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Thermal Property Measurement of Thin Fibers by Complementary Methods

Troy Robert Munro
Utah State University

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THERMAL PROPERTY MEASUREMENT OF THIN FIBERS
BY COMPLEMENTARY METHODS

by
Troy Robert Munro

A dissertation submitted in partial fulfillment
of the requirements for the degree
of
DOCTOR OF PHILOSOPHY
in
Mechanical Engineering

Approved:

Dr. Heng Ban
Major Professor
Prof. Dr. Christ Glorieux
Co-Supervisor

Dr. Randolph V. Lewis
Committee Member
Prof. Dr. Michael Wübbenhorst
Committee Member

Dr. Nicholas Roberts
Committee Member
Prof. Dr. Carmen Bartic
Committee Member

Dr. Thomas Fronk
Committee Member
Prof. Dr. Enrico Carlon
Committee Member

Dr. Mark R. McLellan
Vice President for Research and
Dean of the School of Graduate Studies

UTAH STATE UNIVERSITY
Logan, Utah

2016
ABSTRACT

Thermal Property Measurement of Thin Fibers
by Complementary Methods

by

Troy Robert Munro, Doctor of Philosophy
Utah State University, 2016

Major Professor: Dr. Heng Ban
Department: Mechanical and Aerospace Engineering

To improve measurement reliability and repeatability and resolve the orders of magnitude discrepancy between the two different measurements (via reduced model transient electrothermal and lock-in IR thermography), this dissertation details the development of three complementary methods to accurately measure the thermal properties of the natural and synthetic *Nephila* (*N.*) *clavipes* spider dragline fibers. The thermal conductivity and diffusivity of the dragline silk of the *N. clavipes* spider has been characterized by one research group to be $151-416 \text{ W m}^{-1} \text{ K}^{-1}$ and $6.4-12.3 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$, respectively, for samples with low to high strains (zero to 19.7%). Thermal diffusivity of the dragline silk of a different spider species, *Araneus diadematus*, has been determined by another research group as $2 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ for un-stretched silk. This dissertation seeks to resolve this discrepancy by three complementary methods. The methods detailed are the transient electrothermal technique (in both reduced and full model versions), the 3ω method (for both current and voltage sources), and the non-contact, photothermal, quantum-dot spectral shape-based fluorescence thermometry method. These methods were also validated with electrically conductive and non-conductive fibers. The resulting thermal conductivity of the dragline silk is $1.2 \text{ W m}^{-1} \text{ K}^{-1}$, the thermal diffusivity is $6 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, and the volumetric heat capacity is $2000 \text{ kJ m}^{-3} \text{ K}^{-1}$, with an uncertainty of about 12% for each property.

(197 pages)
Thermal Property Measurement of Thin Fibers
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Thin fibers are prevalent in many engineering materials. Measuring how well heat transfers in such small fibers can be difficult to determine, and previous methods have led to erroneous results. This dissertation details three proposed methods to improve the measurement of the thermal conductivity, thermal diffusivity, and volumetric heat capacity of thin fibers. Of particular interest is natural and synthetic spider silks because previously published values of the natural silk thermal conductivity was similar to copper, an excellent thermal conductor.

The three methods developed are the improved transient electrothermal technique (which was redeveloped to include radiation and convection heat losses and improve accuracy), the $3\omega$ technique (where alternating the power into the fiber allows for a stronger signal to be measured and being able to directly measure all the thermal properties of interest), and the non-contact, photothermal, quantum-dot spectral shape-based fluorescence thermometry method (which takes advantage of the temperature dependent light produced by quantum dots when exposed to laser light).

The results with these methods are that spider silk, while having excellent mechanical properties such as strength and toughness, is not a remarkable thermal conductor. However, the ability to produce synthetic silks with variable properties and the stability and strength of the silk has the potential (with further development) as lightweight, insulative supports in cryogenic systems.
ACKNOWLEDGMENTS

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Then there are the funding sources that have given me the resources to accomplish this work, including SDL and USTAR for project funding, and for the USU Graduate School PDRF program & KU Leuven for my fellowship as I pursued this dual degree. Also thanks are to be had for all my Committee members for supporting this trans-Atlantic endeavor.

Additionally, my collaborators in Randy Lewis’ spider silk lab, particularly my friend Cameron Copeland, as well as my labmates in the MTL (especially Tiger and Ben) and ATF (especially Liwang) are to be acknowledged for helping to develop the equipment for this research and for their friendship.

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NOTATION

**Lowercase Roman**

- \(a\) Radius of cylinder
- \(b_{mag}\) Intercept of axial-based magnitude decay
- \(b_{phase}\) Intercept of axial-based phase delay
- \(c_p\) Specific heat
- \(e_{k, rad}\) Percent error from radiation of thermal conductivity
- \(e_p\) Percent uncertainty of parameter \(p\)
- \(f\) Modulation frequency
- \(f_{req_{phase}}\) Phase delay due to frequency scan
- \(h\) Heat transfer coefficient
- \(h_c\) Convective heat transfer coefficient
- \(h_r\) Radiation heat transfer coefficient
- \(i\) Imaginary unit
- \(k\) Thermal conductivity
- \(k_{axial}\) Axial thermal conductivity
- \(k_e\) Effective thermal conductivity of fiber
- \(k_f\) Thermal conductivity of fiber
- \(k_{radial}\) Radial thermal conductivity
- \(k_{rr}\) Radial thermal conductivity
- \(k_s\) Thermal conductivity of surface
- \(k_{zz}\) Axial thermal conductivity
- \(m^2\) Complex term arising in \(3\omega\)
- \(m_{mag}\) Slope of axial-based magnitude decay
- \(m_{phase}\) Slope of axial-based phase delay
- \(p\) Arbitrary parameter
- \(q_i\) Wavenumber (spacial FFT)
- \(q''\) Volumetric heating
- \(t\) Time
\( t_{Au} \) Thickness of gold coating
\( t_0 \) Initial time
\( t^* \) Non-dimensional time
\( t_{end} \) Final time of simulation
\( t_s \) Steady state time
\( v \) Speed of sound in material
\( x \) Axial dimension
\( x^* \) Non-dimensional axial dimension
\( z \) Axial position
\( z_{mag} \) Amplitude of thermal wave at axial position \( z \)
\( z_{phase} \) Phase of thermal wave at axial position \( z \)

**Uppercase Roman**

\( A \) Peak of Gaussian
\( AC \) Alternating current or oscillatory component of waveform
\( A_f \) Area of fiber
\( A_l \) Lateral surface area
\( A_{Pl,0} \) Intercept of peak intensity linearized temperature relationship
\( B_{PWL,0} \) Intercept of peak wavelength linearized temperature relationship
\( Bi \) Biot number
\( C_{FWHM,0} \) Intercept of full-width half maximum linearized temperature relationship
\( C_p \) Volumetric heat capacity
\( D \) Diameter
\( D_{0} \) Intercept of baseline linearized temperature relationship
\( Fo \) Fourier number
\( H_e^2 \) Effective heat transfer coefficient
\( I \) Current
\( I_v \) Current from voltage source
\( I_0 \) DC current amplitude
\( L \) Length
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_{\text{Au}}$</td>
<td>Lorenz number</td>
</tr>
<tr>
<td>$L_{\text{th}}$</td>
<td>Thermal diffusion length</td>
</tr>
<tr>
<td>$N$</td>
<td>Number of samples</td>
</tr>
<tr>
<td>$P_0$</td>
<td>Power absorbed by laser</td>
</tr>
<tr>
<td>$P_{\text{PI},0}$</td>
<td>Intercept of peak intensity linearized temperature relationship</td>
</tr>
<tr>
<td>$R'$</td>
<td>Temperature versus resistance slope</td>
</tr>
<tr>
<td>$R_0$</td>
<td>Initial resistance</td>
</tr>
<tr>
<td>$R_1$</td>
<td>Other bridge resistor</td>
</tr>
<tr>
<td>$R_1$</td>
<td>Steady state resistance</td>
</tr>
<tr>
<td>$R_2$</td>
<td>Other bridge resistor</td>
</tr>
<tr>
<td>$R_b$</td>
<td>Bridge resistance</td>
</tr>
<tr>
<td>$R_s$</td>
<td>Steady state resistance</td>
</tr>
<tr>
<td>$S_D$</td>
<td>Linearized sensitivity of baseline to temperature</td>
</tr>
<tr>
<td>$S_{\text{FWHM}}$</td>
<td>Linearized sensitivity of full-width half maximum to temperature</td>
</tr>
<tr>
<td>$S_p$</td>
<td>Sensitivity to parameter $p$</td>
</tr>
<tr>
<td>$S_{\text{PI}}$</td>
<td>Linearized sensitivity of peak intensity to temperature</td>
</tr>
<tr>
<td>$S_{\text{PW}}$</td>
<td>Linearized sensitivity of peak wavelength to temperature</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$T_0$</td>
<td>Initial temperature</td>
</tr>
<tr>
<td>$T_{\text{AC}}$</td>
<td>Periodic temperature</td>
</tr>
<tr>
<td>$T_{\text{DC}}$</td>
<td>Constant temperature</td>
</tr>
<tr>
<td>$T_{\text{end}}$</td>
<td>Final temperature of simulation</td>
</tr>
<tr>
<td>$T_{\text{NN}}$</td>
<td>Neural network reconstructed temperature</td>
</tr>
<tr>
<td>$\tilde{T}(a,z)$</td>
<td>Complex surface temperature of cylinder</td>
</tr>
<tr>
<td>$T_{\text{True}}$</td>
<td>True temperature</td>
</tr>
<tr>
<td>$U_p$</td>
<td>Measurement uncertainty of parameter $p$</td>
</tr>
<tr>
<td>$V_0$</td>
<td>Voltage amplitude from voltage source</td>
</tr>
<tr>
<td>$V_3$</td>
<td>3$^{\text{rd}}$ harmonic voltage</td>
</tr>
<tr>
<td>$V_{3v}$</td>
<td>3$^{\text{rd}}$ harmonic voltage response from voltage source</td>
</tr>
<tr>
<td>$V_c$</td>
<td>Monitored voltage from current source</td>
</tr>
</tbody>
</table>
\( V_s \quad \text{Volume of sample} \)

**Lowercase Greek**

- \( \alpha \quad \text{Thermal diffusivity} \)
- \( \alpha_s \quad \text{Thermal diffusivity of surface} \)
- \( \alpha_T \quad \text{Temperature coefficient of resistivity} \)
- \( \delta_i^2 \quad \text{Combination of spatial and temporal FFT terms} \)
- \( \epsilon \quad \text{Emissivity} \)
- \( \gamma \quad \text{Dimensionless non-constant heating} \)
- \( \gamma \quad \text{Non-dimension thermal diffusion length} \)
- \( \lambda \quad \text{Wavelength} \)
- \( \mu \quad \text{Thermal diffusion length} \)
- \( \varphi \quad \text{Phase} \)
- \( \rho \quad \text{Density} \)
- \( \rho c_p \quad \text{Volumetric heat capacity} \)
- \( \rho_e \quad \text{Electrical resistivity} \)
- \( \rho_{e,\text{side}} \quad \text{Electrical resistivity at center} \)
- \( \rho_{e,\text{center}} \quad \text{Electrical resistivity at edge} \)
- \( \sigma \quad \text{Stefan-Boltzmann constant} \)
- \( \omega \quad \text{Angular frequency} \)
- \( 1\omega \quad 1^\text{st} \text{harmonic} \)
- \( 2\omega \quad 2^\text{nd} \text{harmonic} \)
- \( 3\omega \quad 3^\text{rd} \text{harmonic} \)
- \( \xi \quad \text{Dimensionless radiation} \)

**Uppercase Greek**

- \( \Delta T \quad \text{Temperature rise from ambient} \)
- \( \Delta T \quad \text{Change in temperature} \)
- \( \Delta T_c \quad \text{Constant temperature} \)
\( \Delta T_c \) Length averaged constant temperature
\( \Delta T^* \) Non-dimensional temperature
\( \Delta T^\ast \) Length averaged non-dimensional temperature
\( \Delta T_p \) Periodic temperature
\( \Delta T_p^\ast \) Length averaged periodic temperature
\( \Delta T_s \) Steady state temperature rise from ambient
\( \Delta T^*_s \) Non-dimensional steady state temperature
\( \Delta T^\ast_s \) Length averaged non-dimensional steady state temperature
\( \Delta T^\ast_t \) Homogeneous non-dimensional temperature
\( \Delta V \) Voltage rise
\( \Delta V_s \) Steady state voltage rise
\( \Lambda \) Mean free path
ACRONYMS

<table>
<thead>
<tr>
<th>Acronyms</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>CdSe/ZnS</td>
<td>Cadmium selenium zinc sulfur core-shell quantum dot</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>COMSOL</td>
<td>Multiphysics finite element software</td>
</tr>
<tr>
<td>CTE</td>
<td>Coefficient of thermal expansion</td>
</tr>
<tr>
<td>CW</td>
<td>Continuous wave</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current or bias of mean value of waveform</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis</td>
</tr>
<tr>
<td>DMM</td>
<td>Digital multimeter</td>
</tr>
<tr>
<td>DMTA</td>
<td>Dynamic mechanical thermal analysis</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast fourier transform</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full-width half maximum</td>
</tr>
<tr>
<td>GET</td>
<td>Generalized electrothermal technique</td>
</tr>
<tr>
<td>HFIP</td>
<td>Hexafluoroisopropanol</td>
</tr>
<tr>
<td>II</td>
<td>Integrated intensity</td>
</tr>
<tr>
<td>IPA</td>
<td>Isopropanol</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>LN₂</td>
<td>Liquid nitrogen</td>
</tr>
<tr>
<td>MaSp1</td>
<td>Major ampullate spidroin 1</td>
</tr>
<tr>
<td>MaSp2</td>
<td>Major ampullate spidroin 2</td>
</tr>
<tr>
<td>MEMS</td>
<td>Microelectromechanical systems</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multiwall carbon nanotube</td>
</tr>
<tr>
<td>MWNT</td>
<td>Multiwall nanotube</td>
</tr>
<tr>
<td>NA</td>
<td>Numerical aperature</td>
</tr>
<tr>
<td>NN</td>
<td>Neural network</td>
</tr>
<tr>
<td>PBT</td>
<td>Polybutylene terephthalate</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
</tr>
<tr>
<td>PEEK</td>
<td>Polyether ether ketone</td>
</tr>
<tr>
<td>PEK</td>
<td>Polyether ketone</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PI</td>
<td>Peak intensity</td>
</tr>
<tr>
<td>PID</td>
<td>Proportional-integral-derivative control</td>
</tr>
<tr>
<td>PIPD</td>
<td>Poly2,6-diimidazo[4,5-b:4’,5’-e]-pyridinylene-1,4(2,5-dihydroxy)phenylene</td>
</tr>
<tr>
<td>PT1000</td>
<td>Platinum resistor</td>
</tr>
<tr>
<td>PTR</td>
<td>Photothermal radiometry</td>
</tr>
<tr>
<td>QD</td>
<td>Quantum dot</td>
</tr>
<tr>
<td>PW</td>
<td>Peak wavelength</td>
</tr>
<tr>
<td>PWL</td>
<td>Peak wavelength</td>
</tr>
<tr>
<td>R</td>
<td>Ratio of peak intensity and integrated intensity</td>
</tr>
<tr>
<td>RH%</td>
<td>Relative humidity percentage</td>
</tr>
<tr>
<td>RhB</td>
<td>Rhodamine B</td>
</tr>
<tr>
<td>RMS</td>
<td>Root mean square</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SThM</td>
<td>Scanning thermal microscopy</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>SWNT</td>
<td>Single wall nanotube</td>
</tr>
<tr>
<td>TDTR</td>
<td>Time domain thermal reflectance</td>
</tr>
<tr>
<td>TET</td>
<td>Transient electrothermal technique</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>TMA</td>
<td>Thermal mechanical analysis</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
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</table>
CHAPTER 1
INTRODUCTION

1.1 Background

Thermal characterization of materials is essential for design, to provide a basic understanding of the behavior of materials in demanding environments, and then to extend this fundamental understanding of the materials into the realm of application. While understanding of a material’s thermal properties is necessary for first principle predictions, the greatest benefit is for developing new materials for advanced applications and using the fundamental understanding of the material behavior to tune the biosynthetic material to fit a need. Thermal properties such as specific heat, thermal diffusivity, and thermal conductivity are of particular interest because of their expression in the fundamental heat transport equations. Generally, determination of these properties involves quantification of the thermal (heat applied and temperature response) behavior of a material so that the system response can be related to the transient or steady state solution of the heat equation.

One class of materials where thermal property measurement techniques need to be developed for greater accuracy are individual thin (<200 µm) fibers. Traditionally used techniques and standards such as hot wire \([1]\), laser flash \([2]\), guarded hot plate \([3]\), or hot disk \([4]\) cannot be applied in their standard form to the study of individual thin fibers due to small scales, higher uncertainties (using indirect measurements for conductivity), or insufficient sensitivity. To fill in that gap, several different techniques have been created for individual fibers: DC thermal bridge \([5]\), modified hot wire \([6]\), 3ω \([7]\), generalized electrothermal technique \([8]\) and variants \([9]\), Raman shift \([10]\) and variants \([11, 12]\), and lock-in IR thermometry \([13, 14]\). Some of the issues with these are: need to know thermal contact resistance, only obtaining \(k\) or \(\alpha\), neglect of heat transfer modes, small signals, insufficient calibration (Table 1.3).

Fiber measurement has generally been accomplished in bundles (yarns, tows, etc.) \([15]\), by measuring bulk thermal properties and assuming that the bulk material property is the same as the fiber \([16]\), measuring the composite of the fiber and mostly resin and subtracting the resin effect \([17]\), curve-fitting the thermal conductivity based on 100% to 0% fiber content \([18]\). These are not sensitive enough to measure a single fiber, nor do they deal well with the anisotropy of the fiber.

One fibrous material of particular interest is dragline spider silk, which forms the spokes and frame of
the web as well as a line to catch the spider if it falls [19]. The dragline silk (major ampullate) is one of six silks and one glue [19, 20] produced by orb-weaver spiders, especially the golden orb-weaver Nephila (N.) clavipes. Mechanically, the N. clavipes dragline has been extensively studied because of its high tensile strength, low density, biocompatibility, high energy to break, and high extensibility [21, 22]. The silk is comprised of two proteins, MaSp1 and MaSp2 (major ampullate spindroin [23]), and is produced in the major ampullate gland as an aqueous solution [24]. The proteins contain highly repetitive amino acid sequences [25] (which are also conserved over many different spider species, including A. diadematus [26]), which give rise to distinct secondary structures which provide the silk with its favorable properties. These include (Figure 1.3) zippers (Gly II Helix) and springs (β-turn spirals) which are believed to be responsible for its extensibility [26], anti-parallel [27, 28], alanine-rich β-sheets, which are believed to be responsible for its strength [26], and unknown spacers. When silk is required, the spider pulls on its spinnerets, and withdraws the fiber, which passes through several ducts [29], which quickly turns the aqueous protein solution into a water-insoluble fiber in a matter of ms [30]. During the extraction, the ducts change the pH [31] and remove ions from the solution [32], which behavior has been partially repeated in small amounts of fiber with microfluidic devices [33]. Upon proper extrusion, the natural spider silk is typically 3 µm in diameter (Figure 1.1), with crystalline regions (from the β-sheets) that align with the axis of the fiber (Figure 1.2). A summary of many of silks properties are presented in Table 1.1.

The thermal conductivity of spider silks was investigated in 2012 [40]. The researchers used the TET with a curve-fit and calibration to measure the thermal diffusivity and conductivity, respectively, of the dragline silk of the N. clavipes spider. They determined that its un-strained values were of thermal conductivity and diffusivity were 151–416 W m$^{-1}$ K$^{-1}$ and 6.4–12.3 × 10$^{-5}$ m$^2$ s$^{-1}$ respectively, with the highest properties being observed at the highest strains. The reasoning for having thermal properties similar to copper and greater than the highest measured conductivity of a polymer (104 W m$^{-1}$ K$^{-1}$ for an ultra-drawn polyethylene fiber [53]) were the crystalline β-sheet regions and that stretching the silk caused them to align further along the fiber axis, resulting in increased properties. However, another group measured only the thermal diffusivity of a different spider’s (Araneus diadematus) dragline silk via non-contact, frequency-based lock-in IR thermometry, with the value being 0.20 ± 0.01 mm$^2$ s$^{-1}$, a value 400X lower than that of the 2012 study [54]. Although the fibers were from different spiders, the amino acid sequence and structures (including the highly conserved repetitive sequences [25], including β-sheet crystals) is not sufficiently different to account for such a discrepancy. Furthermore, a molecular dynamics simulation of the β-sheets investigated the phonon dispersion and thermal conductivity as a function of sheet size, and determined that the expected
Fig. 1.1: SEM images of different spider silks both natural and synthetic (as spun, stretched and dipped, and Rhodamine B coated).

Fig. 1.2: XRD of synthetic spider silk fibers compared to natural dragline silk to show improvement of crystallinity and alignment based on processing, after [34–37].
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTE [K⁻¹] by TMA [38]</td>
<td>$-6.59 \times 10^{-4}$ for 50–186.4 °C</td>
</tr>
<tr>
<td></td>
<td>$-8.2 \times 10^{-3}$ for 186.4–250 °C</td>
</tr>
<tr>
<td></td>
<td>(Larger than Kevlar and Twaron [39] - aramid fibers)</td>
</tr>
<tr>
<td>Initial $k$ [W m⁻¹ K⁻¹]</td>
<td>151 [40]</td>
</tr>
<tr>
<td>Initial $\alpha$ [m² s⁻¹]</td>
<td>$6.4 \times 10^{-5}$ [40]</td>
</tr>
<tr>
<td>Initial $c_p$ [kJ kg⁻¹ K⁻¹]</td>
<td>1725 by TET [40]</td>
</tr>
<tr>
<td>$c_p$ [kJ mol⁻¹ K⁻¹]</td>
<td>12–15 by DSC of the block co-polymers [41]</td>
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<tr>
<td>$\rho$ [kg m⁻³]</td>
<td>1360 [40]</td>
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<tr>
<td>$T_g$ [K]</td>
<td>459.55 by TMA [38]</td>
</tr>
<tr>
<td></td>
<td>203.15 by DMTA [42]</td>
</tr>
<tr>
<td></td>
<td>205.15 as predicted [42]</td>
</tr>
<tr>
<td></td>
<td>483.15 by DMA [43]</td>
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<td>Degradation [K]</td>
<td>503.15 by TGA [43]</td>
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<tr>
<td></td>
<td>side chains 607.15–615.15 and amino acids 928.15–932.15 [38]</td>
</tr>
<tr>
<td>Young’s Modulus [GPa]</td>
<td>4–22 [44–46] at 300 K</td>
</tr>
<tr>
<td></td>
<td>7–15 in LN₂ [46]</td>
</tr>
<tr>
<td></td>
<td>9.7–35 based on silking rate [43]</td>
</tr>
<tr>
<td>Full elastic tensor</td>
<td>[47]</td>
</tr>
<tr>
<td>Crystallinity</td>
<td>17.5–30% [38, 48]</td>
</tr>
<tr>
<td>Ultimate tensile [GPa]</td>
<td>0.7–4 [38, 43, 49] with improvements in cryogenic temps [45, 46, 50]</td>
</tr>
<tr>
<td>Extensibility [%]</td>
<td>6–35 [43, 45, 50, 51], 0.23–11.8 in cryo [46, 50]</td>
</tr>
<tr>
<td>Toughness [kJ kg⁻¹]</td>
<td>100–400 [45, 49]</td>
</tr>
<tr>
<td></td>
<td>95 in LN₂ [46]</td>
</tr>
<tr>
<td>Supercontraction</td>
<td>Length shrink in presence of water (51–86%) [38, 49, 52]</td>
</tr>
<tr>
<td></td>
<td>Diameter increase 6.1–81.8% from RH % 22–97% [38]</td>
</tr>
<tr>
<td>Diameter [µm]</td>
<td>2.19–6.29, based on silking rate [43]</td>
</tr>
</tbody>
</table>
Fig. 1.3: Constituent structures of spider silk, after [26].

thermal conductivity is in the range of 2–4 W m\(^{-1}\) K\(^{-1}\) [27, 55]. This value is about 100X lower than the 2012 study, and is expected to be even lower because of the contribution of the amorphous regions. One of the sources of this discrepancy from the 2012 study to the other literature values is that the property was overestimated based on neglect of radiation heat losses and insufficient vacuum levels to neglect convection in the thermal property extraction model. However, it is therefore necessary to resolve this discrepancy by applying complementary methods (that are similar to both the original TET and lock-in IR thermometry) to measure the thermal conductivity and diffusivity of the *N. clavipes* dragline silk, which is the focus of this work.

The focus thus far has been on naturally produced spider silk, forcibly extracted (silked) [58] from the spider. However, for commercial uses of spider silk (Table 1.2), the production of silk from spiders is not feasible because they are territorial and cannibalistic, nor can the silk be easily removed from the web because of the other silks included in web making (flagelliform, aggregate, minor ampullate). To that end, synthetic production (Figure 1.4) of spider silk fibers is proposed to meet the scale of production necessary. Transgenic goats are bred to express either the MaSp1 or MaSp2 protein in their milk [30, 59, 60], although other vectors are being developed (*E. coli* [61], alfalfa [62], tobacco [63], and hybrid silk with silkworms [64]) but are not the focus of this work. The protein is then purified from the milk [65], resulting in a white powder. The MaSp1 and MaSp2 proteins are then solubilized in a spin dope with HFIP at the desired ratio (generally, 80% MaSp1,
20% MaSp2), with additional solvents to improve the spinning of the fiber [66]. Recent advances for aqueous solutions of the recombinant proteins (which is a similar environment experienced in the spider’s gland) will not be considered in this work [24]). The protein dope is then placed into a modified plastic extruder where it is injected and coagulated into an “as spun” fiber in a pure IPA bath. These fibers are incredibly weak, brittle and amorphous (XRD of as spun in Figure 1.2, [36]). Research has shown [67] that manual stretching of the fibers in an alcohol bath can improve the crystalline formation and alignment. A machine has been built [66] to perform the initial coagulation, 1–3X stretch in methanol or IPA & water bath 2nd 1–2X stretch in a pure water bath. XRD results [36] show that this mechanized process provides more repeatability in the properties, improves crystallinity and alignment, and that the mechanical properties are improved, even though they are not at the same magnitude as the natural silk. An improvement of the thermal conductivity from the “as spun” fiber to the stretched fiber is expected in a similar manner. Additionally, the ability to capture the effect of processing on the thermal (and mechanical) properties can aid in the development of tunable fibers. A summary of the relevant properties in literature for spider silk is given in Table 1.1.

This thesis focuses on the characterization of silk (major & minor ampullate and synthetic), in addition to other fibers for validation (platinum, glass) and other general fibers (carbon, etc.) via three complementary methods: an improved transient electrothermal technique, extended and corrected 3ω, and quantum dot fluorescence, shape-based, neural network thermometry. A short description of each will be included here, with extensive explanations in future chapters (each based on published journal papers).

1.1.1 State of the art

Several difficulties arise when attempting to measure the thermal behavior of nano- and micro-sized fibers because of small dimensions, accurate temperature measurements, and fully accounting for all the heat transfer mechanisms that occur, while trying to make all of these behaviors conform to an expected thermal model. The current state of the art for these methods include the modified hot wire [6], 3ω [7], DC thermal bridge [5], general/transient electrothermal technique [68] (for thin films [69]), microfabricated device [70], MEMS fluorescence temperature sensor [71], laser flash Raman [72], Joule Raman shift [10], and lock-in IR thermography [13, 73]. Some difficulties with each method are listed in Table 1.3.

Furthermore, the thermal properties of a selection of fibrous materials is presented in Table 1.4.
Fig. 1.4: Simplified production process of synthetic spider silk: expression in goat’s milk (1), purification of protein (2), protein dope (3), DACA-inspired machine for spinning (4), collection of silk (5), and SEM comparison of natural and spider silk (6).

Table 1.2: Potential applications for synthetic spider silk.

<table>
<thead>
<tr>
<th>Mechanical</th>
<th>Thermal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sutures</td>
<td>Low heat loss suspension for cryogenic suspension [56, 57]</td>
</tr>
<tr>
<td>High performance fabrics</td>
<td>Thermal protective clothing</td>
</tr>
<tr>
<td>Tendons, ligaments</td>
<td></td>
</tr>
<tr>
<td>Airbags</td>
<td></td>
</tr>
<tr>
<td>Gels</td>
<td></td>
</tr>
<tr>
<td>Films</td>
<td></td>
</tr>
<tr>
<td>Scaffolds</td>
<td></td>
</tr>
</tbody>
</table>
Table 1.3: Shortcomings of fiber measurement techniques.

<table>
<thead>
<tr>
<th>Method</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot Wire [6]</td>
<td>Effected by thermal contact resistance</td>
</tr>
<tr>
<td></td>
<td>Uniform sample geometry needed</td>
</tr>
<tr>
<td></td>
<td>Only $k$ measured</td>
</tr>
<tr>
<td></td>
<td>Radiation and convection lumped</td>
</tr>
<tr>
<td></td>
<td>Only conductive fibers</td>
</tr>
<tr>
<td>3ω [7]</td>
<td>Validated only with conductive fibers</td>
</tr>
<tr>
<td></td>
<td>Temperature coefficient of resistance needed</td>
</tr>
<tr>
<td></td>
<td>Does not consider resistance of whetstone bridge</td>
</tr>
<tr>
<td>DC Bridge [5]</td>
<td>Contact resistance ignored</td>
</tr>
<tr>
<td></td>
<td>Uniform sample geometry</td>
</tr>
<tr>
<td></td>
<td>Only $k$ measured</td>
</tr>
<tr>
<td></td>
<td>Radiation ignored</td>
</tr>
<tr>
<td></td>
<td>Steady state measurement</td>
</tr>
<tr>
<td>TET [68]</td>
<td>Ignore contact resistance during validation</td>
</tr>
<tr>
<td></td>
<td>Uniform sample geometry</td>
</tr>
<tr>
<td></td>
<td>Validated only with conductive fibers</td>
</tr>
<tr>
<td></td>
<td>Radiation and convection ignored</td>
</tr>
<tr>
<td></td>
<td>Temperature coefficient of resistance needed</td>
</tr>
<tr>
<td>MEMS Device [70]</td>
<td>Need for microfabrication facility</td>
</tr>
<tr>
<td></td>
<td>Heat losses</td>
</tr>
<tr>
<td>Fluoro MEMS [71]</td>
<td>Contact resistance</td>
</tr>
<tr>
<td></td>
<td>Need for microfabrication facility</td>
</tr>
<tr>
<td>Laser Flash Raman [72]</td>
<td>Weak signal</td>
</tr>
<tr>
<td></td>
<td>Raman signal calibration required</td>
</tr>
<tr>
<td>Raman [10]</td>
<td>Weak $G$-band signal</td>
</tr>
<tr>
<td></td>
<td>Raman signal calibration required</td>
</tr>
<tr>
<td>Lock-in IR [13,73]</td>
<td>Limited to low frequencies</td>
</tr>
<tr>
<td></td>
<td>Difficulty finding the fiber</td>
</tr>
</tbody>
</table>
Table 1.4: Axial $k$ and $\alpha$ of select fibers near room temperature.

<table>
<thead>
<tr>
<th>Material</th>
<th>$k$ [W m$^{-1}$ K$^{-1}$]</th>
<th>$\alpha$ [mm$^2$ s$^{-1}$]</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>120</td>
<td></td>
<td>Lock-In IR [73]</td>
</tr>
<tr>
<td>Ni</td>
<td>19</td>
<td></td>
<td>Lock-In IR [73]</td>
</tr>
<tr>
<td>Ti</td>
<td>8.8</td>
<td></td>
<td>Lock-In IR [73]</td>
</tr>
<tr>
<td>AISI-302</td>
<td>3.8</td>
<td></td>
<td>Lock-In IR [73]</td>
</tr>
<tr>
<td>AISI-302</td>
<td>3.6</td>
<td></td>
<td>Lock-In IR [73]</td>
</tr>
<tr>
<td>Carbon T650/35</td>
<td>6.4</td>
<td></td>
<td>Lock-In IR [73]</td>
</tr>
<tr>
<td>Carbon P100</td>
<td>310</td>
<td></td>
<td>Lock-In IR [73]</td>
</tr>
<tr>
<td>PEEK</td>
<td>0.54</td>
<td></td>
<td>Lock-In IR [73]</td>
</tr>
<tr>
<td>Human hair</td>
<td>0.14</td>
<td></td>
<td>Lock-In IR [73]</td>
</tr>
<tr>
<td>DNA bundle</td>
<td>0.4</td>
<td>2.5-3.75</td>
<td>TET [74]</td>
</tr>
<tr>
<td>TiO$_2$ nanowire</td>
<td>0.05-0.35</td>
<td>1.2-3.5</td>
<td>TET [75]</td>
</tr>
<tr>
<td>CNT bundle</td>
<td>25</td>
<td>1.5</td>
<td>Raman [76]</td>
</tr>
<tr>
<td>ZylonHM</td>
<td>23</td>
<td></td>
<td>TDTR [77]</td>
</tr>
<tr>
<td>Vectra</td>
<td>1.8</td>
<td></td>
<td>TDTR [77]</td>
</tr>
<tr>
<td>Kevlar</td>
<td>3</td>
<td></td>
<td>TDTR [77]</td>
</tr>
<tr>
<td>M5AS (PIPD)</td>
<td>9</td>
<td></td>
<td>TDTR [77]</td>
</tr>
<tr>
<td>ZylonAS</td>
<td>19</td>
<td></td>
<td>TDTR [77]</td>
</tr>
<tr>
<td>Dyneema (PE)</td>
<td>14</td>
<td></td>
<td>TDTR [77]</td>
</tr>
<tr>
<td>PBT</td>
<td>12</td>
<td></td>
<td>TDTR [77]</td>
</tr>
<tr>
<td>Spectra2000 (PE)</td>
<td>15</td>
<td></td>
<td>TDTR [77]</td>
</tr>
<tr>
<td>Spectra900 (PE)</td>
<td>11</td>
<td></td>
<td>TDTR [77]</td>
</tr>
<tr>
<td>Silkworm</td>
<td>0.54</td>
<td>0.39</td>
<td>TET [78]</td>
</tr>
<tr>
<td>PEK/CNT</td>
<td>1.1-17</td>
<td></td>
<td>DC bridge [5]</td>
</tr>
<tr>
<td>Single CNT</td>
<td>1600-3600</td>
<td></td>
<td>4-Probe Pt [79]</td>
</tr>
<tr>
<td>Polyester</td>
<td>0.526</td>
<td></td>
<td>TET [8]</td>
</tr>
<tr>
<td>SWCNT</td>
<td>27.3</td>
<td></td>
<td>TET [8]</td>
</tr>
<tr>
<td>SWNT</td>
<td>2400</td>
<td></td>
<td>Raman Shift [10]</td>
</tr>
<tr>
<td>MWNT</td>
<td>1400</td>
<td></td>
<td>Raman Shift [10]</td>
</tr>
<tr>
<td>CNT in water</td>
<td>1200</td>
<td></td>
<td>Fluorescent pillars [80]</td>
</tr>
<tr>
<td>Ultradrawn PE</td>
<td>0.3-40</td>
<td></td>
<td>Pulse PTR [81]</td>
</tr>
<tr>
<td>Ultradrawn PE</td>
<td>50-104</td>
<td></td>
<td>AFM Cantilever [53]</td>
</tr>
<tr>
<td>Carbon fiber (methylnaphthalene)</td>
<td>123-544</td>
<td></td>
<td>Hot Wire [6]</td>
</tr>
<tr>
<td>MWCNT</td>
<td>300</td>
<td></td>
<td>4-point $3\omega$ [82]</td>
</tr>
<tr>
<td>Glass rod</td>
<td>0.24</td>
<td></td>
<td>Micromanipulator [83]</td>
</tr>
<tr>
<td>Polyimide</td>
<td>0.0648</td>
<td></td>
<td>Micromanipulator [83]</td>
</tr>
<tr>
<td>CNT in water</td>
<td>701</td>
<td></td>
<td>Fluorescent [71]</td>
</tr>
<tr>
<td>CNT in air</td>
<td>480</td>
<td></td>
<td>Fluorescent [71]</td>
</tr>
<tr>
<td>Kevlar 49</td>
<td>3.7</td>
<td></td>
<td>Steady state [15]</td>
</tr>
<tr>
<td>Animal proteins</td>
<td>0.193-0.5</td>
<td></td>
<td>Various [84]</td>
</tr>
<tr>
<td>MWCNT</td>
<td>1400-1700</td>
<td>820-1050</td>
<td>Laser flash Raman [72]</td>
</tr>
<tr>
<td>MWCNT</td>
<td>9.82-12.3</td>
<td>49.5</td>
<td>TET Raman [9]</td>
</tr>
</tbody>
</table>
1.1.2 TET

The TET method includes suspending the fiber across two heat sinks, coating it with gold (if not already electrically conductive), pasting the fiber to the heat sinks with silver paste to reduce both thermal and electrical contact resistance, attaching electrical leads to the heat sinks, calibrating the resistance of the gold coating to temperature, placing the fibers in high vacuum ($10^{-5}$ mbar or lower) to eliminate convection and conduction in the vicinity of the fiber, having multiple different lengths of fibers to curve-fit to a “zero-length” property where radiation heat loss does not contribute, passing several different constant currents to each fiber and tracking the voltage response (related to temperature rise through a resistance change), and curve fitting the normalized transient average temperature rise for thermal diffusivity & absolute temperature rise and input power for thermal conductivity. The improvement over the previous (hereafter referred to as reduced) versions of the TET model is the incorporation of radial convective and radiative heat losses, which become more significant as the fiber of interest has long $L$, smaller $D$, or smaller $k$. A full model incorporates these considerations and increases the accuracy of the $k$ and $\alpha$ measurements.

1.1.3 $3\omega$

The $3\omega$ technique uses the same sample preparation as the TET, but rather than using a step DC input, an AC-modulated voltage or current is input into the sample. Because the current and voltage are oscillating at $1\omega$, the power responds at $2\omega$ which is the driving force for a change in temperature (also at $2\omega$), resulting in a change in resistance at $3\omega$, which is then measured by a change in voltage at $1\omega$ and $3\omega$ [85]. The $3\omega$ portion of the signal is of interest versus the other harmonics because it does not contain additional noise from the original input source. Use of a lock-in amplifier allows for adequate attenuation of signals at other frequencies besides the harmonics of the input signal, resulting in a significantly higher signal-to-noise ratio (up to -100 dB signal detection attainable in some cases [86]). The lock-in maps the signal into the frequency domain, where the amplitude and phase are measured at the $3\omega$ frequency. Based on the fiber properties and the frequency of the original $1\omega$ signal, the amplitude and phase have an attenuation and delay that can be used to extract the $C_p$, $k$, and $\alpha$ directly, depending on the frequency range used. The improvement with the proposed method over previous ones is the inclusion of either a current source or a voltage source for the modulation (which is a typical output of a lock-in amplifier) and corrections for use of a whetstone bridge to cancel out the $1\omega$ signal & the ratio of the bridge resistance to sample resistance.
1.1.4 Shape-based, quantum dot, fluorescence thermometry

The spectral shape-based, quantum dot, fluorescence thermometry method is an extension and combination of several fields, each of which will be lightly treated in this section: quantum dots, fluorescence & fluorescence thermometry, solution of the inverse problem via artificial neural networks, and photothermal and thermal wave techniques.

To understand fluorescence, a simple three-level model (ground, excited, and relaxed level) is described for fluorescent dyes. An electron in a fluorescent dye absorbs a photon, raising its energy and placing it in the excited energy level, at which point the electron experiences some vibrational and other relaxations which reduce its energy, and finally drops back to the ground level, emitting a red-shifted (Stokes shift) photon compared to the originally absorbed photon [87]. The lifetime of this excited state is typically on the order of nanoseconds and is also sensitive to temperature, but lifetime thermometry is beyond the scope of this work [88]. In organic dyes, this behavior occurs because of many conjugated (alternating double and single) bonds [89], with Rhodamine B (Figure 1.5) being a well used dye, including for thermometry [90], as has green fluorescent protein [91].

Quantum dots are semiconductors (typically III-V types) where the band gap is such that the radius of the hole-electron pair (exciton) “orbit” is similar to the physical size of the dot [92, 93] (several nanometers), resulting in the quantum confinement phenomena. This results in a fluorescent color that is dependent on the size of the dot, with larger dots being more red [94]. This emitted, almost Gaussian shaped fluorescent spectra is temperature dependent [95], as are several spectral features (peak intensity [96], integrated intensity [97], the PI/II ratio [98], peak wavelength [99], FWHM [99]). This can be used to determine the temperature of the dots and the substrate surface they are on, based on the spectra at known temperature & data reduction methods to relate the feature of interest to its temperature. Traditional methods are generally linear or exponential curve fits and simple sigmoids to create this temperature-feature relationship.

The current work proposes to use artificial neural networks to reconstruct the surface temperature based on using multiple spectral features as inputs to the network. The neural network used in this work is a supervised machine learning algorithm composed of three layers of neural nodes: input nodes, hidden nodes which weight the sums of the input nodes, and an output node which also has weighted sums of the hidden nodes. Training data, where the desired output is known, are used to “train” the neural network, meaning varying the weights of each node, until the inputs produce the expected output (in this case temperature). The varying of the weights is guided by reduction of the RMS error from neural network output compared expected output by a Levenberg-Marquardt algorithm. To ensure that the network is not overtrained, randomly selected sub-
sets from the pool of training data is used as a test to ensure that network does not erroneously converge to an incorrect result. The neural network is able to take into consideration non-linear effects, which can be seen in some of the features, with the intent of improving the accuracy of non-contact thermometry from quantum dots below the typical $\sim1–2$ K currently observed [100].

To further extend fluorescence thermometry in the realm of thermal property determination, the current method takes advantage of photothermal or thermal wave techniques. The photothermal effect is where incident electromagnetic radiation is absorbed by a material and via non-radiative transitions of the excited atom or molecule, the energy is converted to heat [86]. By sinusoidally modulating the intensity of the light, the temperature of the material responds in an oscillatory manner down to a certain depth of the material. This temperature variation is often called a thermal wave (although it does not transport energy like traditional waves [101]) and it experiences both an attenuation and phase delay that are functions of the material’s properties, the distance from the modulated source, and the modulation frequency. Traditionally, photothermal techniques use a pump beam to induce the temperature variation, and some techniques also include a probing beam or sensor to measure the material’s response. These probes include [86]: reflectivity of the surface (modulated optical reflectivity [102, 103]), photoacoustic [104], piezoelectric [105], pyroelectric [106], Mirage or optical beam deflection [107], photothermal displacement [108], infrared photothermal radiometry [109, 110]. The current project uses surface temperature reconstructed from the fluorescent signal, induced by a green probe laser beam, to measure the material response to an IR pump beam. Furthermore, the amplitude and phase decay are determined by an FFT-based method that extracts the phase and amplitude at the modulation frequency while the axial spacing between the laser beams is varied (axial scan) and by
varying the modulation frequency (frequency scan). The thermal diffusivity can then be extracted by fitting the data to a frequency domain solution of the transient heat equation for a cylindrical sample with a modulated surface heating condition [73].

1.2 Motivation

The motivation for this work can be broken down into two general areas, methods and materials.

• Methods
  – Need reliable way to measure thermal conductivity and diffusivity of individual, thin fibers
  – Push limits of non-contact thermometry
  – Verify properties by complementary approaches

• Materials
  – Spider silk was originally reported to have thermal properties ($k$ and $\alpha$) similar to copper, while other researchers reported significantly lower properties
  – Ability to compare properties of synthetic and natural silks

1.3 Objectives of the research

• Develop techniques to measure the thermal properties of thin fibers
  – Exploit both DC and AC measurement techniques to verify new techniques
  – Verify new models with reference materials
  – Combine work on photothermal, machine learning, and fluorescence thermometry for new method

• Characterize natural and synthetic spider silk
  – Resolve discrepancy in the literature
  – Determine affect of processing variations on thermal properties
  – Relate thermal properties to microstructure of fibers
1.4 Outline of the dissertation

This thesis is a compilation of several published journal articles of which I have been a major or first author, with the permission letters from the co-authors in Appendix A.1 and for copyright from the journals in Appendix A.2. To fill in details not included in the papers, there are connecting chapters that expand on topics of interest. The chapter breakdown is as follows:

- Chapter 2 is based on the first paper that details the full model of the TET method and how its use improves upon the bias error that occurs when convection and radiation is neglected. The paper was originally published in 2013 as “Analysis of the Electrothermal Technique for Thermal Property Characterization of Thin Fibers” in the *Measurement Science and Technology* journal with the authors being Changhu Xing, Troy Munro, Colby Jensen, and Heng Ban.

- Chapter 3 is a bridge chapter, focused on the convection and coating effect (including annealing) of the TET, limitations of the method, and validation of the method with platinum and glass fibers, including at cryogenic temperatures. Citations for other experimental work with the improved TET method are also included.

- Chapter 4 is based on the second paper that details the derivation and application of the $3\omega$ technique for thin wires for both current and voltage sources, and verifies the measurement technique with a numerically simulated platinum wire. The paper was originally published in 2014 as “Thermal Property Characterization of Fine Fibers by the 3-omega Technique” in the *Applied Thermal Engineering* journal with the authors being Changhu Xing, Colby Jensen, Troy Munro, Benjamin White, and Mihai Chirtoc, and Heng Ban.

- Chapter 5 is a bridge chapter that focuses on the limitations of the $3\omega$ method, a flow chart to aid in the practical application of both the TET and $3\omega$ techniques, and images of the hardware used for both the TET and $3\omega$ methods. Discussions on the size limitations of the two methods and anisotropic considerations are included. Citations for other experimental work with the $3\omega$ method are also included.

- Chapter 6 reports the thermal property measurement of the natural and as spun synthetic spider silk via the TET method to meet the objective of resolving the discrepancy in the literature. The paper was originally published in 2014 as “Thermophysical Properties of the Dragline Silk of *Nephila clavipes* Spider” in the *Polymer* journal with the authors being Changhu Xing, Benjamin White, Troy Munro, Heng Ban, and Cameron Copeland, and Randolph Lewis.
• Chapter 7 is a bridge chapter that discusses issues with the timescale for a TET/3ω measurement, the motivation for developing a non-contact thermometry method, justification for use of neural network for temperature reconstruction, as well as a description for the procedures used to create the synthetic spider silk studied in this work.

• Chapter 8 reports the quantum dot fluorescence shape-based thermometry and the experimental and numerical simulations to analyze its validity and accuracy in preparation for thermal property measurements. The paper was originally submitted in 2015 as “CdSe/ZnS Quantum Dot Shape-based Thermometry via Neural Network Reconstruction” in the Journal of Applied Physics with the authors being Troy Munro, Liwang Liu, Christ Glorieux, and Heng Ban.

• Chapter 9 reports the FFT-based method to determine the phase and amplitude of the quantum dot fluorescence thermometry signal to verify measurement of thermal diffusivity in both an axial and frequency scan by numerical simulation, with initial experimental results. The paper will be submitted in 2016 as “FFT-based Method for Thermal Property Determination of Micro-Sized Fibers via Photothermal Quantum Dot Fluorescence-based Thermometry” in the Applied Thermal Engineering journal with the authors being Troy Munro, Liwang Liu, Heng Ban, and Christ Glorieux.

• Chapter 10 is a bridge chapter that provides further detail on the limitations of the FFT-based method due to noise in the neural network reconstructed temperature and images of the hardware systems created at Utah State and KU Leuven and an explanation for the limit of the method to detect a good signal at higher frequencies.

• Chapter 11 summarizes the measured properties of all fibers measured in this study, as well as thermal applications of synthetic spider silk and potential future work.

• Chapter 12 presents the overall conclusions of the work.
References


[37] Lewis, R., “PowerPoint - Using Synthetic Biology to Produce Spider Silk,” 2013.


CHAPTER 2
ANALYSIS OF THE ELECTROThERMAl TECHNIQUE FOR THERMAL PROPERTy
CHARACTERIZATION OF THIN FIBERS

This chapter is based on a paper published in Measurement Science and Technology, 24, doi:10.1088/0957-0233/24/10/105603 with the original author list being: Changhu Xing, Troy Munro, Colby Jensen and Heng Ban. My contribution to this work was aiding in derivation of the models, initial tests with reduced model, setup of equipment for TET method, data analysis, and document preparation.

2.1 Abstract

The transient electrothermal technique has been developed to measure the thermal conductivity and thermal diffusivity of electrically conductive or non-conductive nano-to-microscale fibers. In this work, a full theoretical model was developed in detail including the effects of radiation heat loss and non-constant heating as a result of sample temperature rise during measurement, and was compared to the more commonly used reduced model, which neglects these effects.

Non-dimensional parameters were derived representing radiation heat loss and non-constant heating to identify the true parameter dependencies on these effects. A numerical model was used to perform parametric analyses on the experimental setup providing results that were fitted with the full and reduced models to find thermal conductivity and thermal diffusivity. Additionally, the numerical model was used to investigate nonlinear radiation heat losses and spatially non-uniform heating effects resulting from uneven coating of the conductive layer on electrically non-conductive samples. As a result, these influences were shown to require careful consideration in the application of this technique. A clear linear relationship was found between the non-dimensional parameters and measurement error, which provides a measure for the proper estimation of systematic error induced by these effects. Using the reduced model for data reduction results in measurement percentage error equal to ten times the radiation and non-constant heating dimensionless parameters under the assumption of linear radiation heat losses (small sample temperature rise compared to ambient temperature).

2.2 Introduction

The exceptional mechanical and/or thermal properties of high-performance fibers (e.g. carbon fibers, carbon nanotubes, synthetic spider silk, etc) play many important roles in current and potential technological
applications. Reliable techniques are required to characterize the thermal capabilities of such fibers that can have micro- or even nanosize diameters. General thermal property characterization techniques for fine fibers include the hot wire [1], Raman shift [2], $3\omega$ [3, 4], transient/generalized electrothermal technique (TET or GET) [5] and DC thermal bridge [6] methods.

Initially developed for metallic thin film measurements [7], the TET [8] models heat transfer through an electrically conductive or a non-conductive fiber coated with a thin conductive layer, with the fiber being suspended between two heat sink blocks. With an electrical current passing through the sample, the temperature of the sample increases due to Joule heating. The final steady-state temperature is a function of the thermal conductivity of the sample. The transient temperature response, normalized to the steady-state value, is a function of the sample’s thermal diffusivity. Therefore, the thermal properties of the fiber can be obtained from the steady-state and transient temperature responses.

In the derivation of the TET thermal model [5], simplifying assumptions of negligible heat losses from the sample surface and constant heating in the sample were made, resulting in the solution that has been widely used, referred to as the ‘reduced’ model in this paper. Clearly, application of the reduced model will only be valid when heat losses through radiation or convection in imperfect vacuum are small, and when heat generation variation due to the change in resistance as a function of temperature rise is negligible. If the temperature rise during measurement is small relative to the environmental temperature so that radiation heat transfer can be linearized (based on a first order Taylor series expansion), the radiation heat loss is usually a strong function of the overall environmental temperature, sample geometry (surface to volume ratio) and material properties (emissivity, thermal conductivity, and so on) but not related to the magnitude of temperature rise [9]. At low vacuum level, convective heat transfer may also have significant influence on the measurement result due to the large aspect ratio. Radiation loss in the $3\omega$ technique was investigated by Hou et al [10]. Although their result is particular to their measurement setup, they begin to illustrate the importance of sample sizing on model assumptions. In [11, 12], non-constant heating effects were observed. The inclusion of these effects in the mathematical model results in what will be called the ‘full’ model, similar to that derived in [7].

In this work, the full model is described in detail and compared to the reduced model. Unique to this work, the full model is non-dimensionalized revealing non-dimensional relationships for the effects of sample heat losses and non-constant heating. Using these theoretical models, the effects of radiation heat losses, non-constant heating and non-uniform heating on thermal property measurement are quantified for the TET technique. A finite element model was created in COMSOL which was used to perform ‘numerical
experiments’ allowing for easy variation of system parameters. Using the full and reduced analytic models, the resulting temperature profiles, taken from the COMSOL calculations, were used to extract $k$ and $\alpha$. The derived non-dimensional relationships for heat losses and variable heat generation contributions each result in a linear relationship with respect to calculated error.

2.3 Theory

2.3.1 Full TET model

Figure 2.1 presents a schematic diagram of the TET measurement where a fiber sample is suspended between the two heat sinks while providing good electrical/thermal contact between sample and the heat sink through silver paste. The sample has a high aspect ratio, $L/D$, so that radial temperature gradients are negligible. With the application of a constant current to the sample (Joule heating) through a current source, the voltage variation induced by the change of the sample’s resistance (due to temperature increase) is measured. With known temperature versus resistance relationship ($R'$) of the sample, which is often directly measured by changing the environment temperature, the resulting temperature/voltage profile can be used to extract the thermal conductivity and diffusivity of the sample.

The constant current, $I$, supplied to the sample with average electrical resistance $R(T)$ provides volumetric heat generation in the sample (since the volume of the coating is less than 1% of the volume of the fiber) equal to $I^2R(T) = I^2R_0 + I^2R'\Delta T$ where $R_0$ is the electrical resistance of the sample measured at $T_0$ using a small, negligible current, and $R'$ is the slope of the resistance/temperature relation. $R_0$ can also be calculated from $R_0 = 4\rho_e L / \pi D^2$, where $\rho_e$ is the electrical resistivity.

Radiation and convection/conduction heat transfer from the lateral surface are accounted for using heat transfer coefficients, $h_r$ and $h_c$, respectively. For a gray body and small changes of temperature, $\Delta T$, above the

![Fig. 2.1: Schematic of the TET measurement configuration.](image)
expressed as
\[ \Delta = \text{ambient}, T_0, \] the radiation heat transfer contribution is linearized by the Taylor expansion so that \( h_r \approx 4T_0^3 \varepsilon \sigma \) [9].

In this way, the full model accounts for heat losses from the lateral surface and heat contribution from change of resistance with temperature of the sample in a single term, \( H_x^2 = [(h_r + h_c)A_l - I^2R']/V_k \) in a one-dimensional (1D) model while the temperature-independent volumetric heating term is \( q''_0 = I^2R_0/V_s \). In the definition, \( V_s \) is the volume equal to \( \pi D^2 L/4 \) for a cylinder sample and \( A_l \) is the lateral surface area equal to \( \pi DL \). The transient, 1D governing equation for the TET method is then written as

\[
\frac{1}{\alpha} \frac{\partial \Delta T}{\partial t} = \frac{\partial^2 \Delta T}{\partial x^2} - H_x^2 \Delta T + \frac{q''_0}{k}.
\] (2.1)

The boundary and initial conditions for Equation (2.1) are those of a constant temperature heat sink, \( \Delta T(x = 0, t) = \Delta T(x = L, t) = \Delta T(x, t = 0) = 0 \). Equation (2.1) can be non-dimensionalized using the following relationships: \( \Delta T^* = \Delta T/(q''_0 L^2/k), t^* = \alpha t/L^2 = Fo \) (Fourier number), and \( x^* = x/L \).

\[
\frac{\Delta T^*}{\partial Fo} = \frac{\partial^2 \Delta T^*}{\partial x^2} - L^2 H_x^2 \Delta T^* + 1.
\] (2.2)

The solution of the above equation, \( \Delta T^*(x^*, Fo) \), is found as the sum of the solutions of the spatial dependent terms (steady-state) and the homogeneous equation or \( \Delta T(x^*, Fo) = \Delta T^*_s(x^*) + \Delta T^*_r(x^*, Fo) \) where

\[
\Delta T^*_s = \frac{1}{L^2 H_x^2} \left[ 1 - \frac{\sinh(LH_x x^*) + \sinh[LH_x(1 - x^*)]}{\sinh(LH_x)} \right],
\] (2.3)

\[
\Delta T^*_r = -4 \sum_{m=1}^{\infty} e^{-(2m-1)^2 \pi^2 + L^2 H_x^2} \sin[(2m-1)\pi x^*]/(2m-1)^2 \pi^3 + L^2 H_x^2 (2m-1)\pi.
\] (2.4)

The steady-state average temperature is found by integrating Equation 2.3 with respect to \( x^* \) and is expressed as

\[
\Delta T^*_s = \frac{1}{L^2 H_x^2} \left[ 1 - 2 \cosh(LH_x) - 1 \right].
\] (2.5)

Spatially integrating the full solution, \( \Delta T^*(x^*, Fo) \), and normalizing by the above equation yields

\[
\frac{\Delta T^*}{\Delta T^*_s} = 1 - \frac{8L^2 H_x^2}{1 - 2 \cosh(LH_x) \sinh(LH_x)} \times \sum_{m=1}^{\infty} e^{-(2m-1)^2 \pi^2 + L^2 H_x^2} \sin[(2m-1)\pi x^*]/(2m-1)^2 \pi^3 + [LH_x(2m-1)\pi]^2.
\] (2.6)
The thermal diffusivity $\alpha$ of the sample is then obtained by fitting the above equation to the measured voltage (temperature) response of the sample (typical response of normalized voltage as a function of time is shown in Figure 3.1 in section 3.1). The full model for thermal conductivity $k$ is found by substituting the resistance/temperature relationship $\Delta T = (R_1 - R_0)/R'$ in Equation 2.5 giving

$$1 = \frac{I^2 R_0 R'}{V_f k H_e^2 (R_1 - R_0)} \left[ 1 - 2 \frac{\cosh(LH_e - 1)}{LH_e \sinh(LH_e)} \right].$$ (2.7)

To obtain an explicit relationship for $k$, the cosh and sinh terms can be expanded as infinite series. If $LH_e$ is small and neglecting terms higher than order 4 (all odd orders divide out and $k \propto H_e^{-2}$), $k$ can be expressed explicitly by the following equation:

$$k = \frac{I^2 R_0 R' L^2}{12 V_f (R_1 - R_0)} - \frac{L^2 k H_e^2}{6}.$$ (2.8)

For $H_e = 0$, the expression simplifies to the form of the “reduced” model. The second terms represents the effect of additional heat losses (radiation or convection) and/or gains ((non-constant Joule heating).

If radiation heat loss is the dominant term in $H_e$, $k$ is over-predicted by the reduced model, where from the full model $k$ may be expressed as

$$k = \frac{I^2 R_0 R' L^2}{12 V_f (R_1 - R_0)} - \frac{2 \gamma_0^2 \kappa \sigma L^2}{3D}.$$ (2.9)

When non-constant heating is dominant, $k$ can be expressed as Equation 2.10 and would be under-predicted by the reduced model (when $R'$ is positive):

$$k = \frac{I^2 R_0 R' L^2}{12 V_f (R_1 - R_0)} + \frac{2 I^2 R' L}{3 \pi D^2}.$$ (2.10)

### 2.3.2 Reduced TET model

The reduced model developed in [5, 8] neglects surface heat losses and non-constant heating ($H_e = 0$ in Equation 2.1). Expanding cosh and sinh in Equation 2.5 and neglecting the $LH_e$ term, Equation 2.5 is reduced to a constant, $\Delta T_s = 1/12$. Then for $k$, the reduced model can be expressed as an explicit relationship as the first term of equations 2.8-2.10:

$$k = \frac{I^2 R_0 R' L^2}{12 V_f (R_1 - R_0)}.$$ (2.11)
The reduced model for $\alpha \ (LH_e \rightarrow 0 \text{ in Equation 2.6})$ is

$$\frac{\Delta T}{\Delta T_s} = 1 - \frac{96}{\pi^2} \sum_{m=1}^{\infty} \frac{e^{-(2m-1)^2/4}}{(2m-1)^4}$$

(2.12)

In the full model, $k$ does not have an explicit solution because $H_e$ is a function of $k$. A nonlinear root finding method such as the Newton-Raphson method can be used to find $k$, using the reduced model to find a good initial guess value. In both the reduced and full models, a nonlinear curve fitting method may be used to find $\alpha$. For this work, the Levenberg-Marquardt algorithm [13] was selected as it is commonly used for such applications and is well suited for such a procedure (the typical transient response to be curve-fit for the reduced model, as well as $T(x,t)$ is given in Figure 3.1 in section 3.1).

2.4 Numerical model and procedure

Using COMSOL Multiphysics software, the heat transfer through a 1D wire sample was simulated. In the model, the 1D transient heat equation was solved over the domain including the effects of an additional source term for spatially non-uniform Joule heating and nonlinear radiation exchange, $\varepsilon\sigma A_i(T^4 - T_0^4)$. These effects were turned off/on to study the effect of the other independently. The mesh consisted of a single line of 240 elements and was checked to ensure grid independence. The simulation uses a constant temperature boundary condition at the end nodes of the sample with radiation losses from the lateral surfaces to the ambient temperature (see Figure 2.1). Convection heat transfer was not considered since it would be negligible in high vacuum.

To check the 1D assumption, an axisymmetric model was created and meshed with 240 elements in the axial direction and 15 elements in the radial direction. For the case of a perfectly insulated sample, the temperature field is radially uniform. To ensure that the 1D assumption is valid for all configurations explored in this work, the conditions corresponding to the largest contribution of lateral heat loss were applied to the model. A comparison of the temperatures between the center and the surface of the sample at the location of highest temperature (the midspan of the sample) revealed a difference of only 0.45 mK ($1.5 \times 10^{-4}\%$). Therefore, the 1D model is valid for results in this study.

For the radiation studies, the applied electrical current was adjusted first so that the average temperature rise was $\sim 0.1$ K. In this way, the assumption of linearized radiation is valid. In order to evaluate the non-linear contribution from the radiation heat transfer, larger electrical currents were passed through the sample inducing larger temperature rise. The average temperature of the sample was obtained by integrating the temperature over the sample in COMSOL.
The purpose of the numerical simulation was to replicate the experimental measurement procedure while having easy flexibility in adjusting sample properties and geometry. The numerical simulation, allowing for all parameters to be adjusted, was used to calculate transient and steady-state temperature profiles for different sample properties and geometries. The full and reduced models were then fitted to these numerically calculated profiles to estimate \(k\) and \(\alpha\) for each case.

To quantify the effects of radiation and non-constant heating, three representative materials were selected for the numerical simulation covering a large range of \(k\), \(\alpha\), and \(\varepsilon\). The three representative materials were carbon fiber, platinum wire and spider silk. Table 1 contains a list of parameter values used and specifies the parameters varied in different calculated cases while other parameters were held constant. For the spider silk, \(\varepsilon\) is assumed to be \(\sim 0.5\) because of the one-side gold sputter coating that would be applied in experimental measurements. Although electrically non-conductive, the electrical resistivity of the spider silk sample is represented as the value calculated from gold-coating resistance (Table S1 in supporting information of [8]).

2.5 Model considerations

The full model of the TET method allows for modeling heating/cooling effects to be neglected in the reduced model. In particular, these effects include heat losses from the surface including convection (and conduction) and radiation heat transfer, non-constant heating due to change of sample resistance with temperature rise. For this study, convection heat transfer is not considered in detail as the measurement is typically carried out in vacuum where convection heat loss may be justifiably neglected (see Section 3.3). In addition to the utility of the full model, the numerical model allows for easy study of the spatial dependent phenomena. In this case, the effect of non-uniform heating in the sample is of great practical application.

The non-dimensional coefficient on the second term on the right-hand side of Equation 2.2 can be expanded and simplified to give two non-dimensional terms related to lateral heat losses and non-constant heating as

\[
L^2 H_e^2 = \frac{4(h_r + h_c)L^2}{kD} - \frac{4I^2 R'L}{\pi kD^2}. \quad (2.13)
\]

2.5.1 Radiation heat loss

To better identify and quantify the effect of radiation heat loss on measured \(k\) and \(\alpha\), the dimensionless term on the right-hand side of Equation 2.13 (assuming \(h_c = 0\) and \(I = 0\)) is defined as \(\xi\):
Table 2.1: Thermal parameters of representative samples used in the finite element model for parameter study. Properties taken at room temperature.

<table>
<thead>
<tr>
<th>Material</th>
<th>$k$</th>
<th>$\alpha \times 10^6$</th>
<th>$\varepsilon$</th>
<th>$\alpha_T$</th>
<th>Varied parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon fiber [14]</td>
<td>6.83</td>
<td>3.38</td>
<td>0.98 [15]</td>
<td>-0.0005</td>
<td>$L, T_0, D$</td>
</tr>
<tr>
<td>Platinum [16]</td>
<td>71.6</td>
<td>25.1</td>
<td>0.05</td>
<td>0.0039</td>
<td>$D, L, I$</td>
</tr>
<tr>
<td>Spider silk [8]</td>
<td>415.9</td>
<td>123</td>
<td>0.5</td>
<td>0.0011110</td>
<td>$L; I$</td>
</tr>
</tbody>
</table>

\[ \xi = \frac{4(h_r)\varepsilon T_0^3 L^2}{kD} = \frac{16\varepsilon \sigma T_0^3 L^2}{kD} \]  
(2.14)

which represents the ratio of radiation heat loss to axial heat conduction in the sample. As seen in Equation 2.13, $\xi$ dependencies can easily give the effect of $h_c$ as well through $L^2H_2^2$. Experiments are typically carried out in high vacuum where $h_c = 0$ and is thus not explicitly included in this analysis.

### 2.5.2 Non-constant heating

Small sample temperature rise is desirable to have negligible non-constant heating effects but becomes a trade-off with signal-to-noise ratio. Especially when measuring high $\alpha$ materials, a fast sampling rate with good (small) resolution is needed to capture the transient behavior. A low signal-to-noise ratio and a fast sampling rate will result in large measurement uncertainty. To improve the measurement accuracy, the applied current and thus the measured temperature associated with voltage change in the sample should be increased. Therefore, the error associated with non-constant heating effect is an important consideration. A second dimensionless parameter, $\gamma$, is defined from the second term on the right-hand side of Equation 2.13 ($h_r = h_c = 0$):

\[ \gamma = \frac{4F^2 R'L}{k\pi D^2} = \frac{16F^2 \alpha_T \rho L^2}{k\pi^2 D^4}. \]  
(2.15)

The above equation represents the effect of non-constant heating and can be thought of as the ratio of heat generation variation due to a temperature change of resistance relative to axial heat conduction in the sample.

### 2.5.3 Non-uniform heating

For non-conductive fibers, a thin coating (usually 10 nm) of metal (gold) is required to be deposited on the sample. The uniformity of the coating along the sample length, however, affects the measured behavior significantly. Any variations of coating thickness can cause variations of local electrical resistance and thus
variations of local heat generation, even for constant current. For example, inside a plasma sputter coater, the coating thickness may vary from the center to the edge or from one side to the other on the fiber, resulting in a local resistance difference on a coated sample.

To evaluate the effect of non-uniform heating, two distributions of coating thickness (resistance/unit length) were studied: (1) the resistivity changes parabolically from sample center to edge; (2) the resistivity varies linearly from one side of the sample to the other. The overall resistance of the sample is computed from the integration over the length of the sample.

2.6 Results and discussion

2.6.1 Radiation heat loss

Neglecting non-constant heating and convection effects, Figures 2.2 and 2.3 present percentage error of the fit $k$ and $\alpha$ from the numerical temperature profile with respect to dimensionless variable $\xi$ (Equation 2.14) when the temperature rise is $\sim$0.1 K. All parameters found in $\xi$ were changed by different materials and studies. For both $k$ and $\alpha$, using the simplified models infers an error linearly proportional to $\xi$. If the

![Fig. 2.2: Numerical results for the effect of radiation heat loss on measured thermal conductivity shown as the percentage deviation of values calculated by different models from true values. The legend shows varied parameter and modeled material. Lines have been drawn to show the trends. Marked $\xi$ values represent values used to study nonlinear effects in Figure 2.6.](image-url)
Fig. 2.3: Radiation effect on thermal diffusivity - per cent deviation of measured from true values. Platinum wires, carbon fibers and spider silk were used under different models (Exploitation of the linear behavior of this error relationship is detailed in Section 5.1).

Fig. 2.4: Variation of steady-state average temperature rise with respect to the effect of radiation heat loss.
reduced model (Equation 2.11 for \( k \) and Equation 2.12 for \( \alpha \)) is used, the resulting error in each case has a slope of around 10 (the fitted slope is 9.95 for \( k \) and 10.28 for \( \alpha \)). When the full model is used (equations 2.6 and 2.7), nearly zero error is obtained for the whole range demonstrating the improved accuracy of the model. Additionally, Figure 2.2 shows the result of using Equation 2.9 for calculating \( k \), resulting in error between the full and reduced models.

The results from Figures 2.2 and 2.3 are instructive when considering sample preparation. The effect of radiation loss is a function of both thermal and geometric parameters. Radiation heat loss can be lessened by reducing the length-to-diameter aspect ratio. However, care must be exercised to not violate the assumption of negligible radial temperature gradients (1D axial). This could be checked using a simple Biot number calculation where \( Bi = (h_r + h_c)D/(4k) \) (internal conduction resistance to external heat transfer resistance) should be \( \ll 1 \) to meet this requirement. From \( \xi \), the radiation effect is more sensitive to length than diameter. These results also show that a small ratio of \( \epsilon \) to \( k \) is favorable for neglecting radiation losses.

Figure 2.4 presents the ratio of steady-state average temperature rise with radiation effect to that without radiation effect with respect to dimensionless \( \xi \) when the parameters and materials used in Figures 2.2 and 2.3 are studied parametrically. The result illustrates why \( k \) is artificially higher when calculated from the reduced model. Radiation loss decreases the steady-state temperature rise creating the effect of a lower

![Normalized transient average temperature change](image)

Fig. 2.5: Normalized transient average temperature change with respect to dimensionless time when the radiation influence is different.
Fig. 2.6: Contribution of nonlinear radiation effects (using the numerical model) to the calculated error for three values of $\xi$ marked in Figure 2.2, plotted as the ratio of average sample temperature rise to ambient temperature. $\Delta T/T_0 = 0$ represents the results from the linear models as shown in Figure 2.2. Results for thermal conductivity and thermal diffusivity are shown. All parameters in $\xi$ were varied in these results.

Fig. 2.7: Non-constant heating effect on thermal conductivity - per cent deviation of measured from true values. Platinum wires, carbon fibers, and spider silk were used under different models.
Figure 2.8: Non-constant heating effect on thermal diffusivity - per cent deviation of measured from true values. Platinum wires, carbon fibers, and spider silk were used under different models.

sample resistance change \((R_1 - R_0)\) and thus a higher \(k\) (Equation 2.9) for the reduced model.

Figure 2.5 presents the normalized transient average temperature rise, \(\frac{\Delta T}{\Delta T_s}\), with respect to dimensionless time, \(Fo\), where \(\xi\) is varied for each curve. With the help of \(Fo\) and under the assumptions of the reduced model \((\xi = 0)\), all materials and geometries result in the same relationship. With an increase of \(\xi\), the time to reach steady-state conditions becomes shorter. Using the reduced model, Equation 2.12, then results in a fit \(\alpha\) that is larger than its true value.

Although convection heat losses were not directly addressed in this study, as mentioned in section 2.5.1, the radiation heat transfer coefficient, \(h_r = 4T_0^3 \varepsilon \sigma\), in Equation 2.14 could be replaced with \(h_c\). The effects of convection heat losses would result in the same relationship shown in Figure 2.2 for dimensionless \(\xi\).

The \(\Delta T_s\) in the aforementioned results is maintained small relative to \(T_0\), so the linearized radiation heat transfer coefficient is a valid approximation. Figure 2.6 presents the additional error contribution of nonlinear radiation heat losses as \(\Delta T_s\) increases. In this figure, three \(\xi\) values were selected to represent a range of values. For each \(\xi\) value, all independent variables were changed to reach different steady-state average temperature rises \((\Delta T_s)\). The errors of the calculated \(k\) and \(\alpha\) found from the results of the nonlinear numerical model were then plotted with respect to the ratio of the average sample temperature rise to the reference temperature \((T_0)\). In this figure, \(\Delta T_s/T_0 \approx 0\) represents the error from the linear models corresponding to those shown in Figure 2.2. Increasing \(\Delta T_s/T_0\) results in increasing error.
The sensitivity (slope) of measurement error to nonlinear radiation effects is greater for large $\xi$. Smaller $\xi$ results in a smaller gradient of additional error with respect to $\Delta T/T_0$ and vice-versa. For measuring $k$, the error profiles from the reduced and full models have the same gradient for the same $\xi$. Fitted $\alpha$ does not show the same relationship between the full and reduced models, but the reduced model results in greater error for a given $\Delta T/T_0$. These results provide guidance for error from nonlinear radiation effects related directly to the average temperature rise in the sample, whereas the previous linear results (Figure 2.2) have no dependence on the average temperature rise.

Figure 2.6 indicates that with the same average temperature rise, $\Delta T_s$, the nonlinear radiation contribution is more significant with lower $T_0$, implying that low environmental temperature might render larger systematic uncertainty (see section 3.2). It is only partially applicable for the full model because $\xi$ will be significantly reduced ($T_0^3$ in $h_r$), which causes lower deviation. With a decrease of $T_0$, the linear radiation contribution from Figure 2.2 is reduced significantly for the reduced model, making it more appropriate for the cryogenic temperature.

### 2.6.2 Non-constant heating

Figures 2.7 and 2.8 present the percentage error of the calculated $k$ and $\alpha$, respectively, versus the non-dimensional variable $\gamma$ (Equation 2.15). Similar to the radiation effect, the result of using a simplified model to fit the resulting transient and steady-state average temperature changes is a linear relationship of error with respect to $\gamma$. The slope of the error is around -10 (the fitted slope is -10 for $k$ and -10.25 for $\alpha$). The full model again provides the result of nearly zero error. Using Equation 2.8 for determining $k$, results in an overestimation of the sample thermal conductivity.

Figure 2.9 presents the ratio of steady-state average temperature change with variable heating to that with constant heating with respect to $\gamma$ when parameters and materials used in Figures 2.7 and 2.8 are studied parametrically. Figure 2.10 plots the normalized average temperature rise, $\Delta T/\Delta T_s$, with respect to Fourier number, $Fo$. The results are again similar to Figures 2.4 and 2.5, but with opposite trends. With an increase of $\gamma$, the steady-state average temperature and the time to reach steady-state become larger, which explain the phenomena shown in Figures 2.7 and 2.8. The reduced model then under-predicts the heat input in the calculated $k$ and $\alpha$, causing negative error. If the sample has a negative $\alpha_T$ (such as carbon fiber), the effects are opposite resulting in positive error.

Similar to the radiation effect, a larger thermal conductivity material causes lower error when keeping other parameters the same. The measurement is more sensitive to diameter than length in regard to the
Fig. 2.9: Variation of steady-state temperature rise with respect to the non-constant heating effect.

Fig. 2.10: Normalized transient average temperature change with respect to dimensionless time when the heat generation is non-constant.
Fig. 2.11: Comparison of normalized steady-state temperature distribution for different non-uniform heating conditions (linear and parabolic spatial variation of electrical resistance).

Fig. 2.12: The effect of non-uniform heating on calculated thermal conductivity and diffusivity shown as the per cent deviation of values calculated from the numerically calculated temperature distributions from the true values. Results are shown for linear and parabolic spatial variation of electrical resistance.
2.6.3 Non-uniform heating

Figure 2.11 shows the numerically calculated temperature profiles in the sample resulting from non-uniform resistance in the sample as from a sample that has an uneven conductor coating distribution. The temperature field through the sample is greatly influenced by the coating. For the linearly distributed case, the maximum temperature shifts towards the side of larger resistivity. However, the average temperature evolution is nearly the same as for the uniformly distributed coating. To separate the non-uniform heating effect, the radiation heat loss and non-constant heating effects were not considered in the models. Figure 2.12 shows that the $k$ and $\alpha$ calculated with these profiles have no error because of the averaging effect of the integration on temperature distribution.

For the parabolically distributed case, the shape of the temperature profile becomes wider or narrower depending on whether the resistivity distribution is concave upward ($\rho_{e, center}/\rho_{e, side} < 1$) or concave downward ($\rho_{e, center}/\rho_{e, side} > 1$). If $\rho_{e, center}/\rho_{e, side} > 1$, the calculated $k$ and $\alpha$ are less than the true values. The opposite is true for concave upward, because averaging the resulting temperature profile does not give the same result as for uniform heating. Figure 2.12 also shows that compared to $\alpha$, $k$ is more sensitive to a parabolic heating distribution. If the two ends have less coating (concave upward), the measured result has more significant bias error. The only way to reduce this type of systematic error is to ensure coating uniformity.

2.7 Summary and conclusions

A full theoretical model of the TET method has been derived in detail to include the effects of linearized radiation heat transfer and non-constant heating caused by temperature induced change of electrical resistance (both neglected in the reduced model). Using the flexibility of a numerical model, parametric studies were performed to quantify radiation (and convection), non-constant heating, and non-uniform heating conditions in the TET technique with the theoretical models.

Dimensionless parameters representing radiation heat losses, $\xi = 16\varepsilon\sigma T_0^3 L^2 D^{-2} k^{-1}$, and non-constant heating, $\gamma = 4I^2 R L \pi^{-1} D^{-2} k^{-1}$, may be used with the figures in this work to estimate the error introduced in the measurement when using the reduced model for data extraction. Because radiation and resistance are modeled as linear effects of temperature, results show a linear relationship between measurement error and the dimensionless parameters. Under the assumption of linearized radiation (small $\Delta T_s/T_0$), the magnitude of radiation heat loss is not dependent on the sample’s average temperature rise but on its geometry, material properties and ambient temperature. The nonlinear radiation effects caused by large $\Delta T_s/T_0$ have
been quantified for a range of values of $\xi$. Generally, smaller $\xi$ provides a lower sensitivity to $\Delta T_s/T_0$. In the case of electrically non-conductive samples requiring a thin conductive coating for measurement, nonuniform heating introduced by coating non-uniformities can affect measurement results significantly.

For small values of $\xi$ and $\gamma$, the reduced model can be used to extract $k$ and $\alpha$. Otherwise, the full model should be used with the disadvantage of extra parameter dependencies. A comparison of these numerical results with experiment will be performed in a following work.
References


CHAPTER 3
BRIDGE BETWEEN TET AND $3\omega$ PAPERS

Further explanations of procedures and considerations to obtain accurate and reliable measurements by the TET are included in other publications ([1,2]), but this chapter will focus on several of the most relevant. These present practical considerations of sample preparation, data reduction, annealing, convection effects, model selection, initial resistance $R_0$ determination, non-linear radiation effects, experimental exploration of non-constant heating, and coating thickness. The TET is then calibrated with both platinum wires and gold-coated glass fibers (previous TET developments in the literature [3] validated only with conductive fibers), with a measurement error of $\sim 7\%$ and $\sim 4\%$ for the thermal conductivity and thermal diffusivity, respectively.

3.1 Temperature distribution of TET

This chapter also provides a representation of the axial temperature distribution as a function of time for the fiber during a TET measurement (Figure 3.1), as well the shape of a typical normalized transient curve used to curve-fit for thermal diffusivity with the reduced model.

3.2 Platinum validation in cryo

Fig. 3.1: Axial temperature distribution as a function of time (left) with the corresponding average axial temperature (right) showing thermal diffusivity curve-fit.
Attempts were made to extend the TET measurement to cryogenic temperatures, with the intent of understanding the silk as it went through one of its glass transitions [4] and eventually where boundary scattering is observable [5]. To that end, the thermal conductivity and diffusivity of several different platinum wires of 25.4 µm diameter (soldered to heat sinks, pasted to heat sinks, heat sinks placed on a pure copper substrate, and extremely short - ∼1 mm - wire) were measured with the reduced model TET. The results are given in Figure 3.2. The thermal diffusivity measurements of most wires showed good agreement with literature [6], except the short length fiber. The deviation for this fiber is expected to be because the contact resistance to the heat sink was about the same as the fiber, which invalidated the assumption in the model of constant temperature boundaries. The thermal conductivity measurement is particularly sensitive to this resistance effect, which explains how poorly the measured thermal conductivity matches literature values. Furthermore, the reduced model is expected to have greater systematic uncertainties as the environment temperature decreases.

Fig. 3.2: Thermal conductivity (a) and thermal diffusivity (b) of platinum wire by TET at cryogenic temperatures.

To provide the cryogenic environmental temperature, two systems were used: flowing LN₂ through the plate the sample was placed on in the vacuum chamber, and a sterling engine cryocooler with a custom designed sample enclosure on the cold finger (Figure 3.3). These systems are further detailed in [7].

Ultimately, the measurement of the silk at cryogenic temperatures was deemed beyond the scope of the current project.
Convection effect

The previous chapter neglected the effect of convection on the measured thermal conductivity and diffusivity by both the full and reduced models, because of the assumption that the vacuum level was sufficiently low to neglect convection. Section 5.4 of a later publication on the TET [8] demonstrated the effect that the vacuum level has on convection and the property measurement. Figure 3.4 shows error in the diffusivity measurement of a platinum wire in a high vacuum (\(<0.001\) Pa) and poor vacuum (2 Pa) by the reduced model, the full model neglecting convection, and the full model approximating \(h_c\) for convective considerations in the model. The results show that the high vacuum measurements match well with the literature value of platinum, except where the reduced model is used for longer samples, where radiation heat loss begins to become significant. A predicted heat transfer coefficient \(h_c\) near 2 Pa was determined to be \(1.5\) W m\(^{-2}\) K\(^{-1}\), based on the error of the measured values from literature. As expected, neglect of convective heat transfer over-predicts the measured thermal property.

Coating effect

The previous chapter commented on the effect of the uniformity of the gold coating on the error of the property determination (section 2.6.3). This section seeks to expand upon that area by considering in general the contribution of the gold to the effective property of the fiber measured by the TET. The thickness of a uniform coating and its effect on silk is mentioned in a future chapter (section 6.5.1), but the details of that experiment (and one done on a glass fiber) are given here.

Ref. [9] proposes a model based on a parallel thermal resistance to separate the measured property of the fiber from the gold coating effect in Equation 3.1,
Fig. 3.4: The influence of vacuum level on the TET technique presented as percentage error of thermal diffusivity from the reference values of platinum, from [8].

\[ k_f = k_e - \frac{L_{Au}TL}{RA_f} \]  

(3.1)

where \( k_f \) is the thermal conductivity of the fiber. The variables that are measured during a typical experiment are \( k_e \) as the effective measured thermal conductivity of the fiber, \( L \) as the length of the fiber, \( T \) as the temperature, \( R \) as the resistance of the coating, and \( A_f \) as the cross-sectional area of the fiber. The key unknown in this model is the Lorenz number of the gold coating (\( L_{Au} \)), which is not a constant for thin films below a critical thickness of \( \sim 100 \) nm [10] and is larger than the bulk value of \( 2.5 \times 10^{-8} \) W \( \Omega \) K\(^{-2} \) [11]. One study measured \( L_{Au} \) of layers of 6.3 nm thin gold films [12] with the result being that a single film on a silicon substrate has a Lorenz number of \( 7.44 \times 10^{-8} \) W \( \Omega \) K\(^{-2} \). Two other studies [13, 14] measured the Lorenz numbers for 21-37 and 53 nm thick gold films as \( 7.0 \times 10^{-8} \) W \( \Omega \) K\(^{-2} \) and \( 5.0 \times 10^{-8} \) W \( \Omega \) K\(^{-2} \), respectively. It is then expected that \( L_{Au} \) for a 10-20 nm gold coating on spider silk or glass fiber should be between 5.0-7.44 \( \times 10^{-8} \) W \( \Omega \) K\(^{-2} \) for use in Eq. 3.1. Figure 3.5 presents these results when using the data in Table 6.1 at steady state (the results using initial resistance are not appreciably different) and a range of \( L_{Au} \), including the bulk value. No trend can be observed in the calculated fiber \( k_f \), and for the expected film values of \( L_{Au} \), the average calculated thermal conductivity is negative. Because the model assumes uniformity of the gold
coating and the significant variation in the resistances of fibers of similar lengths suggests non-uniformity of the film on the fibers, it cannot be applied to determine the effect of the coating.

To resolve this, the effect of the gold film thickness was then determined experimentally. Figure 3.6 shows the measured thermal conductivity, thermal diffusivity, and initial resistance for gold-coated spider silk and glass fibers after multiple coatings. The same sample was tested first with a 10 nm coating, and was then tested again in identical conditions after two separate additional coatings of 5 nm were performed (15 nm and 20 nm total thickness). It is expected that a thicker coating should increase the effective property of the fiber, but the thermal properties vary within about 5% of the value of the 10 nm film. This variation is within the precision uncertainty of the measurement technique (\(~7\%)\), suggesting that the effect of the coating can be neglected for the spider silk (3 µm diameter) and glass fiber (124.5 µm diameter).

### 3.4.1 Annealing effect

The greatest concern of the film appears to be the tendency of the resistance of the gold coating to change over time, which can affect the property measurement. The solution to this behavior is annealing of the coated fibers for a period of time. Annealing the coating on the fiber causes a reduction and stabilization of the measured resistance, which allows for proper calibration of the temperature-resistance relationship and confidence that the resistance of the coating will not decrease during the operation of a measurement. The effect of annealing on the different measurement parameters is given in Figure 3.7, and shows that there is little variation of the quantities of interest after 12 days of annealing near 100 °C.

### 3.5 Silver paste effect

To investigate the role of the silver paste on the thermal property measurement, a COMSOL model was developed based on the reduced model. The results are still applicable to the full model because the boundary conditions (except for the radial heat losses) are the same. The boundary conditions investigated are presented in Figure 3.8, with the wire embedded inside the silver paste. Electrical and thermal properties for the simulation were based on values provided by the silver paste manufacturer and for a platinum wire. The current flux was selected to provide a typical (1–2 mA) current load through the platinum wire. The axial temperature distribution along the exposed portion of the wire was then averaged at each time step and the normalized, transient, average temperature rise was then used to perform the curve fit to obtain the thermal diffusivity of the platinum wire. The resulting thermal diffusivity with a simulated embedded wire (2.51387 × 10\(^{-5}\) m\(^2\) s\(^{-1}\)) was compared to the thermal diffusivity of the wire without silver paste (2.51355 × 10\(^{-5}\) m\(^2\) s\(^{-1}\)), with the difference being negligible. However, for a thermal conductivity measurement, the low
Fig. 3.5: Application of Eq. 3.1 to determine actual fiber $k$, assuming the thermal conductivity of spider silk by the full model is the effective conductivity of the fiber.

Fig. 3.6: Effect of coating thickness on the measured properties of the coated samples. Data are normalized by values for 10 nm coating thickness, from [2, 8].
Fig. 3.7: Stabilizing effect of annealing on the resistance measured during the TET experiment, from [1].

Fig. 3.8: Boundary conditions for COMSOL model to investigate effect of silver paste on constant temperature boundary condition.
electrical resistance of the platinum wire being on the same order of magnitude as the silver paste resulted in significant errors on the measured thermal conductivity of the platinum. This matches experimental observations on the platinum. Because the resistance of the coating is orders of magnitude higher than the silver paste resistance, this effect is not observed, which is also consistent with the experimental results of the glass fiber thermal conductivity (Table 11.2).

3.6 TET considerations

This section outlines some of the benefits and shortcomings of the TET method, summarized in Table 3.1.

Table 3.1: Benefits and shortcomings of the TET method.

<table>
<thead>
<tr>
<th>Benefits</th>
<th>Shortcomings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Get $k$ and $\alpha$ for known geometry</td>
<td>Long lead time for fiber measurement (~1 month)</td>
</tr>
<tr>
<td>Get $\alpha$ for unknown geometry</td>
<td>Contact resistance for low resistance fibers</td>
</tr>
<tr>
<td>Simple measurement procedure</td>
<td>High fiber breaking potential</td>
</tr>
<tr>
<td>Same samples can be used for TET and $3\omega$</td>
<td>Requires linear calibration of $R'$</td>
</tr>
<tr>
<td></td>
<td>Detectable rise time limited by equipment</td>
</tr>
<tr>
<td></td>
<td>Need for thin coating on non-conductive fibers</td>
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References


CHAPTER 4
THERMAL PROPERTY CHARACTERIZATION OF FINE FIBERS BY THE 3ω TECHNIQUE

This chapter is based on a paper published in Applied Thermal Engineering, 71, dx.doi.org/10.1016/j.applthermaleng.2014.06.022 with the original author list being: Changhu Xing, Colby Jensen, Troy Munro, Benjamin White, Heng Ban, and Mihai Chirtoc. My contribution to this work was aiding in derivation of the models, setup of equipment for 3ω method, data analysis, and document preparation.

4.1 Abstract

The 3ω method is one of few reliable measurement techniques for thermal characterization of micro to nanoscale suspended wires or fibers and has been applied for measurements of carbon nanotubes and silicon nanowires. However, the models described in the past were either complicated for analysis or simplified from a more complete solution. In addition, the past models cannot be implemented directly when using a more reliable measurement configuration with a Wheatstone bridge. In this work, a simpler, explicit model, is developed to describe the heat transfer process through a suspended wire for measurement of its thermal properties. Generic trends and values of the 3ω harmonic voltage amplitude and phase responses clearly indicate the frequency limits for thermal conductivity and heat capacity determination and ideal conditions for thermal diffusivity estimation. Based on a sensitivity analysis, these limits are confirmed and appropriate frequency ranges for thermal conductivity and diffusivity are recommended. Radiation influence on the measurement results is quantified and correlated to a dimensionless radiation parameter. Two methods are presented to determine sample thermal properties independent of lateral heat losses and validated by numerical experiments using COMSOL. Uncertainty analysis is also carried out by Taylor series expansion with calculated parameter sensitivities.

4.2 Introduction

The commonly used configuration of the 3ω method is the heater-on-substrate system [1, 2], in which a thin metal strip is evaporated on a sample surface, acting as both a heater and resistive thermometer. An alternating current (AC), at frequency 1ω, passes through the heater, inducing a temperature change which propagates into the substrate at a frequency of 2ω. By monitoring the voltage response due to the change of resistance with temperature at the third harmonic frequency (3ω), the thermal conductivity can be determined.
With an additional direct current (DC) offset, thermal property information can be obtained from $1\omega$ or $2\omega$ as well, as detailed in Refs. [3, 4]. However, as was concluded in Ref. [3], the $3\omega$ measurement is generally the best choice for extracting thermal properties.

Several models have been presented in the literature for temperature profiles in a suspended wire heated by AC current [4]. Many of these models were intended for modeling the thin wire probe used in scanning thermal microscopy (SThM), where the application is for thermal property measurement of a substrate contacting the probe apex. The $3\omega$ method may also be applied to obtain the thermal properties of the suspended wire itself, as is detailed in this work. Though having similarities to the SThM probe model, for the suspended wire, the heat transfer model does not include the contact boundary condition required for the probe models. Thus, the probe solutions cannot be applied directly.

The $3\omega$ method has been applied to micro- to nanoscale diameter fine fiber thermal conductivity and heat capacity determinations [5–8]. Lu et al. [6] modeled a suspended wire between two heat sinks arriving at a series solution using the impulse theorem. The final solution, used in other studies [8–10] for carbon nanotubes and silicon nanowire measurements, contains only the first term of the infinite series. Expressions for the thermal conductivity and heat capacity were derived from the voltage amplitude measurement because it contains all desired thermal property information; however, the more reliable phase response, which only provides thermal diffusivity, was never used. Hou et al. [7] simulated the coupled suspended wire and substrate system and rendered a complicated solution including the wire-substrate interaction. As demonstrated in the analysis section, their model does not yield considerably different results from the current model when considering only the wire sample. Modeling only the suspended wire removes the requirement for the unknown thermal contact resistance between sample and substrate, which alters the result significantly if inappropriately estimated.

Previously, the sample radiation influence on thermal property determination was either neglected, or only evaluated on a specific sample with no guiding conclusion reached [7]. In a previous study for the electrothermal measurement for fine fibers [11], the deviation of measured thermal conductivity and diffusivity from the reference values, caused by neglecting radiation influence, was related to a dimensionless radiation parameter. With this relationship, data reduction can be made using the simple model that neglects radiation, and then correcting for its influence in a final step.

The objective of this research is to provide a model for thermal characterization of suspended wires by the $3\omega$ technique and to fully quantify its characteristics. It gives a complete and practical approach to measure thermal conductivity and heat capacity of a suspended wire. Radiation influence is evaluated
in terms of the dimensionless radiation parameter. Some practical aspects regarding constant current and constant voltage sources are presented. A methodology is presented by which thermal properties may be obtained independent of sample length (lateral heat losses). Finally, a sensitivity analysis is presented for each measured thermal property.

4.3 Theoretical model

4.3.1 Constant current source

The fin-shaped (where radial heat losses are modeled as a boundary conditions perpendicular to the axial heat flow [12]) governing equation presented in this work is similar to those in Refs. [4,13] for Wollaston-wire probes used for SThM but with different boundary condition and application. Fig. 4.1a presents a schematic diagram of the sample setup for the $3\omega$ method. The sample, with a large length ($L$ [m]) to diameter ($D$ [m]) aspect ratio is suspended between two highly thermally conductive heat sinks. A modulated electrical current is passed through the sample (electrically conductive or metal coated, non-conductive fibers) causing a temperature rise ($\Delta T$ [K]) due to the Joule heating effect. The modulated current, $I$ [A] and heat generation, $q''$ [W m$^{-3}$] can be expressed as

$$I = I_0 \cos \omega t,$$

$$q'' = I^2 R(T)/V_s = I_0^2 (1 + \cos 2\omega t) R(T)/(2V_s),$$

where $I_0$ is the current amplitude [A], $\omega$ is the angular frequency [rad s$^{-1}$], $R(T)$ is the instantaneous resistance [$\Omega$] of the sample at temperature $T$ [K] and $V_s$ is the volume [m$^3$] of the sample. The Joule heating contains constant and periodic components. The sample resistance as a function of temperature change can be expressed as

$$R(T) = R_0 + R' \Delta T = R_0 (1 + \alpha_T \Delta T),$$

where $R_0$ is the sample initial resistance [$\Omega$], $R'$ is the calibrated slope of temperature-resistance relationship [$\Omega$ K$^{-1}$] and $\alpha_T$ is temperature coefficient of resistivity [K$^{-1}$].

Even numbers of $\omega$ in Eq. (4.2) induce even number harmonics of temperature rise $\Delta T$. With knowledge of $R'$, sample temperature rise can be monitored by its resistance change. With constant current, the resistance
change is reflected by the monitored voltage $[V]$ of the sample.

$$V_c = IR(T) = I_0 R_0 \cos \omega t + I_0 R' \cos \omega t \cdot \Delta T(2n\omega t), \quad n = 1, 2, \ldots$$ (4.4)

To use Eq. (4.4), the sample temperature change needs to be solved. Due to the large sample aspect ratio, the heat transfer process can be modeled by 1-dimensional (1D) heat conduction with lumped convection/radiation in the radial direction and a volumetric source/heat generation term. In terms of $\Delta T = T - T_0$ where $T_0$ [K] is the environment temperature, the governing equation can be written as

$$\frac{1}{\alpha} \frac{\partial \Delta T}{\partial t} = \frac{\partial^2 \Delta T}{\partial x^2} - \frac{4h_r}{Dk} \Delta T + \frac{I^2 R(T)}{kV_s}$$ (4.5)

where $k$ is thermal conductivity [W m$^{-1}$ K$^{-1}$], $\alpha$ is diffusivity [m$^2$ s$^{-1}$], $h_r \approx 4T_0^3 \varepsilon \sigma$ is the linearized radiative heat transfer coefficient [W m$^{-2}$ K$^{-1}$] through the sample lateral surface, $\varepsilon$ is the emissivity and $\sigma = 5.67 \times 10^{-8}$ W m$^{-2}$ K$^{-4}$ is the Stefan-Boltzmann constant. The measurement should be conducted in...
high vacuum (<0.001 Pa) so that convective heat loss is negligible.

$\Delta T$ can be split into two parts, a constant ($\Delta T_c$) and periodic ($\Delta T_p$) one. The constant part can be used to estimate the sample average temperature rise in the sample. If $\Delta T$ is too large, the constant temperature assumption of the heat sink may be violated due to the contact resistance between sample and heat sinks. The periodic portion, directly correlated to the periodic voltage change in the wire, is used to extract thermal properties of the sample.

For the constant part, the governing equation is

$$\frac{1}{\alpha} \frac{\partial \Delta T_c}{\partial t} = \frac{\partial^2 \Delta T_c}{\partial x^2} - \left[ \frac{4h_r}{Dk} - \frac{I_0^2 R'}{2kV_s} \right] \Delta T_c + \frac{I_0^2 R_0}{2kV_s} \tag{4.6}$$

The steady state average temperature change caused by the constant part of heat generation is

$$\Delta T_c = \frac{I_0^2 R_0}{2V_s kH_2^2} \left[ 1 - 2 \cosh(LH_e) - \frac{LH_e}{2} \sinh(LH_e) \right] \tag{4.7}$$

where $H_2^2 = \frac{4h_r}{(Dk)} - \frac{I_0^2 R'}{(2kV_s)}$.

For the periodic heating component, the temperature-dependent resistance couples with the modulated current and generates infinite harmonics (due to the $\Delta T(2n\omega t)$ term in Equation 4.4 and $R'\Delta T$ term in Equation 4.3). Solutions accounting for the harmonic coupling can be found in Refs. [14–16]. However, for small heating, the resistance change is significantly smaller than the initial sample resistance, thus justifying the neglect of harmonic coupling [4]. In addition, harmonics larger than two have little influence on the temperature and are neglected as well. The governing equation can be rewritten in terms of exponential functions. For instance, $\cos 2\omega t = 0.5(e^{i2\omega t} + e^{-i2\omega t})$. For the $2\omega t$, Eq. (4.5) is expressed as

$$\frac{\partial \Delta T_p}{\partial x} - \left[ \frac{i2\omega}{\alpha} + \frac{4h_r}{Dk} - \frac{I_0^2 R_0}{2kV_s} \right] \Delta T_p = -\frac{I_0^2 R_0}{4kV_s} \tag{4.8}$$

Note that the contribution from DC heating, $-\frac{I_0^2 R'\Delta T_c}{(4kV_s)}$ on the right hand side of Eq. (4.8) was neglected.

The average temperature oscillation change in terms of $\exp(i2\omega t)$ is

$$\overline{\Delta T_p} = \frac{I_0^2 R_0 \left[ 2 - 2 \cosh(mL) + mL \sinh(mL) \right]}{m^2 L^2 k \pi D^2 \sinh(mL)} \tag{4.9}$$

where $m^2 = \frac{i2\omega}{\alpha} + \frac{4h_r}{(Dk)} - \frac{I_0^2 R'}{(2kV_s)}$. 

In experiments, the temperature rise is usually maintained small, so the last term in $m^2$ is negligible. Radiation contribution is dependent on material properties and geometry and will be quantified in the next section.

For the $-i2\omega t$ component of the periodic expression above, the average temperature change is the conjugate of $\Delta T_p$.

The sample voltage change, Eq. (4.4), has the 1st and 3rd harmonic components. This is the basis for the use of 1$\omega$ in literature [3]. However, the 1st harmonic response is strongly influenced by the sample initial resistance and has large uncertainty in application (examining the resistance change (O(-3) of $R_0$) from $R_0$) while the 3rd harmonic has better signal to noise ratio (resistance change is excluded from the final expression). The voltage of the 3rd harmonic, $V_3$ [V], comprised of contributions from $\pm 3\omega$, is expressed as

$$V_3 = \frac{I_0^3 R_0 R' L}{i 2 \omega \rho c_p \pi D^2 L} \left[ 2 - 2 \cosh(mL) + mL \sinh(mL) \right] \left[ k \pi D^2 (mL)^3 \sinh(mL) \right] (4.10)$$

The voltage amplitude is the modulus of $V_3$ and phase, $\phi$, is determined by the angle of imaginary and real parts.

Similar to the analysis by Lu et al. [6], Eq. (4.10) has a low and high frequency limit considering radiation contribution later. The limits are derived by rewriting Eq. (4.10) in infinite series form. At low frequencies, the $mL$ dependent terms are negligible and Eq. (4.10) becomes

$$V_3 = \frac{I_0^3 R_0 R' L}{12 k \pi D^2} (4.11)$$

At low frequencies, the voltage is independent of sample diffusivity and, consequently, a function of sample thermal conductivity only. Correspondingly, the phase is zero at the low limit. Eq. (4.11) is a complete solution but slightly different from the expression presented by Lu et al. [6].

At high frequencies (the infinite $mL$ term is dominant), Eq. (4.10) is reduced to

$$V_3 = \frac{I_0^3 R_0 R' L}{i 2 \omega \rho c_p \pi D^2 L} \left[ 2 - 2 \cosh(mL) + mL \sinh(mL) \right] (4.12)$$

where $\rho c_p$ is the volumetric heat capacity [J m$^{-3}$K$^{-1}$] and $\rho$ [kg m$^{-3}$] is the density and $c_p$ [J kg$^{-1}$ K$^{-1}$] is the heat capacity.

Although Eq. (4.12) is only a function of heat capacity, in order to apply this limit with reasonable uncertainty, the frequency needs to be sufficiently large. At high frequency, the voltage amplitude becomes very low (decreasing exponentially with frequency), thus becoming susceptible to the influence of system
noise (especially if the 1st harmonic is not canceled out). Therefore, special care is required for application of this limit. At the high frequency limit, the phase is -90° (positive \( R' \)). The magnitude of Eq. (4.12) has the same expression given by Lu et al. [6].

The first approach to determine material thermal properties is to use the amplitude as it contains all property information of interest. Eqs. (4.11) and (4.12) require only one measurement point if frequency requirements are met. If amplitude is measured over a range of frequencies, the \( k \) and \( \rho c_p \) may be obtained simultaneously by fitting Eq. (4.10) to middle range frequencies. Because the fitting is with two parameters and they are correlated to some extent, the measurement accuracy may not be as good as using Eqs. (4.11) and (4.12) independently (with curve fits on experimental data for \( k \) and \( \rho c_p \) shown in Figure 5.3 in Section 5.6 and Ref. [17]).

The second approach in determining the thermal conductivity and diffusivity is to use amplitude and phase independently. Eq. (4.10) indicates that if radiation is negligible or considered later, the phase is independent of sample thermal conductivity, making it a function of thermal diffusivity only. Thus, diffusivity and conductivity can be obtained independently from the phase response in Eq. (4.10) and amplitude in Eq. (4.11) respectively. If the frequency required in Eq. (4.11) is very low, requiring a long time to reach steady state, the diffusivity determined from the phase response of Eq. (4.10) can be applied to the amplitude response for thermal conductivity determination at higher frequencies.

The two approaches can be combined together to obtain thermal conductivity, diffusivity, and heat capacity independently to improve measurement accuracy and provide some additional validation. Direct determination of thermal properties avoids the propagation of uncertainties when calculating an unknown from two known properties.

### 4.3.2 Direct measurement

If a voltage source (e.g. lock-in output) is used in a measurement, Fig. 4.1b, the amplitude (\( L_0 \)) of the current, synchronous to the supply voltage, is not a constant but a function of \( \Delta T \). The current based on the voltage amplitude, \( V_0 \) can be expressed as

\[
L_i = \frac{V_0}{R_b + R(T)} = \frac{V_0}{R_b + R_0} \left[ \frac{V_0 R' \Delta T}{(R_b + R(T))^2} \right] + \cdots \\
\approx \frac{V_0}{R_b + R(T)} \left( 1 - \frac{R' \Delta T}{R_b + R_0} \right) = I_0 \left( 1 - \frac{R' \Delta T}{R_b + R_0} \right) \tag{4.13}
\]

where \( R_b \) is the balance resistance of \( R_0 \) in the circuit. Eq. (4.13) includes only the first two terms.
of the expansion since the magnitudes of other harmonics ($\Delta T$ terms) are negligibly small. For the heat generation term, the $\Delta T$ dependent term may also be neglected due to low temperature rise. Using the $I_0$ of the voltage source (constant amplitude), the expressions of the average temperature change in terms of the second harmonic are the same as those of the constant current source, making Eq. (4.9) applicable for the voltage source. However, the monitored 3rd harmonic voltage is slightly different from Eq. (4.10) because the current amplitude in Eq. (4.13) has a second harmonic term coupling to the first term in Eq. (4.4). Instead of $I(t)R'\Delta T$ for a constant current source, the measured sample 3rd harmonic voltage response is expressed as $V_{3v} = I_0R'\Delta T[1 - R_0/(R_0 + R_b)]\cos(\omega t)$ for the voltage source. To use Eq. (4.10) for thermal characterization, the measured $V_{3v}$ has to be converted to $V_3$.

$$V_3 = \frac{R_0 + R_b}{R_b}V_{3v}$$

(4.14)

The voltage source cannot be connected directly to the sample like Fig. 4.1a. Without a $R_b$, $V_{3v} = 0$. For this configuration, the voltage relationship between current source and voltage source is in agreement with that in Ref. [3]. However, there is no advantage using this configuration compared to the current source.

### 4.3.3 Wheatstone bridge

The voltage source with a Wheatstone bridge is presented in Fig. 4.1c. In this configuration, the voltage of the bridge, $V_b$, is monitored by the lock-in amplifier. The sample 3rd harmonic voltage $V_3$ used in Eq. (4.10), needs to be converted from $V_b$. The voltage of the bridge is a function of the supply voltage, $V_0$, and the relationship of the resistors, $V_b = V_0[\frac{R_0}{(R_0 + R_b)} - \frac{R_2}{(R_1 + R_2)}]$. With the Joule heating, the bridge voltage can be expressed as

$$V_b = I_v\cos(\omega t)(R_0 + R'\Delta T) - V_0\frac{R_2}{(R_1 + R_2)}$$

$$= I_0R'\Delta TR_b/(R_0 + R_b)\cos\omega t = V_{3v}$$

(4.15)

Similarly, $V_3 = V_b(R_0 + R_b)/R_b$ for Eq. (4.10) when determining thermal properties as was shown in Ref. [4].

For the voltage source, if the balance resistance is much larger, $R_b \gg R_0$, the voltage, $V_b$, can be used directly for thermal property calculation. If $R_b$ is equivalent to or smaller than $R_0$, the expression in Eq. (4.15) may be violated due to the neglected terms in Eq. (4.13).
4.3.4 Quantification of radiation induced bias error

Theoretical error analysis

Eq. (4.11) presents thermal conductivity, neglecting radiation heat loss, in the low frequency limit. Eq. (4.10) however, contains the radiation influence. The percentage error of measured thermal conductivity, \( e_{k, rad} \), caused by the radiation heat loss, can be calculated by comparing Eqs. (4.10) and (4.11).

\[
e_{k, rad} = \frac{(m^3L^3 - 12mL) \sinh(mL) - 24 + 24 \cosh(mL)}{24 - 24 \cosh(mL) + 12mL \sinh(mL)}
\] (4.16)

Eq. (4.16) can be rewritten in infinite series form. In the low frequency range, where \( m \) is only radiation dependent (reduced to \( H_e \)), by neglecting \( O(m^6L^6) \), Eq. (4.16) can be simplified to

\[
e_{k, rad} = m^2L^2 \left( 1 - \frac{m^2L^2}{8400} \right)
\] (4.17)

Since frequency and temperature rise are negligible, \( m \) is dependent on radiation effects only. If \( m^2L^2 \) < 10, which corresponds to less than \( \sim 100\% \) error of the thermal conductivity by radiation, the expression \( e_{k, rad} = 0.1m^2L^2 \) is accurate enough (0.1 vs. 0.099) to estimate the error.

In the high frequency limit, the \( mL \) term is dominant. In order to have a dominant \( m \), \( i2\omega/\alpha \gg 4h_e/(Dk) \). For this situation, the radiation influence is negligible in the \( \rho c_p \) calculation by Eq. (4.12). Similar direct quantification of radiation influence on thermal diffusivity is not feasible due to implicit functional dependency. Since \( \alpha = k/\rho c_p \), \( \alpha \) should be influenced in a similar manner as \( k \) by radiation.

Experimental data reduction

By measuring the same sample with different lengths, the influence of radiation heat losses can be shown. If the radiation induced error is not too great (within several hundred percent), a linear fit can be made on the measured thermal conductivity or diffusivity values with respect to the square of sample length (\( L^2 \)). The intercept represents the thermal properties at infinitesimal length where radiation influence in the \( H_e \) or \( mL \) term becomes negligible. This process is supported by Eq. (4.17).

If radiation influence is sufficiently large such that Eq. (4.17) deviates from Eq. (4.16), regression should be used to estimate thermal conductivity (Eq. (4.10)) or the thermal diffusivity (phase in Eq. (4.10)). Regression from amplitude yields thermal conductivity and emissivity, while from the phase it provides thermal diffusivity and the \( H_e \) term. This method is equivalent to the linear fit in the last paragraph but is
slightly more complicated. As an example, radiative and convective heat losses significantly influence the measured accuracy of the single fibers [18].

4.4 Numerical experiment

To validate the models discussed in Section 4.3, experimental measurements are necessary. However, as an initial validation, a numerical simulation is performed in this work.

To conduct the numerical experiment, a 2-dimensional axisymmetric domain representing a test sample was created in the commercial finite element software, COMSOL (Fig. 4.2). The domain was meshed using rectangular grids with 100 and 10 divisions in the axial and radial directions, respectively. An electrothermal coupled multi-physics analysis was applied inside the domain where property values for platinum [19] were taken. Coupling of the two physics was through the temperature-dependent electrical resistivity (electric module) and heat generation by Joule heating (heat transfer module).

Boundary conditions are shown in Figure 4.2. For the heat transfer side, a constant environmental temperature was applied on the two axial ends and nonlinear radiation was selected on the lateral surface. For the electric boundary conditions, one axial end was set as an electrical ground and the other was set as a distributed current as applied in real experiment (I). Electrical insulation was applied on the sample lateral surface and the axis of symmetry was chosen at the center line for both the electric and heat transfer studies.

The sample voltage response, $V_c$, represented in Eq. (4.4), is reflected from the monitored voltage with time after reaching steady state. To get the third harmonic voltage amplitude and phase, a Fourier transformation of $V_c$ is calculated by integration with respect to the 3rd harmonic functions of sine and cosine over several periods [20]. With the phase and amplitude, thermal diffusivity and conductivity are obtained from Eqs. (4.10) and (4.11), respectively.

Following the discussion in Section 4.3.4, multiple samples with different lengths were simulated. Results from the simulations will be presented in the next section.

4.5 Results and discussions

4.5.1 Generic amplitude and phase responses

Amplitude and phase responses can be determined by Eq. (4.10). The frequency-dependent thermal diffusion length is defined as $L_{th} = \sqrt{\frac{2\alpha}{\omega}}$ [4]. Using a non-dimensional length ratio, $\gamma = L/L_{th}$, as a parameter, the phase and normalized amplitude responses are generic for any material and sample length. [1]
Fig. 4.2: Schematic of the numerical model created in COMSOL with labeled electrical and thermal boundary conditions.

Fig. 4.3a presents the amplitude response normalized to Eq. (4.11) with respect to $\gamma$. It clearly indicates the low frequency limit. If $\gamma < 0.5$, using Eq. (4.11) renders a theoretical error less than 0.5% and if $\gamma < 0.9$, the error is less than 5%. These conditions provide criteria for using the low frequency limit to determine conductivity. The amplitude decreases exponentially with an increase of $\gamma$ because the heat dissipation range is limited by the $L_{th}$.

Fig. 4.3b presents the amplitude normalized to Eq. (4.12) with respect to $\gamma$. Note that Eq. (4.12) is not a constant value but changes with $\gamma$. At low $\gamma$, Eq. (4.12) renders much larger amplitude than that by Eq. (4.10), thus the normalized amplitude is close to zero. With an increase of $\gamma$, amplitudes from Eq. (4.12) approaches that from Eq. (4.10). Different from the low frequency limit, the error caused by using Eq. (4.12) to get $\rho c_p$ decreases slowly as $\gamma \rightarrow \infty$ ($\gamma = 141.2$) to reach 0.5% uncertainty. For 95% accuracy, however, the high frequency limit ($\gamma = 13.8$) is relatively easy to achieve.

Fig. 4.3c presents the phase response with respect to $\gamma$. The phase is bounded by zero and $-90^\circ$, representing the low and high frequency limits. For 99.5% accuracy, the phases corresponding to the two limits are $-5.7^\circ$ and $-89.7^\circ$ and for 95% accuracy, they are $-18^\circ$ and $-86.9^\circ$ respectively. For an unknown sample measurement, $\gamma$ is unknown in advance. However, the phase is generic for any sample. With the observation of the phase, the satisfaction of low and high frequency limits can be judged. The results of Fig. 4.3 show the typical characteristics of a low pass filter. Similar trends are shown in Ref. [4].
Fig. 4.3: Comparison of $3\omega$ voltage amplitude and phase responses with respect to the ratio of sample length to thermal diffusion length: a) amplitude is normalized by the low frequency limit, b) amplitude is normalized by the high frequency limit, c) phase is mostly influenced by sample thermal diffusivity.
4.5.2 Radiation effect on amplitude and phase response

Eq. (4.10) contains the contribution from radiation heat losses. The influence of radiation on amplitude and phase is demonstrated in Fig. 4.3. A dimensionless parameter $\xi = H_e L^2$ (when temperature rise is low, the 2nd term in $H_e$ is negligible) or $m^2 L^2$ in the low frequency range can be defined to quantify the radiation effect. With an increase of $\xi$, Fig. 4.3a, the amplitude in the range $\gamma < 2$ tends to decrease. Since $k$ is inversely proportional to amplitude (Eqs. (4.10) and (4.11)), the measured $k$ increases with $\xi$. In Fig. 4.3b, the decrease of amplitude is also clearly seen. The amplitude at high $\gamma$, however, is affected little. Therefore, the determination of $\rho c_p$ using Eq. (4.12) is not affected by radiation.

Fig. 4.3c presents the radiation influence on the phase response. In the middle range of $\gamma$, the phase tends toward zero (moving upward) with the increase of $\xi$. Evaluation of diffusivity with this phase results in a positive error using the model neglecting radiation.

4.5.3 Thermal properties from numerical experiment

The determined thermal conductivities and diffusivities for a set of platinum wires with 2.5 $\mu$m diameter and different lengths, using the model neglecting radiation influence, are presented in Fig. 4.4 with respect to the square of length ($L^2$). As mentioned in Section 4.4, the voltage amplitude and phase were obtained from the numerical experiment by COMSOL.

A linear regression was used to fit the measured thermal properties. The y-intercepts representing values
at “zero” length are 71.8 W m$^{-1}$ K$^{-1}$ and 2.5 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ respectively, both close to the input values, 71.6 W m$^{-1}$ K$^{-1}$ and 2.51 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$, respectively. This figure demonstrates the accuracy of the 3$\omega$ measurement. The emissivity of a material varies with surface conditions (e.g. roughness, oxidation, etc.) and can vary greatly for a given material. Therefore, it is typically unknown or has large uncertainties associated with it. To account for this, length dependencies should be carefully considered before reporting the thermal properties of a measured material.

### 4.5.4 Sensitivity analysis on precision error

In any measurement, the bias and precision uncertainties should be considered. For the model neglecting radiation, the radiation contribution from Fig. 4.4 can be used to estimate its induced bias error. For the 3$\omega$ measurement system, however, precision uncertainty needs to be considered further.

In Eq. (4.10), the voltage is dependent on many parameters, including current, amplitude, sample initial resistance, the temperature coefficient of resistance, sample length, diameter, conductivity, and diffusivity. To determine the contribution of each parameter, the relative sensitivity, $S_p = (p/y)(\partial y/\partial p)$, can be defined where $y$ represents thermal conductivity, heat capacity or diffusivity and $p$ represents the parameter of choice. In this way, the sensitivity represents the power of the parameter in the functional dependency, e.g. directly proportional means $S_p = 1$, square root means $S_p = 0.5$, etc.

In the analysis, thermal conductivity and heat capacity are determined from the amplitude response, and thermal diffusivity is obtained from phase responses. Thermal diffusivity is only dependent on $L$ and measured phase. Thermal conductivity depends on the measured amplitude, $I_0$, $R_0$, $R'$, $L$, and $D$, as well as $\alpha$, if outside of the low frequency limit. Volumetric heat capacity is a function of measured amplitude, $I_0$, $R_0$, $R'$, $\omega$, $D$, and $L$ in the high frequency limit. For the explicit parameters, direct derivatives are possible while for the implicit parameters, numerical derivatives are calculated.

As discussed previously, thermal property measurements can be done using either point measurement or by fitting a frequency spectra of data. The advantage of the regression approach is that measurement accuracy can be improved if the data covers the range of $\gamma$ with significant sensitivity. The disadvantage is the longer time required for the measurement. Point measurement is faster and if appropriate $\gamma$ is selected, the measurement uncertainty can be minimized. Uncertainty analysis for the fitting approach may be done using the Monte Carlo stochastic method, while for the explicit formulations, the direct Taylor series method of propagation of uncertainties can be used.

The sensitivities of $k$ to $I_0$, $R_0$, $R'$, $V_3$ and $D$ are 3, 1, 1, -1, and -2 respectively. The sensitivities of $\rho c_p$
to \( I_0, R_0, R', V_3, \omega, D \) and \( L \) are 3, 1, 1, -1, -1, -2, and -1 respectively. These results are seen by looking at the power of each term in Eqs. (4.11) and (4.12). For the implicit parameter in \( k \) and \( \alpha \), the sensitivities are presented in Fig. 4.5. The sensitivity of \( k \) to \( L \) varies from 1 to -1 with \( \gamma \) going from low to high, which is explainable from the two frequency limits demonstrated in Eqs. (4.11) and (4.12). Sensitivity of \( k \) to \( L \) changes sign at \( \gamma \approx 1.6 \). The sensitivity of \( k \) with respect to a plot shows that the uncertainty of \( \alpha \) does not affect the \( k \) measurement at the low frequency limit, which is in accordance with Eq. (4.11). The sensitivity gradually increases to 1, corresponding to Eq. (4.12) \((\rho c_p = k/\alpha)\). These sensitivity studies demonstrate the relationship between Eq. (4.10) and Eq. (4.11) or (4.12).

The sensitivity of \( \alpha \) with respect to phase is acquired by differentiating with respect to degrees instead of percentage change of the measured phase, because at any phase measurement, the system noise would be similar. The uncertainty of phase has minimum influence on \( \alpha \) at \( \gamma \approx 1.6 - 1.7 \) at which the sensitivity is 3.5% per degree uncertainty of phase (0.035 in the figure) and has larger influence at the two limits represented by Eqs. (4.11) and (4.12). The uncertainty of \( L \) has a constant sensitivity of 2 on diffusivity for any \( \gamma \).

Based on the analysis, intermediate values of \( \gamma \) (\( \sim 1.7 \)) corresponding to the phase of \(-49^\circ\) are more appropriate for \( \alpha \) determination by phase and the low frequency limit is better for \( k \) determination by amplitude. For \( \rho c_p \), the parameters are all explicit in the high frequency range.

To evaluate the sensitivity of thermal diffusivity to measured phase when using the fitting approach,
the Monte Carlo method was employed. Eq. (4.10) was used to form a reference data set. Each term in the
data set was randomly perturbed using a normal distribution having a standard deviation of 1° (standard
deviation is half the parameter uncertainty based on a 95.4% confidence level). The diffusivity was obtained
by fitting the perturbed data. This process was repeated 100,000 times (converged after 10,000 iterations).
The sensitivity of $\alpha$ to phase based on fitting process is found to be 0.9% per degree uncertainty of phase, almost $\frac{1}{4}$ of the sensitivity by point evaluation.

With the sensitivities of the properties, the overall uncertainties of the system from Eq. (4.10) can be
evaluated by the Taylor series method for propagation of uncertainty [21] and are expressed as

$$
e_k^2 = S_h^2 e_h^2 + S_R^2 e_R^2 + S_P^2 e_P^2 + S_D^2 e_D^2 + S_L^2 e_L^2 + S_{V_3}^2 e_{V_3}^2 \tag{4.18}
$$

$$
e_{\rho c_p}^2 = S_h^2 e_h^2 + S_R^2 e_R^2 + S_P^2 e_P^2 + S_D^2 e_D^2 + S_L^2 e_L^2 + S_{V_3}^2 e_{V_3}^2 + S_{\omega}^2 e_{\omega}^2 \tag{4.19}
$$

$$
e_{\alpha}^2 = S_L^2 e_L^2 + S_{\alpha}^2 U_{\alpha}^2 \tag{4.20}
$$

where $S_p$ takes the values discussed above for $k$, $\rho c_p$, or $\alpha$ respectively, $e_p$ is the percentage uncertainty
and $U_p$ is the measurement uncertainty of the parameter. The uncertainty analysis will be performed for real
experimental results in a following study.

### 4.6 Conclusions

The modeling of a suspended fiber experiencing modulated Joule heating has been described in detail
for the application of measuring its thermal properties. This model is simpler in form and more accurate than
other modeling approaches found in literature for this application. Implications of voltage vs. current sources
are presented. Data reduction on results from numerical experiments by COMSOL was used to validate the
analytic model.

The power of the 3$\omega$ approach was shown by describing several complementary approaches to determine
thermal conductivity, heat capacity and thermal diffusivity from the same model. The frequency limits for
the property determination can be judged by given generic amplitude and phase plots and are justified with a
sensitivity analysis. Specific limits were quantified for the ratio of sample length to thermal diffusion length,
$\gamma$, to use simplified, explicit formulas for calculation of thermal conductivity (for $< 5\%$ error, $\gamma < 0.9$) and
volumetric heat capacity (for $< 5\%$ error, $\gamma > 13.8$). A Monte Carlo approach showed that fitting thermal
diffusivity to frequency spectrum effectively reduces measurement sensitivity (and uncertainty) to \( \frac{1}{4} \) of the minimum using evaluation from a single point.

Radiation influence on the thermal conductivity and diffusivity measurement was quantified. The contribution of radiation heat losses can be accounted for by two methods: obtaining the intercept for “zero” sample length by fitting the measured thermal properties with respect to the square of lengths or evaluating the percentage error \( e_{k,\text{rad}} \) by regression and dividing \( (1 + e_{k,\text{rad}}) \) from the determined properties.
References


CHAPTER 5
BRIDGE BETWEEN 3ω AND SILK PROPERTIES PAPERS

The previous chapter described the development and application in a numerical experiment of the 3ω method, but neglected any experimental considerations. For details on the experimental application of the 3ω measurement, refer to [1], which calibrates the method by measuring the properties of platinum wires with a current and voltage source, and with and without 1ω canceling, as well as accounting for sample resistance compared to Wheatstone bridge resistance. The measurement uncertainties are then reported as \( \sim 9\% \), \( \sim 4\% \), and \( \sim 11\% \) for thermal conductivity, diffusivity, and volumetric heat capacity, respectively.

5.1 Practical application of TET and 3ω

For ease of application of the TET and 3ω methods, a flow chart was developed to guide experimenters through the process. This flow chart is detailed in Figure 5.1. Preparation of the samples for TET and 3ω are identical, and the flow chart reflects this, providing details on heat sink preparation for rigid or flexible fibers, handling of electrically conductive or non-conductive fibers, and pasting of samples to the heat sinks (further detailed in [2,3]). The selection criteria for 3ω over TET is based on the properties to be determined (\( k, \alpha \) with TET, and potentially \( k, \alpha, \) and \( \rho c_p \) with 3ω) and the rise time to reach steady state (if too quick for TET, near 100 ms, use of 3ω is preferred, but the measurement process is significantly longer). Initiation of Joule heating, as well as radiation considerations are also described. The flow chart mentions the possibility to use the bias error based on radiation heat loss (Figures 2.2 and 2.3), with an error term \( (e_{kb} = 0.1L^2H_e^2) \), to modify the reduced models for improved accuracy. This is expressed in

\[
k = \frac{I^2R_0R'L^2}{12V_s(R_1 - R_0)\left(\frac{1}{1 + e_{kb}}\right)}. \tag{5.1}
\]

\[
\frac{\Delta T}{\Delta T_s} = 1 - \frac{96}{\pi^4} \sum_{m=1}^{\infty} \frac{e^{-(2m-1)^2\pi^2\alpha t/L^2}}{(2m-1)^4} \left(\frac{1}{1 + e_{kb}}\right). \tag{5.2}
\]

5.2 Fiber size limitations

To explore the size limitations of the applicability of the TET (and 3ω) method, several things must be
Fig. 5.1: Flow chart of processes involved in obtaining a reliable measurement via the TET or $3\omega$ methods.
considered. As the fiber diameter reduces, the conductive gold coating contribution to the effective thermal property of the fiber becomes more significant and must be taken into account. Further, for the 1D axial heat flow assumption to be valid, $10D < L$. However, the greatest consideration that limits the applicability of the TET (and $3\omega$) method is the mean free path of the heat carrier.

The biggest consideration to determine the lower bound of the size limitations is when the mean free path ($\Lambda$) of the heat carrier approaches the dimensions of the fiber. This is based on a simple kinematic model, $k = \frac{1}{3} \rho c_p v \Lambda$, where $v$ is the speed of sound of the material, with typical mean free paths for bulk materials ranging from 10 nm – 1000 nm [4] at room temperature. At small dimensions approaching the size of the mean free path, the energy carriers will collide with the boundaries of the material. This classical size effect reduces the mean free path of the carrier and can reduce the thermal conductivity of the material. Further, the transport of these energy carriers becomes ballistic rather than diffusive at these small scales, and renders measurement of the thermal conductivity by TET to be invalid because of it’s applicability only in the diffusive regime.

To ensure that the TET is valid for spider silk, the mean free path of the silk will be approximated based on the kinematic model of phonons, due to the insulating nature of silks. Literature values of density ($\rho = 1360 \text{ kg m}^{-3}$ [5, 6]), specific heat ($c_p = 1470 \text{ kJ kg}^{-1} \text{ K}^{-1}$ – current study), speed of sound ($v = 6.5 \text{ km s}^{-1}$ [5]), and the measured thermal conductivity ($k$ – current study) will be used. Conductivity will also be varied by 4 orders of magnitude to determine the mean free paths that would provide limits with all other factors being the same. The mean free path of silk is approximately 0.29 nm, which is very similar to the mean free path of water at 300 K (Table 5.1), meaning that the TET measurement is not affected by size considerations in this particular work.

<table>
<thead>
<tr>
<th>Material</th>
<th>$k$ (W m$^{-1}$ K$^{-1}$)</th>
<th>$\Lambda$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silk</td>
<td>1.24</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>0.0023</td>
</tr>
<tr>
<td>Water (300 K)</td>
<td>0.61</td>
<td>0.30</td>
</tr>
</tbody>
</table>

5.3 Anisotropy considerations

Many fibers are anisotropic in nature because the formation process of the fiber induces an axial preference to the microstructure of the fiber. This is observed in the case of carbon fiber, where an onion-like
or radial structure is observed in the cross-section of the fiber [7]. However, silk does not have this onion-like structure because it is formed from fibrils [8], although there is still a preferential axial alignment to the microstructure. Still, the models for TET and $3\omega$ were derived for an isotropic conductivity, and the role of anisotropy should be discussed. Although the models will not be re-derived, the governing heat transfer equation to solve is given in Equation 5.3.

$$\rho c_p \frac{\partial T}{\partial t} = k_{rr} \frac{\partial^2 T}{\partial r^2} + \frac{k_{rr}}{r} \frac{\partial T}{\partial r} + k_{zz} \frac{\partial^2 T}{\partial z^2} + q_0'''$$  (5.3)

The effect of anisotropy on the measured properties was investigated through numerical, finite element simulation for the natural silk. An axisymmetric model was used, where boundary conditions are fixed temperatures at the fiber ends and radiation heat transfer of the fiber surface (where $h_r \approx 4\epsilon \sigma T_0^3 \approx 5$). A parametric sweep was performed where the $k_{radial}/k_{axial}$ ratio was from 0.01-100. The fiber was assumed to be orthotropic. The results showed negligible variations in the average axial temperature when $k_{axial} = 1.24 \text{ W m}^{-1} \text{ K}^{-1}$, and $k_{radial}$ varies from 0.01 to 100 W m$^{-1}$ K$^{-1}$ (> 0.005 K). Further, the measured axial diffusivity varied less than 1%, suggesting that axial thermal properties can be measured accurately despite the anisotropic nature of the fiber.

Based on the presented methods, the $3\omega$ provides the greatest potential to be applicable to measure the radial thermal properties. In it’s currently derived form, only axial $k$ can be measured (because of the maximum frequency of 100 Hz used). However, the thermal diffusion length (Equation 5.4) being a function of frequency can be used to probe into the radial dimension. Care should be taken and considerations need to be made when $\mu \approx t_{Au}$. Still a frequency scan that allows $t_{Au} < \mu < D$ of fiber, has potential but a detailed investigation is beyond the scope of this project. Based on the kinematic model for thermal conductivity above, assuming similar mean free path and using the measured radial speed of sound ($v = 2.9 \text{ km s}^{-1}$ [5]), the approximate value of the thermal conductivity is 0.55 W m$^{-1}$ K$^{-1}$ (a little less than half of the axial value). Assuming a similar reduction in thermal diffusivity ($\alpha$), this frequency range would be $\sim$300 kHz – 1 GHz to probe into the radial dimensions of the fiber.

$$\mu = \sqrt{\frac{2\alpha}{\omega}}$$  (5.4)

### 5.4 $3\omega$ considerations

This section outlines some of the benefits and shortcomings of the $3\omega$ method, with the summary given in 5.2.
Table 5.2: Benefits and shortcomings of the $3\omega$ method.

<table>
<thead>
<tr>
<th>Benefits</th>
<th>Shortcomings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Get $k$, $\alpha$, and $C_p$ for known geometry</td>
<td>Long time for a single measurement (frequency scan and length/radiation effect)</td>
</tr>
<tr>
<td>Good for short fibers and thermally conductive fibers</td>
<td>High fiber breaking potential</td>
</tr>
<tr>
<td>Developed model includes method to consider radiation</td>
<td>Requires linear calibration of $R'$</td>
</tr>
<tr>
<td></td>
<td>Need thin coating on non-conductive fibers</td>
</tr>
</tbody>
</table>

5.5 Equipment

Presented in Figure 5.2 is the hardware used for both TET and $3\omega$ measurements. The vacuum chamber includes an isothermal copper enclosure connected to a circulating water bath for resistance-temperature calibration as well as a constant environmental temperature during testing. The chamber is pumped down with a rotary pump and turbo pump connected in series to eliminate convection.

5.6 Summary

Presented in Tables 11.2, 11.3, 11.6, 11.7, and 11.8 are a summary of the thermal properties of platinum wires and gold-coated glass fibers from both the TET and $3\omega$ techniques to provide validate for the two methods. The curve-fits of the amplitude signal for the experimental results on a platinum wire using a current source with $1\omega$ cancellation are given in Figure 5.3, from Ref. [1].
Fig. 5.2: DMM, constant current source, and switch used during TET and $3\omega$ measurements (top), as well as the vacuum chamber where the samples are placed in (bottom).
Fig. 5.3: Measurement of platinum wire samples with current source and $1/\omega$ cancellation, a) voltage amplitude and c) determined volumetric heat capacity. Points are measured values and lines are fits. Error bars represent 1\,\sigma deviation. From [1].
References


CHAPTER 6
THERMOPHYSICAL PROPERTIES OF THE DRAGLINE SILK OF NEPHILA CLAVIPES SPIDER

This chapter is based on a paper published in Polymer, 55, dx.doi.org/10.1016/j.polymer. 2014.05.046 with the original author list being: Changhu Xing, Troy Munro, Benjamin White, Heng Ban, Cameron Copeland, and Randolph V. Lewis. My contribution to this work was sample preparation, data acquisition, initial tests with reduced model, setup of equipment for TET method, data analysis, and document preparation.

6.1 Abstract

The thermal conductivity and diffusivity of the dragline silk of the Nephila (N.) clavipes spider has been characterized by one research group to be 151-416 W m$^{-1}$ K$^{-1}$ and 6.4-12.3 $\times$ 10$^{-5}$ m$^2$ s$^{-1}$, respectively, for samples with low to high strains (zero to 19.7%). Thermal diffusivity of the dragline silk of a different spider species, Araneus diadematus, has been determined by another research group as 2 $\times$ 10$^{-7}$ m$^2$ s$^{-1}$ for unstretched silk. To improve measurement reliability and repeatability and to resolve the orders of magnitude discrepancy between the two different measurements, this paper measured 13 unstretched dragline silk samples of the N. clavipes spider with different lengths using the same electrothermal technique as the first group but with a much higher vacuum level and an improved heat transfer model. The measured thermal conductivity is 1.2 W m$^{-1}$ K$^{-1}$ and thermal diffusivity is 6 $\times$ 10$^{-7}$ m$^2$ s$^{-1}$. The measured thermal diffusivity of the N. clavipes spider silk is in the same order of magnitude as that of the A. diadematus spider but is 1/100-1/200 of the value by the first group. The measured thermal conductivity is 1/150-1/400 of that measured in literature. The discrepancy between this research and the first group may reside in the vacuum level and the improved heat transfer analysis. The difference in thermal diffusivity measurement between the current research and the results of the second group may be because of different species.

6.2 Introduction

The dragline silk of the Golden Orb Weaver, N. clavipes, is among the strongest known materials [1]. The combination of both high tensile strength and elasticity/extension make dragline silk a desirable material for applications such as sports materials and specialized ropes or cords. It has been found that spider silk elicits almost no immunological response and may be applicable as a medical biomaterial for sutures, growth
matrices, tendons, and ligaments [2–5]. Dragline silk is one of six silks that is produced by *N. clavipes* [6]. This silk is produced in the major ampullate gland and is comprised of two different proteins, major ampullate spidroin 1 (MaSp1) [7] and major ampullate spidroin 2 (MaSp2) [8]. Both proteins are highly repetitive proteins that contain unique motifs that contribute to the mechanical properties of spider silk [9]. A poly-alanine motif (present in both proteins, see Figure 1.3), forms a crystalline $\beta$-sheet region that is generally thought to provide spider silk with its tensile strength [9–11], while MaSp2 contains a GPGXX motif which makes up much of the presumed amorphous region of the protein and is believed to form a $\beta$-spiral responsible for the high elasticity of dragline silk [12] (also see Figure 1.3).

Although the structure and mechanical properties have been studied extensively, the thermal properties, especially the thermal conductivity ($k$, [W m$^{-1}$ K$^{-1}$]) and thermal diffusivity ($\alpha$, [m$^2$ s$^{-1}$]), which determine how much and how fast a material conducts heat, have not been investigated convincingly. Huang et al. [13] measured the thermal conductivity and diffusivity of the dragline silk of a *N. clavipes* using the transient electrothermal technique (TET). The paper reported the conductivity for samples under different strains ranges (3.9% to 19.7%) from 151 to 416 W m$^{-1}$ K$^{-1}$ (if linearly-extrapolating from the sample measurements under strain to where there was 0% strain, the unstretched thermal conductivity would be 324 W m$^{-1}$ K$^{-1}$, more than double of the directly measured value) and diffusivity spans from 6.4 to 12.3 $\times$ 10$^{-5}$ m$^2$ s$^{-1}$. With these values, the thermophysical properties of spider silk are equivalent to, or even higher than, those of the best thermal conductive metal, copper or silver. However, Fuente et al. [14] measured the dragline of an *Araneus diadematus* (European garden) spider by means of a lock-in infrared (IR) thermography and found that the diffusivity is $2 \times 10^{-7}$ m$^2$ s$^{-1}$, over 400 times smaller than the measurement by Huang et al. [13] and consistent with typical polymer values. Since both *N. clavipes* and *Araneus diadematus* are orb weaving spiders, the process each one uses to produce silk is very similar. Additionally, the amino acid sequence between the two species is highly conserved [15]. These two reasons make it unlikely that a difference in species should produce such a radical change in thermal properties.

This paper will therefore present the measured thermal conductivity and diffusivity of the *N. clavipes* (the same species used in Ref. [13]) spider dragline silk. To have a direct comparison, this paper will employ the same measurement technique that was adopted in Ref. [13]. However, as mentioned in a previous paper [16], the model used in Ref. [13] is a reduced form from a full model describing the heat transfer process through the sample. This paper will present the results obtained under the reduced and full model and analyze the differences.
6.3 Thermal characterization

A simplified heat transfer model has been described previously [13]. The thermal characterization mechanism of this technique is the Joule heating of the sample and subsequent thermal response. Fig. 6.1 presents a schematic setup of the measurement technique. When a constant current, $I$ [A], is passed through a sample with an unheated resistance, $R_0$ [$\Omega$], the electrical energy is converted to thermal energy, which is introduced as a volumetric heat source to the sample, $I^2R_0/V_s$ where $V_s$ [m$^3$] is the volume. For the cylindrical silk, the $V_s = \pi D^2L/4$, where $D$ is the diameter [m] and $L$ is the length [m]. The heat induces a temperature rise, $\Delta T$ [K], over time, which finally reaches the steady-state temperature rise $\Delta T_s$ [K]. The magnitude of $\Delta T_s$ depends on the thermal conductivity; and the time to reach steady-state ($t_s$ [s]) is affected by the thermal diffusivity. Using a calibrated temperature coefficient of resistance, $R'$ [$\Omega K^{-1}$], the temperature change is linked to the resistance variation. Thus the steady-state resistance under heating is, $R_s = R_0 + R' \Delta T_s$. $R'$ can be rewritten as $R' = \alpha_T R_0$, where $\alpha_T$ is the temperature coefficient of resistivity [K$^{-1}$], which depends only on material and not the shape of the sample.

The full model [16] considers other influential factors on the heat transfer process, for instance heat losses including radiative heat transfer, $h_r \approx 4\varepsilon\sigma T_0^3$ [W m$^{-2}$ K$^{-1}$] where $\varepsilon$ is emissivity, $\sigma$ is Stefan-
Boltzmann constant, and $T_0$ is environment temperature [K], convective heat transfer, $h_c$ [W m$^{-2}$ K$^{-1}$] and variable heating, all of which were lumped into an equivalent heat transfer term, $H_e^2 = [(h_r + h_r)A_l - P^2R']/(kV_s)$, where $A_l$ is the lateral surface area [m$^2$]. For a cylindrical sample, the thermal conductivity and diffusivity are evaluated by Eqs. (6.1) and (6.2) respectively.

$$k = \frac{4I^2R_0R'L}{\pi D^2(R_s - R_0)} \frac{2 - 2\cosh(LH_e) + LH_e \sinh(LH_e)}{(LH_e)^3 \sinh(LH_e)} \quad (6.1)$$

$$\Delta T_s = 1 - \frac{8(LH_e)^3}{2 - 2(LH_e) + LH_e \sinh(LH_e)} \times \sum_{m=1}^{\infty} e^{-[2(m-1)^2\pi^2 + (LH_e)^2]x/L^2} \quad (6.2)$$

If the $H_e$ term approaches zero, Eqs. (6.1) and (6.2) can be formulated as the reduced model used in literature [13].

$$k = \frac{I^2R_0R'L}{3\pi D^2(R_s - R_0)} \quad (6.3)$$

$$\Delta T_s = 1 - 96 \sum_{m=1}^{\infty} e^{-(2m-1)^2\pi^2 x/L^2} \quad (6.4)$$

Spider dragline silk thermal properties will be characterized using Eqs. (6.1-6.4) for comparison of both models.

### 6.4 Sample preparation

The dragline silk was collected from adult *N. clavipes* spiders from the state of Florida, USA, using the method described by Xu et al. [7]. Briefly, spiders were subjected to CO$_2$, anesthetizing them and allowing them to be restrained on the top of a petri dish. Using tweezers, silk was teased out of the major ampullate gland with the assistance of a dissecting microscope and was attached to a reel, which gathered approximately 100 m of silk. Spiders were misted during the reeling process to prevent dehydration.

The uniformity and profile of the dragline silk were observed under Scanning Electron Microscope (SEM), from which the diameter of the silk, 3.1$\pm$0.2 µm was measured. Fig. 6.2 presents the silk at different sections under SEM imaging.
Fig. 6.2: Profile of the dragline silk of *N. clavipes* spider under SEM imaging. The diameter is $3.1 \pm 0.2 \, \mu m$.

To characterize the thermal properties, several spider silk samples of different lengths were mounted following the configuration recommended in Ref. [13] to form a set. The silk was secured on the two outer ends of the heat sinks by silver paste at the beginning, endured a 10 nm gold film sputter coating (controlled by a Cressington thickness monitor) and secured on the inner edges of the heat sinks. All of the samples were tightly mounted on the outer heat sink ends by rheologic silver paste pulling without inducing stress or strain. To improve the contact at the inner edge and the accuracy of length measurement, the heat sinks were sloped slightly. After coating, a copper sheet drove the silver paste rheologically to the inner edge to finalize a sample. Many samples in a set had infinite resistance, typically due to an incomplete coating, meaning no measurement could be conducted. Some of the successfully coated samples were burned by heating or broken in air before or after testing. However, even with these difficulties, 13 samples from 4 different sets/batches of coating had successful measurements. The length of each sample was determined by high resolution camera using a reference having a resolution of 0.001 mm.

The coated samples could not be measured immediately because the resistance of the coated film keeps decreasing with time. To stabilize the sample resistance (slow down its change at room temperature) and remove coating related measurement bias error, the samples were annealed in a furnace for a week. As a basis for the temperature limit for annealing, the temperatures of phase transition behavior of the spider
silk were obtained from the literature (details of phase transitions are given in Table 1.1. Based on the Thermogravimetric Analysis (TGA) and Dynamic Mechanical Analysis (DMA) measurements, Cunniff et al. noticed that the properties of spider silk were stable below 210 °C [17]. Using Thermal Mechanical Analysis (TMA), Rengasamy et al. [18] found that the transition temperature of the dragline silk was at 186 °C. Based on the literature studies, an annealing temperature below 100 °C was adopted to maintain the structure of the silk upon heating. Several annealing temperatures were tested but no appreciable thermal property difference beyond precision error was found.

6.5 Calibration and test

In order to obtain $k$ of the dragline by Eq. 6.1 or 6.3, the temperature coefficient of resistance should be known. For a wire or coated film without a theoretical $R'$, a calibration is necessary. A set of samples was placed in a copper enclosure inside a vacuum chamber for the in-situ calibration in air before testing in high vacuum (Fig. 6.1). The temperature of the enclosure was controlled and maintained for ~10-15 min by a Cole-Parmer Polystat circulating water bath before collecting the calibration data. A type K thermocouple, soldered on the common heat sink and electrical leads for the samples with a 4-wire resistance measurement configuration were passed through the vacuum chamber by means of thermocouple and electrical feedthroughs respectively. The simultaneous acquisition of temperature and resistance were conducted by an Agilent 34970a data acquisition unit. A linear regression was employed to fit the measured resistances at different temperatures and the slope is $R'$. Fig. 6.3 presents the determined $R'$ for the 13 samples. All of the calibrations have a coefficient of determination ($R^2$) larger than 0.99. For the 1st set where only one sample was successfully coated, the calibration temperature range is slightly small, but it was still larger than the measured temperature rise.

The calibrated $R'$ and other quantities are summarized in Table 6.1 where the $\alpha_T$ is also presented. The sample temperature coefficients of resistivity of the coated gold film are mostly between 0.0008 and 0.001 K$^{-1}$, which is about one-quarter to one-third of the bulk gold value (0.0034 K$^{-1}$). Even though the measured values deviate considerably from that of the bulk material, the consistency of the measured coefficients demonstrates the accuracy of the calibration and its effect on spider silk thermal conductivity measurement.

After calibration, the temperature of the samples was maintained at room temperature (22 °C) and the pressure inside the chamber was reduced by the combination of Adixen Pascal 2015SD rotary vane and Pfeiffer HiPace 300 turbo pumps. The measurement could begin after the pressure reading from a PKR 251 full range gauge dropped below ~0.001 Pa.
A constant current through the sample, having a settling time of 2 µs was provided by the Keithley 6221 current source. A Keithley 3706 digit multimeter was connected to the other two wires for the voltage measurement. In the computer code, setting commands and a trigger signal were sent to the multimeter. Once the multimeter started sampling voltage data, a trigger from the computer was sent to the current source to activate the Joule heating. The heating lasted less than 2 s for all of the samples (for the long samples, radiation significantly reduced the time required to reach steady-state). After sampling, the code automatically transferred data from the multimeter buffer to the computer for processing.

For the spider silk samples, the $\Delta T_s$ needs to be limited to a low value so that the non-constant heating ($I^2$ term) in $H_e$ term is negligible. Due to the characteristic of the film coating (resistance drop), measured thermal properties under large $\Delta T_s$ do not follow the theory. However, to reduce the precision error and improve signal to noise ratio, $\Delta T_s$ needs to be larger. A compromise has to be made in the measurement. For each sample, several electrical currents were applied in the experiment to find the compromise between avoiding the non-constant heating effect and having a sufficiently high signal to noise ratio. The measurement cases that had better resolution and did not yield results that were significantly deviated from those at other applied currents were selected for the final data reduction.

The noise and transition (a few points) were removed from the collected data, leaving only the Joule heating portion. The steady-state resistance, converted from the measured voltage and constant current, was input into Eq. (6.3) for the thermal conductivity ($k$) evaluation by the reduced model similar to literature [13]. Once measurements on all of the samples were finished, a regression code was applied on Eq. (6.1) for simultaneous $k$ and $\varepsilon$ determination based on varying length and then radiation effects.

The transient data were normalized by $\Delta T / \Delta T_s$ (actually the non-dimensional voltage response, $\Delta V / \Delta V_s$, because of the linear $R'$ and constant $I$). The normalized transient data were input into Eq. (6.4) for thermal diffusivity ($\alpha$) evaluation by the reduced model because the dependence is only on one parameter, $L$. After $k$ is determined from the full model, the same datasets were regressed by Eq. (6.2) for a evaluation considering lateral heat loss using the improved $k$ value.

In the data processing of $k$ and $\alpha$ by the full model, the $I^2R'$ term in $H_e$ was nulled because the measured value did not decrease with the increase of $\Delta T_s$ (positive $R'$). With the high vacuum level, $h_c = 0$, leaving only the radiation influence.

### 6.5.1 Results and discussions

Table 6.1 summarizes the measured data for the 13 samples. It contains parameters, measurement results
Table 6.1: Measured quantities for the 13 spider silk samples and determined \( k \) and \( \alpha \) by reduced (R) or full (F) model.

<table>
<thead>
<tr>
<th>Set#</th>
<th>( L ) (mm)</th>
<th>( I ) (µA)</th>
<th>( R' (\Omega K^{-1}) )</th>
<th>( \alpha_T (K^{-1}) )</th>
<th>( R_0 (\Omega) )</th>
<th>( R_s (\Omega) )</th>
<th>( \Delta T_s (K) )</th>
<th>( t_s ) (s)</th>
<th>( k ) (W m(^{-1})K(^{-1}))</th>
<th>( \alpha ) (mm(^2) s(^{-1}))</th>
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<tr>
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<td></td>
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<td></td>
<td>1.23</td>
<td>0.62</td>
</tr>
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</table>

Note: \( k \): Thermal conductivity, \( \alpha \): Thermal diffusivity.
Fig. 6.3: Calibration of the temperature coefficient of resistance of the samples.

\((R_s \text{ and } t_s)\) and determined \(k\) and \(\alpha\) for the dragline silk. The determined \(k\) and \(\alpha\) by reduced or full model will be presented in the following figures for analysis.

The conductivity of each sample is determined by the reduced model with the parameters from \(L\) to \(R_s\), and presented in Fig. 6.4 with respect to its length. The reduced \(k\) increases quadratically with respect to \(L\), with a minimum of 1.2 and a maximum of 190 W m\(^{-1}\) K\(^{-1}\). In literature [13], the reported thermal conductivity of an unstretched dragline silk with a length of 4.1 mm is 151 W m\(^{-1}\) K\(^{-1}\) by direct measurement whereas it became 324 W m\(^{-1}\) K\(^{-1}\) by extrapolating from the stretched cases. If an interpolation is used for...
the 4.1 mm sample, the $k$ measured by this research is $10 \text{ W m}^{-1} \text{ K}^{-1}$ by the reduced model, around 1/15-1/30 of the reported value. Since the same material is measured by the same technique and determined by the same model, the significant difference has to be ascribed to the different vacuum level used in the two studies (detailed in Section 3.3). A similar significant difference is found in the reduced $\alpha$ in Fig. 6.5. The reported thermal diffusivity of the unstretched dragline silk is $6.4 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ whereas this research yields a reduced $\alpha$ of $\sim 6 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$, around 1/10 of the reported value. Note that the diameters of the dragline silks are slightly different because in literature [13], the diameter of the silk is 4.7 µm, which is slightly larger than the silk collected in this research. However, the reduced model, Eq. (6.4), contains only one parameter, sample length. Thus different sample diameter should not influence the determined diffusivity.

In literature [13], it was found that the thermal conductivity and diffusivity became larger when both length and strain increased and they ascribed the enlargements to the amount of stretching. However, if their measured quantities were plotted with respect to the sample length, a strong length dependent increase would be found similar to Figs. 6.4 and 6.5. Therefore, this paper speculates that the explanation in Ref. [13] was not appropriate unless the length dependency could be removed by the more suitable full model. However, since stretching was not studied in this research, the possibility that stretching induced a thermal property increase cannot be fully ruled out.

![Fig. 6.4](image.png)

Fig. 6.4: Strong length dependence of thermal conductivities of the dragline silk of *N. clavipes* spider measured below $\sim 0.001 \text{ Pa}$ by reduced model which neglects lateral heat loss. All samples were tightly mounted without strain. At the same conditions except vacuum level, the result is $\sim 1/15$ of the literature value.
Fig. 6.5: Strong length dependence of thermal diffusivities of the dragline silk of *N. clavipes* spider measured below $\sim 0.001$ Pa by reduced model which neglects lateral heat loss. All samples were tightly mounted without strain. At the same conditions except vacuum level, the result is $\sim 1/10$ of the literature value.

![Graph showing thermal diffusivity vs. length](image)

Fig. 6.6: Unbiased thermal conductivities of the dragline silk of *N. clavipes* spider measured below $\sim 0.001$ Pa by the full model. All samples were tightly mounted without strain. The regressed result is $< 1/100$ of the literature value.

![Graph showing true thermal conductivity vs. lateral heat loss influence](image)
Fig. 6.7: Unbiased thermal diffusivities of the dragline silk of *N. clavipes* spider measured below ∼0.001 Pa by the full model. All samples were tightly mounted without strain. The regressed result is <1/100 of the literature value.

Because of the significant variation of \( k \) and \( \alpha \) with respect to the sample length, the reduced model is inappropriate for the data reduction, so the full models, Eqs. (6.1) and (6.2), have to be employed. The parameters and measured \( R_s \) were put in a regression code for simultaneous \( k \) and \( \varepsilon \) estimation by Eq. (6.1). The regressed \( k \) is 1.23 W m\(^{-1}\) K\(^{-1}\) and \( \varepsilon \) is 0.73. The significant drop in \( k \) of the long samples is because of the consideration of radiation heat loss from the lateral surface. If radiation is not considered, the thermal property is over estimated. The influence by radiation can be viewed from \( t_s \) (when \( \Delta T \gg 0.99\Delta T_r \)) in Table 6.1 where the \( t_s \) increases with length until reaching a plateau at ∼1.5-1.6 s for any length sample. If radiation effect is negligible, \( t_s \) is proportional to \( L^2 \).

With the determined \( k \) and \( \varepsilon \), the dimensionless parameter \( L^2H_\varepsilon^2 \) can be evaluated for each sample. The individual \( k \), convenient for measurement uncertainty analysis, is presented in Table 6.1 and Fig. 6.6. The \( k \) for each sample scatters around the regressed \( k \). With the determined \( k \) and \( \varepsilon \), evaluation of \( \alpha \) using the full model in Eq. (6.2) becomes trivial. The determined \( \alpha \) is presented in Table 6.1 and Fig. 6.7 as \( 6.2 \times 10^{-7} \) m\(^2\) s\(^{-1}\). If the measurement is perfect, the determined \( \alpha \) would scatter evenly around the mean value. However, in this figure, the \( \alpha \) by the full model still shows slight length dependency when the longest two samples were included. This may be caused by the imperfect coating and associated resistance effects. As indicated in Table 6.1, the resistances of similar length samples may differ significantly. Previous research [16] demonstrated that the coating non-uniformity affects the thermal properties determination.
Fig. 6.8: Unbiased thermal conductivity and diffusivity of the dragline silk of *N. clavipes* spider obtained by linear fitting on the results determined by reduced model with respect to the square of lengths.

The coated gold film has the possibility to increase the measured thermal properties because gold has much larger conductivity. However, as Ref. [19] indicated, the film conductivity was significantly reduced from its bulk value. To estimate the coating influence in the experiment, the same silk sample, after having a 10 nm gold coating, had another two additional 5 nm coatings. Other parameters are fixed because the same sample was used, leaving only the coating thickness as a variable. The subsequently measured \( k \) and \( \alpha \) indicated that there is no definite increase from 10 nm to 15 nm coating and slight augment, 3-5\%, from 15 nm to 20 nm coating (within precision error range). Therefore, for the 10 nm coating, the influence may be in the range of precision error (further details in Section 3.4).

After obtaining consistent \( k \) and \( \alpha \) values for the dragline silk with different lengths, they may be compared with the previous researches. The measured \( k \) is around 1/150-1/400 and \( \alpha \) is 1/100-1/200 of the measurements in Ref. [13] for the same material using the same Joule heating technique. The measured \( \alpha \) is 3 times the value measured in Ref. [14] using a lock-in IR thermography, however, the measurements were on two different species of spider. To confirm the results, the 3\( \omega \) technique [20] may be employed to measure \( k \) and \( \alpha \) in a steady-state manner.

Another approach to obtain an unbiased \( k \) and \( \alpha \) is presented in Fig. 6.8, where the measured quantities by reduced model were plotted with respect to \( L^2 \). This figure employs the linear characteristic of the error [16] of results by reduced model from the full model if the error is within several hundred percent. In this
Using a linear fit, the unbiased values at ‘zero’ length indicate that the $k$ and $\alpha$ are $1.18 \text{ W m}^{-1} \text{ K}^{-1}$ and $6.3 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ respectively, close to those by the full model.

Uncertainty of the measurements can be found in Table 6.1. The measured $k$ and $\alpha$ both have 12% uncertainty after using the full model.

### 6.6 Conclusions

Thermal conductivity and thermal diffusivity of the dragline silk of *N. clavipes* spiders were measured using the electrothermal technique. The found thermal conductivity is $1.2 \text{ W m}^{-1} \text{ K}^{-1}$ and thermal diffusivity is $6 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$. The deviation in the measurements on this spider silk in the previous literature may be because of two facts: poor vacuum level contributing to the convective heat transfer and neglected radiation through the sample lateral surface, both augmenting the measured values.
References


CHAPTER 7
BRIDGE BETWEEN SILK AND FLUORESCENCE PAPERS

The previous five chapters have summarized and reported the TET and $3\omega$ methods for thin fibers, and reported the results of applying these techniques to natural spider silks. These methods are generally classified as contact methods. The forthcoming chapters detail the development, simulation, and application of non-contact, quantum dot fluorescence, shape-based thermometry and its application to a frequency domain based thermal wave model to determine the thermal diffusivity of thin fibers, particularly synthetic spider silk.

7.1 Motivation for QD fluorescence thermometry

Because of the long lead time for a sample measurement (several weeks from fiber reception to final property measurement, shown in Figure 7.1) and the likelihood of several of the fibers on a single mount being broken during the entire process, there exists a need for a thermal property measurement that has a faster turn-out rate than the TET and $3\omega$ methods. This is one of the main driving forces to develop the fluorescence measurement technique, as well as use of a measurement technique not affected by non-negligible thermal contact resistance. Its main features are to use the spectral features of fluorescent dyes coated on the surface of a fiber as a temperature sensor via training of a neural network based on the spectra at known temperatures. The decay of a photothermally induced thermal wave can then be measured and related to the thermal diffusivity of the fiber. The lead time for this method is short because the fibers can easily be coated with the fluorescent dye, then placed in the focal plane of the laser path, the spectral features can be measured at calibrated temperatures, and then the scanning of the fiber for the thermal wave decay can all happen in the space of several days, rather than weeks.

One other motivation for developing the fluorescence shape-based thermometry was to increase the

<table>
<thead>
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<th>Sample Mount Construction</th>
<th>Week 1</th>
<th>Week 2</th>
<th>Week 3</th>
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</table>

Fig. 7.1: Timeline for the preparation and application of the TET or $3\omega$ methods to samples.
accuracy of quantum dot fluorescence thermometry beyond what is commonly observed (Figure 7.2). A neural network was chosen to accomplish this for two major reasons. The first is that commonly used shape factors (like peak intensity and full-width half maximum) become non-linear over certain temperature ranges, which the neural network can easily handle. The second reason is it provides a robust way to combine multiple features in an attempt to improve temperature reconstruction accuracy. The current study selects a small temperature range (∼ 10 K) to train the neural network on and analyze via numerical simulation for simplicity. For a wider application and measurement of thermal properties, temperature ranges where non-linear effects occur would also be desirable [1].

7.2 Silk processing and measurement summary

A summary of the thermal conductivity and diffusivity by the TET method for natural and synthetic spider silks is given in Chapter 11. The results show that the dragline (major ampullate) silk has the highest relative properties, followed next by the minor ampullate silk (which has similar secondary protein structures as the major ampullate silk, but lacks the elastic β-spiral [3]), then the processed synthetic silks, and finally the as spun synthetic silk. Furthermore, the thermal conductivity of the synthetic silks are not presented because non-uniformities along the fiber diameter cause significant uncertainty in correct determination of the fiber geometry, which is essential for an accurate thermal conductivity measurement. However, the diffusivity values can be used to compare the effect of the processing on the thermal properties. All processing techniques result in a higher $\alpha$ compared to the as spun fiber, with the largest improvements being observed for high stretching ratios and use of methanol/H$_2$O in the stretch bath. These improvements are also observed in the mechanical properties and crystallinity of the synthetic silk [4]. This improvement in crystallinity was observed in XRD results, with increased formation and alignment of β-sheets due to stretching in the alcohol/water bath that more closely resembled XRD data of the natural silk. Again, the greatest crystallinity improvement occurs in the methanol bath [4].

Additionally, the custom-made, DACA-inspired machine that actually spins the silk is given in Figure 7.3. This system allows the user to control the rate of silk extrusion into the isopropanol bath for fiber coagulation (A in Figure 7.4), the concentration of the first stretch bath (B in Figure 7.4), the rate of spinning via spinning Godets (C in Figure 7.4), the length of the second water bath (D in Figure 7.4), monitor the size, and spool the silk. This has resulted in the differently processed synthetic spider silks investigated in this work (Figure 7.4), based on the variations in the extrusion machine.
Fig. 7.2: Typical accuracy of thermometry methods, after [2], with proposed improvements via neural network reconstruction of the fluorescent signal.

Fig. 7.3: Custom-made synthetic silk spinning machine.
Fig. 7.4: Process variations from the extrusion machine leading to the different synthetic silks investigated in this work.
References


CHAPTER 8
CdSe/ZnS QUANTUM DOT SHAPE-BASED THERMOMETRY VIA NEURAL NETWORK RECONSTRUCTION

This chapter is based on a paper submitted to Journal of Applied Physics with the original author list being: Troy Munro, Liwang Liu, Christ Glorieux, Heng Ban. My contribution to this work was development of the numerical model, setup of equipment for fluorescence thermometry method, experimental data acquisition, data analysis, and document preparation.

8.1 Abstract

As a system of interest gets small, due to the influence of the sensor mass and heat leaks through the sensor contacts, thermal characterization by means of contact temperature measurements becomes cumbersome. Non-contact temperature measurement offers a suitable alternative, provided a reliable relationship between the temperature and the detected signal is available. In this work, exploiting the temperature dependence of their fluorescence spectrum, the use of quantum dots as thermomarkers on the surface of a fiber of interest is demonstrated. The performance is assessed of a series of neural networks that use different spectral shape characteristics as inputs (peak-based – peak intensity, peak wavelength; shape-based – integrated intensity, their ratio, full-width half maximum, peak normalized intensity at certain wavelengths, and summation of intensity over several spectral bands) and that yield at their output the fiber temperature in the optically probed area on a spider silk fiber. Starting from neural networks trained on fluorescence spectra acquired in steady state temperature conditions, numerical simulations are performed to assess the quality of the reconstruction of dynamical temperature changes that are photothermally induced by illuminating the fiber with periodically intensity-modulated light. Comparison of the five neural networks investigated showed that using neural networks trained on the a combination of the spectral characteristics improves the accuracy over use of a single independent input, with the greatest accuracy observed for inputs that included both intensity-based measurements (peak intensity) and shape-based measurements (normalized intensity at multiple wavelengths), with an ultimate accuracy of 0.29 K via numerical simulation based on experimental observations. The implications are that quantum dots can be used as a more stable and accurate fluorescence thermometer for solid materials and that use of neural networks for temperature reconstruction improves the accuracy of the measurement.
8.2 Introduction

Because of the crucial role of temperature in many phenomena, there is a continuous interest in improved temperature measurements in a variety of conditions, especially with non-contact methods [1]. One avenue of research has been the use of fluorescent dyes as thermometers, because of their emission being sensitive to temperature variations. Fluorescent dyes have been used in many instances including labeling structures in cells [2], single photon imaging [3], and as temperature sensors, relating the individual spectral features such as peak intensity, peak wavelength, or the ratio of different spectral peaks [4], as well as fluorescent lifetime measurements [5]. Specifically, Rhodamine B dye has been used as a non-contact temperature sensor in microfluidic devices [6], [7], to probe the surface temperature between two plates [8], and as an additive in PDMS to measure the thermal conductivity of carbon nanotubes [9], [10]. However, all of these applications assumed a linear relation between a single spectral feature (usually the peak intensity) and the temperature. In reality, these relations are substantially nonlinear, and it is worthwhile to refine them and exploit the information content in multiple features simultaneously.

As will be shown in this paper, for the goal of photothermal experiments on fibers (which involve quite time consuming frequency and detection position scans), the stability of organic dyes can be problematic, as photobleaching effects [6] hamper accurate calibration at set temperatures, and an improved fluorescent probe must be selected. Inorganic compounds, such as quantum dots, are not affected by this, and therefore have the potential for more robust signals. However, the spectral signal is sensitive to pH [11], salt concentrations, and electron coupling [12], in addition to temperature, but these factors are maintained as a constant in the current study. To this end, quantum dots rather than organic fluorescent dyes were selected in the current investigation.

Quantum dots are nanometer-sized semiconductors, whose emission spectra are controlled by their size. While their fluorescence spectrum is also temperature dependent, compared to organic fluorescent dyes, they exhibit improved stability (including after repeated thermal cycling [13]), a higher quantum yield, and a longer lifetime [14]. They also do not contribute significantly to the thermal diffusivity of the material of interest [15], so that they have desirable properties for use as a fluorescent thermoprobe. Additionally, on the timescale of photothermal experiments (with the integration time of the spectrometer on the order of ms), the blinking commonly associated with quantum dots (related to the lifetime of the fluorophore on the order of tens of ns) is not an issue [16]. Another incentive to select quantum dots for the current experiment is the earlier demonstration of their successful integration into both silk worm [17] and spider [18] silk (although the purpose of this coating was merely for appearances). The thermal properties of spider silk materials
have previously been investigated [19], and a synthetically produced silk is the substrate used in the current investigation for future thermal characterization by photothermal methods. The typical accuracy of quantum dot fluorescence thermometry is typically on the order of 1–2 K [20], but this work seeks to improve upon that temperature accuracy.

As mentioned above, in order to further improve the use of quantum dots as temperature sensors, an interesting pathway is to simultaneously use multiple spectral features to extract the temperature. Recently [21], the feasibility of using spectral features of organic dyes as inputs for an artificial neural network (NN) and training it to reconstruct the associated temperature, has been demonstrated. Neural networks have been used to solve the inverse problem for depth profiling of heat source distribution [22], optical penetration via photothermal radiometry [23], to relate sea color from satellite imagery to chlorophyll concentrations [24], and to determine the thermal diffusivity of a slab of insulation material [25]. By making use of nonlinear functions such as hyperbolic tangent sigmoids, neural network approaches are particularly efficient in dealing with non-linear aspects of the inverse problem [26], [27]. This is an improvement over a simple, standard least squares fit by a sigmoidal function of the spectral feature [28] required to create the non-linear temperature relationship.

In this work, we verify using a neural network approach for extracting temperature from the fluorescence spectrum of inorganic fluorophores, in the time domain. This paper details a photothermal, inorganic fluorescent thermometry accomplished by a time domain temperature reconstruction via neural networks (with inputs to the network based on spectral features of the fluorophore at calibrated temperatures), based on modulated laser heating experiments and simulation.

8.3 Experimental setup

8.3.1 Equipment description

The experimental setup consisted of a pump and probe laser system and a sample holder with temperature measurement and control. The fluorescence spectra of Rhodamine B and quantum dots on the sample surface were collected by a microscope objective lens and collimated into the fiber of a USB4000 spectrometer. The optical system that focused the light of the pump laser onto a small spot on the fiber was placed on a position scanning stage (Figure 8.1). A 532 nm Coherent Compass CW laser was used to induce the fluorescence at the fiber surface. The laser beam was focused to a spot size of 30 micron by means of a half lens. A mechanically chopped laser beam from a 1064 nm Coherent Vector laser was used to photothermally generate temperature oscillations along the fiber surface. The pump beam diameter on the fiber surface was
about 90 µm. The longer wavelength of the heating laser was selected because it does not induce additional fluorescence in the quantum dots, since the quantum dot absorption is almost negligible at long wavelengths, and the pump wavelength is longer than the one of the fluorescence light [16]. Besides the IR light that was used for the photothermal excitation, the laser beam of the Coherent Vector laser also contained a weak residual green component. This was reflected and filtered out prior to arriving at the fiber sample. The reflected green light was sent to the spectrometer to provide to the spectrometer a reference signal synchronous with the photothermal excitation. The IR pump light passed through a half lens, which was placed on a linear motor stage with sub-micron resolution, so as to provide accurate axial positioning along the fiber. The half lenses that focused respectively the probe and pump beam to the fiber were placed right on top of each other, in order to have their focal points near to each other, while retaining the possibility to individually scan the focal point of the pump laser beam along the fiber axis by moving the respective half lens along with the beam.

The sample fiber was placed on an aluminum plate, which provided four heating resistors for control of the sample temperature. The temperature of the plate was measured by both a PT1000 (measured by an HP-34401) and a type T thermocouple (via HP-34970A) to ensure that the ends of the fiber were near the same temperature, with their location shown on Figure 8.1. The temperature control of the plate was based on the PT1000 using a PID subroutine in Labview, which controlled the heating resistor voltage supplied by an Agilent E3631A power supply. The sample mount plate was placed inside of a Janis cryostat in order to combine optical access with a vacuum environment. At a pressure of $10^{-5}$ mTorr, the thermal conductivity of the surrounding medium was sufficiently low to allow heat conduction via the air to be neglected in modeling and analyzing the heat transport in and around the fiber. The collection of the emitted fluorescent light was done by a microscope objective (10X,0.25 NA), which was focused onto a fiber optic connected to the Ocean Optics USB4000 spectrometer, after passing through several filters (visible bandpass, shortpass, and green notch filters). The green reference signal reflected from the pump laser was also collected in the spectrometer without passing through the filters.

The operation of the experiment was controlled automatically by Labview and began with stabilization of the fiber temperature. Once the temperature variation was under 0.015 °C for 15 minutes, the spectrometer collected 250 spectra while keeping track of the temperature as measured by the PT1000 resistance. The means and standard deviations of 1750 spectra between 300 K and 312 K were determined and the individual spectra were stored in order to serve as training data for the neural network.

After the spectral calibration was done, the pump and probe beams were aligned on the fiber, and the
position of the pump laser was scanned in steps of 50 micron along the fiber in order to map the thermal wave decay versus pump-probe distance between 2000 µm and −2000 µm. The pump laser was turned on to full power (1 W) via serial communication to provide sufficient modulated heating of the fiber to produce a photothermal signal, a waiting period of 5 seconds occurred to allow a steady state of the DC heating of fiber to be more readily reached so that only the AC variation would be present in the signal, and the spectrometer was set to measure as quickly as possible (after a single measurement from the PT1000 to verify the initial temperature), collecting enough spectra to record 100 periods per pump-probe distance. The temperature of the sample mount could be set at any temperature of interest, allowing performance of frequency and/or position scans, in view of applying the setup in the future to determine the temperature dependence of the thermal diffusivity of the fiber.
8.3.2 Fluorophore selection

Two types of fluorophore-coated fibers were investigated using Rhodamine B and quantum dots as thermoprobes, with the quantum dot coated fiber showing greater stability. The experimental system was first tested on a synthetic spider silk that had Rhodamine B integrated into the fiber during its production, similar to how Rhodamine B had been integrated into an optical fiber for use as a temperature sensor in Ref. [29]. The production process [30] involved coagulation of a fiber in an IPA bath, passing through a methanol/water bath where it was stretched 1.5x, and then through a water bath, where 65 mg of Rhodamine B was dissolved in 200 mL of distilled water, and stretched again 1.5x. This allowed the Rhodamine B to be integrated throughout the fiber surface, although at an unknown concentration. However, the concentration did not change during the calibration nor the experiment and hence should have little effect on the results. The fiber diameter was about 25 µm, and thus could be considered to be thermally thin for the used modulation frequencies between 0.5 Hz and 4 Hz, i.e. the temperature oscillation was rather uniform throughout the fiber, and signal variations were mainly along the fiber axis, with increasing distance from the pump laser spot.

Rhodamine B was initially selected as a thermosensitive probe because it had successfully been used as a temperature sensor in an application for photothermal, shape-based neural network temperature determination, which was aimed at depth profiling of an optical absorbance profile in glycerol [21]. An important issue encountered with using the Rhodamine B embedded fibers was that the stability of the peak intensity and fluorescent emission spectra was not-consistent over the time needed for a measurement. For this reason, we have started using the more stable Lumidot™ 640nm peak wavelength, CdSe/ZnS quantum dots. The stabilities over several hours (a typical photothermal experiment at low frequencies and multiple axial positions can take an entire work day) of a synthetic spider silk embedded with Rhodamine B, and the same type of synthetic spider silk coated with the quantum dots, are compared in Figure 8.2. Quantum dots showed greatly improved stability of the peak intensity. In order to coat the fiber surface with quantum dots, they were first suspended in toluene and then diluted from 5 mg/mL to 0.5 mg/mL. Next, a drop was placed on the fiber and the toluene was allowed to evaporate, leaving the dots behind on the fiber and glass slide. The final concentration on the fiber was unknown, but it was sufficiently high so that the color of the fiber was changed to the color of the dots in solution (red-orange).

8.4 Methods

In order to explain quantum dot fluorescence spectrum-based thermometry, the following sections cover the procedure to train a neural network based on different spectral features to reconstruct the surface temper-
Fig. 8.2: Comparison of the stability over several hours of the peak intensity of Rhodamine B (blue) and quantum dot coated synthetic spider silk (red). Also, the integrated intensity of the fluorescence peak of the quantum dot coated synthetic spider silk is shown.

Central to the quantum dot fluorescence spectrum shape-based thermometry method is the ability to accurately relate measured spectra to the corresponding fiber surface temperature. In the following, we cover the relation between different spectral features and the DC temperature (without photothermal excitation), and detail the data reduction process to use these spectral features as inputs to train a neural network.

8.4.1 Neural network training and temperature reconstruction

Temperature Behavior of Spectra

Central to the quantum dot fluorescence spectrum shape-based thermometry method is the ability to accurately relate measured spectra to the corresponding fiber surface temperature. In the following, we cover the relation between different spectral features and the DC temperature (without photothermal excitation), and detail the data reduction process to use these spectral features as inputs to train a neural network.

The temperature dependent behavior of the quantum dots’ spectra and shape-based factors (spectral features) such as peak intensity (PI), integrated intensity (II) [31], the PI/II ratio (R) [32], peak wavelength (PW or PWL [8]), FWHM [8], and the summed spectral bands are shown in Figure 3. As expected [32], [31],...
as the temperature increases, the spectral content shifts towards longer wavelengths, broadens, and decreases in intensity (Figure 8.3b). The spectral features mimic this behavior (insets Figure 8.3a).

The temperature behavior of the fluorescent probe (being established as sufficiently stable), allowed tackling of the inverse problem for extracting the surface temperature from the fluorescence spectrum by means of neural network recognition. The neural network data acquisition process began by combining the 250 calibration spectra from each calibration temperature into a single file and performing a moving, rectangular-windowed average (10 data points), where the intensity of the counted intensity was averaged over 10 wavelengths, in order to reduce the noise and determine the features of interest (peak intensity, integrated intensity, peak wavelength, ratio of peak to integrated intensity, FWHM, peak normalized intensities, and summed bands) more accurately and more easily.

A 3rd order polynomial was fit to the smoothed spectra, the derivative was taken, and the peak intensity and peak wavelength were found at the maximum of the fit curve. The selection of the polynomial order was motivated by the desire to have a numerical stable derivative and to be able to be a more general fit because of the different shaped-spectra of the Rhodamine B and quantum dot spectra. The integrated intensity was then taken as the sum of the intensity values under the curve of the smoothed spectra. Also, the ratio between the peak intensity and the integrated intensity of the spectra was calculated. The FWHM of the spectral peak was determined as well. The spectra were normalized to their peak value and the “normalized intensity” values at 40 evenly spaced wavelengths from 536 nm to 764 nm were used as inputs for the neural networks. Finally, five bands of 25 wavelength measurements each (≈5 nm wide) were summed, and these five “sum bands” would provide the inputs for one of the neural networks.

Fig. 8.3: Experimentally determined temperature behavior of the fluorescent spectra of quantum dots with inset showing the temperature dependence of the PI, Ratio, PWL, and FWHM of the spectra (a). Also the trend of the spectral features with increasing temperature is schematically illustrated (b).
Neural Network Training

The different spectral features were used as inputs to create five different, simple neural networks containing 2 hidden nodes, with varying inputs based on the different spectral features just described and summarized below:

1. PI, II, PWL – with 2 hidden nodes
2. PI, II – with 2 hidden nodes
3. PI, II, R, FWHM, PWL – with 2 hidden nodes
4. PI, 40 Normalized Intensities – with 2 hidden nodes
5. Sum Bands – with 2 hidden nodes

These were selected to represent traditional methods for temperature correlations (peak intensity and wavelength), shape-based methods (FWHM and integrated intensity), and combinations of both methods (normalized intensity and sum bands).

The actual training of the neural network used 80% of the calibrated spectra for training the network and 20% for testing how well the output matches expectations on new data. Each spectrum was randomly assigned to either group, for cross-validation. The weights of the different nodes (Figure 8.4a, with the results of the training presented in Figure 8.4b) were varied at each iteration until the RMS error of the NN output temperature to the expected temperature (from the PT1000 measurement) was sufficiently small, with the variation of the weights of the nodes in each layer being guided by a Levenberg-Marquardt algorithm. The weights of the neural networks were stored and then applied to each measured spectra, in order to determine the modulated temperature of the fiber during photothermal heating. Note that over the temperature range experienced in the experiment, the temperature dependence of most NN input quantities was quite linear (Figure 8.3a).

Figure 8.4b shows that over the temperature range of interest, 300–312 K, there is a satisfactory correlation between the temperature values extracted by the NN from the spectra on one hand, and the actual temperatures on the other hand. Figure 8.4c shows that the average reconstruction error for the training and test data is less than 10 mK, with a spread similar on the order of 100 mK (Figure 8.4d).

8.4.2 Numerical experiment for NN accuracy

As mentioned above, the future application of interest in this work is the use of photothermal excitation and fluorescence-based thermometry to extract the thermal diffusivity along the axis of a fiber from the axial
pump-probe distance dependence of the photothermally induced temperature oscillation amplitude and phase delay with respect to the intensity modulation. In order to determine which neural network provides the best temperature reconstruction, a numerical simulation of the quantum dot spectra and their variation due to temperature was created, with the experimental to simulation comparison given in Figure 8.5.

The time dependence of the detection temperature was simulated (see further) and noise was added to it to produce simulated spectra. Additional noise was added to the spectra, based on the signal-to-noise
Fig. 8.5: Schematic illustration of the experimental procedure for calculating the thermal diffusivity of a fiber by determining the dependence on the photothermal signal amplitude and phase as a function of the laser intensity modulation frequency and of the pump-probe distance along the fiber (a) and numerical simulation model (b).
ratio of the spectrometer. The simulation took advantage of the almost Gaussian-shape of the quantum dot fluorescence spectra. Based on the experimental observations in Figure 8.3, the different spectral features were assumed to be linearly related to temperature \( A = P_{PT,0} + S_{PT} T \) over the narrow temperature range of interest (300–312 K). The resulting temperature determined by the different neural networks could then be compared to the actually modulated temperature that was used to create the spectra.

The Salazar et al. [33] model for an infinitesimally narrow laser line heating source was used to represent the complex temperature field of a cylinder for a given periodic intensity modulation, in vacuum, with linearized radiation, and the fiber radius much smaller than the diffusion length of the thermal wave, Eqs. 8.1 and 8.2. For the sake of simplicity, the fluorescent spot was assumed to be a point.

\[
\tilde{T}_s(a, z) \approx \frac{P_0}{2\pi k_s q'_s} e^{-q'_s|z|} \tag{8.1}
\]

\[
q' = \sqrt{\frac{i\omega}{\alpha_s} + \frac{2h}{k_s a}} \tag{8.2}
\]

The model predicts a linear dependence of the phase delay and of the logarithm of the amplitude on the pump-probe distance, Eqs. 8.3 and 8.4.

\[
z_{\text{mag}} = \exp (m_{\text{mag}} |z| + b_{\text{mag}}) \tag{8.3}
\]

\[
z_{\text{phase}} = m_{\text{phase}} |z| + b_{\text{phase}} \tag{8.4}
\]

The slope is determined by the modulation frequency and the thermal diffusivity of the fiber, Eq. 8.5.

\[
m_{\text{phase}} \times m_{\text{mag}} = -\pi f \alpha_s^{-1} \tag{8.5}
\]

To mimic the time domain behavior of the experiment, the complex temperature (modeled as an AC signal, Eq. 8.6) was superimposed onto a gradual DC temperature rise (Eq. 8.7), with a power law shape with exponent \( n = \frac{1}{2} \), although any fractional exponent \( < 1 \) is reasonable.

\[
T_{\text{AC}}(z \text{ or } f, t) = \frac{f_{\text{req mag}}}{f_{\text{req mag, max}}} \frac{z_{\text{mag}}}{z_{\text{mag, max}}} \times \cos \left[ 2\pi f(t - t_0) - z_{\text{phase}} - f_{\text{req phase}} \right] \tag{8.6}
\]
\[ T_{DC}(z \text{ or } f, t) = [T_{end} - T_0] \left( \frac{t - t_0}{t_{end}} \right)^n + T_0 \] (8.7)

The time domain temperature evolutions were then used to create Gaussian fluorescence spectra at different times, Eq. 8.8, using the linear dependencies of the spectral features \((A_{PI,0}, S_{PI}, \text{ etc})\) on temperature from calibration experiments, with the inputs to the model given in Table 8.1. A reference signal, synchronous with the intensity oscillation underlying the simulated temperature evolution was used to create a trapezoidal curve between 526 nm and 535 nm, thus simulating the green light directed into the spectrometer.

\[ \text{Spec}[\lambda, T(z, t)] = (A_{PI,0} + S_{PI} T) \times \exp \left[ -\frac{4ln(2)(\lambda - (B_{PW L,0} + S_{PW L} T))^2}{(C_{FWHM,0} + S_{FWHM} T)^2} \right] + (D_0 + S_D T) \] (8.8)

To fully mimic the experiment, this simulation also created calibration files of spectra at fixed temperatures to train the neural network, and then created spectra from a modulated temperature at a fixed frequency and axial position, with similar uncertainties to those seen during the experiment, also presented in Table 8.1.

<table>
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<tr>
<th>Sim. Parameters</th>
<th>Nominal Values</th>
<th>Uncertainty</th>
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</thead>
<tbody>
<tr>
<td>(\lambda) Resolution</td>
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<td>0.19 nm</td>
</tr>
<tr>
<td>PT1000 Temp</td>
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<tr>
<td>Time Spacing</td>
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<td>0.000727 sec</td>
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<td>217 counts</td>
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<td>(A_{PI,0})</td>
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<td>42.58 counts</td>
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<tr>
<td>(B_{PW L,0})</td>
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<tr>
<td>(C_{FWHM,0})</td>
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<td>0.00032 nm</td>
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<td>(D_0)</td>
<td>1500 counts</td>
<td>50 counts</td>
</tr>
<tr>
<td>(S_{PI})</td>
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<td>1.391 counts/K</td>
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<td>(S_{PW L})</td>
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<td>0.000404 nm/K</td>
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<tr>
<td>(S_{FWHM})</td>
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<tr>
<td>(S_D)</td>
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<tr>
<td>(m_{mag})</td>
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<td>(\alpha_s)</td>
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<td>(h)</td>
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</table>
8.5 Results

8.5.1 NN Accuracy via simulation compared to experiment

An example of experimentally determined temperature evolutions using the five NNs investigated is shown in Figure 8.6 for an axial pump-probe spacing of 1 mm and at an initial temperature near the lower limit of the calibration range (302 K). All evolutions show the expected DC temperature rise and modulated temperature. However, there is a significant variation in the reconstructed temperature by the different networks, with the normalized intensity NN having the least variation (Figure 8.6, inset) and the NN with the most spectral features (PI, II, Ratio, FWHM, PWL) having the most variation. The substantial discrepancy between the different results was the incentive to perform this analysis on simulated data, for which the reconstructed data can be unambiguously evaluated by comparison with the known temperature evolution underlying the simulation.

The numerical simulation was based on the nominal values of uncertainty on the different spectral features and other system parameters (Table 8.1). The calibration spectra were created based on the magnitude of the neural network parameters observed during the experiment as shown in Figure 8.3. The neural net-

![Fig. 8.6: Neural network reconstructed temperature evolutions for five types of neural network inputs investigated based on experimental data. The inset shows the normalized temperature evolutions.](image)
works were then trained on those data. Next, the simulation assumed a temperature evolution as described in Section 8.4.2. For each temperature, a spectrum was generated with the corresponding characteristics (FWHM, peak intensity, peak wavelength) with noise superimposed onto the created spectra. Finally, the trained neural networks were then used to determine the temperature evolution from the generated spectra. The reconstructed temperature evolutions were compared with the original one, in order to determine which provides the greatest accuracy.

The RMS error on the temperature evolution extracted by the different NNs is included in the legend in Figure 8.7. The most accurate NN reconstruction was based on the normalized intensities with an RMS error lower than that traditionally observed in fluorescent dyes [20]. The discrepancy observed in the experimental temperature can be attributed to a large DC heating during the initial five seconds when the pump laser was on but the spectrometer was not collecting data. However, this discrepancy was not observed in the simulated temperature.

Fig. 8.7: Reconstructed temperature signals by 5 different neural networks and reconstruction by linear fit to peak intensity (symbols), compared to the original temperature (full line), with the RMS error of each (in Kelvin) in the legend. The normalized intensity based neural network matches the input temperature most accurately. From simulation.
Table 8.2: RMS error (K) of spectral inputs at 1% uncertainty of each input, with the FWHM being the most sensitive to uncertainty.

<table>
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<tr>
<th></th>
<th>NN#1</th>
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<th>NN#3</th>
<th>NN#4</th>
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<td>0.11</td>
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<td>0.10</td>
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<td>4.22</td>
<td>1.60</td>
<td>1.60</td>
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<td>0.09</td>
<td>0.09</td>
<td>0.10</td>
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<td>0.11</td>
<td>0.10</td>
<td>0.10</td>
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<tr>
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<td>0.10</td>
<td>0.10</td>
<td>0.19</td>
</tr>
<tr>
<td>Slope of PI</td>
<td>0.12</td>
<td>0.12</td>
<td>0.09</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Intercept of PI</td>
<td>0.12</td>
<td>0.12</td>
<td>0.09</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Slope of FWHM</td>
<td>0.14</td>
<td>0.48</td>
<td>0.47</td>
<td>0.16</td>
<td>0.10</td>
</tr>
<tr>
<td>Intercept of FWHM</td>
<td>8.88</td>
<td>4.70</td>
<td>10.47</td>
<td>37.47</td>
<td>34.57</td>
</tr>
<tr>
<td>Modulation Freq</td>
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<td>0.49</td>
<td>0.50</td>
<td>0.17</td>
<td>0.10</td>
</tr>
<tr>
<td>Slope of Baseline</td>
<td>0.14</td>
<td>0.48</td>
<td>0.47</td>
<td>0.16</td>
<td>0.10</td>
</tr>
<tr>
<td>Intercept of Baseline</td>
<td>0.14</td>
<td>0.48</td>
<td>0.47</td>
<td>0.16</td>
<td>0.10</td>
</tr>
</tbody>
</table>

\[
RMS_{\text{error}(K)} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (T_{\text{NN}} - T_{\text{True}})^2} / N
\]  

Furthermore, the numerical simulation provides an excellent vehicle to determine the sensitivity of the method to different experimental errors. The inputs of Eq. 8.8 into the simulation were fixed at their nominal value, except for one, in which the bias and precision uncertainty was 1% of the nominal value. The numerical experiment was repeated for each input for a fixed axial position and frequency, which then fixed the decay and phase delay terms Eq. 8.6 as a constant. Calibration spectra and modulated spectra at the lowest temperature of the calibration range were created. The neural network calibration and application was applied to the simulated, modulated spectra and the final variation from the true modulated temperature compared to the neural network determined temperature was determined. Table 8.2 presents the RMS (Eq. 8.9) error in Kelvin of the reconstructed temperature, resulting from a 1% uncertainty in the investigated variables. Apparently, the FWHM based NN is the most sensitive to deviations. This can be explained by the rather low sensitivity of the FWHM to temperature (about 0.18%/K) and the limited wavelength resolution of the spectrometer (∼0.2 nm).

8.6 Conclusions

CdSe/ZnS quantum dots have been shown to be viable fluorescent dyes to be used as a non-contact temperature sensor, with the surface temperature being reconstructed from their fluorescence spectrum by an artificial neural network and improved performance in terms of stability, compared to Rhodamine B,
an organic dye. Out of the five neural networks investigated in this work, based on the different spectral shape features, numerical simulations pointed out that the neural network based on the normalized intensity provides the greatest accuracy. The overall RMS uncertainty from simulation of the method to reconstruct the temperature was 0.29 Kelvin compared to 1 Kelvin based on reconstruction by only peak intensity. This improvement allows for improved thermal characterization of materials and monitoring of thermal processes via a less intrusive temperature measurement.
References


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CHAPTER 9
FFT-BASED METHOD FOR THERMAL PROPERTY DETERMINATION OF MICRO-SIZED FIBERS VIA PHOTOTHERMAL QUANTUM DOT FLUORESCENCE-BASED THERMOMETRY

This chapter is based on a paper to be submitted to Applied Thermal Engineering with the original author list being: Troy Munro, Liwang Liu, Heng Ban, and Christ Glorieux. My contribution to this work was derivation of method, development of the numerical model, setup of equipment for fluorescence thermometry method, experimental data acquisition, data analysis, and document preparation.

9.1 Abstract

Because of difficulties with thermal characterization at small scales, there is a need to develop non-contact temperature measurements to eliminate the influence of sensor mass, contribution to thermal properties, and heat loss in the measurement of thermal properties. This work details the use of quantum dots as non-contact thermomarkers to measure the surface temperature of thin fibers and the FFT-based method to relate the measured temperature to the thermal diffusivity of the fiber, based on modulated laser heating. Neural networks are trained on fluorescence spectra at calibrated, steady-state conditions (in experiment and simulation), and then used to reconstruct the surface temperature in time domain. Then fluorescence data, obtained in a time domain photothermal experiment and mapped to the frequency domain via FFT, are analyzed in the framework of verifying the feasibility of applying the method for determining the thermal properties of micro-sized fibers from the spatiotemporal dependence of the photothermally generated temperature field dynamics.

9.2 Introduction

Quantum dots as temperature sensors have been considered for use as nano-sized temperature probes [1], because of their increased stability over organic dyes [2], their small size [3], and their applicability in a variety of applications. They are nanometer-sized semiconducting crystals, with their peak wavelength and emission spectra being a function of their size. CdSe/ZnS quantum dots are one of multiple probes considered for nanothermometry [4], particularly to study the thermal behavior at the cellular level, where improved temperature resolution is required [3, 5, 6]. They (and other fluorophores) have been used for thermal characterization of the solution they are suspended in [7, 8], for spectroscopic investigation of materials via the
thermal lens and optical absorption methods [7], and as contrast agents in photoacoustic and photothermal microscopy [9]. Their contribution to the effective thermal diffusivity of the system of interest is negligible [7], which is necessary for improved temperature accuracy (typically on the order of 1 K [3]). Quantum dots have the benefit of an order of magnitude increase in stability over single dye molecules, with the intensity being decreased by oxygen [10].

One avenue where an improved quantum dot thermometry can benefit is the use of frequency domain-based methods. Many fluorescence spectroscopy measurements in the frequency domain have been focused on lifetime-based measurements [11], with the emphasis being on understanding decay kinetics of chemical systems. These frequency domain lifetime measurement were coupled with a fast Fourier transform (FFT) and intensity-modulated light source to induce fluorescence in a fiber optic-based temperature sensor [12], thereby improving the detected signal and aiding in fitting the lifetime decay as a function of temperature. However, there is the possibility of increase accuracy for thermal property measurements by fluorescence thermometry in the frequency domain-based on the spectroscopic signal of the fluorophore, rather than its lifetime.

The current study seeks to expand shape-based, neural network reconstructed, time-domain fluorescence thermometry [8] with quantum dots into the frequency domain to determine the decay and phase delay of the thermal wave along a thin fiber caused by intensity-modulated laser heating. Because neural networks have successfully been used to reconstruct the surface signal for photothermal radiometric experiments [13], they have the potential to improve the temperature accuracy of the quantum-dot shape-based thermometry.

Accurate measurements of the thermal properties of fibers are of interest, because of large uncertainties in the measured property for spider silk [14–16] and polyethylene nanofibers [17], which are induced by thermal contact resistance [18], modeling biases [19], and spatial resolution [20]. Additionally, axial thermal conductivity (and to a lesser extent, thermal diffusivity $k = \alpha / \rho c_p$) and Young’s Modulus are properties of interest because they are the most sensitive characteristics to measure chain extension and continuity in polymers [21]. One proposed way to improve the accuracy of their measurement is to use non-contact temperature techniques and to exploit modulated excitation.

In this work, a neural network approach is used for extracting temperature from the fluorescence spectrum of inorganic fluorophores, both in time and frequency domains. This neural network reconstructed temperature in the time domain can be used for thermal characterization, particularly with photothermal methods, via successful mapping into the frequency domain. An FFT (Fast Fourier Transform)-based method is proposed and detailed to perform this mapping operation and obtain the needed amplitude and phase at the
modulation frequency. Laser heating experiments and simulations are investigated to determine the feasibility of this approach to measure the thermal diffusivity of thin fibers.

9.3 Experimental setup

The experimental setup was a pump-probe laser system with the sample fiber mounted on a sample holder capable of measuring and controlling its temperature (Figure 9.1). Quantum dots deposited on the surface of the fiber were illuminated with the probe beam (532 nm Coherent Compass CW laser) at a spot size of 30 µm, and the resulting fluorescent emission was collected with an Olympus microscope objective (10X, 0.25 NA) into the fiber optic of an Ocean Optics USB4000 spectrometer, after having passed though band pass filters to remove the probe light. After passing through an optical chopper, the pump laser (a 1064 nm Coherent Vector) was focused onto the fiber with a half lens mounted on a position scanning stage, with a resulting spot size of 90 µm. This laser contained some residual green light, which was filtered out prior to arriving at the sample, and the reflected light from the filter was focused onto the spectrometer to provide a reference for the intensity-modulation of the laser light for photothermally generated temperature variations.

The longer wavelength of the pump beam was selected to not induce fluorescence of the quantum dots because the absorption of the quantum dots at IR wavelengths is insignificant and it did not interfere with the emitted fluorescence spectra. Focusing of the lasers by half lenses allowed independent motion of the pump laser from the probe laser, as well as maintaining the same focal plane for both collimated laser beams.

The sample holder consisted of an aluminum plate with four heating resistors that provided control of the sample temperature from a Labview-controlled PID control routine. The fiber was placed in a slit on the plate to allow optical access from both sides. Temperature was measured by both a PT1000 (measured by an HP-34401 via GPIB control) and a type T thermocouple (measured by an HP-34970A via GPIB). Samples were placed inside a Janis cryostat to provide optical access and high vacuum (10^{-5} mTorr). Photopyroelectric measurements of the thermal diffusivity of air demonstrated that at 2.6 Torr the diffusivity of air at 3.55 × 10^{-3} m^2 s^{-1} [22], and the significantly decreased vacuum pressure allows for the neglect of convective contributions to the heat transfer of the fiber.

To relate the fluorescence spectra to the fiber surface temperature, a calibration is needed. The calibration process of the experiment begins by stabilization of the fiber at ±0.015 °C for 15 minutes, after which 250 spectra are acquired, while recording the sample mount temperature measured by the PT1000 resistor. Temperature increments of 2 K (between 300 K and 312 K) resulted in 1750 total recorded calibration spectra to provide the training data for the neural network.
Upon a successful calibration and alignment of the pump and probe beams, the position of the pump laser with respect to the probe laser is scanned between -2000 and 2000 µm, with scanning steps of 50 µm. At each position, the laser is turned to full power (1 W) to provide enough modulated heating on the fiber to produce a sufficient photothermal signal. After a waiting period of 10 seconds (to allow for a steady state of the DC heating, resulting in mainly AC variation), the spectrometer began measuring as quickly as possible, with the sampling time long enough to collect 100 periods for an improved phase measurement during the FFT analysis.

### 9.4 Methods

Central to the quantum dot fluorescence shape-based thermometry and its application to a frequency domain axial temperature model, the following sections will focus on the neural network training process for time domain temperature reconstruction, the Fast Fourier Transform (FFT) procedure to find the amplitude and phase of the complex temperature (compared to the FFT of commonly used spectral features), develop-
ment of a numerical simulation of the temperature behavior of the fluorescence spectra (assuming a linear relation between spectral features and temperature) at the modulation frequency, and extending the numerical simulation to verify the ability of this method to extract the thermal diffusivity of the fiber from axial and frequency scans.

9.4.1 Neural network training and temperature reconstruction

Temperature behavior of spectra

To reconstruct the temperature of the fiber surface, the relationship between different spectral features and temperature (acquired during steady probe laser illumination but without probe laser-induced photothermal heating) is detailed. Being placed in vacuum and maintaining all other variables to be constant, factors such as quenching, dipole interactions, pH [23], salt concentrations, and electron coupling [24] were not expected to vary during the duration of the experiment, meaning that the spectral changes are solely functions of temperature. The process to train the neural network based on these spectral features as inputs is detailed below.

Several temperature dependent spectral features of the quantum dots (shape-factors) have been used independently in the literature and include: peak intensity (PI) [25], peak normalized intensity [26], integrated intensity (II) [27], the PI/II ratio (R) [28], peak wavelength (PW or PWL [29]), FWHM [29], and the summed spectral bands [30]. These features as a function of temperature are shown (along with the overall spectra) in Figure 9.2.

With a sufficiently stable temperature relation between the different spectral features, application of neural networks to solve the inverse temperature problem is sufficient. The process began with compiling the 250 spectra at each calibration temperature and then a rectangular-windowed averaging on a moving window on the intensity values of 10 wavelengths was performed. This had the effect of reducing the noise induced by the spectrometer. A 3rd order polynomial (for numerical stability) was then fit to the smoothed spectra, the derivative was taken, and the peak intensity and peak wavelengths were calculated at the maximum value. The integrated intensity was measured as the sum of the intensity values under the fit curve, and the ratio of peak intensity to integrated intensity was also calculated. The FWHM was also calculated based on the fitted curve. The “sum bands” consisted of the summed values of five \(\approx 5\) nm wide bands between 536 nm and 664 nm, similar to how photodiodes with notch filters would perform. Finally, the intensity values of 40 evenly spaced wavelengths of the spectra between 536 nm and 664 nm were normalized to the peak intensity.
Fig. 9.2: Fluorescent spectra of quantum dots at the calibrated temperatures (a) and the temperature dependence of the PI, Ratio (b), 40 peak normalized intensities (c), 5 sum bands (d), and PWL and FWHM (e) of the spectra.

and these values (in addition to the peak intensity) were ultimately selected as inputs for the neural network, based on providing the lowest RMS of the trained neural network.

**Neural Network Training**

Based on previous research and simulation, the neural network that provided the greatest accuracy was one where the inputs were based on 40 peak-normalized intensities and the peak intensity, containing 2 hidden nodes. The performance of this neural network is compared to the traditional use of peak intensity as a means to reconstruct the temperature in the time and frequency domains.

For cross-validation purposes, the temperature calibrated spectra were randomly distributed between training spectra (80%) and testing spectra (20%). The training data was used to vary the weights of the different nodes until the RMS error of the neural network output temperature compared to the expected temperature was minimized, guided by a Levenberg-Marquardt algorithm. The testing spectra was then used to confirm that the neural network was not over-trained. The weights of this trained neural network was then applied to spectra acquired during modulated heating to reconstruct the surface temperature of the fiber. Figure 9.3 shows the general NN architecture, the expected vs output temperature of a trained neural network, and the averaged and unaveraged RMS error of the reconstructed temperature.
Fig. 9.3: NN architecture for peak intensity and normalized intensities inputs (a), results of expected vs output temperature values from NN (b), and averaged RMS (c) and unaveraged (d) error values versus temperature from the NN training with training spectra results in blue circles and test spectra in red dots. From experiment.

9.4.2 Complex surface temperature by FFT

In order to map the spectral data sequences from the time domain to frequency domain, a Fast Fourier Transform (FFT)-based method was used. In order to cope with some jitter on the pump laser intensity modulation by the optical chopper, together with the fluorescence light, a part of the modulated pump light was sent to the spectrometer, so that the reference signal of the experiment could be accurately monitored synchronously with the fluorescence spectra acquisition, by determining the surface under the spectral peak magnitude at 532 nm for every acquired spectrum. An FFT was performed on the time dependence of the
reference signal, yielding the intensity modulation frequency, the modulation amplitude, and the modulation phase with respect to the chosen time scale. The modulation phase was stored, to later be subtracted from the phase of the other signals, and determine the absolute phase delay between the extracted photothermal temperature modulation and the intensity modulation.

An FFT was then performed on the NN-reconstructed temperatures. Also the periodically modulated part of the fluorescence peak intensity signal was analyzed in that way, as it is a commonly used spectral feature in the literature to relate fluorescence to temperature, and because it has a higher dynamic range (about 1/30000) than the NN-reconstructed temperature due to discretization effects of most of the other features (about 0.1 nm/35 nm for FWHM and 0.1 nm/631 nm for PWL). The time varying part of the latter was determined by fitting a 3rd order polynomial to its time dependence signal, and subtracting the polynomial in order to remove effects of the slow temperature evolution due to the steady state component of the optical heating.

After performing the Fourier transform, the amplitude and phase of each signal (with respect to the phase of the reference signal) at the modulation frequency (as determined by the reference signal) was stored.

The purpose of mapping the surface temperature in frequency domain was to be able to use Salazar et al. [31] frequency domain model for an infinitesimally small laser line heating source on a cylinder.

9.4.3 Numerical experiment for NN accuracy and FFT validity

In order to verify the ability of the FFT-based method to accurately transform the spectral signals into the frequency domain for the purpose of measuring the thermal diffusivity of a thin fiber, a numerical simulation of the quantum dot spectra (approximated as a Gaussian distribution) and their behavior due to temperature variations was created for different modulation frequencies and pump-probe distances, mimicking the operation of a real life experiment, as illustrated in Figure 9.4.

The time varying temperature was simulated, with noise based on experimental data (Table 9.1) imposed on the temperature and temperature-dependent spectral features, resulting in Gaussian shaped spectra. Additional noise was added to the spectra to mimic the signal to noise ratio observed with the spectrometer. The spectral features were assumed to be linear (based on experimental observations seen in Figure 9.2, \( A = P_{H0} + S_{H} T \)) over the 300–312 K range of interest. In actuality, the different features become non-linear as the temperature range is increased, but the neural network is able to account for these non-linearities. The simulated spectra were then processed with the proposed FFT-based thermal property extraction method in the same way as the experiment, with the intent to compare the expected thermal properties to the calculated
Table 9.1: Inputs and uncertainties used for the simulation.

<table>
<thead>
<tr>
<th>Sim. Parameters</th>
<th>Nominal Values</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$ Resolution</td>
<td>520–770 nm</td>
<td>0.19 nm</td>
</tr>
<tr>
<td>PT1000 Temp</td>
<td>300–312 K</td>
<td>0.05 K</td>
</tr>
<tr>
<td>Time Spacing</td>
<td>0.001 sec</td>
<td>0.000727 sec</td>
</tr>
<tr>
<td>Spectrometer Noise</td>
<td>0 counts</td>
<td>217 counts</td>
</tr>
<tr>
<td>$A_{PI,0}$</td>
<td>329356 counts</td>
<td>42.58383 counts</td>
</tr>
<tr>
<td>$B_{PWL,0}$</td>
<td>613.51 nm</td>
<td>0.123523 nm</td>
</tr>
<tr>
<td>$C_{FWHM,0}$</td>
<td>16.153 nm</td>
<td>0.000322 nm</td>
</tr>
<tr>
<td>$D_0$</td>
<td>1500 counts</td>
<td>50 counts</td>
</tr>
<tr>
<td>$S_{PI}$</td>
<td>-1014 counts/K</td>
<td>1.391491 counts/K</td>
</tr>
<tr>
<td>$S_{PWL}$</td>
<td>0.059 nm/K</td>
<td>0.000404 nm/K</td>
</tr>
<tr>
<td>$S_{FWHM}$</td>
<td>0.0616 nm/K</td>
<td>0.000105 nm/K</td>
</tr>
<tr>
<td>$S_D$</td>
<td>0 counts/K</td>
<td>0 counts/K</td>
</tr>
<tr>
<td>Motor Position</td>
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<td>0.0011 mm</td>
</tr>
<tr>
<td>$m_{phase}$</td>
<td>2000 rad/m</td>
<td></td>
</tr>
<tr>
<td>$m_{mag}$</td>
<td>600 I/m</td>
<td></td>
</tr>
<tr>
<td>$\alpha_t$</td>
<td>0.13 and 0.16 mm$^2$/s</td>
<td></td>
</tr>
<tr>
<td>$P_0$</td>
<td>1000 a.u.</td>
<td></td>
</tr>
<tr>
<td>$k_s$</td>
<td>0.24 W/mK</td>
<td></td>
</tr>
<tr>
<td>$h$</td>
<td>6 W/m$^2$K</td>
<td></td>
</tr>
<tr>
<td>$f$</td>
<td>0.5 and 2–10 Hz</td>
<td>0.05 Hz</td>
</tr>
</tbody>
</table>

thermal properties.

A model for heating of a cylinder by an intensity modulated, infinitesimally small laser line heating source [31] represented the complex temperature distribution on the fiber, with the following conditions: sample in vacuum to neglect convection, linearized radiation, and the cylinder radius being significantly smaller than the diffusion length of the thermal wave, Eqs. 9.1, 9.2, and 9.3.

\[
\tilde{T}_s(a,z) \approx \frac{P_0}{2\pi k_s q_s'} e^{-q_s'|z|} 
\]  

(9.1)

\[
q' = \sqrt{\frac{i\omega}{\alpha_s} + \frac{2h}{k_s a}}
\]  

(9.2)

\[
\mu = \sqrt{\frac{2\alpha}{\omega}}
\]  

(9.3)

The model predicts a linear dependence of the phase delay and of the logarithm of the magnitude based on the pump-probe distance, Eqs. 9.4 and 9.5.
Fig. 9.4: Illustration of the process to calculate the thermal diffusivity of a fiber, with respect to the photothermal signal amplitude and phase as a function of pump-probe spacing and laser (heating) intensity modulation frequency, experimental process (a) and numerical simulation (b).
\[ z_{\text{mag}} = \exp(m_{\text{mag}}|z| + b_{\text{mag}}) \] (9.4)

\[ z_{\text{phase}} = m_{\text{phase}}|z| + b_{\text{phase}} \] (9.5)

The slopes of the phase and natural log of the magnitude are determined by the modulation frequency and the fiber’s thermal diffusivity, Eq. 9.6.

\[ m_{\text{phase}} \times m_{\text{mag}} = -\pi f \alpha_s^{-1} \] (9.6)

Two types of scans were numerically investigated, a frequency scan at a fixed axial pump-probe spacing of 0.5 mm microns and an axial scan at a fixed frequency of 0.5 Hz. During the axial scan, the frequency was fixed at 0.5 Hz, resulting in values for the phase and magnitude slopes (Eqs. 9.4 and 9.5) of 2000 rad/m\(^{-1}\) and 500 m\(^{-1}\), for a chosen diffusivity ($\alpha_s$) value of $1.3 \times 10^{-7}$ m\(^2\) s\(^{-1}\) (Eq. 9.6).

To mimic the time domain behavior of the experiment, the AC temperature variations (indicative of the complex temperature), Eq. 9.7) were superimposed onto a gradual DC temperature rise (Eq. 9.8), with a power law shape with exponent 1/2, which was indicative of the sample heating that occurred from the laser.

\[ T_{\text{AC}}(z \text{ or } f, t) = \frac{f_{\text{reqmag}}}{f_{\text{reqmag,max}}} \frac{z_{\text{mag}}}{z_{\text{mag,max}}} \times \cos\left[2\pi f(t - t_0) - z_{\text{phase}} - f_{\text{reqphase}}\right] \] (9.7)

\[ T_{\text{DC}}(z \text{ or } f, t) = [T_{\text{end}} - T_0] \left(\frac{t - t_0}{t_{\text{end}}}\right)^n + T_0 \] (9.8)

The linearly dependent spectral features ($A_{\text{PI,0}}, S_{\text{PI}}, B_{\text{PW,L}}, S_{\text{PW,L}}$, etc), with values measured from experiment (Table 9.1), were used to create the Gaussian shaped spectra as a function of time Eq. 9.9. The green reference signal from the modulated laser was simulated as a trapezoidal curve between 526 nm and 535 nm and was added to the simulation at the heating modulation frequency.

\[ \text{Spec}[\lambda, T(z \text{ or } f, t)] = (A_{\text{PI,0}} + S_{\text{PI}}T) \times \exp\left[-\frac{4\ln(2) (\lambda - (B_{\text{PW,L,0}} + S_{\text{PW,L}}T))^2}{(C_{\text{FWHM,0}} + S_{\text{FWHM}}T)^2}\right] + (D_0 + S_D T) \] (9.9)
The simulation created calibration spectra for the training of the neural network, in addition to the modulated spectra. Experimental uncertainties (Table 9.1) were used in the generation of both types of spectra.

9.5 Results

9.5.1 FFT behavior via simulation

Using the simulated data from the previous section (where the nominal values and uncertainty in the inputs were based on experimental data), the data processing described in Figure 9.4 was extended to the reconstruction of photothermally induced temperature evolutions. As mentioned earlier, an FFT was performed on the reference signal to find the modulation frequency. Figure 9.5 shows the simulated results of the amplitude of the FFT for a simple sinusoidal modulation. A peak at 0.5 Hz is observed in the reference signal and corresponding peaks are seen in the reconstructed NN temperature and the peak intensity of the signal.

The results in Figure 9.5 demonstrate that mapping the fluorescent spectral features signal into the frequency domain via FFT can provide the amplitude and phase at the modulation frequency, and that the

![Graph showing FFT spectra for numerical simulation (sine modulation)](image)

Fig. 9.5: FFT spectra for numerical simulation (sine modulation) showing the dominant frequency present in the reference with corresponding FFT peaks in the spectral signals (NN temperature and peak intensity) at the modulation frequency of the original temperature.
modulation frequency can be determined by the FFT of the reference signal.

Additionally, the windowing of the entire signal was selected to observe the effect of including the curved baseline (caused by DC portion of heating) compared to subtracting a 3rd order polynomial fit from the signal prior to implementation of the FFT. The subtracted signal provides the lowest error on the phase of the signal, and still maintains the high amplitude of the signal. Compared to subtracting the baseline, an error of 1.1% on the amplitude of the signal is observed due to the gradual temperature rise and the effect on the phase (compared to the true phase) is 1.24 degrees with and 0.11 without the 3rd order polynomial subtraction.

### 9.5.2 Frequency scan and axial scan simulation

In the following, we verify if the dependence of the reconstructed temperature oscillation amplitude and phase on the modulation frequency and pump-probe distance, as calculated by simulated spectra, are well reconstructed.

As explained in Section 9.4.3, the model derived by Salazar et al. [31] was used for a simulated frequency scan of the temperature. The phase and amplitude of 81 linearly spaced frequencies between 2 Hz and 10 Hz were determined at a fixed axial spacing of 0.5 mm (Eqs. 9.1 and 9.2) and then used as inputs in Eq. 9.7, where the amplitude was normalized to the maximum value observed at the lowest frequency. The spectra, calculated as explained in Section 9.4.3, were then presented to the neural networks [32]. For each scanning frequency, the FFT method described above was applied to the reference signal, the NN reconstructed temperature, and the peak intensity. The resulting frequency dependence of the amplitude and phase of the photothermal signal was compared to the one of the temperature underlying the simulation, to verify the performance of the reconstruction procedure. The results of the frequency scan (Figure 9.6) show good agreement at low frequencies between the frequency dependence of the temperature used to create the NN inputs, and the NN-reconstructed data. However, at higher frequencies, the NN-reconstructed signal at the modulation frequency is buried in the noise and signal decay with frequency saturates at the noise floor. (Table 9.1) gives these noise values, which results in a noise level of about -14 dB on the peak intensity and the noise floor observed in the frequency scan is about -13 dB).

The simulation was also run to mimic an axial scan, with the input amplitude and phase data calculated by Eqs. 9.1 and 9.2, at a frequency of 0.5 Hz. The two-sided results (Figure 9.7) of the output phase and amplitude compared to the input agree well. One thing of note during operation of the simulation was that the preferred range of frequencies (to avoid significant attenuation of the signal, while still operating within
Fig. 9.6: Simulated results – amplitude (a) and phase (b) – of FFT-based method for frequency scan with respect to the NN reconstructed temperature and peak intensity signals. The reconstruction approach is effective in reconstructing the input amplitude and phase lower frequencies, but is limited due to the signal being buried in the noise at higher frequencies.

Fig. 9.7: Simulated results of the FFT-based NN method for an axial scan of a photothermally generated temperature field. The reconstruction method is correctly determining the amplitude and phase of the modulated signals.
the acceptable range of the spectrometer) was between 0.5 Hz to 20 Hz for a frequency scan, and near 0.5 Hz for an axial scan. However, the method is severely limited by the level of noise that exists in the reference signal (i.e. -10 dB of noise superimposed on the reference signal makes it difficult to correctly identify the modulation peak in the reference signal while the peak is still discernible with -20 dB of noise) to get an accurate reconstruction of the phase delay. Further work is to be done on improving the reference signal. Assuming that there is no radiation heat loss, the slope of the phase delay is the same as the natural log of the magnitude decay. In this case, the measured thermal diffusivity of the fiber (based on the axial scan in Figure 9.7) is near $3 \times 10^{-7}$ m$^2$s$^{-1}$, which is an order of magnitude higher than the typical value for synthetic spider silks. It is therefore necessary to have an accurate measurement of the phase delay.

9.5.3 Experimental results

The application of the neural network temperature determination thus far described was also extended to the experiment described in an earlier Section 9.3. The used experimental setup via optical chopper and recorded by spectrometer did not provide a sufficiently large range of frequencies to be tested to use a frequency scan (minimum allowable frequency $\approx$1.8 Hz, limited by optical chopper; maximum allowable frequency $\approx$5 Hz, limited by integration time of spectrometer to acquire sufficient signal). For the numerical simulations, the normalized intensity neural network was selected to analyze the experimental behavior of photothermally heating a fiber.

The decay with pump-probe distance of the amplitude (normalized intensity NN) of the photothermal signal as reconstructed from the time dependent fluorescence spectra at different pump-probe distances is presented in Figure 9.8a. The scanning step was 50 µm, with a scanning distance of -2 mm to 2 mm spacing between the pump and probe beams, the sampling frequency of the spectrometer at 13.8 Hz, and an average of 825 spectra per position. To improve the accuracy of the FFT of the signal, the slow temperature rise was removed by fitting of a 3rd order polynomial to the signal, and then subtracting the fit, so that the AC-portion of the signal remained. This was obtained via the same FFT process described previously, including selecting only the values of the FFT signal at the fundamental frequency. Figure 9.8b shows the amplitude of the FFT of the peak intensity of the fluorescence signal and neural network temperature compared to the amplitude of the reference signal at a fixed axial spacing (1.0 mm). Although in the experiment, the light was modulated in a square wave fashion via optical chopper, only the fundamental frequency component could be considered.

Figure 9.8a, illustrates the decay of the experimentally probed thermal wave with increasing pump-probe distance, with the broad central peak reflecting the finite size of the excitation spot and of the probed area.
Fig. 9.8: Natural log of amplitude portion of the FFT signal of the peak intensity as a function of axial location (a). The FFT spectra at a chopper modulation frequency of 2 Hz at one of the axial positions (b) showing dominant frequencies present in the reference with corresponding FFT peaks in the spectral signals (NN temperature and peak intensity) at the fundamental frequency clearly. Because of the uneven duty cycle of the 2 Hz square wave modulation via optical chopper, higher frequency components of the reference signal are observed at all harmonics of the 2 Hz signal, while only the 4 Hz peak is observed in the NN temperature and the 2 Hz, 4 Hz, and 12 Hz peaks are observed in the peak intensity. Finally, the modulated behavior of the reference and temperature dependent signals is shown (c).
The absolute phase delay of the reference signal phase subtracted from the temperature signal phase was erratic at the different axial positions due to too much noise in the reference signal. This noisy reference signal is the limiting factor in accurately applying this method to determine thermal properties, as explained in the end of Section 9.5.2.

Figure 9.8b, shows the FFT spectra of the experimental square wave modulation reference, the NN reconstructed temperature, and the peak intensity signals, with higher harmonic elements observable. Figure 9.8c, shows the modulated behavior of the fluorescence peak intensity signal based on the experimental reference signal (based on both the green light and some residual IR light that entered the spectrometer). The values were normalized to their peak values and show, as expected, that when the pump laser was on (high reference signal), the fluorescence peak intensity decreased due to the increase in temperature from the laser heating.

The numerical simulations for the axial thermal wave decay had assumed an infinitely narrow laser beam and no effect from the background at low signal noise levels. However, in practice this is not valid and therefore, the more complete model by Salazar [31] must be used and are presented in Eq. 9.10

\[
\tilde{T}_s(a,z) \approx \int_{-\infty}^{\infty} e^{i\lambda z} \frac{P_0}{4\pi k_s \delta_s} \delta_s a \frac{e^{-\lambda^2 \delta^2/8}}{k_s \delta_s \delta_s a \ln(\delta_s a)} + \frac{h}{k_s \delta_s} d\lambda, \tag{9.10}
\]

where \(\delta^2 = q_i^2 + \lambda^2\) and \(q_i = \sqrt{i\omega/D}\).

The data presented in Figure 9.8a, where only data above the noise floor was selected, was used to curve fit the magnitude of Eq. 9.10, with the thermal diffusivity and beam width being the two curve fitting parameters. The selection of beam width being a fitting parameter was because of the uncertainty in the degree of overlap between the IR pump beam (about 90 \(\mu\)m in diameter) and the green probe beam to induce fluorescence (about 30 \(\mu\)m in diameter). The results of the curve fit are presented in Figure 9.9, with the measured thermal diffusivity based on amplitude alone being 3.2 ± 0.8 \(\times\) 10\(^{-7}\) m\(^2\) s\(^{-1}\) and the fitting beam width being 110 \(\mu\)m, which is near the summed diameter of the two beams. This diffusivity value is comparable to some of the more recent synthetic silks as measured by the TET (see Synth #9 in Table 11.1), which demonstrates the proof of concept of the proposed method. Similar to the frequency scan in Figure 9.6, the modulated temperature signal becomes buried in the noise at about a 1 mm axial spacing between the lasers, with the noise floor being about -15 dB.

The FFT spectrum of the neural network reconstructed temperature in Figure 9.8c does not show other harmonics besides the fundamental. A similar behavior is seen in the peak intensity signal and this is also
expected to be because the signal is buried in the noise floor of the background noise.

9.6 Conclusions

CdSe/ZnS quantum dot shape-based thermometry via neural network has been shown to be a viable basis for an FFT-based detection of photothermally induced temperature variations. A numerical experiment reconstructing the frequency and pump-probe distance dependence of a photothermal signal from fluorescence spectra demonstrated the intrinsic feasibility of the approach for thermal property determination. Experimental results for an axial scan qualitatively confirm that the amplitude of the signal decays with pump-probe distance in an expected manner. Methods to improve measurement of the phase will be investigated in a future article and will aid in the determination of the thermal diffusivity of thin fibers.
References


Section 9.5.2 presented the results of a simulated frequency and axial scan and commented briefly on the noise floor observed during the frequency scan, resulting in a deviation from theory. To further explain this and the limits of the FFT-fluorescence method, the neural network reconstructed temperature at several frequencies (Figure 10.2) and the corresponding FFT spectrum of that temperature and the reference signal (Figure 10.1) are presented. Figure 10.2 shows an observable sinusoidal modulation at 2.1 and 3.1 Hz (blue and black), but at the higher frequencies (red and green), the magnitude of the oscillations are on the same order as the reconstructed temperature noise. The FFT spectrum also supports this observation where peaks are only apparent at the lower frequencies.

10.1 Hardware

A picture of the two different fluorescence setups are shown in Figure 10.3 for the setup at KU Leuven and Figure 10.4 for the setup at Utah State.

Fig. 10.1: Amplitude of the FFT spectrum of the reference signal (dotted lines) and NN reconstructed temperature at 2.1, 3.1, 5.1, and 9.1 Hz.
Fig. 10.2: Simulated temperature variations, offset to illustrate how the AC temperature variation is buried in noise, matching the coloring scheme of Figure 10.1 at 2.1 Hz (blue), 3.1 Hz (black), 5.1 Hz (red), and 9.1 Hz (green).

Fig. 10.3: Labeled picture of KU Leuven fluorescence setup.
10.2 QD shape-based fluorescence thermometry considerations

This section outlines some of the benefits and shortcomings of the QD shape-based fluorescence thermometry method in Table 10.1.

<table>
<thead>
<tr>
<th>Benefits</th>
<th>Shortcomings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurement takes 1-2 days</td>
<td>Currently, only rear detection for transparent fibers</td>
</tr>
<tr>
<td>With a reference layered sample, $\alpha$ &amp; $k$ possible</td>
<td>Currently, only $\alpha$ measured</td>
</tr>
<tr>
<td>Non-contact detection</td>
<td>Complexity of setup</td>
</tr>
<tr>
<td>Temperature information in both time and frequency domains</td>
<td>Low frequency range limit due to spectrometer</td>
</tr>
</tbody>
</table>
CHAPTER 11
SUMMARY OF FIBER THERMAL PROPERTY RESULTS

Below is a summary of the thermal properties of the thin fibers measured with the TET, $3\omega$, and fluorescence-based thermometry. Of note are the diffusivity values from the $3\omega$ for the synthetic spider silk. They were performed on only one fiber, rather than multiple lengths to curve fit away the radiation effect. Because of that, they are consistently higher than the TET measured values. However, because they are not exceptionally long (usually 1 mm or so), the radiation effect is sufficiently low that the properties are not too erroneous.

Table 11.1: Synthetic spider silk thermal diffusivity ($\alpha$).

<table>
<thead>
<tr>
<th>Synth # and Process</th>
<th>Thermal Diffusivity</th>
<th>TET</th>
<th>$3\omega$ (1 fiber)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1 As Spun</td>
<td></td>
<td>1.68</td>
<td>2.15</td>
</tr>
<tr>
<td>#2 80:20 IPA:H$_2$O 3x</td>
<td>2.97</td>
<td>2.61</td>
<td></td>
</tr>
<tr>
<td>#3 80:20 IPA:H$_2$O 3x water dipped</td>
<td>2.23</td>
<td>1.91</td>
<td>2.38</td>
</tr>
<tr>
<td>#4 50:50 IPA:H$_2$O 2x</td>
<td>1.91</td>
<td>1.41</td>
<td></td>
</tr>
<tr>
<td>#5 50:50 IPA:H$_2$O 2x water dipped</td>
<td>2.31</td>
<td>2.04</td>
<td>2.78</td>
</tr>
<tr>
<td>#6 80:20 IPA:H$_2$O 2x, water 2x</td>
<td>2.55</td>
<td>2.38</td>
<td></td>
</tr>
<tr>
<td>#7 70:30 IPA:H$_2$O 2x, water 3x</td>
<td>2.42</td>
<td>3.42</td>
<td></td>
</tr>
<tr>
<td>#8 70:30 IPA:H$_2$O 2x, water 2x</td>
<td>2.55</td>
<td>3.42</td>
<td></td>
</tr>
<tr>
<td>#9 FA-25, 2x2x, 1-MeOH:H$_2$O, 2-H$_2$O</td>
<td>3.33</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>

Table 11.2: Glass fiber thermal conductivity ($k$).

<table>
<thead>
<tr>
<th>Thermal Conductivity</th>
<th>Lit Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L^2H_2$</td>
<td>0.04</td>
</tr>
<tr>
<td>Reduced</td>
<td>1.35</td>
</tr>
<tr>
<td>Full</td>
<td>1.35</td>
</tr>
<tr>
<td>Modified</td>
<td>1.35</td>
</tr>
<tr>
<td>Curve Fit (R)</td>
<td>1.35</td>
</tr>
<tr>
<td>Curve Fit (F)</td>
<td>1.35</td>
</tr>
<tr>
<td>Curve Fit (Mod)</td>
<td>1.35</td>
</tr>
</tbody>
</table>

$^1$From fluorescence method, the approximate thermal diffusivity of a similarly produced fiber was $3.14 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$
Table 11.3: Glass fiber thermal diffusivity ($\alpha$).

<table>
<thead>
<tr>
<th></th>
<th>Thermal Diffusivity (10^-7 m^2 s^-1)</th>
<th>Lit Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L^2H_c^2$</td>
<td>0.04 1.18 4.81 11.21 0.26 1.75 3.31 4.39</td>
<td></td>
</tr>
<tr>
<td>Reduced</td>
<td>7.43 8.10 9.48 9.51 10.4 10.7 13.4 18.9</td>
<td>8.00</td>
</tr>
<tr>
<td>Full</td>
<td>7.90</td>
<td></td>
</tr>
<tr>
<td>Modified</td>
<td>7.32 8.16 8.00 7.84 7.69 7.37 8.89 8.21</td>
<td>8.00</td>
</tr>
<tr>
<td>Curve Fit (R)</td>
<td>7.60</td>
<td></td>
</tr>
</tbody>
</table>

Table 11.4: Natural spider silk thermal conductivity ($k$).

<table>
<thead>
<tr>
<th></th>
<th>Thermal Conductivity (W m^-1 K^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>1.23</td>
</tr>
<tr>
<td>Reduced</td>
<td>9.88 2.85 10.96 31.8 1.2 2.32 190.6 66.92</td>
</tr>
<tr>
<td>Full</td>
<td>1.36 1.29 1.14 1.22 1.15 1.19 1.2 1.23</td>
</tr>
<tr>
<td>Curve Fit - Reduced</td>
<td>1.18</td>
</tr>
</tbody>
</table>

Table 11.5: Natural spider silk thermal diffusivity ($\alpha$).

<table>
<thead>
<tr>
<th></th>
<th>Thermal Diffusivity (10^-7 m^2 s^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduced</td>
<td>45.8 12.5 62.4 173 6.50 12.7 1274 415</td>
</tr>
<tr>
<td>Full</td>
<td>5.80 5.50 5.90 5.90 6.10 6.40 6.80 6.60</td>
</tr>
<tr>
<td>Mean - Full</td>
<td>6.20</td>
</tr>
<tr>
<td>Curve Fit - Reduced</td>
<td>6.30</td>
</tr>
</tbody>
</table>

### 11.1 Applications of silk

This work has demonstrated that the dragline of the *N. clavipes* spider is not a highly thermally conductive fiber, as originally expected. Because of this realization, the application of this material based on its thermal properties is more limited than when this project first began. However, the combination of the silks mechanical strength, thermal stability, and relatively low thermal properties provide several avenues of applications including:
Table 11.6: Platinum thermal conductivity ($k$).

<table>
<thead>
<tr>
<th></th>
<th>Thermal Conductivity (W m$^{-1}$ K$^{-1}$)</th>
<th>Lit Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lit Value</td>
<td></td>
</tr>
<tr>
<td>$3\omega$ - I w/o canceling</td>
<td>74 75.3 71.8 74.1</td>
<td>71.6</td>
</tr>
<tr>
<td>$3\omega$ - I w/ canceling</td>
<td>71.9 72.9 74.9 74.0</td>
<td>71.6</td>
</tr>
<tr>
<td>$3\omega$ - Volt w/ canceling</td>
<td>120.5 112.8 94.4 94.0</td>
<td>71.6</td>
</tr>
<tr>
<td>$3\omega$ - Volt w/ cancel &amp; correct</td>
<td>71.4 73.0 74.5 74.5</td>
<td>71.6</td>
</tr>
<tr>
<td>TET - Full Model</td>
<td>75.3</td>
<td>71.6</td>
</tr>
</tbody>
</table>

Table 11.7: Platinum thermal diffusivity ($\alpha$).

<table>
<thead>
<tr>
<th></th>
<th>Thermal Diffusivity ($10^{-7}$ m$^2$ s$^{-1}$)</th>
<th>Lit Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lit Value</td>
<td></td>
</tr>
<tr>
<td>$3\omega$ - Current w/o canceling</td>
<td>255 265 256 255</td>
<td>251</td>
</tr>
<tr>
<td>$3\omega$ - Current w/ canceling</td>
<td>243 261 250 258</td>
<td>251</td>
</tr>
<tr>
<td>$3\omega$ - Voltage w/ canceling</td>
<td>248 257 255 257</td>
<td>251</td>
</tr>
</tbody>
</table>

Table 11.8: Platinum volumetric heat capacity ($\rho c_p$).

<table>
<thead>
<tr>
<th></th>
<th>Volumetric Heat Cap. (MJ m$^{-3}$ K$^{-1}$)</th>
<th>Lit Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lit Value</td>
<td></td>
</tr>
<tr>
<td>$3\omega$ - Voltage w/ canceling</td>
<td>2.95 2.82 2.96 2.84</td>
<td>2.85</td>
</tr>
</tbody>
</table>

Table 11.9: Minor ampullate silk and carbon thermal diffusivity ($\alpha$).

<table>
<thead>
<tr>
<th></th>
<th>Thermal Diffusivity ($10^{-7}$ m$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Spider Minor Silk (20 m/min)</td>
</tr>
<tr>
<td>Curve Fit - Reduced</td>
<td>4.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Carbon Fiber (AS4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curve Fit - Reduced</td>
<td>62.0</td>
</tr>
<tr>
<td>Modified</td>
<td>62.5</td>
</tr>
</tbody>
</table>
• Insulative fabric, similar to silk produced from the silkworm, but with improved mechanical and biocompatibility properties (1–3).

• Instances where Kevlar \((k, 300 \, \text{K} = 3.7 \, \text{W} \, \text{m}^{-1} \, \text{K}^{-1} \, [4])\) or Zylon \((k, 300 \, \text{K} = 19–25 \, \text{W} \, \text{m}^{-1} \, \text{K}^{-1} \, [4])\) is used but with a lower thermal conductivity and similar mechanical properties (including suspension of cryogenic pieces [5–7]). Natural silk was used to suspend an inertial confinement target for fusion testing at Lawrence Liverpool’s Laboratory for Laser Energetics [8].

  – The added benefit is that while Kevlar and Zylon require petrochemical constituents in their production, spider silk does not.

• Flexible electronics (after gold coating) for use in cryogenic applications desiring low heat losses (based on work by a group at FSU with superconducting magnets [9–12]).

• Reinforcing fiber in composites [13].

11.2 Future work

During the course of this work, several potential avenues for future research have been realized:

• Multiplexing and functionalizing QD to adhere to spider silk surface based on different amino acids [14]

• Measurement of transgenic silkworm silk with both spider silk and green fluorescent protein (GFP) [15], which has also been used previously as a temperature sensor [16]

• Measurement of natural silk with the fluorescence thermometry

• Measure fibers at cryogenic temperatures

• Extending TET and 3ω measurements into improved composite predictions

• Due to anisotropy of fibers, measure radial conductivity

• Perform fluorescence thermometry with fiber-optic-based system

• Extend fluorescence thermometry to front detection for opaque materials
References


CHAPTER 12
CONCLUSIONS

This work has detailed the derivation, numerical simulation, and experimental application of three methods to measure the thermal conductivity, thermal diffusivity, and volumetric heat capacity of thin fibers: the transient electrothermal technique (TET), the $3\omega$ technique, and the photothermal quantum dot fluorescence shaped-based thermometry.

A parametric study of the TET method with an improved full model quantified the effect of non-constant heating, non-uniform coating, and radiation (and to some extent convection) heat losses on accurate property measurements. Several non-dimensional parameters were obtained that can be used in conjunction with the reduced model for an improved thermal conductivity and thermal diffusivity measurement. There are then three basic methods of data reduction via TET for an accurate measurement: curve-fit with reduced model results to obtain a “zero-length” value where radiation is negligible, use of reduced models with a correction by the non-constant radiation parameter $\xi$, or use of the full model. These were applied to platinum wires and gold-coated glass fibers (with the thermal conductivity and diffusivity results matching literature values) as well as natural and synthetic spider silks.

Practical considerations for applying the $3\omega$ method with a current source or a voltage source with a bridge (with $1\omega$ canceling and correcting for bridge resistance) were detailed and limits on probing frequency as well as the sensitivity of the method to various sources of error were given. The thermal conductivity, diffusivity, and volumetric heat capacity were measured for platinum wire and matched literature values. Because of their non-uniform geometry, the $3\omega$ method was able to only measure the thermal diffusivity of nine different synthetic spider silks, without correction for radiation. The measured values were slightly higher than the values measured by the TET.

The quantum dot fluorescence shape-based thermometry has been demonstrated as a proof of concept that has an improved temperature accuracy (0.29 K versus 1 K) by use of multiple shape factors rather than a simple peak intensity. The method is able to detect the amplitude decay and phase delay of a photothermally induced modulated temperature on the fiber surface during a frequency and axial scan, and numerical simulations have demonstrated the ability to extract the thermal diffusivity from this complex temperature behavior. Furthermore, experimental results have also detected the thermal wave behavior, but have not successfully been confirmed with a reference sample.
In summary, this work has reached the following conclusions:

- Realistic thermal property measurement of silks (both natural and synthetic spider silks) were obtained, demonstrating that its thermal behavior is not atypical ($k$ of 1.2 W m$^{-1}$ K$^{-1}$, $\alpha$ of $6 \times 10^{-7}$ m$^2$ s$^{-1}$, and $\rho c_p$ of 2000 kJ m$^{-3}$ K$^{-1}$).

- Newly developed models that incorporate radiation (and convection) heat transfer and non-constant Joule-heating provide an accurate thermal property measurement without the systematic error that was present in the original study that reported exceptionally high thermal conductivity values for dragline silk.

- Strain increase of silk properties reported in the initial thermal property investigation has not been investigated because of difficulty decoupling the length dependent radiation contribution from the strain contribution on the thermal properties.

- Processing of the synthetic spider silks during their production have an effect on the orientation and formation of crystalline $\beta$-sheets. These, in turn, resulted in improved mechanical and thermal properties, with the greatest improvement observed for a methanol stretched silk.

- Quantum dots are a potential fluorophore for thermal characterization of materials.

The significance of this dissertation is providing new methods, along with the practical considerations, to measure the axial thermal conductivity and thermal diffusivity of thin fibers. These methods have improved upon the accuracy of previous developments in the literature by incorporating additional heat transfer modes and corrections of systematic behaviors in the realm of contact methods. For non-contact methods, the accuracy of temperature by fluorescent thermometry has been improved by reconstruction via neural networks of quantum dot fluorescence. Combined, these methods have helped to correctly measure the thermal properties of natural and synthetic spider silks. Although spider silk is not the marvelous thermal conductor it was initially reported to be, both natural and especially synthetic silks provide a multipurpose material with tunable properties based on several factors in its production. This lays the groundwork for improved fiber-reinforced composite thermal property prediction (by providing accurate axial properties of thin fibers) and characterizing a strong, lightweight material as a more insulative alternative to petrochemical based fibers.
APPENDICES
Appendix A

Approval forms

A.1 Author approval forms

This appendix is focused on permission letters from both co-authors and publishers to include the previous papers in this work.
November 9, 2015

Troy R. Munro
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Logan, UT 84341
801-558-4780

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Date: ____________________________
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Date: 11-9-15
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Date: Nov. 6, 2015 ____________________________. 
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801-558-4780

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801-558-4780

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Troy R. Munro
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Logan, UT 84341
801-558-4780

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Use of Published Journal Article in PhD dissertation

Troy Munro <troy.munro@aggiemail.usu.edu>

To Whom It May Concern,

As part of my PhD dissertation, I would like to include one of the papers I published in your Applied Thermal Engineering journal, "Thermal property characterization of fine fibers by the 3-omega technique" (doi:10.1016/j.applthermaleng.2014.06.022) and Polymer journal "Thermophysical properties of the dragline silk of Nephila clavipes spider" (dx.doi.org/10.1016/j.polymer.2014.05.046). From your website on scholarly sharing (https://www.elsevier.com/about/company-information/policies/sharing), it says:

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This chapter is based on a paper published in Applied Thermal Engineering, 71, dx.doi.org/10.1016/j.applthermaleng.2014.06.022 with the original author list being: Changhu Xing, Colby Jensen, Troy Munro, Benjamin White, Heng Ban, and Mihai Chirtoc.

This chapter is based on a paper published in Polymer, 55, dx.doi.org/10.1016/j.polymer.2014.05.046 with the original author list being: Changhu Xing, Troy Munro, Benjamin White, Heng Ban, Cameron Copeland, and Randolph V Lewis

Is this acceptable?

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Hop Wechsler
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CURRICULUM VITAE
Troy R. Munro
763 E 1200 N Apt C4
Logan, UT 84341
Phone: 801-558-4780
troy.munro@aggiemail.usu.edu

Education

Katholieke Universiteit (KU) Leuven, Leuven, Belgium  
Spring 2016
Utah State University (USU)  
GPA 4.0

Joint PhD, Mechanical Engineering and Physics
by Transient Electrothermal Technique, 3ω, and Photothermal
Fluorescence Shape-Based Thermography – Application to Natural
and Synthetic Spider Silks”
Co-Advisor (KU Leuven): Prof. Christ Glorieux
Co-Advisor (USU): Prof. Heng Ban

Utah State University  
May 2012
MS, Mechanical Engineering  
GPA 3.75

Thesis: “Heater Geometry and Heat Flux Effects on Subcooled,
Thin Wire, Nucleate Pool Boiling in Microgravity”
Advisor: Prof. Heng Ban

Utah State University  
May 2012
BS, Mechanical Engineering (Mathematics minor)  
GPA 3.88

Capstone Project: “Collection of CO₂ from the Martian Atmosphere
for use as a Propellant for a Radioisotope Powered Mars Research Vehicle”
Advisor: Prof. Byard Wood

Research Interests

- Thermal sciences and heat transfer
- Developing methods for micro/nano-scale probing of materials
- Thermal characterization and behavior of biomaterials
- Energy transport under extreme conditions, especially nuclear environments

Publications

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<tr>
<th>Publication</th>
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<tr>
<td>Polymer</td>
<td>3.562</td>
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<td>Microgravity Science and Technology</td>
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<td>International Journal of Heat and Fluid Flow</td>
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<td>International Journal of Thermophysics</td>
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<td>Applied Thermal Engineering</td>
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<td>Measurement Science &amp; Technology</td>
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<td>Journal of the Utah Academy of Sciences Arts and Letters</td>
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</tr>
<tr>
<td>Journal of Applied Physics</td>
<td>2.183</td>
</tr>
</tbody>
</table>
Journals - Published

Journals – Submitted

Journals – In Preparation

**Conference Proceedings**


**Teaching Experience**

- Instructor on Record for Thermal Fluid Design, MAE5410 (senior elective, 15 students), Spring 2015.
- K-12 curriculum support for science classrooms, 2008-present.

**Grants/Proposals Received**


Undergraduate Research Grant. $60,000 grant to fund Get Away Special undergraduate research team from Research and Graduate Studies Office. Awarded February 2013.


Honors and Awards

Fellowships
- Utah State University Presidential Doctoral Research Fellowship, 2012-present
  - Member of inaugural nine students to the program
- Rocky Mountain NASA Space Grant Consortium Fellowship, 2011-2012
- Get Away Special Undergraduate Research Team Summer Fellowship, 2008

Scholarships
- Nuclear Regulatory Commission Scholarship, 2009-2011
- Utah State University Presidential Scholarship, 2007-2011
- Hansen Scholarship, 2011
- Taylorsville Exchange Club Student of the Year Scholarship, 2005
- ATK Outstanding Student Math Scholarship, 2005

Awards
- Outstanding Engineering Graduate Scholar, USU College of Engineering, 2015
- Graduate Enhancement Award, USU, 2015
- B.S. Magna Cum Laude, USU, 2012
- Honors Program, USU, 2007-2011
- AIAA Region VI Student Conference, Team Category, 2nd place March 2011 and 3rd place March 2012
- Undergraduate Research Scholar Transcript Designation, USU, Fall 2010

Service Activities
- Graduate Student Representative, USU 2015-2016.
- Judge for AIAA Region VI Student Conference, 2013.
- Graduate student selection committee for Robins (university wide) awards, 2013.
- Graduate student selection committee for Graduate enhancement awards, 2013.
- Reviewer for ASME 2013 Summer Heat Transfer Conference.
- Reviewer for ASME 2015 IMECE Conference.
- Reviewer for Applied Thermal Engineering.
- ANS Decommissioning, Decontamination & Reutilization Topical Meeting, Session Host, September 2, 2010.
- Get Away Special Research Team Coordinator, mentoring 35 undergraduates per year in space engineering research, 2011-2013.
- Former team lead for CubeSat project, expected flight in 2017.
- Project lead, three successful microgravity boiling experiments with NASA, 2009-2012.
- Project lead for photoelectric effect on lunar dust charging experiment, 2008.
CV - Munro

- STEM outreach organizer for program that has visited over 74 classrooms, brought K-12 students to USU, and met with over 9,000 students and community members.
- Team media contact for over 70 newspaper articles, television spots, and radio stories.

Professional Associations

- Society of Photographic Instrumentation Engineers (SPIE), 2014-present
  - Vice President and founding member of student chapter at USU (2015)
- Belgian Physics Society, 2014-present
- American Institute of Aeronautics and Astronautics (AIAA), 2010-present
- American Society of Mechanical Engineers (ASME), 2009-present
  - Outreach officer, AIAA student chapter, 2010-2011
- Tau Beta Pi Engineering Honor Society, 2009-present

Presentations

Doctoral Period (2012-2015)

12. Intermountain Graduate Research Symposium, “Probing the Mysteries of Spider Silk’s Uncharacteristically High Thermal Diffusivity,” Utah State University, Logan, Utah, oral presentation, April 12, 2013.


15. nanoUtah, “Thermal Diffusivity of Natural and Synthetic Spider Silks,” University of Utah, Salt Lake City, Utah, poster presentation, October 11-12, 2012.

**Masters Period (2011-2012)**


18. USU Physics Department Colloquium, “Gravitational Effects on Thin-Wire Subcooled Nucleate Boiling Dynamics with Two Dimensional Applications,” Utah State University, Logan, Utah, oral presentation (Invited), September 6, 2011.

**Undergraduate Period (2007-2011)**


Technical Reports

“Report for 2010 URCO Funded FUNBOE Experiment,” Undergraduate Research Office, Utah State University, September 2010.

Skills

• Experimental: Transient electrothermal technique, optical (photothermal) techniques, 3ω methods, hot-wire
• Computational: MATLAB, Fortran, LabVIEW, Mathcad, FEMAP, COMSOL, FLUENT, CAD, CAM, MPI, OpenMP
• Spoken Languages: American Sign Language (Intermediate)

Research Advising

Nathaniel Scheelke (Graduate) 2014-Present
Yuefang Dong (Graduate) 2014-Present
Levi Gardner (Graduate) 2015-Present
Ben White (Undergraduate/Graduate) 2013-2014
Ty Henrie (Undergraduate) 2015
Robert Hansen (Undergraduate) 2015
Luke Scoggins (Undergraduate) 2015-Present
Chris Martinez (Undergraduate) 2015-Present
Alexis Simac (Visiting French Undergraduate) 2015-Present
Julien Guillou (Visiting French Undergraduate) 2015-Present
Jenica Hillyard (SWE Senora Region Collegiate Representative, 2013-2014) 2011-2013
Ryan Martineau (AIAA The Twenty 20s Award, 2014) 2010-2013
Jacob Singleton (Air Force Cadet Research Award, 2014, 1 student nationally) 2011-2013