Nonlinear Photothermal Radiometry and its Applications to Pyrometry and Thermal Property Measurements

Austin Drew Fleming
Utah State University

Follow this and additional works at: https://digitalcommons.usu.edu/etd
Part of the Mechanical Engineering Commons

Recommended Citation
https://digitalcommons.usu.edu/etd/6545
NONLINEAR PHOTOTHERMAL RADIOMETRY AND ITS APPLICATIONS TO PYROMETRY AND THERMAL PROPERTY MEASUREMENTS

by

Austin Fleming

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

DOCTOR OF PHILOSOPHY

in

Mechanical Engineering

Approved:

Heng Ban, Ph.D. Mihai Chirtoc, Ph.D.
Major Professor Committee Member

Nick Roberts, Ph.D.
Committee Member

Nicolas Horny, Ph.D.
Committee Member

Mathieu Francoeur, Ph.D.
Committee Member

Jean-Luc Battaglia, Ph.D.
Committee Member

Mark R. McLellan, Ph.D.
Vice President for Research and Dean of the School of Graduate Studies

UTAH STATE UNIVERSITY
Logan, Utah

2017
ABSTRACT

Nonlinear Photothermal Radiometry and its Applications to Pyrometry and Thermal Property Measurements

by

Austin Drew Fleming, Doctor of Philosophy

Utah State University, 2017

Major Professor: Dr. Heng Ban
Department: Mechanical and Aerospace Engineering
Co-Major Professor: Dr. Mihai Chirtoc
University: Université de Reims Champagne-Ardenne, Reims, France

Accurate temperature and thermal property measurements are critical for the modeling and prediction of heat transfer. In many industries thermal management is a limiting factor of performance, and rely on advanced modeling techniques to develop and design methods to better manage thermal energy. While there are standard measurement techniques for both temperature and thermal properties, each technique has its own limitations. One of these standard techniques is photothermal radiometry (PTR) which measures thermal properties by measuring a materials thermal response due to optical heating. PTR measures the emitted thermal radiation from a sample to determine the thermal response. The work presented here further develops the PTR theory by including the nonlinear dependence of thermal emission with respect to temperature.

This more advanced PTR theory is numerically and experimentally explored in this work. Three new measurement techniques are developed and experimentally tested by
including this nonlinear dependence in the PTR theory. Two of these techniques are new pyrometry techniques, and the other is a direct noncontact thermal effusivity measurement technique.

The first pyrometry technique allows for accurate temperature measurement during a traditional PTR measurement. This has many applications when the sample is sensitive to an increase in temperature and possibly damaged due to overheating. This provides significant advantages because PTR is used in many nondestructive testing conditions where the sample can be destroyed or irreversibly damaged due to high temperature.

The second pyrometry technique developed has several advantages over current pyrometry techniques. Mainly it does not require emissivity to be known, measured, or rely on a gray body assumption. These characteristics are very desirable for pyrometry measurements, but it does has significant limitations. Specifically, the measurement can be influenced greatly by any error in the bandwidth of optical filters used in the measurement, and it is very sensitive to any nonlinearity in the detection system. From the experimental results, design guidelines are provided to minimize these two drawbacks of the technique for future exploration.

The direct thermal effusivity measurement developed allows for a non-contact, direct measurement of thermal effusivity of a homogenous material. This type of measurement has not been achieved with any other technique. This technique combined with values of specific heat and density can provide thermal conductivity. Alternatively, this technique combined with laser flash can provide a reliable non-contact measurement of thermal conductivity without any previously known parameters of the material.
These three techniques clearly show there is much additional information obtained in the nonlinear dependence of the PTR signal. Certainly more applications of this theory will be developed in the future to provide more advanced measurement capabilities.
PUBLIC ABSTRACT

Nonlinear Photothermal Radiometry and its Applications to
Pyrometry and Thermal Property Measurements

Austin Drew Fleming

Accurate temperature and thermal property measurements are critical for the modeling and prediction of heat transfer. In many industries thermal management is a limiting factor of performance, and rely on advanced modeling techniques to develop and design methods to better manage thermal energy. This study expands the thermal property and pyrometry measurement capabilities by developing three new techniques based on thermal emission’s nonlinear dependence on temperature.
ACKNOWLEDGMENTS

I would like to thank my major advisors Dr. Heng Ban and Prof. Mihai Chirtoc. Both have significantly influenced me academically, professionally, and personally through the opportunities, guidance, and advice they have provided. I cannot express my gratitude for my major advisors enough. I am thankful for all of the guidance and feedback provided by all of my committee members. Their diverse backgrounds have provided unique perspectives of the research. I would like to recognize Nicolas Horny and Georges Hamaoui for their assistance from an academic and administrative standpoint. Their help has been immeasurable, and I am very grateful for all of the discussions I’ve had with them about research ideas. I am appreciative for the funding of my work from the Region of Champagne-Ardenne, France. I also acknowledge the support from the Microscopy Core Facility at Utah State University for their help with sample preparation.

The advice from people who have gone down a path before you is priceless, therefore I am largely in debt to Colby Jensen. The obstacles avoided due to his advice are innumerable, not to mention his help overcoming the obstacles I encountered. I have been blessed to work with some of the best people I know, and I am very grateful for the time I’ve been able to spend with them. To list a few: Colby Jensen, Charlie Folsom, Zilong Hua, Kurt Harris, Tyson Watkins, and Georges Hamaoui. They are such good friends these gentlemen they are closer to brothers than coworkers.

I am thankful for the extensive support from my family. My parents and my sister have been excellent role models for me. I attribute many of my achievements to their influence. Finally, I am grateful for the love and support from my wife, Shantele. Her
support and selflessness have enabled my success, and I am lucky to have her companionship.

Austin Drew Fleming
CONTENTS

Page

ABSTRACT ................................................................. iii
PUBLIC ABSTRACT ......................................................... vi
ACKNOWLEDGMENTS ..................................................... vii
LIST OF TABLES ........................................................... xii
LIST OF FIGURES .......................................................... xiii
ACRONYMS ................................................................. xvii
NOMENCLATURE ........................................................... xviii

CHAPTER

1. INTRODUCTION ......................................................... 1
   1.1. Motivation ....................................................... 1
   1.2. Overview ........................................................ 5

2. OBJECTIVES .......................................................... 7

3. THEORETICAL BACKGROUND AND CONSIDERATIONS .............. 8
   3.1. Thermal Conduction in Solids .................................. 8
       3.1.1. Heat Conduction Parameters .............................. 9
   3.2. Thermal Radiation ............................................... 11
       3.2.1. Planck’s Law ................................................. 11
       3.2.2. Stefan-Boltzmann Law .................................. 12
       3.2.3. Other Blackbody Distributions .......................... 13
       3.2.4. Blackbody vs Real Emitters ............................. 15
   3.3. Pyrometry Measurements ....................................... 17
       3.3.1. Single Wavelength .......................................... 18
       3.3.2. Two Wavelength ............................................ 19
       3.3.3. Three Wavelength .......................................... 20
       3.3.4. Multi Wavelength .......................................... 22
       3.3.5. Emissivity Enhancement Methods ......................... 22
3.3.6. Active Pyrometry ................................................................. 23

3.4. Conduction with Periodic Boundary Conditions ........................................ 26
  3.4.1. Semi-Infinite Homogenous Slab with Periodic Boundary Condition .... 26

3.5. Non-Contact Thermal Wave Detection Techniques .................................... 27
  3.5.1. Photo-Acoustic ................................................................. 28
  3.5.2. Thermoreflectance ......................................................... 28
  3.5.3. Photothermal Radiometry ................................................ 29
  3.5.4. Mirage ........................................................................ 30

3.6. Thermal Effusivity Measurement Techniques .............................................. 30

3.7. Infrared Radiation Detectors .................................................................. 31
  3.7.1. Responsivity ..................................................................... 33
  3.7.2. Noise Equivalent Power ...................................................... 33
  3.7.3. Specific Detectivity ............................................................ 34

3.8. Lock-in Amplifier .................................................................................. 34

4. MATERIALS AND METHODS ................................................................. 39
  4.1. Photothermal Radiometry ................................................................... 39
    4.1.1. Description of Measurement System ........................................ 40
    4.1.2. Lasers ............................................................................. 41
    4.1.3. Laser Modulation ............................................................. 42
    4.1.4. Mirrors ........................................................................... 45
    4.1.5. Detectors ......................................................................... 45
    4.1.6. Lock-in Amplifiers ............................................................ 46
    4.1.7. Photothermal IR Radiometric Signal ..................................... 46

5. RESEARCH PLAN .................................................................................. 52
  5.1. Development of NL-PTR Theory and Modeling Tools .......................... 53
  5.2. Determine Potential Applications of NL-PTR .................................. 53
  5.3. Experimentally Test Possible Applications of NL-PTR ...................... 53
  5.4. Evaluate the Overall Feasibility of NL-PTR Techniques
      Compared to Standard Techniques .............................................. 54

6. NL-PTR THEORETICAL DEVELOPMENT .............................................. 56
  6.1. Signal Calculation ............................................................................ 56
  6.2. Harmonic Generation ....................................................................... 59
6.3. Ratio of 1st and 2nd Order Radiation Terms ........................................64

7. RELATIVE TEMPERATURE MEASUREMENT ........................................70
   7.1. PTR Signal ..................................................................................70
   7.2. Experimental Configuration ..........................................................72
   7.3. Transient Heating Temperature Monitoring ...................................74

8. DIRECT THERMAL EFFUSIVITY MEASUREMENT .................................77
   8.1. Method for Direct Thermal Effusivity Measurement .........................77
   8.2. Determining T_{AC} Using Harmonic Generation by NL-PTR ..............79
   8.3. Experimental Considerations .......................................................80
       8.3.1. Satisfying One Dimensional Assumption .....................................81
       8.3.2. Incoming Flux .........................................................................82
       8.3.3. Absorption ............................................................................82
       8.3.4. Alternating Temperature Measurement .....................................84
   8.4. Experimental Results .....................................................................90

9. ABSOLUTE TEMPERATURE MEASUREMENT .....................................95
   9.1. Theoretical Development ..............................................................95
   9.2. Emissivity, Transmissivity, and Responsivity Independence ..............98
   9.3. Graphical Representation .............................................................100
   9.4. Experimental Results .................................................................103
   9.5. Discussion & Summary ...............................................................110

10. CONCLUSIONS ................................................................................113
    10.1. Relative Temperature Measurement .............................................113
    10.2. Thermal Effusivity Measurement ................................................116
    10.3. Absolute Temperature Measurement ...........................................120

REFERENCES ......................................................................................122

CURRICULUM VITAE ..........................................................................128
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>52</td>
</tr>
<tr>
<td>5.2</td>
<td>55</td>
</tr>
<tr>
<td>6.1</td>
<td>63</td>
</tr>
<tr>
<td>6.2</td>
<td>64</td>
</tr>
<tr>
<td>8.1</td>
<td>93</td>
</tr>
<tr>
<td>8.2</td>
<td>94</td>
</tr>
</tbody>
</table>

5.1 Outline of main tasks to accomplish the objectives of the dissertation

5.2 Approximate schedule for major tasks and their locations

6.1 The multiplicative coefficients at different frequencies for nonlienerarity coefficients ranging from 2 to 5.

6.2 Ratios between first and second order terms that are provided in Table 6.1.

8.1 Experimentally measured absorptivity, heat flux, $T_{DC}$, $PTR(f_1X2)/PTR(f_1)$ ratio, and the ratio 95% confidence interval uncertainty. Using the measured ratio, $T_{AC}$ is calculated for the mean ratio, and the end points of the 95% confidence interval. These results are presented for Rubber, Glassy Carbon, and coated Steel, and Aluminum.

8.2 Summary of the thermal effusivity literature and measured values of rubber, glassy carbon, steel, and aluminum. The corresponding uncertainty values on the measurement are provided along with the error from the literature value.
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Spectral radiance according to Planck’s law for blackbodies at 300 K, 350 K, and 400 K</td>
</tr>
<tr>
<td>3.2</td>
<td>Comparison between Wien’s approximation, Planck’s law, and the Rayleigh-Jeans approximation for emission at 300 K</td>
</tr>
<tr>
<td>3.3</td>
<td>Diagram showing the three types of interaction irradiation has when it encounters an object. Also shows the classification of Irradiance and Radiosity [W/m²]</td>
</tr>
<tr>
<td>3.4</td>
<td>Diagram of one-dimensional, periodic flux boundary condition for a semi-infinite medium</td>
</tr>
<tr>
<td>4.1</td>
<td>Diagram of a standard PTR system</td>
</tr>
<tr>
<td>4.2</td>
<td>Images of PTR systems used: a. located at URCA, France b. located at USU, USA</td>
</tr>
<tr>
<td>4.3</td>
<td>Acousto optical modulators (AOM) utilize bragg scattering to diffract the laser. The acoustic waves can be controlled by piezo-electric transducer and therefore the magnitude of the diffraction can be controlled</td>
</tr>
<tr>
<td>4.4</td>
<td>Specific detectivity of Kolmar Technologies Mercury Cadmium Telluride (MCT) detector KLD-1-J1/11/DC</td>
</tr>
<tr>
<td>4.5</td>
<td>Emission according to Planck’s law at 400 K, MCT detectivity, and their product plotted over a range of wavelengths. The shaded area is proportional to the detector signal and can be calculated by Equation (4.2)</td>
</tr>
<tr>
<td>4.6</td>
<td>Detector signal vs sample temperature T calculated using Equation (4.2) neglecting $V_{bias}$ and assuming constant values for emissivity and transmissivity. The detector responsivity used can be seen in Fig. 4.4. The value of the product $GADF \rightarrow S$ is chosen such that the result is scaled to be on the order of 1 V</td>
</tr>
<tr>
<td>6.1</td>
<td>Detector signal vs sample temperature calculated by Equation (6.1) neglecting $V_{bias}$ and assuming constant values for emissivity and transmissivity. The detector responsivity used can be seen in Fig. 4.4. The value of the product $GADF \rightarrow S$ is chosen such that the result is scaled to be on the order of 1 V</td>
</tr>
</tbody>
</table>
6.2 The nonlinearity coefficient of the detector signal vs temperature. Determined by fitting Equation (6.2) over small temperature ranges in Fig. 6.1

6.3 Temperature and emission vs time for a sample with the superposition of two frequency modulations. The \( A(f_1) \) denotes the instantaneous amplitude of the PTR\( (f_1) \). The amplitude change of \( A(f_1) \) is seen to be periodic at frequency \( f_2 \). This periodic amplitude change is defined as \( PTR(f_1 X_2) \).

6.4 The modulation of \( A(f_1) \) at frequency \( f_2 \). This modulation is defined as the PTR\( (f_1 X_2) \). The horizontal line is representative of PTR\( (f_1) \).

6.5 Power spectrum of the Fourier transform of the emission due to a modulating temperature with \( f_1 \) and \( f_2 \) of 1 and 15 Hz, respectively, and \( T_{AC1} \) equivalent to \( T_{AC2} \).

6.6 Ratio of PTR\( (f_1 X_2)/PTR(f_1) \) vs \( T_{AC2} \) for three different values of \( T_{AC1} \). It is clear that all three plots lay on top of each other, and therefore that the ratio is independent of the value of \( T_{AC1} \).

6.7 Ratio of PTR\( (f_1 X_2)/PTR(f_1) \) vs \( T_{AC2} \) for three different values of \( T_{DC} \). These confirm the predictions of Table 6.2 that the slope would be altered by the value of \( T_{DC} \), and that the ratio would still be linear with respect to \( T_{AC2} \).

7.1 RS vs sample temperature. The RS given by product of Planck’s Law and the detectivity integrated over all wavelengths at each temperature. The y-axis scale is arbitrary since this curve is multiplied by the constant \( K \) which depends on electrical, optical, and thermal properties of the sample and system. The vertical sine waves have identical amplitudes which correspond to different amplitudes for the horizontal sine waves.

7.2 PTR Signal vs temperature.

7.3 Diagram of experimental configuration for the relative temperature measurement using nonlinear photothermal radiometry (approximately 5mm x 5mm x 15mm).

7.4 PTR signal over a range of temperatures for different surface treatments. These three surface treatments provide different values of emissivity to test the technique under different conditions.

7.5 Measured sample temperature vs time for both PTR measured temperature and thermocouple. The transient heating is due to the DC heating of the laser.
8.1 Homogenizing optics with microlens (beam shaping diffuser) are used to evenly distribute the flux from a laser to create one dimensional heat transfer conditions. ................................................................. 81

8.2 Diagram of the parallel lock-in configuration for nonlinear photothermal radiometry setup. This configuration uses two lock-in amplifiers that simultaneously measure the PTR signals at \( f_1 \) and \( f_1 \pm f_2 \). ................................................................. 86

8.3 Diagram of the series lock-in configuration for nonlinear photothermal radiometry setup used to measure the amplitude of the periodic temperature modulation. Lock-in amplifier \#1 is used to measure the instantaneous amplitude of the PTR signal at frequency \( f_1 \). The output is then the input for lock-in amplifier \#2 which measures the modulation of the amplitude at frequency \( f_2 \). The time constant on lock-in amplifier \#1 needs to be short enough to not filter the modulation at \( f_2 \). A detailed discussion on the time constant requirements is provided in Section 8.3.4.2. ................................................................. 88

8.4 The double demodulation configuration for measuring the \( \text{PTR}(f_1 X_2)/\text{PTR}(f_1) \) ratio. This configuration eliminates the need for a second lock-in amplifier. Not all lock-in amplifiers are capable of this operation. For this configuration to work, the ratio operation needs to be performed before the low pass filters in the lock-in amplifier. ................................................................. 89

9.1 Radiometric signal vs sample temperature at three different wavelengths ................................................................................................................. 101

9.2 Nonlinearity coefficient, \( B \), fitted from the curves in Fig. 9.1. Notice the dependence on both the temperature and wavelength. ................................. 102

9.3 Plot of \( \Gamma \) over a range of temperatures for values of \( \lambda_1 \) and \( \lambda_2 \). ................................................................. 103

9.4 Experimentally measured values of the \( \Gamma \) ratio corresponding to the filters with center wavelengths at 2.5 \( \mu \text{m} \) and 4.5 \( \mu \text{m} \). The values are measured over a range of temperatures. The solid line is the theoretical prediction of \( \Gamma \) based on a gray body assumption of emissivity over the filter bandwidth, and uniform filter transmission over the bandwidth. The dotted line corresponds to \( \Gamma \) calculated at 2.25 \( \mu \text{m} \)/4.75 \( \mu \text{m} \) which is the highest possible value of \( \Gamma \) with wavelengths that are contained within the two filter bandwidths. Likewise the dot dash line corresponds to \( \Gamma \) calculated at 2.75 \( \mu \text{m} \)/4.25 \( \mu \text{m} \) which is the lowest possible value of \( \Gamma \). ................................................................. 105

9.5 Experimentally measured values of the \( \Gamma \) ratio corresponding to the filters with center wavelengths at 2.5 \( \mu \text{m} \) and 6.5 \( \mu \text{m} \). The values are measured over a range of temperatures. The solid line is the
theoretical prediction of $\Gamma$ based on a gray body assumption of emissivity over the filter bandwidth, and uniform filter transmission over the bandwidth. The dotted line corresponds to $\Gamma$ calculated at 2.25 $\mu$m/6.75 $\mu$m which is the highest possible value of $\Gamma$ with wavelengths that are contained within the two filter bandwidths. Likewise the dot dash line corresponds to $\Gamma$ calculated at 2.75 $\mu$m/6.25 $\mu$m which is the lowest possible value of $\Gamma$. .................................106

9.6 Experimentally measured values of the $\Gamma$ ratio corresponding to the filters with center wavelengths at 4.5 $\mu$m and 6.5 $\mu$m. The values are measured over a range of temperatures. The solid line is the theoretical prediction of $\Gamma$ based on a gray body assumption of emissivity over the filter bandwidth, and uniform filter transmission over the bandwidth. The dotted line corresponds to $\Gamma$ calculated at 4.25 $\mu$m/6.75 $\mu$m which is the highest possible value of $\Gamma$ with wavelengths that are contained within the two filter bandwidths. Likewise the dot dash line corresponds to $\Gamma$ calculated at 4.75 $\mu$m/6.25 $\mu$m which is the lowest possible value of $\Gamma$. .................................108

9.7 The nonlinearity coefficient $B$ plotted for the three filters used over a range of temperatures. ..................................................109
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>alternating current</td>
</tr>
<tr>
<td>AOM</td>
<td>acousto-optical modulator</td>
</tr>
<tr>
<td>DC</td>
<td>direct current</td>
</tr>
<tr>
<td>FD-PTR</td>
<td>front-detection-photothermal radiometry</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>MOR</td>
<td>modulated optical reflectance</td>
</tr>
<tr>
<td>NEP</td>
<td>noise equivalent power</td>
</tr>
<tr>
<td>NL-PTR</td>
<td>nonlinear photothermal radiometry</td>
</tr>
<tr>
<td>PA</td>
<td>photoacoustic spectroscopy</td>
</tr>
<tr>
<td>PBD</td>
<td>photothermal beam deflection</td>
</tr>
<tr>
<td>PPE</td>
<td>photopyroelectric</td>
</tr>
<tr>
<td>PTD</td>
<td>photothermal displacement</td>
</tr>
<tr>
<td>PTR</td>
<td>photothermal radiometry</td>
</tr>
<tr>
<td>RS</td>
<td>radiometric signal</td>
</tr>
<tr>
<td>URCA</td>
<td>Université de Reims Champagne-Ardenne, Reims, France</td>
</tr>
<tr>
<td>USU</td>
<td>Utah State University, Logan, Utah, USA</td>
</tr>
</tbody>
</table>
## NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>Multiplicative factor in the radiometric signal</td>
</tr>
<tr>
<td>$A_s$</td>
<td>Surface Area [m²]</td>
</tr>
<tr>
<td>$A_\theta$</td>
<td>Surface area normal to the direction of radiation propagation [m²]</td>
</tr>
<tr>
<td>$B$</td>
<td>Nonlinearity coefficient</td>
</tr>
<tr>
<td>$B_{sys}$</td>
<td>System Nonlinearity</td>
</tr>
<tr>
<td>$c$</td>
<td>Speed of light, [m²s⁻¹]</td>
</tr>
<tr>
<td>$D^*$</td>
<td>Specific detectivity, [cm·Hz^(1/2)·W⁻¹]</td>
</tr>
<tr>
<td>$E$</td>
<td>Radiant Exitance, [W·m⁻²]</td>
</tr>
<tr>
<td>$E_\lambda$</td>
<td>Spectral Exitance, [W·m⁻³]</td>
</tr>
<tr>
<td>$c_p$</td>
<td>Specific heat capacity at constant pressure, [J·kg⁻¹·K⁻¹]</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Volumetric heat capacity, [J·m⁻³]</td>
</tr>
<tr>
<td>$e$</td>
<td>Thermal effusivity, [J·m⁻²·K⁻¹·s⁻¹/²]</td>
</tr>
<tr>
<td>$f$</td>
<td>Frequency, [Hz]</td>
</tr>
<tr>
<td>$F_{D→S}$</td>
<td>View factor from detector to sample, [sr]</td>
</tr>
<tr>
<td>$F_{S→D}$</td>
<td>View factor from sample to detector, [sr]</td>
</tr>
<tr>
<td>$\mathcal{F}$</td>
<td>Fourier Transform</td>
</tr>
<tr>
<td>$h$</td>
<td>Planck constant, [J·s]</td>
</tr>
<tr>
<td>$q''$</td>
<td>Heating flux intensity, [W·m⁻²]</td>
</tr>
<tr>
<td>$L$</td>
<td>Thickness of a homogeneous sample, [m]</td>
</tr>
<tr>
<td>$L_{e,\Omega,\lambda}$</td>
<td>Spectral Radiance according to Planck’s Law, [W·sr⁻¹·m⁻³]</td>
</tr>
<tr>
<td>$L_{e,\Omega,\lambda,W}$</td>
<td>Spectral Radiance according to Wien’s Law, [W·sr⁻¹·m⁻³]</td>
</tr>
</tbody>
</table>
$L_{e,\Omega,\lambda,RJ}$ Spectral Radiance according to Rayleigh-Jeans Law, [W\cdot sr^{-1}\cdot m^{-3}]

$k$ Thermal conductivity, [W\cdot m^{-1}\cdot K^{-1}]

$k_B$ Boltzmann Constant, [m^2\cdot kg\cdot s^{-2}\cdot K^{-1}]

$R$ Detector Responsivity, [V\cdot W^{-1}]

$\mathcal{R}$ PTR Ratio

$t$ Generic time, [s]

$T$ Generic temperature, [K]

$T_{DC}$ Absolute temperature of a body, [K]

$T_{AC1}$ Amplitude of alternating temperature at frequency $f_1$, [K]

$T_{AC2}$ Amplitude of alternating temperature at frequency $f_2$, [K]

$V$ Generic voltage, [V]

$V_{noise}$ Voltage of noise in detector, [V]

$z$ Axial directional coordinate, [m]

$\alpha$ Thermal diffusivity, [m^2\cdot s^{-1}]

$\alpha_{absorb}$ Absorptivity

$\varepsilon$ Total hemispherical emissivity

$\lambda$ Wavelength, [m]

$\Delta\lambda$ Optical Filter Bandwidth, [m]

$\lambda_{max}$ Wavelength corresponding to maximum emission, [m]

$\lambda_{prop}$ Set of spectral properties for system

$\Gamma$ Ratio of PTR Ratio’s

$\rho$ Density, [kg\cdot m^{-3}]

$\rho_r$  Reflectivity

$\sigma$  Stefan-Boltzmann constant, [W·m$^{-2}$·K$^{-4}$]

$\tau$  Transmissivity

$\mu$  Thermal diffusion length, [m]
CHAPTER 1
INTRODUCTION

The ability to predict and control heat transfer is essential in our daily lives. It is especially critical in power generation, energy conversion, electronics, and aerospace applications. To perform reliable thermal analysis, it is essential to accurately measure thermal properties and temperature. Many standard techniques already exist to measure both temperature and thermal properties. However, specific scenarios often limit the techniques that can be utilized for a measurement. Often specific conditions require the development of new techniques or variations of existing techniques to accommodate the requirements.

Photothermal Radiometry (PTR) is a well-established technique for measuring thermal properties. It has been applied to thermal property measurements over a wide range of samples, and some applications to pyrometry, to a lesser extent. This work expands the PTR theory to account for the nonlinearity of the PTR signal with respect to temperature. It will be shown that much information can be obtained by observing the nonlinearity of the PTR signal.

1.1. Motivation

Temperature measurements have been thoroughly investigated, and pyrometry has been an active field of study since the 1800’s. Much development occurred around the year 1900 when Wien’s displacement law, Rayleigh-Jeans approximation, and Planck’s law were developed. Throughout the 1900’s scientists and engineers developed techniques to utilize these laws to measure temperature. There are two common problems that have plagued pyrometry techniques.
The first problem is distinguishing the emitted radiation from the desired target, and the radiation from the surrounding environment. This problem is significant when the surrounding environment is at an elevated temperature, and the target is reflective, such as a metal. This problem has largely been solved through various forms of active pyrometry. An excellent example of an application of active pyrometry is provided by Amiel et al [1].

The second problem arises from the unknown value of target emissivity. A wide variety of techniques have been developed to alleviate this problem. A notable technique first proposed by Campbell in 1925 is the use of a pyrometer at two wavelengths [2]. This later would develop into what is known as two-color pyrometry. Later multi-wavelength pyrometry techniques were developed that can determine the spectral emissivity and temperature simultaneously from spectral measurements. This is done by modeling emissivity as a function of wavelength with \( N \) fit parameters and then conducting \( N+1 \) spectral measurements. These multi-wavelength, or spectropyrometers, are currently an active field of research, and have had varying degrees of success [3–5]. The main limitation of these multi-wavelength techniques is the requirement of assuming the functional form of emissivity without knowledge of how emissivity varies spectrally.

Perhaps the most elegant methods are based on the original work of DeWitt and Kunz [6]. Their technique used a broad wavelength range detector and two heating lasers at different wavelengths 520 & 647 nm. The small temperature increase due to each laser was measured using the detector. The temperature increase is proportional to the sample absorptivity at each laser wavelength. Therefore, the ratio of the temperature increase due to laser heating is equal to the ratio of the absorptivity/emissivity at those wavelengths.
This ratio can then be used with the standard two-color pyrometry measurement technique. This technique and those based on it are reliable and accurate pyrometry techniques. However, with this technique, the choice of wavelengths requires that a light source, at that wavelength, exists with sufficient power to heat the sample. This significantly limits the choices of wavelengths based on lasers that are currently available. This constraint requires suboptimal wavelengths to be chosen, or limits the temperature range these techniques can be applied to because only selective wavelengths are available.

Similar to pyrometry, thermal property measurement techniques have been heavily researched for many years. As a result, there are many accurate techniques that are used as standard methods in characterizing thermal properties. Perhaps the most common technique for thermal diffusivity is known as the laser flash technique, first developed by Parker [7]. This technique uniformly heats one side of the sample with a short duration “flash” and monitors the temperature of the opposite side of the sample. The time required for the pulse of heat to diffuse through the sample is dependent only on the thermal diffusivity and the thickness of the sample. This technique has become a standard technique because of its simplicity and reliability. This is a result of the thermal conditions that create a temperature profile that is dependent on one thermal property instead of a combination of thermal properties. Furthermore, the ability for non-contact measurements further enhances the elegance of the technique.

In contrast to the laser flash method measuring thermal diffusivity, a non-contact, direct thermal effusivity measurement technique for homogenous, non-layered samples does not exist. For this reason, thermal effusivity is generally a calculated thermal property
rather than one that is typically measured. Thermal effusivity is generally described as a measure of a material's ability to exchange heat with its surrounding environment. The interface temperature when two semi-infinite bodies at different initial temperatures are brought into contact is determined by the ratio of thermal effusivities and the initial temperatures of the bodies. Because of the dependence on thermal effusivity at material interfaces, it is commonly measured on layered materials.

A unique technique developed by Bicanic et al. utilizes the photopyroelectric technique without the use of material interfaces [8]. This technique is unique since the sample's thermal response is only dependent on the thermal effusivity. This technique provides a direct thermal effusivity measurement which cannot be done with other techniques. Other techniques rely on a material interface between the sample and material of known effusivity, and therefore result in a comparative technique. While the technique presented by Bicanic et al. has many notable advantages, it also has some drawbacks. The main drawback is the sample is required to be in good thermal contact with the photopyroelectric sensor.

From the discussion provided in this section it is clear there is still a need for the development of a pyrometry technique that does not depend on prior knowledge of emissivity or using lasers to measure the emissivity. Additionally, the lack of a direct non-contact thermal effusivity measurement technique has been discussed. The development of nonlinear PTR theory provides the foundation for precisely these applications.
1.2. Overview

The theory explaining the nonlinearity of the PTR signal with respect to temperature is developed in this work. Based on this theory, three applications are identified and experimentally tested. These applications include two pyrometry techniques and a non-contact, direct measurement technique of thermal effusivity.

The first pyrometry technique uses a simple data reduction method and allows for easy monitoring of sample temperature during PTR measurements. This application is particularly useful when the sample is easily damaged by excessive heating. Measurements of paintings or other delicate works of art, are excellent examples of when monitoring the temperature of the sample would be useful [9].

The second pyrometry approach will utilize the nonlinear theory to develop a technique that does not require prior knowledge of the material emissivity, nor does it require the measurement of emissivity. This technique utilizes two modulated heating lasers, but there are no specific requirements on the wavelength of the lasers. The temperature is determined by observing the temperature modulations due to the laser heating. This results in a technique independent of the radiation from the surrounding environment. Additionally, this technique is independent of changes in emissivity with respect to wavelength or temperature.

The third application of nonlinear PTR is a non-contact, direct thermal effusivity measurement technique. This technique is similar in principle to that developed by Bicanic et al. [8] except the temperature modulation is determined by the emitted infrared radiation.
This technique (measuring thermal effusivity), coupled with the laser flash (measuring thermal diffusivity) can provide non-contact thermal conductivity measurements.
CHAPTER 2

OBJECTIVES

The purpose of this work is to develop the theory of nonlinear photothermal radiometry (NL-PTR) and its applications to pyrometry and thermal property measurements. After the theoretical development of each application, experimental measurements are performed to validate the techniques.

The specific objectives of this work include:

- The development of a theoretical model for NL-PTR that accurately predicts the PTR signal over a range of temperature and wavelengths. Using this model, provide a qualitative and quantitative understanding of the PTR signals spectral and temperature dependencies.
- Using the developed theoretical model, evaluate the feasibility of a:
  - Relative temperature measurement for monitoring sample temperature during PTR measurements;
  - Non-contact, direct thermal effusivity measurement technique for homogenous, non-layered samples;
  - Absolute temperature measurement with unknown emissivity, and independent to changes in emissivity with respect to temperature or wavelength.
- Design and perform experiments testing the validity of each of the three applications.
CHAPTER 3
THEORETICAL BACKGROUND AND CONSIDERATIONS

To achieve the objectives in this study, a firm understanding of the underlying principles is required. This will require a thorough understanding of heat transfer with an emphasis in conduction and radiation. This chapter will begin with a discussion of thermal conduction along with the thermal properties that govern it. Next the governing principles of thermal radiation will be discussed in detail. The following section will provide a wide background on existing pyrometry techniques.

Finally, a literature review of how these principles have been previously applied to thermal property and temperature measurements will be provided. An emphasis on thermal wave techniques and pyrometry will be conducted as they are most relevant to this work.

3.1. Thermal Conduction in Solids

In order to measure thermal properties of solids a comprehensive understanding of the heat transfer in solids is necessary. Heat is transferred in solids by a means called thermal conduction. The amount of heat transfer through conduction depends on the temperature gradients and thermal properties. The governing equation

\[
\frac{1}{\alpha} \frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}
\] (3.1)
is commonly referred to as the heat conduction equation where \( T \) is the temperature, \( x, y, \) and \( z \) are spatial coordinates, \( t \) is time, and \( \alpha \) is the thermal diffusivity. Specific solutions to the heat conduction equation used in this study will be developed later in this chapter.
3.1.1. *Heat Conduction Parameters*

Heat conduction in solids is determined by two independent material properties. However there exists four thermal properties that are often used in engineering problems. These properties include: thermal conductivity, heat capacity, thermal diffusivity, and thermal effusivity. Because there are only two independent properties, if two properties are defined the other two can be defined based on the two originally chosen. The four different properties are useful because they describe specific phenomena and in some cases the heat transfer can be dependent on only the value of one of them, and can therefore simplify the problem if it can be written in terms of one property instead of two. This section will provide a brief discussion of each of the properties and its applications to aid in the conceptual understanding of the heat transfer problems presented later.

3.1.1.1. Thermal Conductivity

Thermal conductivity is a measure of a material’s ability to transfer heat. It is the only thermal property that governs steady state heat transfer, and therefore is very important. A plane wall subjected to a constant heat flux on one side and a constant temperature on the opposite will have a linear temperature profile throughout the wall, assuming a constant thermal conductivity over the temperature gradient. The slope of this temperature profile will be determined only by the material’s thermal conductivity.

3.1.1.2. Heat Capacity

Heat capacity is the product of two well-known properties, specific heat and density \( (C = \rho c) \). In heat transfer they are generally referred to as their product because they only
appear in the governing equations and boundary conditions as a product. Heat capacity is a measurement of a material’s ability to store thermal energy. Because it deals with the storage of thermal energy, it is inherently only important in transient conditions where a material’s thermal energy is either increasing or decreasing with time.

3.1.1.3. Thermal Diffusivity

Thermal diffusivity is defined by thermal conductivity divided by heat capacity \( \alpha = \frac{k}{C} \). It is clear from its dependence on heat capacity that thermal diffusivity is in nature a transient property. More clearly it can be considered as the ratio of a material’s ability to conduct heat against its ability to store heat. This property is more abstract than thermal conductivity and heat capacity, but it can be extremely useful under certain conditions. Most notably it can be a measure of the speed of heat propagation through a material.

3.1.1.4. Thermal Effusivity

Thermal effusivity, like thermal diffusivity, consists of a combination of thermal conductivity and heat capacity. Specifically, thermal effusivity is defined by \( e = \sqrt{Ck} \). This thermal property is probably the least common, but still extremely important and useful. It can be considered as a material’s ability to exchange thermal energy with its surroundings. The most common example to explain thermal effusivity is done by the contact of two semi-infinite materials at different initial temperatures. When these two materials contact each other the interface quickly goes to an interface temperature. This temperature remains constant through time and is determined only by the two material’s
thermal effusivities and initial temperatures. This property is the reason why some materials feel “cold” to the touch while others feel “warm” when both objects are at room temperature.

3.2. Thermal Radiation

All objects with temperature greater than 0 K, emit thermal radiation. This emission is generally characterized by the notion of an “ideal” emitter which is known as a blackbody. In reality materials do not emit as a blackbody, but instead at some fractions of a blackbody. Therefore it is useful to describe objects as emitting at some fraction of a blackbody. The development of a blackbody emitter will be provided in this section.

3.2.1. Planck’s Law

It is well known the emission from a blackbody is described by

\[ L_{\omega, \lambda} = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1} \]  

which is known as Planck’s law. Where \( L_{\omega, \lambda} \), spectral radiance (in some texts it is also referred to as spectral intensity) is the rate at which radiant energy is emitted in a given direction, at wavelength \( \lambda \), per unit area of the emitting surface normal to the direction of propagation, per solid angle. In Equation (3.2) \( h \) is Planck’s constant, \( k_B \) is the Boltzmann constant, \( c \) is the speed of light in a vacuum, and \( T \) is the temperature in degrees Kelvin.

For reference and discussion a plot of Planck’s law for three different temperatures is provided in Fig. 3.1. The following important observation should be made from this plot:

- The maximum of the plots shifts to shorter wavelengths as the temperature increases.
• The magnitude of the spectral radiance increases more rapidly with an increase in temperature at shorter wavelengths than at the longer wavelengths.

• At all wavelengths, the emission always increases with an increase in temperature.

![Graph showing spectral radiance according to Planck’s law for blackbodies at 300 K, 350 K, and 400 K.]

Fig. 3.1. Spectral radiance according to Planck’s law for blackbodies at 300 K, 350 K, and 400 K.

3.2.2. **Stefan-Boltzmann Law**

Planck’s law describes a blackbody’s emitted radiation in a given direction, at wavelength \( \lambda \), per unit area of the emitting surface normal to the direction of propagation, per solid angle. Often the spectral exitance \( E_\lambda \), is desired; which describes the emitted radiation from a surface per unit area at wavelength \( \lambda \). The angles \( \theta \) and \( \phi \) will be used to describe the direction of propagation. Where \( \theta \) the angle from the surface normal vector and \( \phi \) is the azimuthal angle. The area normal to the direction of propagation \( A_\theta \) is defined by

\[
A_\theta = A_s \cos(\theta),
\]  

(3.3)
where $A_s$ is the surface area. The differential solid angle $d\Omega$ is described by

$$d\Omega = \sin(\theta) \, d\theta \, d\phi.$$  \hfill (3.4)

The spectral exitance is found by combining Equation (3.2), Equation (3.3) and Equation (3.4) and integrating over the hemisphere and dividing by $A_s$, shown by

$$E_\lambda = \int_0^{2\pi} \int_0^{\pi/2} L_{e,\Omega,\lambda} \cos(\theta) \sin(\theta) \, d\theta \, d\phi = \pi L_{e,\Omega,\lambda}. \hfill (3.5)$$

The spectral exitance can be integrated with respect to wavelength from zero to infinity to determine the radiant exitance per unit area. Specifically this integral yields

$$E = \int_0^{\infty} E_\lambda \, d\lambda = \sigma T^4 \hfill (3.6)$$

where $E$ is the radiant exitance over all wavelengths per unit area, $\sigma$ is the Stefan-Boltzmann constant with a value of approximately $5.67 \times 10^{-8}$ W/m$^2$K$^4$, and this expression is known as the Stefan Boltzmann Law. It is important to note that the radiant exitance includes the thermal emission power in all directions and at all wavelengths on a per area basis.

**3.2.3. Other Blackbody Distributions**

Wien’s Approximation was developed by Wilhelm Wien in 1896 to describe emitted radiation [10]. Wien’s approximation can be described as

$$L_{e,\Omega,\lambda,W} = \frac{2hc^2}{\lambda^5} e^{-\frac{hc}{\lambda k_B T}}. \hfill (3.7)$$

Wien’s approximation is useful because it matches Planck’s law in the short wavelength/low temperature regime. Specifically the error is less than 1% if $\lambda T<3000$
µm·K [11]. While today it is known that Planck’s law describes the ideal emitter, Wien’s approximation is still used in some pyrometry techniques because of its added simplicity in the short wavelength/low temperature regime [12,13].

Another important contribution from Wien is Wien’s Displacement Law which determines the wavelength at which the maximum spectral exitance occurs. Wien’s Displacement Law can be found by taking a derivative of Planck’s law (or, with a good approximation, of Wien’s law) with respect to wavelength, setting it equal to zero, and solving for the wavelength. Specifically, Wien’s displacement law is

$$\lambda_{max}T = \frac{hc}{5k_B} = 2898 \, \mu m \, K.$$

(3.8)

Rayleigh-Jeans approximation, based on classical dynamics and statistics, is another approximation for radiation emission. This approximation agrees with Planck’s law when $\lambda T \gg 1$, and can be seen as

$$L_{e,\Omega,\lambda,RJ} = \frac{2ck_BT}{\lambda^4}.$$  

(3.9)

While both the Wien approximation and Rayleigh-Jeans approximation can be useful it is important to always consider the temperature and wavelength range they are being applied to, and care should be taken to ensure that they are being used in the region in which they are accurate for. To provide a better understanding of this the Wien approximation, Planck’s Law, and the Rayleigh-Jeans approximation have been plotted over a range of wavelengths for a temperature of 300 K in Fig. 3.2. It is clear to see that Wien’s approximation matches well for the short wavelength range and Rayleigh-Jeans
approximation matches well for the long wavelengths. However, neither one provides a substitute to Planck’s law over the full spectrum. The large deviations should be noted at the short and long wavelength’s that can be several orders of magnitudes different from that of the result from Planck’s Law. However, under the correct conditions these approximations can still be useful.

Fig. 3.2 Comparison between Wien’s approximation, Planck’s law, and the Rayleigh-Jeans approximation for emission at 300 K

3.2.4. **Blackbody vs Real Emitters**

The previously discussed emission laws describe a perfect emitter which is commonly referred to as a *blackbody*. A *blackbody* has specific characteristics that make it an idealization of a real surface. These characteristics include:

- A blackbody absorbs all incident radiation
- At a given temperature and wavelength no surface can emit more energy than a blackbody.
• The radiation emitted from a blackbody is diffuse, and therefore independent of direction.

The idea of emissivity will be introduced since real materials emit less than that of a blackbody. Therefore, by definition emissivity is the fraction of emitted radiation to the radiation of a blackbody at the same temperature. Real emitters do not emit purely diffuse radiation, but indeed have preferential directions to emit radiation. Furthermore, the emission has preferential wavelengths, and therefore emissivity must vary by wavelength. To accommodate all three of these facts, emissivity is most generally defined as a function of wavelength, direction, and temperature. In the work presented here, the emissivity will be assumed to be independent of direction, and therefore only a function of wavelength and temperature. This will be notated as

$$\varepsilon = \varepsilon(\lambda, T).$$

(3.10)

3.2.4.1. Absorptivity, Reflectivity, Transmissivity

So far only the emission of radiation from a surface has been discussed. This section will provide an understanding of how that radiation interacts with other objects. Electromagnetic radiation that is incident on a surface is generally called \textit{Irradiation}. When this radiation contacts a material a combination of three possibilities occurs. These possibilities are reflection, absorption in the material, or transmission through the material. These three must account for all of the incident irradiation. Therefore, it can be written

$$\rho_r + \tau + \alpha_{absorb} = 1$$

(3.11)
where \( \rho_r \) is the reflectivity, \( \tau \) is the transmissivity, and \( \alpha_{\text{absorb}} \) is the absorptivity. This phenomena is shown pictorially in Fig. 3.3. Another useful optical property in radiation physics is the fact that emissivity is equal to absorptivity for a given wavelength (Kirchhoff’s law) assuming the surface is diffuse. This property is important in pyrometry measurements when the emissivity has a large influence on temperature measurements.

![Diagram showing the three types of interaction irradiation has when it encounters an object. Also shows the classification of Irradiance and Radiosity [W/m²].](image)

3.3. Pyrometry Measurements

Pyrometry is the process of determining a material’s temperature by measuring the thermal radiation emitted from the material. The main advantage of pyrometry is its ability to perform non-contact temperature measurements. Pyrometry is a vast research field, and has been for many years. Some of the first pyrometers developed were known as *disappearing filament pyrometers*. These were independently developed in 1901 by L. Holborn and F. Kurlbaum in Germany, and H. N. Morse in the United States [14]. This
clearly demonstrates that pyrometers have been under development for more than a century.

All pyrometers are based on the temperature dependent emission of thermal radiation, described by Planck’s law. However, Planck’s law describes an ideal emitter known as a blackbody, and thermal emission from real materials depend on the value of emissivity. This is the first main obstacle in pyrometry. The second obstacle is separating thermal radiation emitted from the sample and background radiation. Essentially all pyrometry techniques are defined by how they deal with these two obstacles.

This section will discuss different pyrometry techniques that have been developed and their advantages and disadvantages. Next techniques that have been developed to artificially enhance emissivity will be discussed. Finally, techniques to handle to distinction between thermal radiation from a sample and background radiation will be discussed.

3.3.1. Single Wavelength

The simplest form of a pyrometer could be considered the single wavelength pyrometer. In this technique one wavelength of emitted light is measured. This measurement can be conducted in many different manners. The earliest was the use of a red filter in a disappearing filament pyrometer. In these pyrometers, a filament was placed in an optical system that would allow a user to see the filament on top of the target material. Electrical current was then used to vary the temperature of the filament. By adjusting the current until the intensity of the emission from the filament would match that of the sample, and thereby “disappear”. At this point the temperature of the filament was then considered
to be the same as the temperature of the target. The temperature of the filament would be
known from a previous calibration based on the value of the current.

Today single wavelength measurements can be made easily through the use of a
photodetector and an optical filter. However, regardless of the measurement technique both
require the knowledge or assumption of emissivity. The disappearing filament assumed the
emissivity of the target to be the same as the filament. In the use of a photodetector, any
value of emissivity can be used, but it must be known, assumed, or measured.

The signal using a single wavelength technique is governed by Planck’s law.
Specifically, the signal can be calculated by

\[ S(\lambda, T) = A_S F_{S \rightarrow D} \varepsilon(\lambda) E_{\lambda}(\lambda, T) R(\lambda) , \]  

where \( A_S \) is the sample area, \( F_{S \rightarrow D} \) is the view factor from the sample to detector, \( E_{\lambda} \) is the
spectral exitance according to Planck’s law, and \( R \) is the detector responsivity. It is clear to
see that once the wavelength is specified that the signal becomes only a function of the
sample temperature. The detector responsivity and the view factor can be determined
experimentally using a sample at a known temperature and emissivity.

3.3.2. Two Wavelength

One of the most common techniques used in pyrometry is the two wavelength or
two color pyrometry, first proposed by Campbell in 1925 [2]. This technique measures the
thermal radiation at two different wavelengths, and then calculates the ratio of these two
signals. The two wavelength signal can be shown mathematically as
where the subscript on emissivity corresponds to wavelengths. With the assumption that the wavelengths are close and therefore the detector has a similar responsivity to both wavelengths, then Equation (3.13) can be simplified to

\[
S(\lambda_1, \lambda_2, T) = \frac{A_{S}\varepsilon_1 E_2(\lambda_1, T) R(\lambda_1)}{A_{S}\varepsilon_2 E_2(\lambda_2, T) R(\lambda_2)},
\]

This provides a unique scenario where the \( \varepsilon_1 \) is divided by \( \varepsilon_2 \) and therefore if \( \varepsilon_1 = \varepsilon_2 \) the ratio has no dependence on emissivity. This fact is convenient because it holds true regardless of the value, as long as the two emissivities are equivalent. However, if \( \varepsilon_1 \neq \varepsilon_2 \) then the ratio is multiplied by the ratio of emissivities \( \varepsilon_1/\varepsilon_2 \). Under this case the values of the two emissivities are required to be known if they are not assumed to be the same. A thorough discussion on the error associated with non grey bodies is provided by DeWitt and Nutter [13].

3.3.3. Three Wavelength

After the development of two wavelength pyrometry it was shown that additional spectral measurements could be utilized to eliminate the dependence on the knowledge of emissivity. Specifically a three wavelength technique was developed not unlike the two wavelength technique. In this measurement the product of two ratios is measured. The first ratio

\[
R_{12} = \frac{\varepsilon_1 E_2(\lambda_1, T)}{\varepsilon_2 E_2(\lambda_2, T)}
\]

(3.15)
is the signal measured at two different wavelengths, identical to that in the two wavelength measurement. The second ratio

\[ R_{32} = \frac{\varepsilon_3 E_3(\lambda_3, T)}{\varepsilon_2 E_2(\lambda_2, T)} \quad (3.16) \]

is the ratio of two signals at two different wavelengths, with one of the wavelengths being the same as in the first ratio. Therefore the product of these ratios can be described as

\[ R_{12}R_{32} = \frac{\varepsilon_1 \varepsilon_3 E_1(\lambda_1, T) E_3(\lambda_3, T)}{\varepsilon_2^2 [E_2(\lambda_2, T)]^2} \quad (3.17) \]

Hornbeck [15] and by Reynolds [11] provided interesting results under the assumption the emissivity is varying linearly over the measured wavelengths. Specifically if \( \lambda_2 = (\lambda_1 + \lambda_3)/2 \) then emissivities at \( \lambda_1 \) and \( \lambda_3 \) can be defined as \( \varepsilon_1 = \varepsilon_2 \pm \Delta \varepsilon \) and \( \varepsilon_3 = \varepsilon_2 \mp \Delta \varepsilon \). Substituting these definitions into Equation (3.17)

\[ R_{12}R_{32} = \frac{\varepsilon_2^2 - (\Delta \varepsilon)^2}{\varepsilon_2^2} \frac{E_1(\lambda_1, T) E_3(\lambda_3, T)}{[E_2(\lambda_2, T)]^2} \quad (3.18) \]

is obtained. From this it can be shown that this expression is largely independent of emissivity given \( (\Delta \varepsilon)^2 / \varepsilon_2^2 \ll 1 \). Therefore, if the material under consideration has an emissivity that can be approximated as linear across the measurement wavelengths, then the three wavelength measurement can be very useful. It was noted by Hornbeck [10], “this method is never as sensitive as the two-wavelength method operating at well-chosen wavelengths.”
3.3.4. *Multi Wavelength*

The idea of combining spectral measurements to reduce the dependence of emissivity can be extended further past three wavelengths. Many researchers have attempted to generalize this idea into an N measurement technique where N spectral measurements are made. Typically, in this multi-wavelength technique an emissivity model is chosen which has N-1 fit parameters. Then the product of the emissivity model and Planck’s law are fit to the experimental pyrometry measurements. The number of measurements can then be determined by the number of free parameters in the emissivity model plus one for the sample temperature. The key to this technique is selecting an appropriate emissivity model. Since there is no governing model that fits for all materials large errors can be introduced from this technique. This is especially true as the number of fit parameters increases [4,5].

3.3.5. *Emissivity Enhancement Methods*

From the previous sections it is clear that much work has been conducted to develop pyrometry techniques that minimize the influence emissivity on the temperature measurement. An alternative approach that many researchers have taken is to artificially enhance the emissivity. By sufficiently enhancing the emissivity, the material can be considered a blackbody and therefore no assumptions or prior knowledge of emissivity is necessary.

The first and most simple technique is to coat the surface with a high emissivity material such as carbon. While this is a simple and effective solution it is not convenient
and often not feasible. In other scenarios, the geometry has been arranged in such a fashion that the radiation appears to be coming from a cavity, and thereby increasing the effective emissivity. Specifically, if the material can be arranged into a wedge shape or cylinder. Similar results have been obtained by adding a reflective shield to create the appearance of a cavity [13,16,17]. This idea has been exploited more thoroughly through the use of a highly reflecting hemisphere placed near the sample. The detector is then placed at a small hole at the top of the sphere. This method has become known as the “gold cup” method since the hemisphere is often coated in gold for its high reflectivity in the infrared range [16,18].

3.3.6. Active Pyrometry

Up to this point the Pyrometry discussion has been about purely passive measurement techniques. The passive classification comes from the fact that all temperature or spectral information is obtained only by observing the radiation emitted by the sample. In this section different active pyrometry techniques will be discussed.

Probably the simplest active method is only a slight deviation from the passive technique described previously. Recall the main difficulty with a single wavelength pyrometry was accommodating for different and possibly unknown values of emissivity. To remedy this situation researchers have developed in situ measurement techniques of the emissivity. This is conducted by measuring the reflected light from a monochromatic source, such as a laser, at the same wavelength as the pyrometric detection. Combined with the assumption of equal absorptivity and emissivity at the same wavelength, and
Kirchhoff's radiation law, the reflective signal can easily be related to the emissivity of the material. This can significantly improve the accuracy of the single wavelength pyrometry technique on materials with emissivities significantly less than unity.

As discussed in the beginning of Section 3.3, two main difficulties occur during pyrometry measurements. So far, much discussion has been provided to address the unknown values of emissivity. The later problem of background radiation interfering with pyrometry measurements has also been thoroughly researched. Often the solution to this problem is active pyrometry. The strategy of active pyrometry to remedy this problem is to introduce a small temperature variation that will be identifiable in the detected response. First developed by Berthet and Greffet [19], a periodically modulated laser is used to produce surface temperature oscillations on the surface. These temperature oscillations cause an oscillation in the emitted radiation only and do not affect the reflected radiation. Therefore, the signal from the emitted radiation can be separated from the reflected radiation by the use of a lock-in amplifier.

This type of photothermal pyrometry has been applied widely throughout literature. As previously explained its main benefit is the ability to distinguish between the reflected and emitted radiation. Because of this it has been applied in many conditions when the surrounding environment is at an elevated temperature, and the reflected signal is too large to be ignored. An excellent example of an application for this arises in fusion devices such as ITER. In order to monitor the temperature of metal plasma facing components active pyrometry needs to be used. This is mainly due to the high reflectivity of metal, and the
high emission from the plasma. A good application of this technique is provided by Loarer [1].

Photothermal pyrometry has also been proposed as a form of active pyrometry. Specifically it has been applied to temperature measurements of semiconductors by Chen and Borca-Tasciuc [20,21]. In the case of semiconductors more care needs to be taken due to the generation of electron hole pairs if the excitation source has a wavelength shorter than the corresponding bandgap energy wavelength.

An excellent active pyrometry technique was proposed by DeWitt and Kunz [6]. This technique uses two lasers, with wavelengths $\lambda_1$ and $\lambda_2$, to provide small changes in temperature. The change in emitted infrared radiation due to the small changes in temperature is monitored. The temperature increase is proportional to the sample absorptivity at wavelengths $\lambda_1$ and $\lambda_2$. Given equivalent laser power, the ratio of these two signals is equal to the ratio of the absorptivity at $\lambda_1$ and $\lambda_2$. Assuming emissivity and absorptivity are equal, this is effectively a measurement of the emissivity ratio at the two wavelengths. Finally this technique can utilize the passive two color pyrometry at the same wavelengths since the ratio of their emissivity is now know. Several techniques have been based off of this principle with good results [22–25].

A direct measurement of emissivity is another method that has been developed. Typically in this technique the reflection of a laser from the sample surface is measured [26]. The absorptivity can be measured by determining the laser power before and after contacting the sample surface.
3.4. Conduction with Periodic Boundary Conditions

Thermal conduction with periodic boundary conditions has been a topic of study for many years. The periodic temperature profile has many applications in both research and engineering. Often the periodic temperature profile is referred to as thermal waves. This thermal wave idea comes from certain solution methods that treat the interface of at a thermal boundary with an optical approach where part of the heat is reflected and transmitted through the interface [27]. Other notable solution techniques have used the Quadrupoles method [28] and Greens functions [29].

The heat transfer can be treated as a thermal wave, but it is highly attenuated as it propagates through the sample. This attenuation can be described by

\[
\mu = \sqrt{\frac{\alpha}{\pi f}}
\]  

where \(\mu\) is the thermal diffusion length, \(\alpha\) is the thermal diffusivity defined by \(\alpha = k/(\rho c)\), and \(f\) is frequency.

3.4.1. Semi-Infinite Homogenous Slab with Periodic Boundary Condition

The heat transfer presented here will be limited to one dimensional, homogenous, and infinitely thick sample. The sample will have a coordinate system defined as in Fig. 3.4 and subject to a periodic heat flux on the surface such that the surface boundary condition can be written as

\[
-k \frac{dT}{dz}(z = 0) = \frac{q''}{2} (1 + \cos(ft))
\]  

(3.20)
where $k$ is the thermal conductivity, and the heat flux modulates between zero and $q''$ at a frequency $f$. The one-dimensional heat conduction equation can be solved for the periodic surface temperature which can be described by

$$T = T_{AC} \cos(2\pi f t)$$ \hspace{1cm} (3.21)

where $T_{AC}$ is defined as

$$T_{AC} = \frac{q''/2(1-\rho_r)}{e\sqrt{2\pi f}}$$ \hspace{1cm} (3.22)

$\rho_r$ is the sample reflectivity and $e$ is the thermal effusivity defined by $e = \sqrt{k\rho c}$ in which $\rho$ and $c$ are the density and specific heat, respectively.

Fig. 3.4 Diagram of one-dimensional, periodic flux boundary condition for a semi-infinite medium

### 3.5. Non-Contact Thermal Wave Detection Techniques

Solutions for the heat conduction equation were briefly developed in Section 3.4 when subjected to periodic boundary conditions. It is clear from those solutions, that if the boundary conditions are known, then the temperature response is governed by the thermal properties and sample geometry. Therefore, if the temperature response can be measured after applying a known boundary condition to a specific sample geometry, then the sample
thermal properties can be determined. This is the foundation of all thermal property measurements using thermal-wave techniques. The difference between the techniques is located in the phenomenon used to measure the temperature response. The following sections will discuss the temperature detection methods of common measurement techniques, and provide an overview of the benefits and limitations of each technique.

3.5.1. **Photo-Acoustic**

The photo-acoustic effect was famously first discovered by Alexander Graham Bell in 1880 [30]. The photo-Acoustic technique relies on the acoustic signal generated from the heating or cooling a sample. The heating or cooling of a sample creates a heating or cooling of the surrounding air which causes thermal expansion and contractions. These expansion and contractions of surrounding air is the source of the acoustic signal. Since the heat transfer to the surrounding air is dependent on the surface temperature of the sample, the acoustic signal is related to the surface temperature. The acoustic signal is measured by the use of a microphone which is placed in a chamber with the sample [31].

3.5.2. **Thermoreflectance**

The thermoreflectance technique utilizes the change in a material’s reflectivity due to a change in the material’s temperature. This phenomena is exploited through the use a “probe” laser. This probe laser is a continuous laser contacting the sample, and the reflection of the laser off of the sample is measured by a photodiode. Since the power of the reflected beam is directly proportional to the materials reflectivity, any changes in the reflectivity will be represented in the signal measured by the photodiode [32–35].
3.5.3. **Photothermal Radiometry**

Photothermal Radiometry (PTR) was first developed by Nordal and Kanstad in 1979 [36]. Many variations of PTR have been explored since Nordal and Kanstad, but the fundamental measurement technique remains the same. PTR uses the temperature dependent emission of thermal radiation from a material to gather information about a material’s temperature. The emission of thermal radiation is governed by Planck’s law, and therefore is dependent on temperature. Changes in the temperature will result in changes in the emitted radiation. This emitted radiation is typically gathered by infrared optics and focused into an infrared photodetector. Generally, liquid nitrogen cooled photodetectors are used made from mercury cadmium telluride (MCT).

Broadly speaking, PTR can be characterized into three groups based on the heating of the sample. The first group is characterized by a pulse of light, and is generally referred to as pulsed photothermal radiometry (PPTR) [37–42]. The second group uses a light source that is periodically modulated and the temperature response is measured in terms of amplitude and phase relative to the periodic heating [43–45]. The third group can be considered a combination of the other two techniques. This group contains heating configurations that sweep through frequency, or a modulated pulse train [46–48]. All three techniques have been used extensively, but the frequency domain measurements are the most common today. These PTR techniques have been utilized for a wide range of applications. These applications range from thermal analysis on teeth [44,45] to thermal property measurements of ion irradiated materials [49,50] or of polymer nanocomposites [51]. A whole subfield is based on semiconductors measurements [52,53].
3.5.4. **Mirage**

The mirage technique uses the physical phenomena that the index of refraction of air is dependent on the temperature of the air. According to Snell’s Law, when light passes through a material with changing index of refraction, the light will change directions based on the change of the index of refraction. The mirage technique utilizes this phenomena along with the heat transfer from the sample to the surrounding air. The change in surface temperature results in a change in temperature of the air surrounding the sample. This change in air temperature results in a change in the air’s index of refraction. This index of refraction is measured by a laser propagating parallel and in close proximity to the surface of the sample. As the index of refraction changes, the direction of the laser changes. The change in direction is typically measured by using a four-quadrant photodetector some distance after the heated area. Therefore, the measurement of the laser location on the detector is representative of the surface temperature of the sample [54,55].

3.6. **Thermal Effusivity Measurement Techniques**

Thermal effusivity is defined as the square root of the product of heat capacity and thermal conductivity. Generally, it is interpreted as a materials ability to exchange heat with its surroundings. By its definition, it plays an important role at the thermal interface between materials. Specifically, the ratio of thermal effusivities plays an important role in solutions to the heat equation of layered materials [27,29,56].

In engineering and science applications, often thermal conductivity and diffusivity are needed or measured. From these two parameters thermal effusivity can be calculated.
There remains a large benefit from the ability to directly measure thermal effusivity. Thermal effusivity has been used to monitor manufacturing processes, and commercial probes can be purchased [57], based on early models[58]. Direct thermal effusivity techniques have been developed using the photopyroelectric technique in front-detection configuration[59], and it still remains an active area of research [8,60–63]. The main limitation of these techniques is the contact of the pyroelectric sensor to the sample or a coupling fluid.

Other techniques have been developed using thermal wave methods to measure thermal effusivity. However, they rely on the existence of a layered sample with one of the layers having known properties [64,65]. Relative PTR measurements of volumetric heat capacity and effusivity of polymer nanocomposites has been reported [66]. It was assumed that the sample series had the same optical absorptivity and emissivity. Other thermal property techniques can measure thermal conductivity and thermal diffusivity in order to calculate thermal effusivity. These techniques will not be covered here because they are not a direct measurement of thermal effusivity.

3.7. Infrared Radiation Detectors

Many different types of infrared radiation detectors exist today. Their spectral response, sensitivity, noise properties, and dynamic range all have variations depending on the type of detector. This section will discuss a few of the common types of radiation detectors and their properties. Next the figures of merits and parameters that characterize detector performance will be discussed in detail. The understanding of these parameters
and their ramifications to measurements is critical in understanding possible applications of a radiation detector.

Radiation can be thought of as a stream of discrete photons with varying wavelength. The energy of a photon is dependent on its wavelength which gives rise to the two classes of radiation detectors; detectors that measure photons, and detectors that measure the energy from photons. Photon detectors are made from semiconductor materials, and when a photon of sufficient energy (larger than the band gap) is absorbed by the semiconductor an electron-hole pair is created. This electron hole pair is what gives rise to the electric signal of the detector. The most important observation of these types of detectors is that given the incoming photon has sufficient energy no larger signal is created for excess energy. That is only one electron-hole pair is created for each photon [67].

Energy detectors, as the name implies, detect the amount of energy from the photon stream. Therefore the sensitivity with respect to absorbed radiation is independent of wavelength. A bolometer is a good example of this type of detector where a small absorbing element with known thermal capacity absorbs radiation and is connected to a thermal reservoir by a known conductance. Then a temperature measurement of the absorbing element will be proportional to the energy absorbed by the element from photons. Typically, bolometers are constructed of a material with a temperature dependent electrical conductivity so the temperature of the bolometer can be determined by the electrical resistance of the element. Because the bolometer measures the temperature increase due to the radiation, the only spectral dependency of a bolometer is due to the spectral absorptivity [67].
The following subsections will serve the purpose to discuss some properties of optical radiation detectors.

3.7.1. Responsivity

Responsivity is the ratio of output to input. It is generally measured in either output Volts per input of radiant Watts or output of Amps per input of radiant Watts. The responsivity in photon detectors is a function of wavelength and can be defined by

\[ R(\lambda) = \frac{V}{q} \]  

(3.23)

where \( V \) is the voltage output of the detector and \( q \) is the radiant input measured in Watts.

3.7.2. Noise Equivalent Power

The noise equivalent power (NEP) is defined based on the signal to noise ratio and the responsivity of the detector. Using Equation (3.23) the signal from a detector can be calculated from

\[ V = q_{\text{signal}} R(\lambda). \]  

(3.24)

If the noise of the detector, measured in volts, is \( V_{\text{noise}} \), then the signal to noise ratio \( S/N \), can be written as

\[ S/N = \frac{q_{\text{signal}} R(\lambda)}{V_{\text{noise}}}. \]  

(3.25)

The NEP is defined by the \( q_{\text{signal}} \) required to create a \( S/N \) of 1. Using this definition and rearranging Equation (3.25)

\[ \text{NEP} = \frac{V_{\text{noise}}}{R(\lambda)}. \]  

(3.26)
3.7.3. Specific Detectivity

The specific detectivity is a figure of merit for detectors and is one of the best means to compare dissimilar detectors. The specific detectivity is dependent on the NEP, the frequency bandwidth, and the area of the detector. Mathematically it is defined by

\[ D^* = \frac{\sqrt{A d \Delta f}}{\text{NEP}}. \] (3.27)

This definition is particularly useful because the noise of a detector is proportional to the square root of the product of the detector area and frequency bandwidth. Therefore, by normalizing this product by the NEP of the detector, it allows for a fair comparison between detectors of different sizes, and also with different frequency bandwidths. The bandwidth used in Equation (3.27) is dependent on the electrical system that is measuring the detector signal. Generally specific detectivity is reported for a detector area of 1 cm\(^2\) and a bandwidth of 1 Hz. Therefore having units of cm Hz\(^{-1/2}\) W\(^{-1}\) also known as Jones.

3.8. Lock-in Amplifier

Lock-in Amplifiers are utilized to measure a periodic signal. In principle they behave as a very narrow band-pass filter at the measurement frequency. The frequency is set by providing the lock-in with a reference signal. The lock-in then measures the amplitude of the signal at the reference frequency and the phase difference between the measured signal and the reference signal. They are especially useful under conditions where the noise level is considerably high because they limit the noise bandwidth to a very small frequency range. The general operation of lock-in amplifiers is covered here to provide sufficient understanding for the requirements of the measurement techniques.
developed. More detailed information on the operation of lock-in amplifiers can be found in the Stanford Research Systems lock-in amplifier manual [68].

Lock-in amplifiers have a unique manner of operation that allows them to have a narrow bandwidth that is easily adjustable. Specifically, they utilize a trigonometric property that will be shown in the following discussion. The input signal will be described as

\[ S_s = A_s \cos(2\pi f_s t + \phi_s). \]  \hspace{1cm} (3.28)

The reference signal is either provided externally or created internally in the lock-in. The reference signal can be described by

\[ R_0 = A_{\text{ref}} \cos(2\pi f_{\text{ref}} t + \phi_{\text{ref}}). \]  \hspace{1cm} (3.29)

Additionally, a second reference will be used that is separated by the original reference by 90 degrees. Therefore, it can be represented as

\[ R_{\pi/2} = A_{\text{ref}} \cos(2\pi f_{\text{ref}} t + \phi_{\text{ref}} + \pi/2). \]  \hspace{1cm} (3.30)

The input signal is then multiplied by each reference signal which generates

\[ R_0 S_s = A_{\text{ref}} A_s \cos(2\pi f_s t + \phi_s) \cos(2\pi f_{\text{ref}} t + \phi_{\text{ref}}) \]  \hspace{1cm} (3.31)

and

\[ R_{\pi/2} S_s = A_{\text{ref}} A_s \cos(2\pi f_s t + \phi_s) \cos(2\pi f_{\text{ref}} t + \phi_{\text{ref}} + \pi/2). \]  \hspace{1cm} (3.32)

This multiplication is conducted electronically by mixing the signals in the lock-in. These signals can be represented differently by applying the trigonometric identity

\[ \cos(x) \cos(y) = \frac{1}{2} \left[ \cos(x - y) + \cos(x + y) \right]. \]  \hspace{1cm} (3.33)
Applying this identity to Equations (3.31) and (3.32) obtains

\[ R_0 S_s = \frac{A_{ref} A_s}{2} \left[ \cos(2\pi f_s t + \phi_s - 2\pi f_{ref} t - \phi_{ref}) + \cos(2\pi f_s t + \phi_s + 2\pi f_{ref} t + \phi_{ref}) \right] \]  

(3.34)

and

\[ R_{\pi/2} S_s = \frac{A_{ref} A_s}{2} \left[ \cos(2\pi f_s t + \phi_s - 2\pi f_{ref} t - \phi_{ref} - \pi/2) + \cos(2\pi f_s t + \phi_s + 2\pi f_{ref} t + \phi_{ref} + \pi/2) \right]. \]  

(3.35)

If \( f_s = f_{ref} \) then Equations (3.34) and (3.35) become

\[ R_0 S_s = \frac{A_{ref} A_s}{2} \left[ \cos(\phi_s - \phi_{ref}) + \cos(2\pi f_s t + \phi_s + 2\pi f_{ref} t + \phi_{ref}) \right] \]  

(3.36)

and

\[ R_{\pi/2} S_s = \frac{A_{ref} A_s}{2} \left[ \cos(\phi_s - \phi_{ref} - \pi/2) + \cos(2\pi f_s t + \phi_s + 2\pi f_{ref} t + \phi_{ref} + \pi/2) \right]. \]  

(3.37)

After this mixing occurs in the lock-in, both of the signals shown mathematically in Equations (3.36) and (3.37) are filtered by a low pass filter. After this filtering the product of \( R_0 S_s \) is generally referred to as \( X \) and the product of \( R_{\pi/2} S_s \) is referred to as \( Y \). This low pass filter then yields the two signals as

\[ X = \frac{A_{ref} A_s}{2} \cos(\phi_s - \phi_{ref}) \]  

(3.38)

and

\[ Y = \frac{A_{ref} A_s}{2} \cos(\phi_s - \phi_{ref} - \pi/2) \]  

(3.39)

It is easy to see that the results in Equations (3.38) and (3.39) are DC signals only and do not contain any periodic component. Furthermore, the vector component of the signal in phase with the reference signal is given by \( X \) in Equation (3.38) and the vector component 90 degrees out of phase with the reference signal is given by \( Y \) in Equation (3.39).
Therefore by utilizing Equations (3.38) and (3.39) the amplitude of the original signal can be calculated by

$$R = (X^2 + Y^2)^{1/2},$$

(3.40)

and its phase relative to the reference can easily be determined by

$$\phi = \tan^{-1} Y/X.$$  

(3.41)

A simplification was made in the previous discussion which was the assumption that \(f_{\text{ref}}\) was exactly equal to \(f_s\). It is important to recognize that experimentally the signals do not have exactly the same frequency; there exists some bandwidth around \(f_{\text{ref}}\) that is acceptable. This bandwidth is determined by the low pass filters after the multiplications. Different combinations of low pass filters are available on many lock-in amplifiers. These filters have a -3dB cutoff frequency that corresponds to time constant of the filter with the relationship

$$f_c = \frac{1}{2\pi \tau}.$$  

(3.42)

The lock-in amplifiers then have an option to put up to 4 low-pass filters in a row. This creates a filter with a steeper roll off and decreases the \(f_c\) of the system. Specifically, these filters have 6, 12, 18, 24 dB/octave roll of corresponding to 1, 2, 3, 4 low-pass filters, respectively. The -3dB frequency of the filter system can be found by

$$f_{-3dB} = f_c \sqrt{2^{1/n} - 1}$$  

(3.43)

where \(n\) is the number of low pass filters and \(f_c\) is defined by Equation (3.42).

The time constant and slope setting need to be sufficient that \(f_{-3dB}\) is narrow enough that the \(2f\) signal is filtered significantly. The narrower this bandwidth is, the noise is
reduced and a better measurement can be made. The limitation of increasing the time constant is there is a slow measurement response to any changes in the signal being measured. By combining Equations (3.42) and (3.43) a relationship can be obtained that describes the -3dB frequency as a function of time constant and the slope setting of the lock-in amplifier.

\[ f_{-3dB} = \frac{1}{2\pi\tau} \sqrt{2^{1/n} - 1} \]  

(3.44)

If this \( f_{-3dB} \) frequency were equal \( f_{ref} \) then the signal at \( 2f_{ref} \) would be attenuated to the -3dB level which would not be sufficient for an accurate measurement, but does provide a good bound for the lock-in settings. Therefore, it can be written that

\[ f_{ref} > \frac{1}{2\pi\tau} \sqrt{2^{1/n} - 1} \]  

(3.45)

While this takes into account both lock-in settings and provides a good mathematical bound, in practice it is often easier to use the approximation

\[ \tau > 1/f_{ref} \]  

(3.46)

to provide good results.
CHAPTER 4

MATERIALS AND METHODS

In the previous chapter a literature review was provided on the standard techniques that have been used for thermal property and pyrometry measurements. Leveraging the experiences from these techniques, new methods will be developed based on nonlinear PTR (NL-PTR) for both thermal property and pyrometry measurements. The purpose of this chapter is to discuss in detail the measurement methods, and materials that will be used in this work.

The chapter will begin with a detailed discussion of a basic PTR setup, its components, PTR signal calculation, and data reduction techniques. Next the experimental equipment used in the following work will be covered. Finally, a brief description of the materials used for measurement is provided

4.1. Photothermal Radiometry

PTR has developed into a standard technique for measuring thermal properties after many years of use. By definition PTR is the process of heating a sample with light, and monitoring the change in temperature by observing the thermal radiation emitted. Because of this broad definition, there are many configurations on both the heating and radiometry side of the experiment. This section will cover the details of the specific configuration used in this work.
4.1.1. **Description of Measurement System**

The PTR system in this work uses a modulated laser as the source of heating. This is often referred to as frequency domain PTR. In Frequency domain PTR the sample is heated periodically, and therefore the temperature of the sample also responds periodically. The thermal emission from the sample is collected by off-axis parabolic mirrors, and focused into an infrared detector. The detector signal is measured by a lock-in amplifier, which is designed to measure the amplitude and phase of a signal relative to a reference. Detailed information was provided in Section 3.8 about the operation of lock-in amplifiers. The lock-in amplifier provides a reference signal that corresponds to the amplitude modulation of the heat source. The amplitude and phase measured is dependent on the surface temperature of the sample, because the thermal emission is proportional to its temperature. A diagram of the basic system can be seen in Fig. 4.1.

---

**Fig. 4.1** Diagram of a standard PTR system
Because of the collaborative nature of this work, two PTR systems have been used in the measurements presented here. One system is located at the Université de Reims Champagne-Ardenne, France and the other at Utah State University in Logan, Utah, USA. These systems are largely the same, but have some subtle differences. When the measurement systems are being discussed, it will be noted if there is a difference between the systems. If it is not specified which system is being discussed, then that aspect of the measurement systems are equivalent.

![Images of PTR systems used: a. located at URCA, France b. located at USU, USA.](image)

Now that an overview of the PTR systems has been provided, a detailed discussion of each of the components will be provided. This will begin at the heat source and proceed through the system ending at the measurement of the signal.

4.1.2. Lasers

Lasers are used in PTR measurements because of their ability to heat a sample contactless, and the ability to easily periodically modulate their heat flux. The laser is required to have adequate power to heat the sample, since their main purpose is to provide
a periodic heat flux that generates a periodic temperature field in the sample. Generally in PTR measurements laser power ranging from a 100 mW to 1 W is sufficient to induce detectable thermal waves with an adequate signal to noise ratio. For safety and ease of alignment wavelengths in the visible range are desirable. Often NdYAG lasers are used because they are cost effective for the power requirements, and when coupled with frequency doubling optics emit visible light at 532 nm (green).

A variety of lasers have been used throughout this work. They are varied in power, beam shape, and wavelength. As will be seen in the following chapters, the beam shapes are generally modified to suit the specific needs of the measurements, and all of the measurements are independent of the laser wavelength. Likewise, the lasers power is often attenuated based on the power required for the measurement. For these reasons, the specifics of the lasers used in this work will not be covered.

4.1.3. Laser Modulation

In frequency domain PTR it is required to periodically modulate the laser power. In PTR literature there are four dominate methods to modulate the laser. They include directly modulating the laser output, use a spinning wheel with slot cutouts known as a mechanical chopper, acousto optical modulators (AOM), and electrooptical modulators (EOM). EOM’s are generally used for high frequency applications, and therefore have not been used in this work and will not be covered in detail here. The other three techniques were used throughout this work and their mode of operation will be discussed.
Some lasers can be directly modulated and do not require an external device to modulate the power. Generally, laser diodes have the ability to function in this manner, and use a TTL input to control the modulation. This results in a square wave modulation of the laser being off or at maximum power. To reduce the amplitude of this modulation external neutral density filters can be used.

Mechanically chopping the laser is the second modulation technique used in this work. With this technique a disk with slits cut in rotates on a stepper motor at a specific rate. As the disk rotates the laser alternates between passing through the slits and being blocked between the slits. This effectively creates a square wave, given the laser diameter is small compared to the slots on the chopper wheel.

An AOM is the final method used for modulating the laser power. AOM’s are unique from the other methods used because of their ability to provide a sinusoidal modulation of the laser power. AOM’s modulate the laser by utilizing Bragg diffraction. The acoustic waves required for the Bragg diffraction to occur are generated by a piezo-electric transducer. The amplitude of the diffraction can be controlled directly by controlling the magnitude of the acoustic waves though the piezo electric transducer. A diagram of the AOM operation can be seen in Fig. 4.3.
Fig. 4.3. Acousto optical modulators (AOM) utilize bragg scattering to diffract the laser. The acoustic waves can be controlled by piezo-electric transducer and therefore the magnitude of the diffraction can be controlled.

After the AOM, an iris is used to allow only one of the diffraction orders to pass through it and block the others. Typically 0\textsuperscript{th} or 1\textsuperscript{st} diffracted beams are chosen. The 0\textsuperscript{th} order beam has the benefit of the laser alignment can be performed with the AOM on or off, and the position of the AOM in the light path has little effect if the 0\textsuperscript{th} is chosen. However, generally the 0\textsuperscript{th} order is not fully attenuated at the trough of the modulation, meaning the laser is never fully blocked and add unnecessary heat to the sample. The 1\textsuperscript{st} order beam is fully attenuated, but adds complications in the alignment because of the angle change due to the diffraction. Therefore, the alignment needs to be conducted with the AOM in the light path, and any movement of it will have an effect on the alignment.

In the URCA system, an acousto-optical modulator (AOM) is used to modulate the laser. At USU a mechanical chopper (Stanford Research Systems SR 540) was used with one of the lasers, and the other laser was directly modulated by a TTL input. The amplitude
of the modulation was changed by placing neutral density filters in the light path to attenuate the lasers.

4.1.4. **Mirrors**

PTR systems require a method to collect infrared radiation, and focus it into a detector. While there’s several methods to do this the most common is the utilization of off-axis parabolic mirrors. The mirror used in this study are coated with gold due to its high reflectivity in the infrared range, specifically around 10 µm. The gold coatings generally have a reflectivity around 98% and are spectrally flat across the infrared wavelength range. This allows for easy analysis for the optical transmission in the PTR signal.

4.1.5. **Detectors**

An IR detector is required to measure the thermal radiation emitted from a sample. The measurements presented in this work occur over the range from approximately 300 K to 500 K. A result of this temperature range is that peak emission occurs over a range of wavelengths from 6 to 10 µm. In order to obtain the maximum signal to noise ratio, detectors with a maximum responsivity in this spectral range are desirable. Mercury cadmium telluride (MCT) detectors are most commonly used in this spectral range and have excellent responsivity. These detectors are often thermoelectrically cooled or use liquid nitrogen (77 K) to reduce the detector temperature. This is done to prevent thermally excited electrons producing a signal. MCT detectors are highly linear devices which is important for the work in this study.
4.1.6. **Lock-in Amplifiers**

Throughout this work several measurements of periodic signals are necessary. Lock-in amplifiers have been used to accomplish these measurements accurately and efficiently. The general operation of the lock-in amplifiers used can be seen in Section 3.8. Specifically various Stanford Research Systems (SRS) lock-in amplifiers have been used. They include SR850, SR865, SR844. These lock-ins have different operational frequency ranges and slightly different internal configurations. Largely these lock-ins can be used interchangeably given that the measurement frequency is inside of the operational range of the lock-in amplifier. When constraint requires a specific lock-in be used experimentally it will be noted in the text. Otherwise it can be considered that any of these lock-in amplifiers could be utilized.

4.1.7. **Photothermal IR Radiometric Signal**

To understand the nonlinearity of the PTR signal an accurate understanding of the PTR signal is required. This section serves the purpose to describe qualitatively and quantitatively the factors that affect the PTR signal. In this discussion the signal given from the detector without any processing will be referred to as the Radiometric Signal (RS). The PTR signal is specifically the RS that has been processed by an electronic band-pass filter at a specific frequency. Typically the PTR signal is measured using a lock-in amplifier. Therefore this discussion will begin with the elements that compose the RS.

The RS consists of all radiation contacting the detector regardless of the radiation’s origin. Therefore, the RS is composed of radiation emitted from the sample as well as the
surrounding environment. The IR radiation from the sample depends on the amount emitted and the percentage of the emitted radiation that reaches the detector. Therefore the RS is dependent on the sample emission, transmissivity of the system, and geometrical factors.

The irradiation from the surrounding environment obviously depends on the temperature and radiation properties of the surrounding environment, but some convenient simplifications can be made. Since a laboratory room is a large cavity which can generally be regarded as isothermal it can be considered a blackbody emitter at a constant temperature.

Using this knowledge, the RS for a DC-coupled detector can be expressed mathematically by

$$RS(T) = G_A D F_{D\rightarrow S} \int_{0\mu m}^{\infty \mu m} \varepsilon(\lambda, T) E_\lambda(\lambda, T) R(\lambda) \tau(\lambda) d\lambda$$

$$+ G A_D \left(1 - F_{D\rightarrow S}\right) \int_{0\mu m}^{\infty \mu m} E_\lambda(\lambda, T_{BG}) R(\lambda) d\lambda$$

(4.1)

where $E_\lambda$ is the spectral exitance defined by Equation (3.5), $\varepsilon$ is the sample emissivity, $R$ represents the detector sensitivity, $\tau$ represents the system transmissivity, $T_{BG}$ is the temperature of the surrounding environment, $G$ is the electronic amplification, $A_D$ is the detector area, and $F_{D\rightarrow S}$ is the view-factor from the detector to the sample. Recognizing the second term is independent of the sample temperature, and only a function of the background temperature. Furthermore, the zero voltage level after amplification is often arbitrary, therefore the second term will be designated as a function of $T_{BG}, V_{bias}(T_{BG})$ and Equation (4.1) can be rewritten as
There exists a special case of Equation (4.2) where the $R(\lambda)$ and $\tau(\lambda)$ are constants for all values of $\lambda$. In this scenario the integral results in the Stefan-Boltzmann law and therefore the RS can be described by

$$RS(T) = C_1 \varepsilon \sigma T^4 + V_{bias}(T)$$

(4.3)

where $C_1$ is the product of the sensitivity, transmissivity, gain, detector area and view-factor. While there are detectors that have sensitivities that can be considered constant over a spectral range most detectors used in PTR measurements do not have a constant sensitivity. Additionally, the detectors are not typically sensitive over all wavelengths. Generally PTR measurements are conducted under ambient room temperature conditions which according to Wien’s Law the peak emission occurs at a wavelength of approximately 10 µm. Later it will be shown the PTR signal is proportional to the derivative of Planck’s law with respect to temperature. The derivative shifts the maximum spectrally to approximately 8 µm at a temperature of 300 K. Therefore, mercury cadmium telluride (MCT) detectors are often used since they generally have a high detectivity in this spectral range. The normalized spectral detectivity of the MCT detectors used in this study can be seen in Fig. 4.4. It is clear from Fig. 4.4 the MCT detectors used in this study have a detectivity that is dependent on wavelength, and are not sensitive over all wavelengths. For this reason, Equation (4.2) must be used in the analysis of the RS in a PTR system.
Fig. 4.4. Specific detectivity of Kolmar Technologies Mercury Cadmium Telluride (MCT) detector KLD-1-J1/11/DC

To provide a more thorough understanding of Equation (4.2), a plot of Planck’s law, the detector response, and their product is provided in Fig. 4.5. Furthermore, the shaded area represents the value of the integral in Equation (4.2). The evaluation in Fig. 4.5 assumes that the emissivity $\varepsilon$, and transmissivity $\tau$, are independent of wavelength which is also known as the gray body assumption.
Fig. 4.5 Emission according to Planck’s law at 400 K, MCT detectivity, and their product plotted over a range of wavelengths. The shaded area is proportional to the detector signal and can be calculated by Equation (4.2).

As discussed in previous sections, frequency domain PTR measures the periodic component of the sample temperature at the modulation frequency of the heat source. Mathematically this can be described by

$$PTR(f) = \mathcal{F}\{RS(T), f\}$$  \hspace{1cm} (4.4)

where $\mathcal{F}$ is the fourier transform for the RS at frequency $f$. Experimentally a lock-in amplifier is used to measure the alternating component of the detector signal “locked in” at a specific reference frequency, $f$ and filters out all other frequencies including any DC voltage. Because the lock-in amplifier will filter any DC voltage, the PTR measurement is unaffected by the presence of $V_{bias}(T_{BG})$ in Equation (4.2) given that it remains constant during the measurement process. For this reason the $V_{bias}(T_{BG})$ will be neglected in the calculation of the RS and PTR signal from this point forward. This can be thought of as
experimentally adjusting a bias voltage such that the detector would read zero voltage if the sample were at absolute zero.

The RS has been evaluated over a range of temperatures and plotted in Fig. 4.6. This evaluation has been conducted using Equation (4.2) with constant values for emissivity and transmissivity, and the spectral detector responsivity shown in Fig. 4.4 was used. Since the choice of values in the product of $GA_D F_{D\rightarrow S}$ is arbitrary, the product was set to a value which normalized the plot to be on the order of 1 V. No generality is lost by this choice of scaling, and it does not affect the results. It is clear from this plot that the RS, and therefore the PTR signal, is not linear with respect to sample temperature. It is this nonlinearity that will be exploited to develop the pyrometry and thermal properties measurement techniques.

![Graph](image)

**Fig. 4.6.** Detector signal vs sample temperature $T$ calculated using Equation (4.2) neglecting $V_{bias}$ and assuming constant values for emissivity and transmissivity. The detector responsivity used can be seen in Fig. 4.4. The value of the product $GA_D F_{D\rightarrow S}$ is chosen such that the result is scaled to be on the order of 1 V.
CHAPTER 5

RESEARCH PLAN

This chapter presents a task list for accomplishing the objectives of the work. These collaborative efforts will be illustrated through the following task list. Each section in the chapter briefly delineates the process followed for each of the major tasks outlined in Table 5.1.

Table 5.1. Outline of main tasks to accomplish the objectives of the dissertation

<table>
<thead>
<tr>
<th>Section</th>
<th>Tasks</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>Develop the NL-PTR theory and modeling tools</td>
</tr>
<tr>
<td></td>
<td>• Develop numerical tools that can accurately predict the PTR signal as a function of temperature given spectral information.</td>
</tr>
<tr>
<td></td>
<td>• Determine factors that influence the nonlinearity</td>
</tr>
<tr>
<td>5.2</td>
<td>Determine applications of NL-PTR using the modeling tools developed in task 5.1</td>
</tr>
<tr>
<td></td>
<td>• Relative temperature measurement for monitoring sample temperature during PTR measurements</td>
</tr>
<tr>
<td></td>
<td>• Noncontact, direct thermal effusivity measurements for homogenous non-layered samples</td>
</tr>
<tr>
<td></td>
<td>• Absolute temperature measurement independent of changes in emissivity with respect to temperature or wavelength</td>
</tr>
<tr>
<td>5.3</td>
<td>Experimentally test possible applications of NL-PTR</td>
</tr>
<tr>
<td></td>
<td>• Experimentally test both pyrometry techniques</td>
</tr>
<tr>
<td></td>
<td>‒ Measure temperature using NL-PTR and compare to thermocouple measurements</td>
</tr>
<tr>
<td></td>
<td>• Noncontact, direct thermal effusivity measurements</td>
</tr>
<tr>
<td></td>
<td>‒ Measure thermal properties on material with known thermal effusivities covering a large range of values using the NL-PTR technique</td>
</tr>
<tr>
<td></td>
<td>• Quantify uncertainty in measurements</td>
</tr>
</tbody>
</table>
5.4 Evaluate the overall feasibility of NL-PTR techniques compared to standard techniques

- Comparison of measurement requirements between the relative temperature NL-PTR to other pyrometry techniques
- Evaluation of contactless thermal effusivity measurement
- Comparison of measurement requirements between the absolute temperature measurement to standard pyrometry techniques

5.1. Development of NL-PTR Theory and Modeling Tools

A firm understanding of the nonlinearity of the PTR signal is required before any meaningful applications for it can be developed. To fully understand the phenomena both analytical and numerical analysis will be required. Possible applications will be explored for NL-PTR using the tools developed for this analysis. Furthermore, after applications are identified these tools will be utilized to determine the sensitivity of parameters and uncertainty analysis.

5.2. Determine Potential Applications of NL-PTR

NL-PTR provides a new method for interpreting the PTR signal. This new interpretation is useless without applications. Applications will be developed with the modeling tools outlined in task 5.1. Specifically, these applications developed will be for a direct, non-contact, thermal effusivity measurement and two new pyrometry techniques. Using the tools in task 5.1 the feasibility of application will be evaluated.

5.3. Experimentally Test Possible Applications of NL-PTR

The applications that are identified from Section 5.2 will need to be tested experimentally. From the experimental tests specific criteria will be tested: the
measurement accuracy and suitable measurement conditions. These criteria will need to be evaluated for each experimental application developed.

5.4. Evaluate the Overall Feasibility of NL-PTR Techniques Compared to Standard Techniques

To understand the practicality of utilizing NL-PTR for a standard measurement technique it will need to be compared to current standard techniques. The best way to perform this comparison is by comparing the criteria determined from the results of Section 5.2 to the same properties of standard techniques. In addition to these parameters the techniques will need to be compared on the necessary information in order to apply the technique and on the simplicity of the technique.
Table 5.2 Approximate schedule for major tasks and their locations

<table>
<thead>
<tr>
<th>Dates</th>
<th>Location</th>
<th>Research Task</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan. 2015- April 2015</td>
<td>USU, Utah</td>
<td>Literature review of photothermal radiometry, pyrometry and other thermal property measurement techniques</td>
</tr>
<tr>
<td>April 2015- August 2015</td>
<td>URCA, France</td>
<td>Analytically explore NL-PTR theory</td>
</tr>
<tr>
<td>August 2015- October 2015</td>
<td>URCA, France</td>
<td>Develop numerical tools for the analysis of NL-PTR</td>
</tr>
<tr>
<td>October 2015- Dec. 2015</td>
<td>URCA, France</td>
<td>Use numerical models to develop applications for the NL-PTR theory</td>
</tr>
<tr>
<td>Dec. 2015- March. 2016</td>
<td>URCA, France</td>
<td>Begin experimental tests on NL-PTR, checking for the existence of harmonic generation, and PTR signal temperature dependence, etc;</td>
</tr>
<tr>
<td>March. 2016- June 2016</td>
<td>URCA, France</td>
<td>Development, measurement, and analysis of relative temperature measurement technique</td>
</tr>
<tr>
<td>June 2016- Sept 2016</td>
<td>URCA, France</td>
<td>Development and preliminary testing of thermal effusivity measurement technique</td>
</tr>
<tr>
<td>Sept 2016- Nov. 2016</td>
<td>USU, Utah</td>
<td>Configure USU PTR system for NL-PTR measurements, and final testing and analysis of thermal effusivity measurement technique</td>
</tr>
<tr>
<td>Nov. 2016- Jan. 2017</td>
<td>USU, Utah</td>
<td>Development, measurement, and analysis of absolute temperature measurement technique</td>
</tr>
<tr>
<td>Jan. 2017- March 2017</td>
<td>USU, Utah</td>
<td>Prepare manuscript and journal papers for submission</td>
</tr>
</tbody>
</table>
CHAPTER 6

NL-PTR THEORETICAL DEVELOPMENT

The nonlinearity of sample emission with respect to temperature can be extremely useful for both thermal property and temperature measurements. This chapter will discuss the sources of the nonlinearity with respect to temperature and detail its effects on the PTR signal. The following chapters will discuss in detail how the results of this nonlinearity can be utilized in a useful manner.

6.1. Signal Calculation

In Section 4.1.7 a detailed explanation of the PTR signal is provided. This chapter will explain the result of the nonlinear temperature dependence on the PTR signal. This discussion will begin with a plot of the RS from an IR detector over a range of sample temperature, see Fig. 6.1. This plot is identical to Fig. 4.6, and is reproduced here for convenience. Likewise the equation used to calculate the RS is also repeated here

\[ RS(T) = GAD_FD_{\rightarrow}S \int_{5 \mu m}^{\infty} \varepsilon(\lambda, T)E(\lambda, T)R(\lambda)\tau(\lambda)d\lambda + V_{bias}(T_BG). \] (6.1)

It is obvious that this plot is nonlinear with respect to temperature, but the mathematical representation from the calculation of the radiometric signal (RS) is a complicated relationship. As discussed in Chapter 3, there is a special case when the detector is sensitive over all wavelengths and when the emissivity, responsivity, and transmissivity are all independent of wavelength. In this scenario the Stefan-Boltzmann law is obtained. Therefore, it is suggested this curve can be described by an equation of the form
\[ RS = AT^B + C. \] (6.2)

In the case when the Stefan-Boltzmann law is obtained, \( A \) is a function of view-factor, detector area, emissivity, transmissivity, Stefan Boltzmann constant, and detector responsivity. \( B \) is equal to 4. \( C \) is a function of the surrounding temperature, view-factors, detector responsivity, detector area, Stefan-Boltzmann constant, and detector bias voltage.

When detectors are used with non-uniform responsivities and are limited to a spectral range, then the values of \( A \), \( B \), and \( C \) are different. To understand how \( A \), \( B \), and \( C \) are determined in this case, some observations about Equation (6.1) will be made:

- Planck’s law is the only factor that is dependent on sample temperature if emissivity is independent of sample temperature.
- The spectral properties (depending on \( \lambda \)) affect the temperature dependence of \( RS \).
- The surrounding environment temperature only affects the offset.
- The multiplying factors, in front of the integral only scale the value of the integral.

These observations about Equations (6.1) can then be applied to relating the coefficients of Equation (6.2) to Equation (6.1). First it should be stated that Equation (6.2) does not match Equation (6.1) in the non-grey conditions, unless \( A \), \( B \), and \( C \) are allowed to be functions of temperature. However, with that understanding the following observations can be made about what influence each of the values:

- Parameter \( A \) is influenced by: detector area, view-factors, responsivity transmissivity, emissivity, and sample temperature and electronic amplification
- Parameter \( B \) is influenced by: sample temperature, spectral properties
Parameter C is influenced by: detector area, view factors, surrounding temperature, responsivity, transmissivity, and electronic amplification.

Another way to achieve the same conclusion is to recognize in Equation (6.2) the value of B determines if the function is non-linear, and how nonlinear the curve is. Similarly, in Equation (6.1) Planck’s law and the spectral properties are the only parameters that determine the nonlinearity. All other parameters in Equation (6.1) either scale or shift the plot, but do not change the nonlinearity.

![Graph](image)

Fig. 6.1. Detector signal vs sample temperature calculated by Equation (6.1) neglecting $V_{bias}$ and assuming constant values for emissivity and transmissivity. The detector responsivity used can be seen in Fig. 4.4. The value of the product $GA_DF_{D→S}$ is chosen such that the result is scaled to be on the order of 1 V.

To determine the coefficients of A, B, and C, Equation (6.2) can be fit to the curve in Fig. 6.1. As stated earlier, A, B, and C are not constants, but rather functions of temperature. Therefore, during the fitting process, Equation (6.2) is fit over small temperature ranges of the curve in Fig. 6.1. The fit parameters A, B, and C then correspond to the center of the temperature range the fitting is conducted over. The parameter B, also
known as the nonlinearity coefficient, from this fitting process can be seen in Fig. 6.2. It is clear from our observations made previously about what influences A, B, and C, that this curve is independent of the surrounding environment, detector area, view-factors, and signal amplification. Specifically, it is only dependent on the sample temperature and the spectral properties.

![Graph showing nonlinearity coefficient](image)

Fig. 6.2. The nonlinearity coefficient of the detector signal vs temperature. Determined by fitting Equation (6.2) over small temperature ranges in Fig. 6.1

### 6.2. Harmonic Generation

Section 6.1 explained how the RS can be described by Equation (6.2). Using this understanding, the result of this nonlinearity will be explored. Specifically, how the emission from a periodic temperature will be affected.

When a sinusoidal signal undergoes a nonlinear process harmonics are generated, and their magnitude is dependent on both the nonlinearity of the process and the magnitude of the sine wave. This fact can be easily seen through the trigonometric identity

$$\cos^2(\omega t) = \frac{1}{2}[1 + \cos(2\omega t)].$$  \hspace{1cm} (6.3)
If the signal contains two sine waves at different frequencies, the nonlinear process generates signals at harmonics of both frequencies plus signals at the sum and difference of the frequencies. The number of harmonics and side band frequencies is dependent on the nonlinearity of the process. This is the fact that will be utilized to extract information about the sample temperature and thermal properties. This harmonic generation will be developed throughout this section.

It will be assumed that the sample’s temperature has a DC value and is additionally modulating at two frequencies \( f_1 \) (\( \omega_1 = 2\pi f_1 \)) and \( f_2 \) (\( \omega_2 = 2\pi f_2 \)) and therefore the temperature can be described by

\[
T(t) = T_{DC} + T_{AC1} \cos(\omega_1 t) + T_{AC2} \cos(\omega_2 t).
\] (6.4)

In Equation (6.4) \( T_{DC} \) is the DC temperature component of the sample, and \( T_{AC1} \) and \( T_{AC2} \) are the amplitudes for the temperature modulation at frequencies \( f_1 \) and \( f_2 \), respectively. Furthermore, parameters \( b \) and \( c \) will be defined as

\[
b = \frac{T_{AC1}}{T_{DC}} \quad c = \frac{T_{AC2}}{T_{DC}}
\] (6.5)

So that Equation (6.4) can be rewritten as

\[
T = T_{DC}[1 + b \cos(\omega_1 t) + c \cos(\omega_2 t)].
\] (6.6)

In the previous section, it was shown that the emission from a sample can be described by Equation (6.2). In Fig. 6.2 it was shown how the value of B depends on the temperature and the spectral properties. For a thought experiment, it will be assumed that there exists a temperature for which the nonlinearity coefficient B is equal to 4 for a given
set of spectral properties. Using this assumption Equation (6.2) will be used to describe the emission that corresponds to the temperature modulation described by Equation (6.6).

Substituting Equation (6.6) into Equation (6.2) yields

\[ RS = A(T_{dc}[1 + b \cos(\omega_1 t) + c \cos(\omega_2 t)])^4 + C. \]  

(6.7)

Focusing only on the temperature and distributing the exponent yields

\[ T^4 = T^4_{dc}[b^4 \cos^4(\omega_1 t) + 4b^3 c \cos(\omega_2 t) \cos^3(\omega_1 t) + 4b^3 \cos^3(\omega_1 t) + 12b^2 c \cos(\omega_2 t) \cos^2(\omega_1 t) + 12b^2 \cos^2(\omega_1 t) + 6b^2 \cos^2(\omega_1 t) + 4b^2 \cos^2(\omega_1 t) + 6b^2 \cos^2(\omega_1 t) + 12b^2 \cos(\omega_2 t) \cos(\omega_1 t) + 12bc \cos(\omega_2 t) \cos(\omega_1 t) + 6bc \cos^2(\omega_2 t) + 6c^2 \cos^2(\omega_2 t) + 1]. \]

(6.8)

Recognizing that \( b \) and \( c \ll 1 \), any terms greater than second order with respect to \( b \) and \( c \) will be considered negligible. Removing these terms yields

\[ T^4 \approx T^4_{dc}[6b^2 \cos^2(\omega_1 t) + 12bc \cos(\omega_2 t) \cos(\omega_1 t) + 4b \cos(\omega_1 t) + 4c \cos(\omega_2 t) + 1]. \]

(6.9)

This expression will be simplified further through the use of trigonometric identities, therefore Equation (6.9) can be written in the form

\[ T^4 \approx T^4_{dc} \left[ \frac{6b^2}{2} \cos^2(\omega_1 t) + \frac{12bc}{2} \cos(\omega_2 t) \cos(\omega_1 t) + 4b \cos(\omega_1 t) + \frac{6c^2}{2} \cos^2(\omega_2 t) + 4c \cos(\omega_2 t) + 1 \right]. \]

(6.10)

Plugging this result back into Equation (6.2) yields

\[ RS \approx AT^4_{dc} \left[ \frac{6b^2}{2} \cos(2\omega_1 t) + \frac{12bc}{2} \cos(\omega_2 t - \omega_1 t) + \cos(\omega_1 t + \omega_2 t) \right] + 4b \cos(\omega_1 t) + \frac{6c^2}{2} \cos^2(2\omega_2 t) + 4c \cos(\omega_2 t) + 1 \] + C.

(6.11)

The DC components in the first term will now be pulled out and summed with \( C \) since these are indistinguishable and the new variable will be called \( C' \), shown as

\[ RS \approx AT^4_{dc} \left[ \frac{6b^2}{2} \cos(2\omega_1 t) + \frac{12bc}{2} \cos(\omega_2 t - \omega_1 t) + \cos(\omega_1 t + \omega_2 t) \right] + 4b \cos(\omega_1 t) + \frac{6c^2}{2} \cos(2\omega_2 t) + 4c \cos(\omega_2 t) \] + C'.

(6.12)
From this approximation, it is clear that the nonlinear emission process causes the RS to contain components at several frequencies. Specifically these frequencies include the fundamental frequencies the temperature is modulating at, their harmonics, and the sum and difference of those frequencies.

\[
P_{\text{TR}}(f_1) / (A \cdot T_{\text{DC}}^B) = K_3 b 
\]  
\[
P_{\text{TR}}(2f_1) / (A \cdot T_{\text{DC}}^B) = K_1 b^2 / 2
\]  
\[
P_{\text{TR}}(f_2) / (A \cdot T_{\text{DC}}^B) = K_5 c
\]  
\[
P_{\text{TR}}(2f_2) / (A \cdot T_{\text{DC}}^B) = K_4 c^2 / 2
\]  
\[
P_{\text{TR}}(f_1 \pm f_2) / (A \cdot T_{\text{DC}}^B) = K_2 b c / 2
\]  
\[
P_{\text{TR}}(f_{1 \times 2}) / (A \cdot T_{\text{DC}}^B) = K_2 b c
\] (6.13)

Remembering that this approximation was for the special case of when the nonlinearity coefficient \( B \) is equal to 4. It was shown there is a range of possible values for \( B \) depending on the spectral properties and sample temperature. Therefore, it will be written that the general RS can be described as

\[
RS \approx A T_{\text{DC}}^B [K_1 b^2 \cos^2(\omega_1 t) + K_2 b c \cos(\omega_2 t) \cos(\omega_1 t) + K_3 b \cos(\omega_1 t) \\
+ K_4 c^2 \cos^2(\omega_2 t) + K_5 c \cos(\omega_2 t))] + C
\] (6.14)

where the constants \( K_1, K_2, K_3, K_4, \) and \( K_5 \) are the coefficients multiplying the cosine functions. These constants \( K_1 \) through \( K_5 \) are a function of the exponent \( B \). Furthermore, by applying trigonometric identities Equation (6.14) can be rewritten as

\[
RS \approx A T_{\text{DC}}^B \left[ \frac{K_1 b^2}{2} (1 + \cos(2\omega_1 t)) + \frac{K_2 b c}{2} [\cos(\omega_2 t - \omega_1 t) + \cos(\omega_1 t + \omega_2 t)] + \\
+ K_3 b \cos(\omega_1 t) + \frac{K_4 c^2}{2} (1 + \cos(2\omega_2 t)) + K_5 c \cos(\omega_2 t) \right] + C. 
\] (6.15)

By grouping the DC terms with \( C \)
The PTR signal, defined by Equation (4.4), is the RS at a defined frequency. The amplitude of the various PTR signals are easy to identify in Equation (6.16) because they are multiplied by a cosine function at their respective frequencies. The exception to this is the $PTR(f_1 \times 2)$ which is defined by the modulation of $PTR(f_1)$ at frequency $f_2$. Specifically, the definition of this coefficient can be seen from Equation (6.14) in the term that contains the product of the two cosine functions at each frequency. Each of these coefficients can be seen in Equations (6.13 a-f).

The coefficients from this process for integer values of $B$ from 2 to 5 are shown in Table 6.1. From Table 6.1 it should be noted that if the values of $b$ and $c$ are equal then all of the second order coefficients are separated by factors of two. Specifically, that $4PTR(2f_1) = 2PTR(f_1 - f_2) = PTR(f_1 \times 2)$ given $b$ and $c$ are equal.

Table 6.1. The multiplicative coefficients at different frequencies for nonlinearity coefficients ranging from 2 to 5.

<table>
<thead>
<tr>
<th>$T^B$</th>
<th>$f_1$</th>
<th>$f_2$</th>
<th>$2f_1$</th>
<th>$2f_2$</th>
<th>$f_2 \pm f_1$</th>
<th>$f_{1 \times 2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$(K_3b)$</td>
<td>$(K_5c)$</td>
<td>$(K_1b^2/2)$</td>
<td>$(K_4c^2/2)$</td>
<td>$(K_2bc/2)$</td>
<td>$(K_2bc)$</td>
</tr>
<tr>
<td>$T^2$</td>
<td>$2b$</td>
<td>$2c$</td>
<td>$2b^2/4$</td>
<td>$2c^2/4$</td>
<td>$2bc/2$</td>
<td>$2bc$</td>
</tr>
<tr>
<td>$T^3$</td>
<td>$3b$</td>
<td>$3c$</td>
<td>$6b^2/4$</td>
<td>$6c^2/4$</td>
<td>$6bc/2$</td>
<td>$6bc$</td>
</tr>
<tr>
<td>$T^4$</td>
<td>$4b$</td>
<td>$4c$</td>
<td>$12b^2/4$</td>
<td>$12c^2/4$</td>
<td>$12bc/2$</td>
<td>$12bc$</td>
</tr>
<tr>
<td>$T^5$</td>
<td>$5b$</td>
<td>$5c$</td>
<td>$20b^2/4$</td>
<td>$20c^2/4$</td>
<td>$20bc/2$</td>
<td>$20bc$</td>
</tr>
</tbody>
</table>
6.3. Ratio of 1st and 2nd Order Radiation Terms

While the terms in Table 6.1 are insightful to how the PTR signal behaves under different nonlinearity conditions, the table itself is not particularly useful. Specifically, due to the fact that the absolute values have little use since each coefficient in the table is also multiplied by the \((A \cdot T_{BC}^B)\) factor. However, by taking the ratio of two factors in the table would cancel the \((A \cdot T_{BC}^B)\) multiplicative factor, leaving only the ratio of the amplitudes described in the table.

By inspecting Table 6.1, it is determined that taking a ratio between two first-order terms \((PTR(f_1)\) and \(PTR(f_2)\) ) yields only the ratio of \((T_{AC1} \) and \(T_{AC2}\)). Additionally, taking the ratios of the second-order terms \((PTR(2f_1), PTR(2f_2), PTR(f_1 \pm f_1), \) and \(PTR(f_1x2)\) ) yields either a factor of 2 or 4 depending on which second-order terms are chosen, assuming \(b\) is equal to \(c\). Therefore, it is clear that the most useful ratios are those between the first order and second order terms which can be seen in Table 6.2.

Table 6.2. Ratios between first and second order terms that are provided in Table 6.1.

<table>
<thead>
<tr>
<th>(T^B)</th>
<th>(\frac{PTR(2f_1)}{PTR(f_1)})</th>
<th>(\frac{PTR(2f_2)}{PTR(f_2)})</th>
<th>(\frac{PTR(f_1 \pm f_2)}{PTR(f_2)})</th>
<th>(\frac{PTR(f_1 \pm f_2)}{PTR(f_1)})</th>
<th>(\frac{PTR(f_1x2)}{PTR(f_2)})</th>
<th>(\frac{PTR(f_1x2)}{PTR(f_1)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T^2)</td>
<td>(b/4)</td>
<td>(c/4)</td>
<td>(b/2)</td>
<td>(c/2)</td>
<td>(b)</td>
<td>(c)</td>
</tr>
<tr>
<td>(T^3)</td>
<td>(2b/4)</td>
<td>(2c/4)</td>
<td>(2b/2)</td>
<td>(2c/2)</td>
<td>(2b)</td>
<td>(2c)</td>
</tr>
<tr>
<td>(T^4)</td>
<td>(3b/4)</td>
<td>(3c/4)</td>
<td>(3b/2)</td>
<td>(3c/2)</td>
<td>(3b)</td>
<td>(3c)</td>
</tr>
<tr>
<td>(T^5)</td>
<td>(4b/4)</td>
<td>(4c/4)</td>
<td>(4b/2)</td>
<td>(4c/2)</td>
<td>(4b)</td>
<td>(4c)</td>
</tr>
</tbody>
</table>

From Table 6.2 it can easily be seen that the ratios for a given value of \(B\) are separated by either a factor of 2 or 4. More importantly these ratios have eliminated all variables except for one in each case.
Next, a graphical approach will be used to observe the harmonic generation. To demonstrate this method, Equation (6.4) is plugged into Equation (6.1) and evaluated over a range of time. This provides the RS due to a sample temperature alternating at two different frequencies through time. The temperature and emission from this evaluation are plotted in Fig. 6.3.

![Figure 6.3](image)

Fig. 6.3. Temperature and emission vs time for a sample with the superposition of two frequency modulations. The $A(f_1)$ denotes the instantaneous amplitude of the $PTR(f_1)$. The amplitude change of $A(f_1)$ is seen to be periodic at frequency $f_2$. This periodic amplitude change is defined as $PTR(f_{1x2})$.

The distortion due to the nonlinear emission process is easy to see at both frequencies. In the emission plot the peaks of $f_2$ (low frequency) are more pointed and the troughs have flattened out. The instantaneous amplitude of emission at $f_1$ (high frequency) is denoted by $A(f_i)$. The modulation of $A(f_i)$ is easily noted by the difference of $A(f_i)$ at the peaks and troughs of the wave modulating at $f_2$, shown in Fig. 6.3. This modulation of
A\( (f_i) \) is a graphical representation of \( PTR(f_{1x2}) \) discussed earlier. To provide a better understanding of \( PTR(f_{1x2}) \), \( A(f_i) \) has been plotted in Fig. 6.4 for the same data presented in Fig. 6.3. It is easy to see that \( A(f_i) \) oscillates at a frequency of \( f_2 \) around a constant value \( (PTR(f_i)) \). The amplitude of these oscillations is what has been defined as \( PTR(f_{1x2}) \).

![Graphical representation of PTR(f_1x2)](image)

Fig. 6.4. The modulation of \( A(f_i) \) at frequency \( f_2 \). This modulation is defined as the \( PTR(f_{1x2}) \). The horizontal line is representative of \( PTR(f_i) \).

These deviations can be observed differently by taking the Fourier transform of the emission waveform in Fig. 6.3. The power spectrum of the Fourier transform of an emission curve can be seen in Fig. 6.5. For the power spectrum presented in Fig. 6.5 the \( T_{AC1} \) and \( T_{AC2} \) were set to the same value. The frequencies for \( f_i \) and \( f_2 \) were 15 and 1 Hz, respectively. The highest peaks can be seen at frequencies \( f_i \) and \( f_2 \) and secondly the sideband frequencies at \( f_i \pm f_2 \), finally followed by the harmonics \( 2f_i \) and \( 2f_2 \). Previously neglected higher order terms can be seen with this analysis. Specifically, frequencies at \( 3f_i \), \( 3f_2 \), \( f_i \pm 2f_2 \), and \( 2f_1 \pm f_2 \). While there is useful information contained in these 3\(^{rd} \) order terms they are experimentally un-practical to measure since they are approximately 3 orders a
magnitude smaller than the signals at $f_1$ and $f_2$. As discussed previously, the number of significant harmonics generated depends on the nonlinearity of the process. Furthermore, from Fig. 6.2 it was determined that the nonlinearity depends on the sample temperature and spectral properties. Therefore, the temperature and spectral properties will change the number of harmonics in Fourier series as well as their magnitudes.

![Power spectrum of the Fourier transform of the emission due to a modulating temperature with $f_1$ and $f_2$ of 1 and 15 Hz, respectively, and $T_{AC1}$ equivalent to $T_{AC2}$.](image)

Fig. 6.5. Power spectrum of the Fourier transform of the emission due to a modulating temperature with $f_1$ and $f_2$ of 1 and 15 Hz, respectively, and $T_{AC1}$ equivalent to $T_{AC2}$.

Table 6.2 displayed how the ratio of the second to the first order terms eliminates the dependence of one of the $T_{AC}$ values in the temperature modulation. This conclusion was based on ignoring the influence of the higher order terms. This conclusion has been checked by applying the Fourier series, and then taking the ratio of the two peaks in the power spectrum. This ratio was evaluated over a range of $T_{AC1}$ and $T_{AC2}$ values. The results can be seen in Fig. 6.6, and it is clearly visible that $T_{AC1}$ has a negligible impact on this
ratio. Furthermore, it is important to point out that this ratio is linear with respect to $T_{AC2}$, which was also predicted by Table 6.2.

![Graph](image.png)

Fig. 6.6. Ratio of $PTR(f_{IX2})/PTR(f_1)$ vs $T_{AC2}$ for three different values of $T_{AC1}$. It is clear that all three plots lay on top of each other, and therefore that the ratio is independent of the value of $T_{AC1}$.

In Table 6.2, it was predicted that the average sample temperature would scale the relationship between the ratio of $PTR(f_{IX2})/PTR(f_1)$ vs $T_{AC2}$. Similarly, this prediction was made based on neglecting higher order terms. This has been checked through the use of the Fourier series, and the results have been plotted in Fig. 6.7. It is clear that temperature dependence on $T_{AC2}$ remains linear for different values of $T_{DC}$ and the value of $T_{DC}$ changes the slope of the lines, thereby confirming the prediction.
Fig. 6.7. Ratio of \( \text{PTR}(f_{1X2})/\text{PTR}(f_1) \) vs \( T_{AC2} \) for three different values of \( T_{DC} \). These confirm the predictions of Table 6.2 that the slope would be altered by the value of \( T_{DC} \), and that the ratio would still be linear with respect to \( T_{AC2} \).

Some important conclusions can be made concerning NL-PTR from the results in this chapter. They include:

- The nonlinear emission process generates harmonics in the emitted radiation when the surface temperature is modulated.
- These harmonics are governed by the nonlinearity of the emission process, and the amplitude of the temperature modulation.
- The nonlinearity is influenced by the sample temperature and the spectral properties.
- The ratio, \( \text{PTR}(f_{1X2})/\text{PTR}(f_1) \) is only dependent on \( T_{DC}, T_{AC2} \), and the spectral properties (and not on emissivity or the magnitude of \( T_{AC1} \)).
CHAPTER 7

RELATIVE TEMPERATURE MEASUREMENT

In the Chapter 6 the governing principles of the RS and the source of the nonlinearity was discussed at length. Chapters 7-9 will develop specific applications of this nonlinearity, and provide experimental results for each application.

7.1. PTR Signal

The PTR signal, as previously defined, is the periodic component of the RS at a given frequency. If the sample temperature is modulating at a given frequency the RS likewise has a periodic component. Since the RS is non-linearly dependent on the sample temperature, the magnitude of the periodic component of the RS is dependent on the sample temperature. Fig. 7.1 shows the variation in the PTR signal at two different $T_{DC}$ temperatures for the same magnitude of $T_{AC}$. It is clear this is due to the different slopes of the RS at each temperature. Recall from Chapter 6 that the RS is calculated by

$$RS(T) = G_A F_D - S \int_{0.6 \mu m}^{0.6 \mu m} \varepsilon(\lambda, T) E_\lambda(\lambda, T) R(\lambda) \tau(\lambda) d\lambda + V_{bias}(T_{BG}). \quad (7.1)$$

Therefore, the PTR signal can easily be approximated by the derivative of the RS with respect to temperature multiplied by the AC temperature amplitude, assuming emissivity is independent of temperature. Mathematically this approximation is given by

$$PTR(T) \approx T_{AC} \frac{\partial}{\partial T}(RS(T)) = T_{AC} G_A F_D - S \int_{0.6 \mu m}^{0.6 \mu m} \varepsilon(\lambda) \frac{\partial \varepsilon}{\partial T}(\lambda, T) R(\lambda) \tau(\lambda) d\lambda. \quad (7.2)$$

which can be found by using the Taylor series approximation. If gray properties are assumed for emissivity and transmissivity Equation (7.2) can be simplified to
where $K$ is a constant determined by the product of the terms outside the integral as well as transmissivity and emissivity.

\[
PTR(T) = K \int_{0\mu m}^{\infty} \frac{\partial E}{\partial T}(\lambda, T)R(\lambda) d\lambda
\]  

(7.3)

Fig. 7.1. RS vs sample temperature. The RS given by product of Planck’s Law and the detectivity integrated over all wavelengths at each temperature. The y-axis scale is arbitrary since this curve is multiplied by the constant $K$ which depends on electrical, optical, and thermal properties of the sample and system. The vertical sine waves have identical amplitudes which correspond to different amplitudes for the horizontal sine waves.

By using these assumptions, the PTR signal can be calculated over a range of temperatures, and the results can be seen in Fig. 7.2. It is determined from Equation (7.2) that if the spectral properties are known or can be assumed, the PTR signal can be easily predicted over a range of temperatures. Therefore, only one unknown multiplicative parameter remains which contains view-factors, detector area, emissivity, transmissivity, and $T_{AC}$. In Equation (7.3) all of these terms are grouped into the coefficient $K$. This multiplicative factor will be known as the calibration coefficient. It should be noted that if
the calibration coefficient is determined, then the PTR signal is known for all temperatures. Using that knowledge the PTR signal can then be used to determine the sample temperature. The calibration coefficient is easily determined by measuring the PTR signal and sample temperature simultaneously, and then comparing it to the calculated PTR signal. The ratio of the measured and calculated signals provides the calibration coefficient. Probably the most useful application is to monitor the sample heating due to the laser. For this measurement the initial temperature is known since it is generally at room temperature and used to determine the calibration coefficient. Then PTR signal is monitored as the sample is heated to determine the temperature over time.

Fig. 7.2. PTR Signal vs temperature.

7.2. Experimental Configuration

To test this temperature monitoring technique, a temperature controlled sample is needed. Specifically, $T_{DC}$ needs to be varied and measured independently from the NL-PTR method. That way the temperature measurements can be confirmed. To achieve this,
an aluminum block was used with a resistive heater and thermocouple. Aluminum’s high thermal conductivity ensures the temperature gradients inside the sample are small, and therefore it can be considered isothermal. The thermocouple, which is recessed from the surface, provides a good estimation for the surface temperature because of the small temperature gradients. A small hole was drilled to insert the thermocouple into, and thermal grease was used to ensure good thermal contact with the aluminum block. A diagram of this configuration can be seen in Fig. 7.3.

Fig. 7.3. Diagram of experimental configuration for the relative temperature measurement using nonlinear photothermal radiometry (approximately 5mm x 5mm x 15mm).

Using the sample configuration described in Fig. 7.3 the PTR signal was measured over a range of temperatures. The aluminum block sample from Fig. 7.3 was measured three times. The first measurement was conducted with a bare aluminum surface, the second partially blackened with graphite from a pencil, and the third completely blackened with carbon soot from a flame. Since each of these surfaces has a different emissivity, each scenario will have a different calibration coefficient between the data observed and the curve presented in Fig. 7.2. This calibration coefficient was determined for each data set by the first data point. After obtaining each calibration coefficient the data sets were
normalized by this factor such that they match the theory curve. It can be seen in Fig. 7.4 that this normalized data follows the theoretical prediction quite well.

![Normalized PTR Signal vs Temperature](image)

Fig. 7.4. PTR signal over a range of temperatures for different surface treatments. These three surface treatments provide different values of emissivity to test the technique under different conditions.

### 7.3. Transient Heating Temperature Monitoring

Because this technique requires the PTR signal to be measured at a known temperature, it is not ideal for temperature measurements where a calibration cannot be performed. However, it excels at monitoring a sample's temperature as it changes from a known value. For an example of this application the Aluminum block with resistive heater described in Fig. 7.3 will be used. The PTR signal and thermocouple measurements are taken while the block is under ambient conditions with the heater off, while the heater is turned on, and while the block cools. The normalization constant for the temperature curve is taken during the ambient conditions.
Using the measured PTR amplitude and the calibration coefficient, the temperature can be determined at any given time. The results from monitoring the heating and cooling of the aluminum block can be seen in Fig. 7.5. There is good agreement between the temperature measured using the NL-PTR signal and the temperature measured using the embedded thermocouple. It should be noted from Fig. 7.3 that the thermocouple is located between heater and the sample surface being observed by the detector. Therefore, there is a thermal gradient from the heater to the sample surface. This fact shows clearly in the data towards the end of the heating period where the thermocouple is measuring at a higher temperature than the PTR signal.

![Graph showing temperature vs time for PTR and thermocouple measurements.](image)

Fig. 7.5. Measured sample temperature vs time for both PTR measured temperature and thermocouple. The transient heating is due to the DC heating of the laser.

This clearly shows the ability of this technique to accurately monitor sample temperature under transient or steady state conditions. However, there are some limitations to this technique. Specifically, the assumption or required knowledge on the spectral emissivity. This may seem like a significant limitation, but since the detector is only
sensitive between 2-13 µm, the emissivity assumptions or knowledge is only required in this range. If there is a sample which the emissivity varies spectrally over this range, an IR filter could be used to limit the spectral range measured. This would result in a new curve for the PTR signal vs temperature, which would replace the one in Fig. 7.2. This largely solves the problems associated with changes in emissivity with respect to wavelength. However, there are no easy methods to accommodate changes in emissivity with respect to temperature. Large emissivity changes with respect to changes in temperature could significantly reduce the accuracy of this method. An example of this would be if the surface of a sample oxidizes and significantly changes the emissivity. Another limitation of this technique is the assumption that the $T_{AC}$ remains constant over the measurement. This is a good assumption given the thermal properties and absorption at the wavelength of the laser do not change during the measurement. This could provide measurement difficulties on materials with thermal properties that exhibit a strong temperature dependency. However, the temperature measurement could be corrected if knowledge of the temperature dependent thermal properties is known or measured.
CHAPTER 8
DIRECT THERMAL EFFUSIVITY MEASUREMENT

In this chapter a noncontact, thermal effusivity measurement of a homogenous, non-layered sample will be developed. This technique is based on the ability to measure the periodic component of a sample’s surface temperature. This technique will require an approximation of the average surface temperature and the absorbed flux from the heating laser. Thermal effusivity coupled with either heat capacity or thermal diffusivity allows for the determination of thermal conductivity.

Laser flash is often used for a non-contact determination of thermal diffusivity. This is often then coupled with heat capacity to determine thermal conductivity. A precise measurement of sample thickness is required for the laser flash technique, and any error in this thickness measure has a significant impact on the measured thermal diffusivity. Laser flash samples also have to be thin enough that the heat from the flash can propagate through the sample and still have a detectable amplitude by the time it reaches the other side.

This technique directly measures thermal effusivity, which coupled with heat capacity can also determine thermal conductivity. However, this technique has a significant benefit over laser flash, in that it does not require any measurement of thickness and can be performed on thermally thick samples.

8.1. Method for Direct Thermal Effusivity Measurement

Using the heat transfer theory shown in section 3.4.1, a new measurement method for performing a non-contact measurement of thermal effusivity will be developed. This
measurement technique uses a similar strategy to other photothermal effusivity measurements developed by Bicanic et al. [8] and Chirtoc et al [69]. It utilizes the amplitude of the periodic photothermal signal on what can be considered a semi-infinite medium. As was shown in Equation (3.22) and reproduced here

\[ T_{\text{AC}} = \frac{q''}{2(1-\rho_r)} e^{\sqrt{2\pi f}}. \]  

(8.1)

Thermal effusivity is the only thermal parameter that effects the amplitude of the periodic modulation under the semi-infinite conditions.

It should be noted, the accuracy of the semi-infinite sample assumption is dependent on the modulation frequency \( f \). Specifically, it is dependent on the thermal diffusion length, which was discussed in Section 3.4. The magnitude of temperature oscillations decays exponentially through the sample inversely proportional to the thermal diffusion length. Therefore, for practical purposes if the sample thickness is 3 times thicker than the thermal diffusion length then it can be treated as semi-infinite. Furthermore, since the thermal diffusion length is frequency dependent the measurement can be conducted at a higher frequency in order to decrease the thermal diffusion length.

From Equation (8.1) it is clear that if \( T_{\text{AC}} \) and the absorbed flux is known, that thermal effusivity can be solved for directly by

\[ e = \frac{q''(1-\rho_r)}{T_{\text{AC}}\sqrt{2\pi f}}. \]  

(8.2)

The absorbed radiation can easily be measured through the use of laser and a power meter on a polished sample, and can also be measured on diffuse sample with the use of an
integrating sphere. Therefore, the key to this measurement technique is the measurement of the periodic amplitude of the temperature modulation.

8.2. Determining $T_{AC}$ Using Harmonic Generation by NL-PTR

In order to measure $T_{AC}$ for the use of thermal effusivity measurements, a two-frequency heat flux boundary condition will be used, described by

$$q''(t) = \frac{q_1''}{2}(1 + \cos(f_1)) + \frac{q_2''}{2}(1 + \cos(f_2))$$

where $q_1''$ and $q_2''$ are the heat flux at frequencies $f_1$ and $f_2$. Since the heat conduction differential equation is linear, we can superimpose the solution that was provided in Equation (8.1). Therefore, the solutions from each of the flux conditions alone can be additively combined to yield the solution

$$T(t) = T_{AC1} \cos(2\pi f_1 t) + T_{AC2} \cos(2\pi f_2 t) + T_{DC},$$

where $T_{AC1}$ and $T_{AC2}$ are defined by

$$T_{ACi} = \frac{q''/2(1-\rho r)}{e^{\sqrt{2}\pi f_i}}.$$  

It should be noted that Equation (6.4) and Equation (8.4) are identical, and therefore the development of the NL-PTR theory for harmonic generation in Section 6.2 can be utilized. Specifically, the ratio $PTR(f_1x2)/PTR(f_1)$ will be used to measure the value of $T_{AC2}$. It was shown in Section 6.2 that this ratio is only dependent on $T_{AC2}$, $T_{DC}$, and spectral properties. Therefore, given that $T_{DC}$ and the spectral properties are known or can be measured, $T_{AC2}$ can be determined by the $PTR(f_1x2)/PTR(f_1)$ ratio. It is not possible to solve for the $T_{AC2}$
directly, but it can be solved numerically by setting the calculated PTR ratio equal to the measured PTR ratio given by

\[
\frac{\text{PTR}_c(\omega_1 \times 2)}{\text{PTR}_c(\omega_1)} = \frac{\text{PTR}_m(\omega_1 \times 2)}{\text{PTR}_m(\omega_1)} \tag{8.6}
\]

where the subscripts m and c on PTR denote the measured and calculated PTR signals, respectively. The method described in Chapter 6 using the Fourier series is used to calculate the PTR signals at each frequency. This allows for \(T_{AC2}\) to be solved regardless of the value of the nonlinearity coefficient \(B\). Recall that in these calculations the temperature is given by Equation (8.4), and that the ratio is independent of \(T_{AC1}\). Therefore, a numerical root finding method can be applied to Equation (8.6) to solve for the value of \(T_{AC2}\). In this calculation, it is assumed that the spectral properties and \(T_{DC}\) are known. It should also be noted from Table 6.2, that this ratio is monotonic with respect to the value \(T_{AC2}\), and therefore the solution is unique when the measured ratio is equal to the calculated ratio.

### 8.3. Experimental Considerations

In Sections 8.1 and 8.2, an explanation of the technique for direct thermal effusivity measurement has been provided. It is based on measuring the amplitude of the periodic temperature due to a known periodic heat flux. The periodic temperature is measured by comparing the amplitude at different harmonics due to the nonlinearity of the PTR signal. This section discusses the experimental configuration, specific consideration needed for the measurement, provides guidelines for measurement parameters, and some alternative approaches.
In this measurement, there are several practical considerations that will be discussed in this section. They include the measurement of the absorbed radiation and the experimental configuration for measuring the periodic temperature component.

8.3.1. Satisfying One Dimensional Assumption

In the heat transfer solution provided in Equation (8.5), one dimensional heat transfer was assumed. To obtain this condition homogenizing optics should be used to provide a uniform flux distribution across the sample. These homogenizing optics effectively spread out the laser light into a uniform distribution for a defined angle. This allows for the use of a laser with a non-uniform distribution to be used in the measurement process. A diagram showing how the homogenization is obtained can be seen in Fig. 8.1.

![Diagram](image)

**Fig. 8.1.** Homogenizing optics with microlens (beam shaping diffuser) are used to evenly distribute the flux from a laser to create one dimensional heat transfer conditions.
8.3.2. *Incoming Flux*

The absorbed radiation flux on the sample surface is required for the thermal effusivity measurement. The strategy used in this work to obtain the absorbed radiation flux is to measure the incoming flux, and then measure the percentage of the light that is reflected. To obtain the surface flux both the power and the area being illuminated needs to be known. The optical power from the laser should be measured after the diffuser at the optical plane of the sample surface. The flux needs to be measured in the sample plane since the uniform spot is expanding after the diffuser. There are many ways to perform this measurement. In this work a mask was used which has a hole with a known area. This mask only allows light to pass through the hole, and it is placed in the optical plane of the sample, concentric with the viewing area of the detector. Then the light passing through this mask can easily be measured with an optical power meter. Dividing the measured power by the area of the hole in the mask provides the incoming flux.

8.3.3. *Absorption*

The second requirement of determining the absorbed radiation flux is to know what percentage of the incoming flux is reflected or absorbed. Experimentally it is easier to measure the reflection, and thereby calculate the absorption assuming no transmission. There are several techniques that can be used to determine the reflectivity and the appropriate one will depend on the sample material and surface treatment. The following subsections will describe some of the options.
8.3.3.1. Highly Absorptive

In the case of a highly absorptive material (>98% absorption at the laser wavelength) the reflectivity is not as critical since most of the light will be absorbed. An uncertainty on absorption of 1-2% at near unity values of absorptivity cause uncertainties in effusivity at approximately the same range of 1-2%. However, 1-2% uncertainty in absorptivity is much more significant when the value of absorptivity is, say, 5-10%. That would cause uncertainties in thermal effusivity of 20%. Therefore, much more care needs to be taken on highly reflective samples as compared to highly absorptive samples. On highly absorptive materials, often literature values are sufficient since the uncertainty in the other measured parameters can be much greater than the uncertainty on the literature value. However, if a measurement is required, depending on the type of sample the appropriate measurement technique should be chosen out of the following subsections.

8.3.3.2. Reflective and Specular

The most common example of a specular reflecting sample would be a polished metal. A specular reflection is when the incoming light reflects away from the sample with the same angle of incidence when it contacted the sample in a single direction. Meaning that little to no light was scattered in different directions. This scenario makes the measurement of absorptivity rather straightforward. Since the reflected laser beam still behaves like a laser, then the power of the reflected light can be easily measured using a power meter. Therefore, if the laser’s power is measured before the sample and the power of the reflected light is measured, then the difference is the absorbed light.
8.3.3.3. Reflective and Diffuse

A diffusely reflecting sample is the most complicated sample to measure the absorptivity. However, much research has been conducted to develop standard methods to accurately measure these optical properties. The predominant technique uses a device known as an integrating sphere. An integrating sphere consists of a hollow sphere with several ports that allow access to the inside of the sphere. The inside surface of the sphere is coated with a highly reflecting diffuse material. Three of the ports will be used on the integrating sphere for the laser, sample, and detector. The laser is aimed through its port directed at the sample which is locating at a different port. The reflection off the sample, diffuse or specular, will be diffusely scattered through multiple diffuse reflections on the inside of the sphere. Therefore, regardless of the specularity of the sample’s reflection, the light gets evenly distributed throughout the sphere. A detector which is located on a third port measures the portion of the light that exits through that port. These spheres can easily be calibrated to determine the reflectivity of a sample through the use of materials with known reflectivity.

8.3.4. Alternating Temperature Measurement

To this point, there has been no limitation placed on the frequencies $f_1$ and $f_2$ other than they need to be high enough to ensure the sample appears to be semi-infinite based on the criteria in Section 3.4. The choice of the values for $f_1$ and $f_2$ has little effect on the analysis of the data, but there are practical consequences based on the choice and it should
not be arbitrary. Furthermore, the choice of which of the 2\textsuperscript{nd} order frequency should be measured will also be discussed.

8.3.4.1. Experimental Configurations

The experimental configuration is largely influenced by which 2\textsuperscript{nd} order frequency is measured in the determination of $T_{AC2}$. The consideration of which 2\textsuperscript{nd} order frequency should be measured will begin with a discussion about the harmonic terms. Often the processes involved in modulating a laser (AOM/EOM) is a nonlinear process which will cause the flux boundary condition to have components at both $f$ and $2f$. Meaning that the laser modulation is not a perfect sine wave, but will have a component at $2f$. This will generate thermal responses at both $f$ and $2f$ which will be superimposed on each other. The emission due to the temperature response from the heating at $2f$ will have a first order component at $2f$. The emission due to the temperature response at $f$ will have a 2\textsuperscript{nd} order response at $2f$. In a measurement of the emission, these two signals will be indistinguishable from each other. Furthermore, the $2f$ frequency has the smallest coefficient out of the 2\textsuperscript{nd} order terms, and therefore has the lowest signal to noise ratio. For these reasons measuring the signal at $2f$ has been deemed less desirable.

If the two lasers are modulated independent of each other the generation of the 2\textsuperscript{nd} order terms at $f_1 \pm f_2$ and the $f_1 X_2$ can only be generated from the nonlinear emission process. Therefore, they do not suffer from the shortcomings of the $2f$ signal. From Table 6.2, $f_1 \pm f_2$ and $f_1 X_2$ are expected to have signals higher than $2f_1$ by factors of 2 and 4, respectively.
Experimentally there are differences in the configuration to be used for measuring $PTR(f_1 \pm f_2)$ and $PTR(f_1 \times 2)$.

Lock-in amplifiers are commonly used in PTR systems to measure the periodic signal at the excitation frequency. In the case of measuring the $PTR(f_1 \pm f_2)/PTR(f_1)$ the detector signal can be measured directly by the use of two lock-in amplifiers each set at a reference frequency of $f_1$ and $f_1 \pm f_2$, respectively. Since the signal from the detector is measured simultaneously by both lock-in amplifiers this configuration has been called the parallel lock-in configuration, and can be seen in Fig. 8.2.

![Diagram of the parallel lock-in configuration for nonlinear photothermal radiometry setup. This configuration uses two lock-in amplifiers that simultaneously measure the PTR signals at $f_1$ and $f_1 \pm f_2$.](image)

Fig. 8.2. Diagram of the parallel lock-in configuration for nonlinear photothermal radiometry setup. This configuration uses two lock-in amplifiers that simultaneously measure the PTR signals at $f_1$ and $f_1 \pm f_2$. 
The measurement of the $\frac{PTR(f_1 \times 2)}{PTR(f_1)}$ ratio requires different configuration since $PTR(f_1 \times 2)$ is the modulation of amplitude of the signal at $f_1$ at frequency $f_2$. To measure this quantity with two lock-in amplifiers, the first is used to measure the amplitude at $f_1$. This amplitude will be modulating at frequency $f_2$ around a constant value, similar to Fig. 6.4. The amplitude from this lock-in amplifier #1 will then be the input for lock-in amplifier #2. The reference on lock-in amplifier #2 is set at frequency $f_2$. Therefore, lock-in amplifier #2 will measure only the modulating component of the output of lock-in amplifier #1. Since the output of lock-in #1 is fed into lock-in #2 this configuration is named the series lock-in amplifier configuration and can be seen in Fig. 8.3. In order for lock-in amplifier #1 to not filter the amplitude modulation of $f_1$ the time constant should be set to a value less than $1/(50f_2)$. This requirement will be discussed in more detail in Section 8.3.4.2.
88

Fig. 8.3. Diagram of the series lock-in configuration for nonlinear photothermal radiometry setup used to measure the amplitude of the periodic temperature modulation. Lock-in amplifier #1 is used to measure the instantaneous amplitude of the PTR signal at frequency $f_1$. The output is then the input for lock-in amplifier #2 which measures the modulation of the amplitude at frequency $f_2$. The time constant on lock-in amplifier #1 needs to be short enough to not filter the modulation at $f_2$. A detailed discussion on the time constant requirements is provided in Section 8.3.4.2.

There are two configurations that have the ability to measure the $PTR(f_1X2)/PTR(f_1)$ quantity. The first utilizes two lock-in amplifiers as described in Fig. 8.3. The second accomplishes the same measurement with only one lock-in amplifier. In the second configuration the lock-in amplifier reference frequency is set to $f_1$ and a second reference signal from the $f_2$ modulation is provided to the auxiliary input. The ratio of the measured signal to the auxiliary input is then used. By turning on this ratio operation in this configuration it effectively operates as a second lock-in amplifier. For this method to work
the ratio operation with the auxiliary input must occur before the low pass filters in the lock-in amplifier. Since this configuration effectively acts as two lock-in amplifiers it will be referred to as the double demodulation configuration, and can be seen in Fig. 8.4. Not all lock-in amplifiers are configured in this manner, and this technique was not used in this research, but it has been included here because of its potential elegance and reduction of equipment. The double demodulation configuration is described well in the manual for the SR844 lock-in amplifier [68].

Fig. 8.4. The double demodulation configuration for measuring the $\frac{PTR(f_1 \times 2)}{PTR(f_1)}$ ratio. This configuration eliminates the need for a second lock-in amplifier. Not all lock-in amplifiers are capable of this operation. For this configuration to work, the ratio operation needs to be performed before the low pass filters in the lock-in amplifier.
8.3.4.2. Choice of Frequencies

The choice of frequencies $f_1$ and $f_2$ should be made carefully, because it imposes requirements on the measurement equipment. For example, in Section 3.8 it was concluded that for an accurate measurement using a lock-in amplifier that a time constant $> 1/f$ is required. In addition, the lock-in bandwidth only passes frequencies within $1/(2\pi \tau)$ of $f$. It was shown in Chapter 6 that $f_{i2}$ consists of two signals at frequencies $f_1 - f_2$ and $f_1 + f_2$. Therefore, if it is desired to measure $f_{i2}$ by the series lock-in configuration, then the measurement bandwidth of the first lock-in amplifier needs to include the signals at $f_1 - f_2$ and $f_1 + f_2$. Therefore it can be written that

$$\Delta f = \frac{1}{2\pi \tau_1} > f_2 \quad (8.7)$$

where $\Delta f$ is the bandwidth of the lock-in amplifier band-pass filter. If the time constant is too long, the band-pass filter will be too narrow, and therefore attenuate the signals at $f_1 \pm f_2$, leading to erroneous measurement by lock-in amplifier #2. This inequality presented in Equation (8.7) corresponds to the -3dB attenuation, and therefore the measurement should not be conducted with this inequality is close to being equal. If possible, it is recommended that this equation be satisfied for a value of $2f_2$ to ensure minimal attenuation of the signal.

8.4. Experimental Results

A broad range of materials have been measured using this new direct thermal effusivity measurement technique. These materials include rubber, glassy carbon, aluminum, and 1020 steel. The thermal effusivities of these materials range over three orders of magnitude. In these measurements, the series lock-in configuration was used to
measure the $\text{PTR}(f_{1}x_{2})/\text{PTR}(f_{1})$ ratio. The periodic flux was reduced for the materials with lower thermal effusivity to reduce unnecessary heating of the sample. The steel and aluminum samples were coated with approximately 125 nm of carbon through a carbon evaporation process. They were coated to increase the absorption of the laser. This coating method was chosen because it produces a small layer of carbon in good thermal contact with the sample. The layer thickness is small enough to be considered thermally thin and not have a significant impact on the heat transfer solution.

As discussed in the previous sections, the $\text{PTR}(f_{1}x_{2})/\text{PTR}(f_{1})$ is dependent on $T_{DC}$, $T_{AC}$, and the spectral properties. The spectral properties of the detector and the transmission are known. For the materials used, it has been assumed the emissivity can be considered gray over the sensitive spectral range of the detector. The measurements were conducted in ambient room temperature conditions, but because of the laser heating the sample temperatures were elevated. In the case for steel and aluminum, a small hole was drill and a thermocouple was inserted for the temperature measurement of $T_{DC}$. Both of these samples have a high thermal conductivity and therefore small thermal gradients through the sample. This allows the thermal couples to measure the surface temperature accurately. For the glassy carbon and rubber samples, this is not a feasible solution. Therefore, the relative temperature measurement process developed in Chapter 7 was used to obtain the sample temperature. This has proven to be an excellent application example of the relative temperature measurement, because it eliminated the need for a contact temperature measurement and did not require additional equipment for the temperature measurement. Furthermore, the temperature measurement is conducted on the surface of interest.
The measurement of thermal effusivity can be considered a two-step process. The first includes measuring the $\frac{PTR(f_1x_2)}{PTR(f_1)}$ ratio and numerically solving for the $T_{AC2}$ that corresponds to this ratio. The second part uses $T_{AC2}$ along with the other measured values in Equation (8.2) to determine thermal effusivity. During the measurement, 30 samples were taken for $PTR(f_1)$ and $PTR(f_1x_2)$. These sets of samples were taken to provide a better estimation of the ratio, and an estimation of the uncertainty of the ratio. The ratio uncertainty was calculated using the Taylor Series uncertainty propagation technique as defined by

$$\mathcal{R}_u = \sqrt{\left(\frac{\partial \mathcal{R}}{\partial PTR(f_1)}\right)^2 S_{PTR(f_1)}^2 + \left(\frac{\partial \mathcal{R}}{\partial PTR(f_1x_2)}\right)^2 S_{PTR(f_1x_2)}^2}$$

(8.8)

where $S$ is the standard deviation of the mean and $\mathcal{R}$ represents the $PTR(f_1x_2)/PTR(f_1)$ ratio [70]. Substituting the derivatives yields the formula for the uncertainty of the PTR ratio

$$\mathcal{R}_u = \sqrt{\left(\frac{PTR(f_1x_2)}{PTR(f_1)}\right)^2 S_{PTR(f_1)}^2 + \left(\frac{1}{PTR(f_1)}\right)^2 S_{PTR(f_1x_2)}^2}.$$  

(8.9)

The mean values obtained for the ratio are then used to numerically calculate $T_{AC}$. A 95% confidence interval for the ratio is then obtained by adding and subtracting $2\mathcal{R}_u$. These values are then used to obtain the 95% confidence interval of $T_{AC}$. The measured and calculated values can be seen in .
Using the values in, thermal effusivity can now be directly calculated. Likewise with the ratio uncertainty, the Taylor Series uncertainty approximation technique will be used to estimate the uncertainty on thermal effusivity and can be seen as

\[
e_u = \sqrt{\left(\frac{\partial e}{\partial \rho_r}\right)^2 S_{\rho_r}^2 + \left(\frac{\partial e}{\partial T_{AC}}\right)^2 S_{T_{AC}}^2 + \left(\frac{\partial e}{\partial q''}\right)^2 S_{q''}^2 + \left(\frac{\partial e}{\partial f}\right)^2 S_f^2}.
\]  

(8.10)

Frequency is known and controlled very accurately by electronic devices, and therefore the uncertainty is considered to be negligible. Likewise the heat flux is measured very accurately so the uncertainty is negligible compared to the other parameters. Therefore, Equation (8.10) can be simplified to

\[
e_u = \sqrt{\left(\frac{\partial e}{\partial \rho_r}\right)^2 S_{\rho_r}^2 + \left(\frac{\partial e}{\partial T_{AC}}\right)^2 S_{T_{AC}}^2}.
\]  

(8.11)

Substituting the derivatives into Equation (8.11) yields

\[
e_u = \sqrt{\left(\frac{q''}{2T_{AC}\sqrt{2\pi f}}\right)^2 S_{\rho_r}^2 + \left(\frac{q''(1-\rho_r)}{2T_{AC}\sqrt{2\pi f}}\right)^2 S_{T_{AC}}^2}.
\]  

(8.12)

Table 8.1. Experimentally measured absorptivity, heat flux, \(T_{DC}, P_{TR(f_1X2)}/P_{TR(f_1)}\) ratio, and the ratio 95% confidence interval uncertainty. Using the measured ratio, \(T_{AC}\) is calculated for the mean ratio, and the end points of the 95% confidence interval. These results are presented for Rubber, Glassy Carbon, and coated Steel, and Aluminum.

<table>
<thead>
<tr>
<th>Material</th>
<th>Absorption (%)</th>
<th>Flux (W/m²)</th>
<th>(T_{DC}) (K)</th>
<th>(\mathcal{R})</th>
<th>(\mathcal{R}_{u, 95}%)</th>
<th>(T_{AC}) (K)</th>
<th>(T_{AC} 95%) interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubber</td>
<td>99.</td>
<td>4464</td>
<td>315.</td>
<td>0.01730</td>
<td>3.613\times10^{-4}</td>
<td>1.427</td>
<td>1.397 - 1.457</td>
</tr>
<tr>
<td>Glassy Carbon</td>
<td>99.</td>
<td>10540</td>
<td>310.</td>
<td>0.00991</td>
<td>3.133\times10^{-4}</td>
<td>0.7928</td>
<td>0.767 - 0.818</td>
</tr>
<tr>
<td>Steel</td>
<td>77.4</td>
<td>23287</td>
<td>334.</td>
<td>0.00244</td>
<td>1.147\times10^{-4}</td>
<td>0.2251</td>
<td>0.214 - 0.236</td>
</tr>
<tr>
<td>Aluminum</td>
<td>90.7</td>
<td>23287</td>
<td>338.</td>
<td>0.00209</td>
<td>1.681\times10^{-4}</td>
<td>0.1973</td>
<td>0.181 - 0.213</td>
</tr>
</tbody>
</table>
The uncertainty on $T_{AC}$ is determined from the calculations presented in . Based on measurements for the reflectance of the samples, an uncertainty of approximately 3% has been determined to be appropriate. This is based on the repeatability and range of values found for each sample. Using the values in and these uncertainty equations, the thermal effusivity has been calculated along with its uncertainty. These values are reported in Table 8.2 along with values from literature. The error between the literature values and the measured are also reported.

Table 8.2. Summary of the thermal effusivity literature and measured values of rubber, glassy carbon, steel, and aluminum. The corresponding uncertainty values on the measurement are provided along with the error from the literature value.

<table>
<thead>
<tr>
<th>Material</th>
<th>Literature (W·s^{0.5}·m^{-2}·K^{-1})</th>
<th>Measured (W·s^{0.5}·m^{-2}·K^{-1})</th>
<th>Uncertainty (W·s^{0.5}·m^{-2}·K^{-1}) / %</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubber</td>
<td>600</td>
<td>617</td>
<td>22.9 / 3.8</td>
<td>2.9</td>
</tr>
<tr>
<td>Glassy Carbon</td>
<td>2700</td>
<td>2625</td>
<td>114 / 4.3</td>
<td>-2.8</td>
</tr>
<tr>
<td>Steel 1020</td>
<td>16040</td>
<td>15977</td>
<td>970 / 6.0</td>
<td>-0.4</td>
</tr>
<tr>
<td>Aluminum</td>
<td>23688</td>
<td>21372</td>
<td>1855 / 7.8</td>
<td>-9.8</td>
</tr>
</tbody>
</table>
Chapter 9

Absolute Temperature Measurement

Pyrometry remains an active field of research, and has been for many years. Depending on the sample, various techniques can be used, but often significant limitations are applied. In this chapter a new pyrometry technique will be developed that can measure temperature without any knowledge of emissivity. This technique uses the same harmonic generation measurement technique that was described in Chapter 8.

9.1. Theoretical Development

This technique will use the same two frequency temperature modulation that was used in Chapter 8, and originally described in Chapter 6. Specifically, this temperature modulation is described by

\[
T(t) = T_{DC} + T_{AC1} \cos(\omega_1 t) + T_{AC2} \cos(\omega_2 t). \tag{9.1}
\]

Furthermore, this technique will use the PTR signals at \(f_{1x2}\) and \(f_1\) which were defined and explained thoroughly in Chapter 6. Later they were used in the direct effusivity measurement conducted in Chapter 8. These chapters should be consulted for the explanation and definition of these terms.

The theoretical development of this technique will begin with a discussion of some observations from the results in Chapter 6 and 8. From Chapter 6 it was shown the PTR ratio

\[
\mathcal{R} = \frac{PTR(f_{1x2})}{PTR(f_1)}. \tag{9.2}
\]
is a function of $T_{AC}$, $T_{DC}$, and the spectral properties. The spectral properties will be denoted as $\lambda_{prop}$ which includes sample emissivity, transmissivity and detector responsivity. It was shown $T_{DC}$ and $\lambda_{prop}$ influence this ratio, because they determine the nonlinear temperature dependence of the emission. In chapter 6, this nonlinear temperature dependence was denoted as $B$. Therefore it could be written

$$\mathcal{R} = f \left( T_{AC}^2, B(T_{DC}, \lambda_{prop}) \right),$$

meaning that the $\mathcal{R}$ is a function of two parameters, $T_{AC}$ and $B$. Where $B$ is a function of $T_{DC}$ and $\lambda_{prop}$. Recall from Table 6.2, that each row corresponds to a different value for $B$. In Table 6.2, regardless of the row, the ratio $\mathcal{R}$ contains the same $T_{AC2}/T_{DC}=c$ factor. Therefore, this factor is independent of the nonlinearity coefficient, $B$, and it can be factored out. Factoring out $T_{AC2}/T_{DC}$, Equation (9.3) can be rewritten as

$$\mathcal{R} = \frac{T_{AC2}}{T_{DC}} \tilde{f} \left( B(T_{DC}, \lambda_{prop}) \right)$$

(9.4)

where $\tilde{f}$ is now a function of a single variable $B$, which is determined by $T_{DC}$ and $\lambda_{prop}$. By inspection of Table 6.2, $\tilde{f}$ can be determined to be

$$\tilde{f} = B(T_{DC}, \lambda_{prop}) - 1$$

(9.5)

for the PTR($f_{i\rightarrow2}$)/PTR($f_i$) case, where $B$ still remains a function of the temperature and the spectral properties. This function assumes the higher order terms dropped in Table 6.2 are negligible. In the analysis, this assumption is not used, but Equation (9.5) will be used in the results section in an explanatory role.
In this technique two optical filters are used to provide two different spectral property conditions. These two sets of spectral properties will be noted \( \lambda_{\text{prop}1} \) and \( \lambda_{\text{prop}2} \). A form of Equation (9.4) exists for each of these spectral conditions and can be written as

\[
\mathcal{R}_1 = \frac{T_{AC2}}{T_{DC}} \tilde{f}(B(T_{DC}, \lambda_{\text{prop}1})) \tag{9.6}
\]

and

\[
\mathcal{R}_2 = \frac{T_{AC2}}{T_{DC}} \tilde{f}(B(T_{DC}, \lambda_{\text{prop}2})) \tag{9.7}
\]

respectively. The subscripts on the ratio correspond to the two spectral property scenarios. Finally, a new parameter \( \Gamma \), will be defined as the ratio of \( \mathcal{R}_1 \) and \( \mathcal{R}_2 \) such as

\[
\Gamma = \frac{\mathcal{R}_1}{\mathcal{R}_2} = \frac{f(B(T_{DC}, \lambda_{\text{prop}1}))}{f(B(T_{DC}, \lambda_{\text{prop}2}))}. \tag{9.8}
\]

It is clear this new ratio \( \Gamma \) is only dependent on \( T_{DC} \) and \( \lambda_{\text{prop}1} \) and \( \lambda_{\text{prop}2} \). Therefore, \( T_{DC} \) can be determined if the ratio \( \Gamma \) is experimentally measured and the spectral properties of \( \lambda_{\text{prop}1} \) and \( \lambda_{\text{prop}2} \) are known. So far it has been assumed that the spectral properties for emissivity, detector responsivity, and transmissivity are known. Detector responsivity and the filter transmissivity are generally well known. Equation (9.8) can be used if the emissivity variation through wavelength is known or can be assumed gray over the wavelengths sensitive by the detector and within the filter transmission. If the optical filters are wide band-pass filter then the gray assumption on emissivity or specific knowledge of its variation with wavelength is required. If the sample does not satisfy the gray body assumption, then narrow optical band-pass filters can be used. Therefore the measurement is essentially conducted at two specific wavelengths. If narrow filters are used, it eliminates
any spectral dependence on the detector, transmission or emissivity. This will be shown in the following section.

### 9.2. Emissivity, Transmissivity, and Responsivity Independence

In the previous section it was stated that if two narrow band-pass filters are used then the measurement of $\Gamma$ was independent of the emissivity, transmissivity, and responsivity. This section will provide the details of how this independence is achieved.

This discussion will begin with the RS given as

$$\text{RS}(T) = G_A F_{D-S} \int_{\lambda_0}^{\infty} \mu m \epsilon(\lambda, T) R(\lambda) \tau(\lambda) E(\lambda, T) d\lambda + V_{\text{bias}}(T_{BG}).$$  \hspace{1cm} (9.9)

Recognizing from the previous chapter that the $V_{\text{bias}}$ does not affect the measurement, and therefore will be dropped for simplicity. Additionally, assuming the optical filter is centered around $\lambda_1$ and has a bandwidth of $\Delta \lambda_1$ Equation (9.9) can be simplified to

$$\text{RS}_{\lambda_1}(T) = p \Delta \lambda_1 [\epsilon_{\lambda_1}(T) R_{\lambda_1} \tau_{\lambda_1} E_{\lambda_1}(T)]$$ \hspace{1cm} (9.10)

where $p$ is a constant equal to the product of the constants in front of the integral, and the subscript $\lambda_1$ denotes the values of responsivity, emissivity, transmissivity, and Planck’s law at wavelength $\lambda_1$. The periodic temperature modulations are typically on the order of $0.1 - 1 \text{ K}$. Therefore, even if the sample emissivity is temperature dependent, it can be considered a constant because the periodic temperature amplitude is sufficiently small. Rewriting Equation (9.10) with this assumption yields

$$\text{RS}_{\lambda_1}(T) = p \Delta \lambda_1 [\epsilon_{\lambda_1, T} R_{\lambda_1} \tau_{\lambda_1}] E_{\lambda_1}(T)$$ \hspace{1cm} (9.11)
Recognize that Planck’s law at wavelength $\lambda_1$ is now the only temperature dependent property and the sample emissivity, detector responsivity, and transmissivity are just multiplicative constants. Also recall that the PTR signal is defined as the Fourier transform at a specific frequency. Therefore, the PTR signal can be written as

$$P_{TR\lambda_1}(f) = \mathcal{F}\{p \Delta \lambda_1 [e_{\lambda_1}, TR_{\lambda_1}, \tau_{\lambda_1}] E_{\lambda_1}(T), f\}$$

which because of the Fourier transform is a linear operator, Equation (9.12) can be alternatively written as

$$P_{TR\lambda_1}(f) = p \Delta \lambda_1 [e_{\lambda_1}, TR_{\lambda_1}, \tau_{\lambda_1}] \mathcal{F}\{E_{\lambda_1}(T), f\}.$$  \hspace{1cm} (9.13)

The same process can be repeated for a second filter centered at wavelength $\lambda_2$ and has a bandwidth of $\Delta \lambda_2$. The PTR signal for the second filter can similarly be written as

$$P_{TR\lambda_2}(f) = p \Delta \lambda_2 [e_{\lambda_2}, TR_{\lambda_2}, \tau_{\lambda_2}] \mathcal{F}\{E_{\lambda_2}(T), f\}.$$  \hspace{1cm} (9.14)

where the subscript $\lambda_2$ denotes the values of emissivity, detector responsivity, filter transmission, and Planck’s law at wavelength $\lambda_2$. The ratio of Equation (9.13) at modulation frequencies $f_1$ and $f_{1x2}$, as described in Chapter 6, (9.12) yields

$$\mathcal{R}_{\lambda_1} = \frac{P_{TR\lambda_1}(f_{1x2})}{P_{TR\lambda_1}(f_1)} = \frac{\mathcal{F}\{E_{\lambda_1}(T), f_{1x2}\}}{\mathcal{F}\{E_{\lambda_1}(T), f_1\}}.$$  \hspace{1cm} (9.15)

Recognize that this is the same ratio used in Chapter 8 that was determined only dependent on $T_{DC}$, $T_{AC2}$, and the spectral properties. However, due to the narrow filter, all of the spectral properties are constant. It is also clear that all of the spectral properties and filter bandwidths cancel in Equation (9.15), and therefore this ratio is independent of all the spectral properties. Likewise, this ratio for the second filter is given by
Therefore, Equation (9.15) and (9.16) are only dependent on $T_{DC}$, $T_{AC}$, $\lambda_1$, and $\lambda_2$. From Section 9.1 it was shown this ratio contains a multiplicative factor of $T_{AC}/T_{DC}$. This factor is independent of the nonlinearity, and therefore is canceled by the ratio between Equation (9.15) and (9.16) seen as

$$\Gamma = \frac{R_{\lambda_1}}{R_{\lambda_2}} = \frac{P_{TR\lambda_1}(f_{1x2})}{P_{TR\lambda_2}(f_1)} = \frac{F\{E_{\lambda_1}(T),f_{1x2}\}}{F\{E_{\lambda_1}(T),f_1\}} / \frac{F\{E_{\lambda_2}(T),f_{1x2}\}}{F\{E_{\lambda_2}(T),f_1\}}. \tag{9.17}$$

This ratio is only dependent on $T_{DC}$, $\lambda_1$, and $\lambda_2$. Specifically, it should be noted that in the measurement of $R_{\lambda_1}$ and $R_{\lambda_2}$, detector responsivity does not need to be equal and therefore different detectors may be used in the measurements at the different wavelengths $\lambda_1$ and $\lambda_2$. This allows for large differences in wavelength between $\lambda_1$ and $\lambda_2$. Furthermore, optimal optical detectors can be used for each wavelength, and no calibration between the two detectors is required.

### 9.3. Graphical Representation

It is necessary to graphically observe the spectral dependence on the RS to have a good understanding of this technique. The RS is plotted for various wavelengths for temperatures ranging from 300-500 K in Fig. 9.1. The main observation from this plot is the different curvature/nonlinearity of the plots based on their wavelength. The data from this plot has been fit with the same procedure used in Chapter 6 to determine the nonlinearity coefficient as a function of temperature for these three curves. The results from this fitting process can be seen in Fig. 9.2.
Fig. 9.1. Radiometric signal vs sample temperature at three different wavelengths

Similar to the nonlinearity coefficients found in Chapter 6, these curves monotonically decrease with temperature. The difference between this plot and the one presented in Chapter 6, is that this one specifies wavelengths and the other was determined from the integral over all wavelengths. This difference in nonlinearity at the same temperature due to different wavelengths is the physical phenomena that makes this pyrometry technique possible. This different nonlinearity coefficient is what causes the harmonic and sideband frequencies to have different magnitudes, and therefore making the $R_{\lambda i}$ ratio to have different values based on the wavelength.
Finally a plot of $\Gamma$ vs temperature for various wavelengths is provided in Fig. 9.3. From this it can be seen that the sensitivity with respect to temperature is highly dependent on the chosen wavelengths. The further separated the wavelengths are the greater the sensitivity. This is due to the fact that this ratio is dependent on the nonlinearity at each respective wavelength. If the two wavelengths are close to each other then they will have similar nonlinearity coefficients, and therefore little sensitivity to temperature. Therefore, the measurement wavelength should be chosen carefully depending on the temperature range of interest.

The $\Gamma$ ratio sensitivity with respect to wavelength should also be noted. The different curves in Fig. 9.3 are dramatically different for the different wavelengths, as compared to the difference in temperatures. It is easy to see that this ratio is much more sensitive to the wavelengths than the temperature. This requires accurate knowledge of the filter transmission band to perform an accurate temperature measurement. Specifically note that the difference between the 4 $\mu$m/10 $\mu$m and the 6 $\mu$m/10 $\mu$m is about a factor of two.
at the higher temperature range. This two micrometer difference is much more significant than the change of 700 K for any of the ratios. This lack of sensitivity on temperature, and high sensitivity on wavelength is a significant drawback of this technique.

The most unique fact about this measurement technique is that it requires no calibration measurement, and no knowledge of the material emissivity.

9.4. Experimental Results

Three optical band-pass filters have been used in the experimental testing of the absolute temperature measurement. These three filters have a full width half maximum (FWHM) bandwidth of 0.5 μm, and have center wavelengths at 2.5 μm, 4.5 μm, and 6.5 μm. A three dimensional printer was used to create an apparatus to hold these filters directly in front of the IR detector. This apparatus ensured that all light arriving at the detector is required to be transmitted through the filter. It also allowed for the filters to be easily changed during a measurement.

![Graph showing the variation of \( \Gamma \) with temperature for different λ ratios.](image-url)
A glassy carbon sample was placed on a temperature controlled stage, positioned such that the glassy carbon surface is in the focal plane of the parabolic mirrors. The lasers modulating at frequency $f_i$ and $f_j$ had a power of approximately 350 mW and 450 mW, respectively. Both lasers were expanded to have diameters, at the sample, of approximately 5 mm. From Equation (9.17) it is clear the measurement of $\Gamma$ requires the measurement of two ratios $\text{PTR}(f_{i2})/\text{PTR}(f_i)$ with different spectral conditions. The $\text{PTR}(f_{i2})/\text{PTR}(f_i)$ ratio was measured in the same manner described in chapter 8 (series lock-in configuration) with the exception of the filter in front of the detector. At each measurement of $\Gamma$, the sample stage was set to a given temperature and the $\text{PTR}(f_{i2})/\text{PTR}(f_i)$ ratio is measured with each of the three IR filters placed in front of the detector. From these three filters, three values of $\Gamma$ are computed at each temperature. They correspond to $\text{PTR}(f_{i2})/\text{PTR}(f_i)$ measurements with the corresponding filter center wavelengths, 2.5 µm/4.5 µm, 2.5 µm/6.5 µm, and 4.5 µm/6.5 µm. The results from these measurements can be seen in Fig. 9.4 through Fig. 9.6. In these plots, the solid lines correspond to the calculated signal value of $\Gamma$ using the full bandwidth of the corresponding filters used. The dotted lines use the shortest wavelength of the filter in the numerator and the longest wavelength of the filter in the denominator. The dot dash lines use the longest wavelength of the numerator and the shorter wavelength of the denominator. The expected experimental response is given by the solid line. The other two lines are provided to give the readers an idea of the spectral sensitivity of the measurement. They correspond to the highest, and lowest values of $\Gamma$ that can be obtained from any choice of wavelengths included in the two filter’s bandwidth. From all three plots, it is clear the value of $\Gamma$ is highly dependent on the wavelength. There
is significant variability of $\Gamma$ over the spectral ranges of the filters even though they only have a FWHM bandwidth of 0.5 $\mu$m.

Fig. 9.4. Experimentally measured values of the $\Gamma$ ratio corresponding to the filters with center wavelengths at 2.5 $\mu$m and 4.5 $\mu$m. The values are measured over a range of temperatures. The solid line is the theoretical prediction of $\Gamma$ based on a gray body assumption of emissivity over the filter bandwidth, and uniform filter transmission over the bandwidth. The dotted line corresponds to $\Gamma$ calculated at 2.25 $\mu$m/4.75 $\mu$m which is the highest possible value of $\Gamma$ with wavelengths that are contained within the two filter bandwidths. Likewise the dot dash line corresponds to $\Gamma$ calculated at 2.75 $\mu$m/4.25 $\mu$m which is the lowest possible value of $\Gamma$.

In Fig. 9.4 the experimental values of $\Gamma$ are above that predicted, but are well within the bounds of the spectral range of the filters. This error can easily be explained by non-uniform transmission across the spectral bandwidth of the filter, non-gray sample emissivity over the spectral range of the filter, or a combination of both. However, due to the lack of sensitivity to temperature, this error leads to very large error in the temperature measurement.
Fig. 9.5 Experimentally measured values of the $\Gamma$ ratio corresponding to the filters with center wavelengths at 2.5 $\mu$m and 6.5 $\mu$m. The values are measured over a range of temperatures. The solid line is the theoretical prediction of $\Gamma$ based on a gray body assumption of emissivity over the filter bandwidth, and uniform filter transmission over the bandwidth. The dotted line corresponds to $\Gamma$ calculated at 2.25 $\mu$m/6.75 $\mu$m which is the highest possible value of $\Gamma$ with wavelengths that are contained within the two filter bandwidths. Likewise the dot dash line corresponds to $\Gamma$ calculated at 2.75 $\mu$m/6.25 $\mu$m which is the lowest possible value of $\Gamma$.

In Fig. 9.5 and Fig. 9.6 the experimental values of $\Gamma$ corresponding to the filters at 2.5 $\mu$m/6.5 $\mu$m and 4.5 $\mu$m/6.5 $\mu$m are provided, respectively. The experimental data for these plots are outside of the spectral range of the two filters used in each plot. Therefore, these deviations cannot be explained by the non-uniform transmission or spectral variation of emissivity. Therefore the only explanation for these result is the detector/amplifier has a small nonlinear component. Previously it has been assumed the detector acts as a perfect linear sensor, and to this point there has been no evidence to the contrary. However, this presents a contradiction with the other results presented which matched well with the developed theory assuming the detector behaves linearly. To help explain this contradiction Equation (9.5) and Equation (9.8) will be combined as
Working on the premise that some nonlinearity in the system exists and will be termed $B_{sys}$, Equation (9.18) can be rewritten as

$$\Gamma = \frac{R_1}{R_2} = \frac{B(T_{DC}\lambda_{prop1})^{-1}}{B(T_{DC}\lambda_{prop2})^{-1}}. \quad (9.18)$$

The value of $B$ is required, to understand the effect $B_{sys}$ will have on the measurement of $\Gamma$. Therefore, the nonlinearity coefficient $B$ is plotted over a range of temperature in Fig. 9.7 for the three filters used in the experimental results. This plot shows the value of $B$ decreases with increasing temperature, and decreases with increasing wavelength. It is obvious that any system nonlinearity, $B_{sys}$, will have the greatest impact when $B$ is smaller. Specifically $B_{sys}$ will play the most significant role when the temperature is high and the wavelengths chosen are long. $B_{sys}$ will have the least impact when the short wavelengths are chosen and at low temperature. This trend is observed in the measurements presented in this chapter. In all three cases a bias is observed, but it is much more pronounced in the $\Gamma$ values that contain results from the 6.5 $\mu$m filter.
Fig. 9.6 Experimentally measured values of the $\Gamma$ ratio corresponding to the filters with center wavelengths at 4.5 $\mu$m and 6.5 $\mu$m. The values are measured over a range of temperatures. The solid line is the theoretical prediction of $\Gamma$ based on a gray body assumption of emissivity over the filter bandwidth, and uniform filter transmission over the bandwidth. The dotted line corresponds to $\Gamma$ calculated at 4.25 $\mu$m/6.75 $\mu$m which is the highest possible value of $\Gamma$ with wavelengths that are contained within the two filter bandwidths. Likewise the dot dash line corresponds to $\Gamma$ calculated at 4.75 $\mu$m/6.25 $\mu$m which is the lowest possible value of $\Gamma$.

This system nonlinearity reconciles the results presented in this chapter, but it also has ramifications for the previous chapters. In Chapter 8 the results obtained matched the theory very well, and the thermal effusivity values obtained matched literature values quite well. Specifically, all of the values were within 10% of literature values. In Chapter 8 the ratio $\frac{\text{PTR}(f_{1x2})}{\text{PTR}(f_{1})}$ was measured to determine $T_{AC}$. From Equation (9.4) and Equation (9.5) we can express this ratio as

$$R = \frac{\text{PTR}(f_{1x2})}{\text{PTR}(f_{1})} = \left( \frac{B(T_{DC}, \lambda_{prop}) + B_{sys} - 1}{T_{AC}} \right) \frac{T_{AC}}{T_{DC}}. \quad (9.20)$$

At room temperature and without any spectral filters (the scenario used in the effusivity measurements from Chapter 8), the value of $B$ is calculated to be approximately 5.07. To
reconcile the measurements of this chapter with those of Chapter 8, the value of $B_{sys}$ certainly must be less than 10% the value of $B$, but most likely less than 5% the value of $B$. A 5% error of the nonlinearity of 5.07 yields a $B_{sys}$ of 0.254. As a check, this value for $B_{sys}$ will be used in the calculation of $\Gamma$ to determine if these results are consistent. Specifically at 350 °C the nonlinearity coefficients have values of 8.16 and 2.76 corresponding to filters are 6.5 µm and 2.5 µm, respectively. Therefore, assuming the $B_{sys}$ is a value of -0.254, $\Gamma$ is calculated according it Equation (9.19) to be 4.6. This does not exactly match the experimental data, but it certainly accounts for the bias which in addition to spectral uncertainties explains the discrepancies between the experimental and theoretical data. Therefore, the results obtained in Chapter 8 are consistent with those presented in this chapter. It should also be noted, from Chapter 8 an overall negative bias was observed on the error of measured thermal effusivity. This is also consistent with a negative value of $B_{sys}$.

Fig. 9.7 The nonlinearity coefficient $B$ plotted for the three filters used over a range of temperatures.
9.5. Discussion & Summary

In this chapter a new pyrometry technique has been developed based on the nonlinearity of photothermal radiometry. The technique uses two periodic heat fluxes at different frequencies to heat the sample. The nonlinearity in emission with respect to temperature causes mixing between the two frequencies, and therefore radiation is emitted at different frequencies in addition to the original two excitation frequencies. The temperature can be determined by measuring the emission at these alternative frequencies and normalizing by the emission at the original frequencies under two different spectral conditions. For this work band-pass optical filters were used, but this is not a requirement. Long or short pass filter similarly could be used.

This technique is independent of sample emissivity changes with respect to temperature or wavelength. Furthermore, it does not rely on a measurement of emissivity through the use of lasers at specific wavelengths. This technique also does not require knowledge of the view factors, detector responsivity, amplification, or filter bandwidth. It also does not require any calibration.

This technique does have some limitations. Obviously, this technique requires the use of two independently modulated lasers with sufficient power to induce a measurable thermal response. Certainly in a laboratory setting this is not difficult to achieve, but this requirement could cause difficulties for in situ measurements. Another limitation is the requirement of precise knowledge of the filter’s spectral transmission. As seen in section 9.3 the measurement is very sensitive to wavelength and uncertainty in wavelength can cause significant error in the temperature measurement.
Compared to other pyrometry techniques, this could be considered a relatively slow measurement technique. The speed of operation is dependent on the frequencies chosen for the measurement. A thorough discussion on the requirements involved with the choice of frequencies was provided in section 8.3.4.2. For faster operation higher frequencies could be chosen. The thermal signal decreases with frequency as described in Equation (3.22). Therefore, higher laser power is required for the same signal to noise ratio. If the sample has a low thermal effusivity, and high optical absorptivity the laser power requirements are easier to meet. However, for metal samples which typically have high thermal effusivity and low absorptivity, the laser power may be the limiting factor in to induce a measurable temperature modulation. The equipment used to create the laser modulation typically have power limitations. For these reasons, this technique is probably not well suited for high speed pyrometry applications.

This technique uses a rather complex data reduction technique, compared to other pyrometry techniques. After the two optical filters are chosen for a specific measurement, the $\Gamma$ ratio can be calculated for a range of sample temperatures. This allows for the temperature to be determined quickly after the experimental measurement, but the calculation of the $\Gamma$ ratio is more involved than the data reduction of most pyrometry techniques. Specifically, it requires the integration with respect to wavelength of the product of detector responsivity, emissivity, and filter transmission. This integration then needs to be performed at various points in time to adequately model the periodic modulation of temperature at both frequencies. After this time response of emission is
obtained, a Fourier transform is performed to obtain the specific PTR signals required for \( \Gamma \) ratio.

The experimental results displayed two weaknesses of this technique, the high spectral sensitivity and the vulnerability to any nonlinearity in the measurement system. It was determined that both of these caused significant error in the temperature measurement. Due to these factors the experimental results presented here do not match well the theoretical predictions. However, since the cause is known, a pyrometer system could be designed which minimized these effects. To minimize these effects, the nonlinearity due to emission should be designed such that it is large compared to the system nonlinearity. As discussed in the previous section, and shown in Fig. 9.7, the nonlinearity coefficient \( B \) increases with decreasing wavelength and temperature. Therefore, the shorter wavelengths chosen for a given temperature reduces the influence a system nonlinearity could have. Additionally, narrower band-pass filters can be used to limit the spectral dependence on the transmission and sample emissivity. From the results presented in Fig. 9.4 through Fig. 9.6 it is clear that the 0.5 \( \mu \)m FWHM bandwidth is too wide for accurate temperature measurements. While these results have unveiled significant limitations of the technique, with these suggested modifications this could potentially be a reliable pyrometry technique.
CHAPTER 10

CONCLUSIONS

Researchers have extensively used the standard PTR technique in the measurement of thermal properties. Regardless of the widespread use of this technique, the nonlinearity in the PTR signal has not been exploited in any measurements. This work provided a detailed analysis of the PTR signal and its spectral and temperature dependence. Through this analysis, the PTR signal’s nonlinear dependence on temperature was exploited. This nonlinearity was explored and characterized under different conditions. This theory has been utilized to develop numerical methods to accurately model the nonlinearity. From these numerical methods, conclusions about the NL-PTR signal were determined under certain conditions. This analysis was used to develop three application using the nonlinearity of the PTR signal. These applications include two new pyrometry techniques and a direct thermal effusivity measurement technique. While these three techniques are good examples of applications for the NL-PTR theory, surely there are more applications yet to be discovered. This appears to be the beginning of a subfield in PTR research. This chapter summarizes the techniques developed, their results, limitations, and a brief discussion of improvements that could be made on the techniques.

10.1. Relative Temperature Measurement

The first technique developed was the relative temperature measurement. Its name comes from the fact that the PTR signal must be measured at a known temperature. Using that PTR measurement at a known temperature, the sample temperature can then be
determined by measuring the PTR signal. This technique was developed in detail in Chapter 7, but a brief description will be provided here.

Using the NL-PTR theory developed in Chapter 6, the PTR signal can be expressed as a function of temperature. In the approximation developed, there is a multiplicative factor which is the product of sample emissivity, transmissivity, detector area, electronic amplification, viewfactors, and the periodic temperature. This factor was called the calibration coefficient. If this factor can be determined, then the PTR signal can be predicted for any value of temperature. Therefore, the temperature can be determined from the PTR signal after this calibration coefficient is determined. This calibration coefficient was determined by measuring the PTR signal at a known temperature. Because this measurement must be made at a known temperature, the technique was given the name relative temperature measurement.

This technique assumes this calibration coefficient is constant over the range of temperatures. As a result of this assumption, the factors listed previously must be a constant as a function of temperature. Specifically the factors of concern are the sample emissivity and the periodic temperature. The sample emissivity is never explicitly known in this measurement, but it is assumed that it is independent of sample temperature. The periodic temperature for a semi-infinite sample is dependent on the thermal effusivity and the absorbed flux. Therefore, it is assumed the thermal effusivity and the optical absorption at the wavelength of the laser are independent of temperature. The results shown in this work assumed the samples were gray emitters over the spectral range of the sample. However, this assumption is not required. If this is not a good assumption for the sample, an IR band-
pass filter can be used to create a spectral range that is narrow enough that sample emissivity is a constant over that range. Alternatively, if the spectral emissivity is known it can be incorporated into the calculation. This pyrometry technique is unique from others developed as it does not require and explicit measurement of emissivity or any gray body assumption. However, it does require the calibration coefficient to be measured.

The main application foreseen for this technique is the monitoring of sample temperature during a PTR measurement. PTR has been used on delicate samples including ancient documents and valuable works of art. For these samples, temperature rise due to the measurement must be kept to a minimum. This technique could be used to monitor, in real time, the sample temperature. This would allow for precautions to be taken to prevent overheating of delicate samples.

In this work this technique was used to measure the temperature of a temperature controlled aluminum block with a thermocouple inserted in it. This aluminum block was measured with three different surface treatments providing three different emissivity values. The temperature results using this technique matched well with the thermocouple measurements. Additionally, the applicability of this measurement technique was shown under a transient heating of the aluminum block. In this measurement, the temperature was monitored using the relative temperature measurement and the thermocouple in the aluminum block. The heater was turned on for a period of time and then turned off. The temporal temperature response from the thermocouple and the NL-PTR technique were plotted and showed good agreement. This clearly shows the relative temperature measurement is a good application of this the NL-PTR theory.
Because of the assumptions of this technique it is recommended for monitoring the temperature changes around the calibration temperature. Over large temperature changes this technique is not expected to perform as well due to the changes in thermal properties, emissivity, and absorptivity. However this technique clearly satisfies a niche pyrometry application for monitoring the temperature rise due to sample heating from PTR measurements.

10.2. Thermal Effusivity Measurement

The second application developed from the NL-PTR theory is a direct thermal effusivity measurement of a homogenous sample. This technique measures the amplitude of the periodic temperature due to an absorbed periodic flux. By knowing the modulation frequency and the absorbed flux, the thermal effusivity can be directly determined. This allows for a direct, non-contact, thermal effusivity measurement of a homogenous material. Previously noncontact techniques have used comparative measurements which make an assumption about the value of emissivity, and the value of thermal effusivity of one of the samples is required. Other techniques use layered samples and one of the sample layer’s thermal effusivity is required, but it does not require assumptions about the sample emissivity. Alternatively, contact techniques have been developed that are similar to the approach shown here, but have the requirement of good thermal contact. The limitations of the existing techniques are the primary reasons that thermal effusivity is generally calculated from the measurements of other thermal properties rather than measured itself.
Having a noncontact direct thermal effusivity measurement of a homogenous material has many advantages to existing techniques. An excellent example is the ability to obtain noncontact measurements of thermal conductivity. The popular laser flash technique is considered the standard technique for measuring thermal diffusivity. The technique uses a flash of light to heat a thin sample and measures the time it takes for the heat to propagate to the opposite side of the sample. For this measurement, the sample thickness must be known very accurately, and the sample must be thin enough for the temperature rise on the opposite side of the sample to be detectable. Often this measurement is combined with the material’s density and specific heat to calculate thermal conductivity. Similarly, this thermal effusivity technique can be combined with known values of density and specific heat to determine thermal conductivity. However, this technique does not impose the requirements of a thermally thin sample or knowledge of sample thickness. If the density and specific heat are unknown, this technique can be combined with laser flash to calculate the thermal conductivity and heat capacity from the thermal effusivity and diffusivity. Therefore, this combination provides noncontact method for measuring thermal conductivity and heat capacity for homogenous materials.

The novelty of this technique is the noncontact ability to measure the periodic temperature modulation. This periodic temperature measurement is conducted through the use of the NL-PTR signal. The nonlinearity of the PTR signal with respect to temperature causes infrared radiation to be emitted at harmonics of the temperature modulation. In this work, two periodic temperature modulations, at different frequencies, are superimposed which causes emission at the harmonics of each of the fundamental frequencies in addition
to frequencies at their sum and difference. A very useful parameter was given by the PTR signal at one of the 2\textsuperscript{nd} order frequencies normalized by the 1\textsuperscript{st} order. In this work the ratio $\text{PTR}(f_{1x2})/\text{PTR}(f_i)$ was used where $\text{PTR}(f_{1x2})$ is the amplitude modulation of the carrier frequency $f_i$ at frequency $f_2$. It was shown that this ratio only dependent on the spectral properties, average sample temperature, and the periodic temperature at frequency $f_2$. Notably it is independent of the periodic temperature at frequency $f_i$, sample emissivity, viewfactors, and electronic amplification. In this work sample emissivity was assumed to be independent of wavelength over the sensitive spectral range of the detector. However, this assumption is not required, and if a sample does not satisfy this assumption, then an optical bandpass IR filter can be used to eliminate the requirement of this assumption.

In this measurement the periodic temperature is solved for numerically by setting the experimentally measured $\text{PTR}_m(f_{1x2})/\text{PTR}_m(f_i)$ ratio equal to the calculated $\text{PTR}_c(f_{1x2})/\text{PTR}_c(f_i)$ ratio. The experimental measurement procedure was detailed in Chapter 8. The calculated ratio is determined by calculating the detector signal over time with the sample temperature described by two periodic temperature modulations superimposed with a constant temperature, $T_{DC}$. The Fourier transform is then performed on the values of the calculated detector signal through time to determine the detector signal components corresponding to $\text{PTR}_c(f_{1x2})$ and $\text{PTR}_c(f_i)$. The value of $T_{AC2}$ is then modified using a numerical root finding method as this process is repeated until the two ratios are equivalent.

The periodic absorbed flux is required to determine the thermal effusivity. The material absorptivity is easily measured by the power of the reflected laser beam compared
to the incoming laser. If the sample reflects diffusely an integrating sphere can be used to measure the sample reflectivity. The absorbed flux can be determined by measuring the flux contacting the sample surface and multiplying by the material’s absorptivity. In this work, homogenizing optics with microlens were used to create a uniform flux on the surface. A mask with a small hole (with known hole area) was placed at the focal plane of the sample. An optical power meter was used to measure the amount of light passing through the hole. This divided by the known area of the hole provides the flux on the surface.

Thermal effusivity is directly calculated after the absorbed flux and periodic temperature are measured. In this work rubber, glassy carbon, and coated steel and aluminum were measured. The results were compared to those in literature all showing <10% error from their respective literature values. The largest error was for aluminum having the highest thermal effusivity. Because of aluminum’s high thermal effusivity the periodic temperature was the lowest which results in the lowest signal to noise ratio of the experiments. Through the use of a higher power laser this periodic temperature could be increased which would improve the signal to noise ratio, and presumably reduce the error in this measurement. Regardless this has been shown to be an accurate, noncontact, and direct thermal effusivity measurement for homogenous samples, and therefore an excellent application of the NL-PTR theory developed.
10.3. Absolute Temperature Measurement

The third application of the NL-PTR theory is another pyrometry technique. It has been named the absolute temperature measurement because it does not require a calibration measurement at a known temperature. The absolute temperature measurement is built on the experimental setup from the thermal effusivity measurement. It was shown the ratio $\Gamma$ defined by $\text{PTR}_{\lambda_1}(f_{1x2})/\text{PTR}_{\lambda_1}(f_i)$ divided by $\text{PTR}_{\lambda_2}(f_{1x2})/\text{PTR}_{\lambda_2}(f_i)$ is only dependent on the average sample temperature and the wavelengths $\lambda_1$ and $\lambda_2$. Where $\lambda_1$ and $\lambda_2$ are the center wavelength of transmission filters that are placed in front of the detector. Since the filter wavelengths are known, the only unknown parameter of $\Gamma$ is the sample temperature. Therefore, the sample temperature can be determined from a measurement of $\Gamma$.

In this study, three IR bandpass filters were used with center wavelengths at 2.5 $\mu$m, 4.5 $\mu$m, and 6.5 $\mu$m. Each of these filters had a FWHM bandwidth of 0.5 $\mu$m. Therefore, three $\Gamma$ ratios were measured corresponding to the three spectral ratios 2.5 $\mu$m/4.5 $\mu$m, 2.5 $\mu$m/6.5 $\mu$m, and 4.5 $\mu$m/6.5 $\mu$m. These ratios were experimentally measured over a range of temperatures and compared to the theoretically predicted ratios. There were significant discrepancies between the experimental and theoretical $\Gamma$ ratios. This discrepancy was attributed to two sources of error. The first source is the strong spectral dependence on the $\Gamma$ ratio. This makes the ratio very sensitive to any non-uniform transmission of the IR filter and any spectral changes in emissivity over the filter range. The second source was determined to be a small system nonlinearity. This caused a bias in the $\Gamma$ ratios, and large error in the determination of temperature.
Proposed design parameters are suggested that could be used to limit the effects of these sources of error. Specifically, the choice of filters with short transmission wavelengths increase the value of the nonlinearity due to emission, therefore limiting the error imposed by a system nonlinearity. The second suggestion is the use of narrow band-pass filters. More narrow filters will limit the impact of spectral variations of filter transmissivity and sample emissivity (within the bandwidth). With these proposed design modification, this technique could potentially be a reliable pyrometry technique with significant advantages over existing techniques.
REFERENCES


1886.


CURRICULUM VITAE

AUSTIN FLEMING

148 West 1140 North #4
Logan, UT 84341
Phone: 801-696-1027
Email: austin.d.fleming@aggiemail.usu.edu

EDUCATION

2017  Utah State University  Logan, Utah, USA
Université de Reims Champagne-Ardenne  Reims, France
Ph.D. in Mechanical Engineering (Co-tutelle Program)
Dissertation: The Development of Nonlinear Photothermal Radiometry and its Applications to Pyrometry and Thermal Property Measurements (tentative title)
Co-Advisor (USU): Prof. Heng Ban
Co-Advisor (URCA): Prof. Mihai Chirtoc

2014  Utah State University  Logan, Utah, USA
M.S. in Mechanical Engineering  3.72 GPA
Thesis: Uncertainty Quantification of Photothermal Radiometry Measurements Using Monte Carlo Simulation and Experimental Repeatability
Advisor: Prof. Heng Ban

2014  Utah State University  Logan, Utah, USA
B.S. in Mechanical Engineering  3.73 GPA
Successful Completion of the Fundamentals of Engineering Exam (2010)

PROFESSIONAL EXPERIENCE

2015-2016  Université de Reims Champagne-Ardenne  Reims, France
Graduate Research Assistant: Multiscale Thermophysics Group
GRESPI-CATHERM

- Development of Nonlinear Photothermal Radiometry (NLPRTR) theory
- Establishing advanced pyrometry techniques using NLPRTR
- Development of a new thermal effusivity measurement technique based on NLPRTR

2011-present  Utah State University  Logan, Utah, USA
Graduate Research Assistant: Multiscale Thermophysics Laboratory

- Development of Fiber-based modulated optical reflectance system in order to measure thermal diffusivity
- Uncertainty quantification of thermal conductivity measurements using two laser Raman thermometry
- 3-ω measurements of thin films composed of carbon nanotubes and nanoflakes
• Development of a Fiber-based fluorescence thermometry system to measure thermal diffusivity
• Developing a Photothermal Radiometry (PTR) system
• Photothermal Radiometry measurements of multilayered materials and thin films
• Characterization of ion-irradiated material
• Monte Carlo uncertainty analysis on two layer PTR measurements

2013 National Renewable Energy Laboratory Golden, Colorado, USA
Graduate Researcher: Concentrated Thermal Power Division
• Development of analysis tools to predict optical absorption efficiency of multi-cavity receivers using Monte Carlo ray tracing techniques
• Thermal analysis for natural convections losses to the atmosphere from a multi-cavity receiver
• Optimization of receiver design based on efficiency and temperature constraints

2010 Utah State University Logan, Utah, USA
Undergraduate Researcher: Additive Manufacturing Laboratory
• Selective Laser Sintering (SLS) Optimization

2010 Viracon St. George, Utah, USA
(Summer) Engineering Intern: Engineering Department
• Design and build of a Kevlar Roll Wrapping Machine, using Solid Works
• Lean Manufacturing/6 Sigma training
• Overall Equipment Effectiveness Analysis

2009 Nucor Steel Plymouth, Utah, USA
(Summer) Engineering Intern: Engineering Department
• Designed Bundle Weighing System & Fall Arrest Systems using AutoCAD Inventor
• Worked directly with line workers to improve mill efficiency by manufacturing process modification
• 3-D and Scale Model Construction of Arc Melt Furnace & Continuous Caster

RESEARCH INTERESTS
Advanced pyrometry techniques; Nano/microscale heat transfer; Non-contact thermal property measurement techniques using radiometry, optical reflectance, and Raman thermometry; Experimental and computational approaches to thermophysical characterization of materials for energy transport, conversion, generation, and storage for various applications including nuclear energy, solar energy, semiconductor, and advanced manufacturing.

SKILLS, COURSES/TRAININGS, AND LANGUAGES
• Experimental: Multiscaled thermal measurement approaches: Photothermal Radiometry, Modulated Optical Reflectance, classical approaches for thermophysical properties characterization (transient and steady-state)
- **Computational**: Fortran, MatLab, Python, LabVIEW, Mathcad, CFD, COMSOL, FLUENT, Monte Carlo Ray Tracing, SOITrace, SolarPILOT, 3D CAD
- Grant Writers’ Seminars & Workshops, Logan, UT, *Getting Started as a Successful Proposal Writer and Academician Workshop*
- Spoken Language: French (Conversational)

**TEACHING EXPERIENCE**

<table>
<thead>
<tr>
<th>Year</th>
<th>Institution</th>
<th>Location</th>
<th>Position</th>
<th>Courses</th>
</tr>
</thead>
<tbody>
<tr>
<td>2014</td>
<td>Utah State University</td>
<td>Logan, Utah, USA</td>
<td>Supplemental Instructor</td>
<td>Undergraduate Heat and Mass Transfer Course (MAE 3440)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Responsible for 2 hours of supplemental lecture each week</td>
</tr>
<tr>
<td>2012</td>
<td>Utah State University</td>
<td>Logan, Utah, USA</td>
<td>Teaching Assistant</td>
<td>Undergraduate Engineering Numerical Methods 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Conducted help sessions in a classroom setting for 2+ hours/week</td>
</tr>
</tbody>
</table>

**PATENTS**


**PUBLICATIONS**


CONFERENCE PRESENTATIONS & ABSTRACTS


PROFESSIONAL SOCIETIES, ACTIVITIES & ACCOLADES

• Nuclear Regulatory Commission Scholarship ($20,000 for two years)
• Utah State University 4-H Ambassador Scholarship (Tuition for 4 years)
• American Society of Mechanical Engineers (ASME)
• American Nuclear Society (ANS)
• President of the USU Student Section of Tau Beta Pi 2011
• Engineers Without Borders