Thermal Transport of Nanoenergetics in Composite Materials

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By

MATTHEW RIEHN

Dr. Matthew Maschmann, Thesis Supervisor

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The undersigned, appointment by the Dean of the Graduate School have examined the thesis entitled

**Thermal Transport of Nanoenergetics in Composite Materials**

Presented by Matthew Riehn

a candidate for the degree of Master of Science

and here by certify that in their opinion it is worthy of acceptance.

____________________________________
Dr. Matthew Maschmann

____________________________________
Dr. Shubhra Gangopadhyay

____________________________________
Dr. Robert Winholtz
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# TABLE OF CONTENTS

ACKNOWLEDGEMENTS ........................................................................................................... i
ABSTRACT .................................................................................................................................. vii
CHAPTER ONE ............................................................................................................................. 1
  1.1 Scope of Present Work ........................................................................................................ 1
  1.2 Literature review: Photothermal heating of Al – Polymer Energetic Systems .............. 2
  1.3 Literature Review: Thermal Conductivity in Graphene ............................................. 7
CHAPTER TWO .......................................................................................................................... 13
  2.1 COMSOL Multiphysics: An introduction ....................................................................... 13
      2.1.1 Joule Heating Interface ....................................................................................... 15
      2.1.2 Domains .............................................................................................................. 15
      2.1.3 Dependent Variables ........................................................................................... 15
      2.1.4 Initial Values ....................................................................................................... 16
      2.1.5 COMSOL Overview Conclusions ..................................................................... 17
  2.2 Initial Stages of Modeling Nanoparticle Heating ....................................................... 17
  2.3 Phase Change Analysis .................................................................................................... 22
  2.4 Boundary Resistance ....................................................................................................... 28
CHAPTER THREE ..................................................................................................................... 33
  3.1 Introduction ........................................................................................................................ 33
  3.2 Implementation of Electric Field into COMSOL Model ............................................. 33
  3.3 Plasmonic Grating v. Flat Silver Substrate Comparison ............................................. 35
  3.4 Single v. Two Particle Simulation ................................................................................. 38
  3.5 Theoretical Calculation for Achieving the Ignition Temperature .............................. 44
  3.6 Six Particle Simulation ................................................................................................. 48
  3.7. Applying Simulation Method to other Al/Polymer Projects ................................... 51
CHAPTER FOUR ......................................................................................................................... 56
  4.1 Introduction ...................................................................................................................... 56
  4.2 Design Parameters for the thermal conductivity experiment .................................. 57
  4.3 Experimental Setup ....................................................................................................... 61
  4.4 Microfabrication Instrumentation .............................................................................. 62
  4.5 Spin Coating Basics ...................................................................................................... 62
  4.6 Photolithography Summary .......................................................................................... 63
  4.7 Procedure Used for Photolithography Setup .............................................................. 67
  4.8 Sputtering Overview ...................................................................................................... 68
  4.9 Molecular Dynamics Simulation Introduction .............................................................. 69
  4.10 Experiment: Two Point – Probe Measurement .............................................................. 76
  4.11 Conclusions and Future Work ..................................................................................... 80
REFERENCES ............................................................................................................................... 82
LIST OF PUBLICATIONS ........................................................................................................... 86
Journal Publications ................................................................................................................. 86
Conference Proceedings .......................................................................................................... 86
APPENDIX .................................................................................................................................. 87
A.1 Supplemental Data for Chapter 3.7 ................................................................................ 87
A.2 Supplemental Data for Chapter 4. 10 .......................................................................... 88
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 1</td>
<td>Illustration of a surface plasmon wave propagating along the interface of a metal and dielectric material. [11],[12]</td>
</tr>
<tr>
<td>1. 2</td>
<td>Illustration of grating configuration and diagram of surface plasmon momentum</td>
</tr>
<tr>
<td>2. 1</td>
<td>COMSOL Multiphysics 5.2a Window</td>
</tr>
<tr>
<td>2. 2</td>
<td>Flow chart to run a COMSOL Simulation</td>
</tr>
<tr>
<td>2. 3</td>
<td>The geometric model for the initial stages of simulation analysis. (A) Water medium cube (B) the isolated aluminum nanoparticle</td>
</tr>
<tr>
<td>2. 4</td>
<td>Temperature increase of an 80 nm gold nanoparticle embedded in water from (A) reference [21] and (B) from the COMSOL simulation</td>
</tr>
<tr>
<td>2. 5</td>
<td>ΔT v. Distance graph from (A) the paper [21] and (B) from the COMSOL simulation using coupling of both electromagnetic and heat transfer modules</td>
</tr>
<tr>
<td>2. 6</td>
<td>ΔT v. Distance graph from (left) direct heat transfer analysis and (right) from the COMSOL simulation using coupling of both electromagnetic and heat transfer modules</td>
</tr>
<tr>
<td>2. 7</td>
<td>(Left) Rectangular Pulse Profile as specified from experimental setup. (Right) represents the temporal and spatial distribution profile after being coupled together using COMSOL analytical function</td>
</tr>
<tr>
<td>2. 8</td>
<td>(A) 300 nm (B) 500 nm (C) 700 nm temperature change contour plots at 500 (Top row) and 1000 (Bottom row) μs</td>
</tr>
<tr>
<td>2. 9</td>
<td>(A) 300 nm (B) 500 nm (C) 700 nm phase change contour plots at 500 (Top row) and 1000 (Bottom row) μs</td>
</tr>
<tr>
<td>2. 10</td>
<td>(A) Melting Front Distance v. Time Graph (B) Melting Front Speed v. Time Graph</td>
</tr>
<tr>
<td>2. 11</td>
<td>The geometric model for the initial stages of simulation analysis. (A) THV polymer cube (B) the nanoparticle (C) The Alumina Shell and Aluminum Particle distinguished</td>
</tr>
<tr>
<td>2. 12</td>
<td>Diagram of thermal resistance circuit</td>
</tr>
<tr>
<td>2. 13</td>
<td>Temperature v. Distance Simulation with varying thermal resistances at 1000 μs, which is the time interval at which the experimental laser used for this project ended</td>
</tr>
<tr>
<td>3. 1</td>
<td>FDTD simulated E-field distribution of 80 nm Al NPs on different substrates: (a) flat silver (b) silver gratings</td>
</tr>
<tr>
<td>3. 2</td>
<td>MATLAB (A) volumetric Slice Plot of Rsoft Data (B) Single Slice Plane Plot of Rsoft Data</td>
</tr>
<tr>
<td>3. 3</td>
<td>COMSOL Geometry (A) Flat Silver Model (B) Plasmonic Grating Model</td>
</tr>
<tr>
<td>3. 4</td>
<td>Surface Temperature Map (A) Flat Silver Substrate (B) Plasmonic Grating Substrate</td>
</tr>
<tr>
<td>3. 5</td>
<td>Isolated Particle Temperature v. Power Graph Flat Silver v. Plasmonic Grating in steady state</td>
</tr>
<tr>
<td>3. 6</td>
<td>(A) Geometry. Anisotropic properties applied in (B) X direction (C) Y direction</td>
</tr>
<tr>
<td>3. 7</td>
<td>One Particle Surface Temperature plots at 250 μs A) Full map B) Close up of particle</td>
</tr>
</tbody>
</table>
3.8 Two Particles Surface Temperature plots at 250 µs A) Full map B) Close up of particles ........................................................................................................................................ 41
3.9 Left) Temperature v. Time for 1, 2, and 6 particle system with a maximum time of 100 µs Right) Temperature v. Time for 1 and 2 particle system with a maximum time of 0.2 µs ........................................................................................................................................ 42
3.10 Temperature v. Time Graph from the paper, On the self-damping nature of densification in photonic sintering of nanoparticles [38] .................................................................................................. 43
3.11 Laser Fluence v. Pulse Time (Left) Single Particle (Right) Six particle System 47
3.12 Anisotropic properties applied in A) X direction B) Y direction 49
3.13 Electric Field Data Selection for 5 um Model ................................................................. 49
3.14 (A) Isometric surface temperature. (B) Nanoparticle Temperature v. Time 50
3.15 Temperature v. Power for a 1, 2, and 6 particle systems after reaching steady state Graph ........................................................................................................................................ 51
3.16 Al NP Temperature v. Time Results regarding fluorescence based temperature sensor project (Left) Temperature v. Time with Laser Power Input of 60 mW (Right) Temperature v. Time with Laser Power Input of 200 mW 52
3.17 Diagram of altered and unaltered properties. (A) Close up (B) Physical Domain Model ........................................................................................................................................ 53
3.18 MATLAB (A) volumetric Slice Plot of Rsoft Data (B) Single Slice Plane Plot of Rsoft Data ........................................................................................................................................ 53
3.19 Left) Surface temperature map at 100 ms with power 60 mW. Right) Temperature v. Power graph of an isolated particle on two different platforms and comparing them against simulation and experimental results .................................................................................................. 54

4.1 Schematic of suspended graphene decorated with Al nanoparticles. .......................... 57
4.2 Geometry for Microheater ............................................................................................... 58
4.3 Overall design of the MEMS system. Labels and dimensions are on the diagram. ................................................................................................................................. 59
4.4 A 3D image of the MEMS system on top of the commercialized graphene .... 59
4.5 Spincoater diagram and schematics [45] ........................................................................ 63
4.6 Mask Aligner Schematic [48] ....................................................................................... 64
4.7 Darkfield mask and positive photoresist schematic diagram [50] ................................. 65
4.8 Three Exposure Methods. A) Contact Aligner, B) Proximity Aligner and C) Projection Aligner [51] ...................................................................................................................... 66
4.9 Magnetron Sputtering Schematic Overview [53] .......................................................... 69
4.10 Diagram of the Muller Plathe Method .......................................................................... 71
4.11 Thermal Conductivity v. Time for Graphene .................................................................. 74
4.12 Visualization of a force being added to a graphene sheet in the z direction............ 75
4.13 Thermal Conductivity v. Force for Graphene ............................................................... 76
4.14 Two-point probe arrangement for measuring the effective surface resistance. ... 77
4.15 Temperature v. Resistance Calibration for the contact pads ...................................... 78
4.16 T v. R Theoretical and Experimental Calibration for the first contact pad .......... 79
4.17 T v. R Theoretical and Experimental Calibration for the second contact pad .... 79
4.18 T v. R Theoretical and Experimental Calibration for the third contact pad ...... 80
A. 1  (Left) Surface Temperature Plot after 100 ms for Flat Glass Substrate Geometry  
(Right) Temperature v. Time Plot for Flat Glass Substrate Geometry .......................... 87
<table>
<thead>
<tr>
<th>TABLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 1</td>
<td>Graphene Thermal Conductivity values analyzed by other researchers</td>
</tr>
<tr>
<td>2. 1</td>
<td>Validation parameters for Gold NP in water medium</td>
</tr>
<tr>
<td>2. 2</td>
<td>Validation parameters for Gold NP in water medium</td>
</tr>
<tr>
<td>2. 3</td>
<td>Water material properties used for COMSOL simulations</td>
</tr>
<tr>
<td>2. 4</td>
<td>Essential parameters for the case of Aluminum nanoparticle in THV</td>
</tr>
<tr>
<td>2. 5</td>
<td>Aluminum material properties used for COMSOL simulations</td>
</tr>
<tr>
<td>2. 6</td>
<td>THV material properties used for COMSOL simulations</td>
</tr>
<tr>
<td>2. 7</td>
<td>Melting front distance and speed at 300 nm particle size</td>
</tr>
<tr>
<td>2. 8</td>
<td>Melting front distance and speed at 500 nm particle size</td>
</tr>
<tr>
<td>2. 9</td>
<td>Melting front distance and speed at 700 nm particle size</td>
</tr>
<tr>
<td>2. 10</td>
<td>Material properties for thermal boundary resistance calculations</td>
</tr>
<tr>
<td>2. 11</td>
<td>Simulation Outputs for different Thermal Boundary Resistances</td>
</tr>
<tr>
<td>3. 1</td>
<td>Temperature v. Power for Isolated Particle with different substrates in steady state</td>
</tr>
<tr>
<td>3. 2</td>
<td>Temperature v. Power Table</td>
</tr>
<tr>
<td>3. 3</td>
<td>Nanoparticle Temperature v. Power Values</td>
</tr>
<tr>
<td>4. 1</td>
<td>Thermal Conductivity of Graphene with different Time Steps</td>
</tr>
<tr>
<td>4. 2</td>
<td>Thermal Conductivity of Graphene with different Forces added</td>
</tr>
<tr>
<td>A. 1</td>
<td>Material Properties for Al and THV</td>
</tr>
<tr>
<td>A. 2</td>
<td>First Contact Pad Resistance Values</td>
</tr>
<tr>
<td>A. 3</td>
<td>Second Contact Pad Resistance Values</td>
</tr>
<tr>
<td>A. 4</td>
<td>Third Contact Pad Resistance Values</td>
</tr>
</tbody>
</table>
ABSTRACT

Nanoenergetic materials such as nanothermites are made up of a mixture of nanoscale fuel and oxidizer particles separated by small distances to promote rapid reaction. When reacted, they can reach an adiabatic flame temperature approximately 3000 to 4000K and generate a shock wave of approximately 2500 m/s. In this work we studied the effects of plasmonic photothermal heating and its interaction with aluminum nanoparticles. Plasmonic gratings are known to enhance electric fields based on the structure and surface plasmon resonance as a result of light coupling. By understanding the effects of enhanced electric fields caused by plasmonic gratings, we can study the effects it has on nanoparticles and its applications in in-situ temperature mapping. From the results of this investigation via numerical methods, it was found that six nanoparticles in contact were enough to reach beyond ignition temperature of 470°C, and validated the plasmonic grating does enhance the photothermal heating of nanoparticles.

Another facet to this thesis is the investigation of thermal conductivity of graphene with decorated aluminum nanoparticles. Graphene acts as a great platform for spreading thermal energy due to its excellent thermal properties. We investigate the potentially beneficial thermal properties for sustaining combustion during nanoparticle heating. However, the phonon scattering caused by nanoparticles on the surface of graphene is still not completely understood. This work gives preliminary simulation results and experimental designs to the investigation of the thermal conductivity of graphene with decorated nanoparticles.
CHAPTER ONE

Introduction

1.1 Scope of Present Work

In this work, we will explore the thermal transport in two nanoenergetic material systems of contemporary interest. First, the photothermal heating on the Al-polymer energetic thin films supported on a plasmonic grating is investigated using COMSOL Multiphysics. The scope of this study is primarily focused on the transient heat transfer effects of locally heated Aluminum nanoparticles (Al NP) embedded in a tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride (THV) polymer. This study investigates Al NP loading, the effect of enhanced electric field due to the plasmonic grating, and the extent of polymer melting during heating.

The second material system of interest is an Al-decorated graphene system. The thermal conductivity of Al nanoparticle-decorated graphene will be experimentally investigated using various particle loading from 0–10% by area. The graphene is suspended on electrodes above a lithographically defined SOI (silicon on insulator) trench. A central resistive heater region will supply a known heat flux to the suspended graphene sample, while pre-calibrated resistive temperature measurement electrodes will be used to detect temperature differences. Although the thermal conductivity of graphene will itself be a strong function of temperature, measurements will initially be conducted near room temperature to attain the magnitude of conductivity change due to particle loading alone. Also, molecular dynamic simulations will be sought to numerically simulate the thermal
conductivity of graphene and a decorated Al – graphene sheet as a means of understanding the experimental results.

1.2 Literature review: Photothermal heating of Al – Polymer Energetic Systems

Energetic materials contain chemical energy that, when reacted, can facilitate a rapid exothermic reaction much like rocket fuel and fireworks. In recent times, there has been breakthroughs in the synthesis and capabilities in the field of nanoenergetics, the study of energetic material at the nanoscale, towards applications such as explosives and military applications. Nanoenergetic particles have more surface area to volume ratio in comparison to large particles. When excited or reacted, this greater surface area causes a faster reaction rate. Working at the nanoscale, designers can control the rate at which energy is released by changing the size of the nanoparticles, allowing the designers to customize the response for each application [1]. By making energetic systems smaller and more powerful, they can be utilized as lightweight thrusters or even weaponry in small aircraft such as remote-control drones.

Nanothermites typically consist of a heterogeneous mixture of nanoscale particulate fuels and oxidizers [2 – 7]. Nanoenergetic materials are systems possessing high energy densities of approximately 21.6 kJ/cm³, which is three times more than TNT. They are comprised of nanoscale fuel (frequently Al) and oxidizer particles (such as Bi₂O₃), which are separated by small distances in order to promote rapid reaction rates. When triggered by an external energy source, combustion of the nanoscale fuel occurs.

A relatively unexplored area in nanoenergetic material research incorporates direct plasmonic heating of fuel particles. Plasmonics resonance occurs when external
electromagnetic fields interact with free electron oscillations in a metal at their plasma frequency [8]. Surface plasmons are the oscillation of electrons at the interface of a metal and dielectric material, as represented in Fig. 1.1. Beyond the interface, plasmon fields exponentially decay into both the metal and dielectric, resulting in a dense, strong field confinement at the surface [9,10]. Excitation of surface plasmons results in either propagating modes along the metal/dielectric interface called plasmon polariton (PP) or, in a single metallic particle, called localized surface plasmon (LSP) [9,10]. For our purposes, localized surface plasmons are used to generate heat in metal nanoparticles.

![Figure 1.1 Illustration of a surface plasmon wave propagating along the interface of a metal and dielectric material. [11], [12]](image)

In this work, we use metal grating structures to couple incident optical energy at the surface of the metal grating using surface plasmon resonance (SPR). This results in enhanced photothermal heating of nanoenergetic systems. In order for SPR to occur, surface plasmons must be excited in a resonant manner. An incoming incident light beam must strike the surface of the metal grating at an incident angle $\theta$, and its incoming momentum must then match that of a surface plasmon. A wave matching vector shown in Eq. 1.1 must be satisfied in order to achieve SPR, which is derived from Maxwell’s equations.
Here $k_{\text{SPR}}$ is the wave vector for surface plasmon resonance, $\Lambda$ is grating pitch, $m$ is an integer representing the diffraction order, $\omega$ is the frequency of the incident light, $\theta$ is the incident angle of irradiation, $\varepsilon_m$ is the dielectric constant for the grating metal, $\varepsilon_d$ is the dielectric constant for the surrounding medium [13]. Due to the interaction and excitation of the photons from the light beam and the oscillated electrons at the metal surface resonating, it will form an electromagnetic standing wave. The electromagnetic standing wave forms an electric field upon the metal surface (grating) and dielectric material interface. If a nanoparticle is within this field, the field will promote enhanced heat generation.

Figure 1. Illustration of grating configuration and diagram of surface plasmon momentum (courtesy of Dr. Aaron Wood)

To excite our nanoenergetic system, plasmonic grating pitch, Al NP diameter, and laser wavelength were simultaneously selected to achieve plasmonic resonance and rapid Al heating. Localized heating via electromagnetic irradiation is often referred to as photothermal heating. With respect to medicine, gold nanoparticles are often utilized as photothermal agents in the use of cancer therapy treatments [14]. In photothermal therapy (PTT), embedded particles in tumors generate heat in response to exogenously applied laser
light, killing the cancer cell. This technique is documented as a highly effective cancer treatment [15].

We are interested in understanding the thermal response of nanoenergetic materials to photothermal heating on nanoenergetic materials. Photothermal heating provides a non-contact, non-invasive, localized, and rapid heat generation mechanism. To model photothermal heating two inter-related physical models must be solved simultaneously: Maxwell’s equations describing the electromagnetic fields and heat generation, and the heat equation describing material thermal response. For the Al/polymer systems investigated here, the transient thermal response due to the particle sizes, particle aggregates, and irradiation wavelength were examined. Assuming irradiation is applied at \( t = 0 \), the light intensity (W/m\(^2\)) is calculated by [16]:

\[
I(t) = I_0 = \frac{c n E_0^2}{2}
\]

(1.2)

where \( I_0 \) is the uniform light intensity, \( c \) is the speed of light, \( n \) is the refractive index of aluminum, and \( E_0 \) is the electric field strength.

The heat generation in the Al nanoparticles embedded in polymer oxidizers was determined from the total light absorption rate [16]. The total light absorption rate is a complex function of particle size and particle material composition. These complex relationships may be well represented by the absorption cross section of the particle, described as the light intensity divided by the total energy generation rate of the particle. This can be calculated by integrating the energy loss over the volume of a nanoparticle [17]. For the current material system comprised of Al NPs embedded in fluoropolymers, the absorption cross section of a given particle diameter is determined using finite difference time domain (FDTD) simulations. For a given light intensity, a larger absorption
cross section results in a greater energy generation rate. The scattering cross section can be
determined in a similar fashion. The absorption ($\sigma_{abs}$) and scattering ($\sigma_{sca}$) cross section
can be defined [18]:

$$\sigma_{abs} = \frac{W_{abs}}{I} \quad (1.3)$$

$$\sigma_{sca} = \frac{W_{sca}}{I} \quad (1.4)$$

where $W_{abs}$ represents the energy rate absorbed and $W_{sca}$ represents the energy rate
scattered by the Al nanoparticle.

Typically, the optical absorption and scattering of one single homogeneous metal
nanoparticle with radius of $r$ embedded in an optically homogeneous matrix was modelled
by Mie theory, so $\sigma_{abs}$ and $\sigma_{sca}$ can be expressed as [18]:

$$\sigma_{abs} = \frac{8\pi^2r^3}{\lambda} \text{Im} \frac{\varepsilon_{particle} - \varepsilon_{medium}}{\varepsilon_{particle} + 2\varepsilon_{medium}} \quad (1.5)$$

$$\sigma_{sca} = \frac{128\pi^5r^6}{3\lambda^4} \left( \frac{\varepsilon_{particle} - \varepsilon_{medium}}{\varepsilon_{particle} + 2\varepsilon_{medium}} \right)^2 \quad (1.6)$$

where $\varepsilon_{particle}$ and $\varepsilon_{medium}$ is the relative permittivity of the metallic sphere and dielectric
mediums, respectively.

If we assume that the wavelength of incident light is much larger than the
nanoparticle radius ($\lambda >> r$), the photothermal energy of a single, spherical Al nanoparticle
can be simplified with the expression shown in Eq. 1.7 [16]:

$$Q = \frac{\omega}{8\pi} E_0^2 \left[ \frac{3\varepsilon_{medium}}{2\varepsilon_{medium} + \varepsilon_{particle}} \right]^2 \text{Im}\varepsilon_{particle} \quad (1.7)$$
Here $Q$ is the volumetric heat rate, $k_0$ is the thermal conductivity of the medium, $\omega$ is the angular frequency of the light, $\varepsilon_{\text{particle}}$ and $\varepsilon_{\text{medium}}$ is the relative permittivity of the metallic sphere and dielectric medium, respectively. Note $\text{Re}[i(1 - \varepsilon(r))] = \text{Im} \varepsilon(r) = \text{Im} \varepsilon_{\text{particle}}$. Since Al nanoparticles act as heat sources, the temperature decreases as the distance increases from the Al nanoparticle. Therefore, the maximum temperature occurs at the core of Al nanoparticle. The maximum nanoparticle temperature gain $\Delta T_{\text{max}}$ is calculated using the Eq. 1.8 [16]:

$$
\Delta T_{\text{max}}(E_0) = \frac{R_{\text{NP}}}{3k_0} \text{Re} \left[ i\omega \frac{1 - \varepsilon(r)}{8\pi} \frac{3\varepsilon_{\text{medium}}}{2\varepsilon_{\text{medium}} + \varepsilon_{\text{particle}}} \right]^2 E_0^2
$$

Here $R_{\text{NP}}$ is radius of the nanoparticle, $k_0$ is the thermal conductivity of the medium, $\omega$ is the angular frequency of the light, $\varepsilon_{\text{particle}}$ and $\varepsilon_{\text{medium}}$ is the relative permittivity of the metallic sphere and dielectric medium, respectively, $r$ is the radial coordinate, $\varepsilon(r)$ is the dielectric constant, $I_o$ is the light intensity inside the matrix, $c$ is the speed of light in free space. Note: $\text{Re}[i(1 - \varepsilon(r))] = \text{Im} \varepsilon(r) = \text{Im} \varepsilon_{\text{particle}}$.

By understanding photothermal heating with respect to an Al/THV polymer system, we can then utilize different areas of analysis with respect to the transient thermal behavior of the system.

1.3 Literature Review: Thermal Conductivity in Graphene

Assembling nanoenergetic materials using graphene as a scaffold is of significant interest, as it facilitates a high density of nanoparticles without particle aggregation and sintering. As such, thermal transport in complex graphene-particle systems is also of
significant interest. Recently, there is hasty growth within the scientific and engineering communities regarding transport properties in the nanoscale. While the high thermal conductivity of pristine graphite may enhance the combustion rate of graphene nanoenergetic composite materials, the small physical dimensions of graphene used in material assembly, possible defects introduced by the nanoenergetic material assembly process, and the intimate contact between graphene and nanoenergetic particles may all lead to a dramatic decrease in the effective thermal conductivity of graphene in the assembled material.

Metals are frequently considered the best thermal conductors for practical engineering applications. For example, copper has a thermal conductivity of approximately 401 W/(m·K), and is great for electrical and thermal conductive properties with respect to various real-world applications. This is attributed to the fact electrons transport most of the energy in comparison to phonon transport. According to the Wiedemann – Franz Law, the thermal conductivity is proportional to the electrical conductivity of metals (σ) and temperature (T), which can be expressed as [19]:

\[ k = L\sigma T \]  (1.9)

Here \( L \) is the Lorentz number constant equal to \( 2.44 \times 10^{-8} \text{ W} \Omega \text{K}^2 \).

In the case of non-metals, the electronic contribution towards thermal transport is negligible. Rather, lattice vibrations known as phonons transport heat. For phonon-dominated transport, the thermal conductivity (k) is shown in Eq. 1.10. Here \( v_g \) is the phonon group velocity, \( C_V \) is the specific heat, and \( \Lambda \) is the effective phonon mean free path [20].
\[ k = \frac{1}{3} v_g A_C v \]  \hspace{1cm} (1.10)

We note here that the phonon mean free path may be expressed as

\[ \Lambda_{eff} = v_g \tau_{eff} \]  \hspace{1cm} (1.11)

where \( \tau_{eff} \) represents the effective mean free path determined from

\[ \tau_{eff}^{-1} = \tau_B^{-1} + \tau_i^{-1} + \tau_U^{-1} \]  \hspace{1cm} (1.12)

Here the subscript \( B \) represents boundary scattering, \( i \) represents impurity scattering, and \( U \) represents inelastic Umklapp processes. At room temperature, a single sheet of graphene has a thermal conductivity value of approximately 5000 W/mK [21]. Graphene is on the subject of interest now because the properties it exhibits are beyond the values we see in common materials.

Most research regarding the thermal conductivity of graphene has been conducted using Raman spectroscopy. The method is advantageous in terms of being a quick, non-invasive, and a nondestructive method in which a laser light focuses on a specific spot on a sample. After the sample is exposed to the laser beam, the sample then reflects light energy back to a probe, which then relays the light intensity to a detector [22]. Once detected, the data is then analyzed as an intensity v. wavelength. The position of the local peaks is then used to determine characteristics of the sample.

Though an easy and quick method, it is rather tedious for doing analysis as one has to consider the magnification of the microscope, the amount of power to be induced on to the sample, and how the power will affect the sample of interest. Additionally, focusing one spot too often for multiple tests can damage the sample and skew results. Due to the weaknesses of techniques such as Raman spectroscopy, we will microfabricate a
microheater design to measure the thermal conductivity of graphene. Utilizing a MEMS design allows one more control over parameters such as power input, resistance, and provides accurate high temperature control. This approach is beneficial for the purposes of understanding graphene’s thermal conductivity in an experimental manner.

Researchers have utilized molecular dynamics for understanding the thermal conductivity of graphene. Because measuring the thermal conductivity of graphene is a rather delicate and can be inconsistent between measurement methods, molecular dynamics (MD) provides a consistent method for evaluating systems at the atomic level and can complement experimental work. In previous work, researchers used classical MD with Bresnen Potential to measure the thermal conductivity of graphene nanoribbons (GNR) as a function of temperature. They found with increasing temperature, thermal conductivity increases [23]. This is the inverse relation with respect to metal’s thermal conductivity temperature dependence.

Other results from academic researchers found the thermal conductivity of few-layered graphene exceeds the thermal conductivity of bulk graphite. In fact, monolayered graphene has a thermal conductivity value of approximately 5350 W/mK. In comparison, graphite has an approximate in-plane thermal conductivity value of about 1,000 W/mK, which is five times smaller than graphene [24]. In addition, other researchers were able to make correlations between graphene flake size and thermal conductivity. Evaluating the thermal conductivity as a function of grain size, they found with the thermal conductivity of graphene films with a grain size of 5 nm is extrapolated to be 19.2 W/mK, 300 times the decrease in thermal conductivity in comparison to pristine graphene [25]. Moreover, Table
1.1 gives a few measured thermal conductivity values of graphene with accordance to other researchers.

### Table 1.1 Graphene Thermal Conductivity values analyzed by other researchers

<table>
<thead>
<tr>
<th>Method</th>
<th>$k$ (W/mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raman Spectroscopy</td>
<td>710 (at 500K) to 1800 (at 325K)</td>
</tr>
<tr>
<td>Raman Spectroscopy</td>
<td>4840 to 5350</td>
</tr>
<tr>
<td>Raman Spectroscopy</td>
<td>630 (at 660K)</td>
</tr>
<tr>
<td>Raman Spectroscopy</td>
<td>1400 (at 500K) to 2500 (at 350K)</td>
</tr>
<tr>
<td>Raman Spectroscopy</td>
<td>2600 (at 350K) to 3100 (at 350K)</td>
</tr>
<tr>
<td>Classical MD</td>
<td>3080 to 5030</td>
</tr>
<tr>
<td>Theory: relaxation - time approx.</td>
<td>1000 to 5000</td>
</tr>
<tr>
<td>Theory: valence force field, Boltzmann Transport</td>
<td>2000 to 5000</td>
</tr>
</tbody>
</table>

Though numerous studies on the thermal conductivity of graphene have been reported, the influence of external particle loading on the effective thermal conductivity has not been explored. Because significant phonon energy is transported from the out-of-plane acoustic phonon polarity (ZA-branch), the inherent mass and material mismatch of nanoparticle-decorated graphene could drastically diminish thermal transport. It is anticipated that the contact points between surface particles and graphene will serve as phonon scattering sites, decreasing the phonon mean free path and conductivity. As shown in Eq. 1.10, thermal conductivity is dependent upon the phonon free path. We hypothesize that the role of nanoparticle decoration on graphene may act in a similar capacity as an artificial boundary that locally reflects phonons. Conversely, the surface particles may act as localized impurities which would scatter phonons selectively based on their frequency

$$\tau_i^{-1} = B_i \omega^4 \quad (1.13)$$

where $B_i$ is a constant and $\omega$ is the phonon angular frequency.
Regardless of the specific scattering mechanism, surface particle decoration is expected to contribute to additional scattering. Molecular dynamics (MD) simulations will be utilized to model the phonon transport in an isolated graphene ribbon with and without external nanoparticle decoration. Further, the effective thermal conductivity of graphene will be measured on a MEMS heating and temperature sensing device. These investigations will facilitate greater insights into the fundamental transport mechanisms in decorated graphene and provide practical guidance relative to the role of graphene in nanoenergetic-graphene composite materials.
2.1 COMSOL Multiphysics: An introduction

The photothermal heating of aluminum nanoparticles (Al NPs) embedded within a low melting-temperature polymer is difficult to solve analytically. Within the system, multiple constituent martials (Al, THV polymer, Ag grating, PMMSQ layer, Si substrate) are present, polymer phase change may occur, and heat generation is determined via electromagnetic interactions with the Al NP. These complicating factors dictate that a numerical approach is necessary to determine the transient thermal response of the nanoenergetic composite material system.

In this work we used numerical methods to study photothermally heated nanoparticle simulated using COMSOL, a powerful multi-physics finite element analysis (FEA) solver. This simulation tool offers coupled systems such as Joule heating, AC/DC, electrical, heat transfer, chemical, plasma, biological, and other general physics. With the built-in interfaces and support for defining material properties, the program allows one to design models and implement the suitable physical boundaries, constraints, sources of energy such as electrical and heat fluxes, and material properties without the need to specify underlying equations [26]. Users can define their own expressions, variables, and analytical tools for analysis. A basic COMSOL window is shown in Fig. 2.1. In addition, a simple flow chart describes basic processes needed to complete a COMSOL simulation with respect to this thesis.
To begin the simulation, users have to add physics with specific sub-physics (i.e. specific areas of simulation/operation for selected physics) and then have to define the type of study for analysis. The term “study” indicates if the analysis going to be stationary/steady state, be transient/time dependent, frequency – domain, etc. Note,
COMSOL users can change/add studies during the simulation process. For the current study, the simulation used the Joule Heating Multiphysics package. Within the package, it was necessary to use the electromagnetic wave frequency domain module and the heat transfer in solids module to simulate plasmonic photothermal heating. Furthermore, the simulation was time dependent because the laser pulse was a time duration pulse.

2.1.1 Joule Heating Interface

For the current study, the “joule heating” module was utilized to convert electric fields induced by laser radiation into a volumetric heat source. Such COMSOL simulations are presented in this chapter. The joule heating physics module combines two different modules: “electromagnetic wave interface” which is part of the wave optics module, and the “heat transfer in solids” interface which is a branch of the heat transfer module.

2.1.2 Domains

COMSOL requires a user to select specific domains in which given physics packages will be applied. For example, users must select the domain(s) on which joule heating is applied, otherwise all domains are selected by default. For the current problem, each Al NP within the system is selected for joule heating. All domains were selected to experience both an electric field map and temperature change.

2.1.3 Dependent Variables

The interface node in COMSOL uses the following heat balance equation when evaluating the heat transfer in solids mathematical model:

\[
Q = \rho C_p \frac{dT}{dt} - \nabla (k \nabla T) \quad (2.1)
\]
where \( \rho \) is mass density, \( C_p \) is heat capacity, \( k \) is thermal conductivity, \( Q \) is the volumetric heat source or sink. Note that the heat conduction equation above does not contain contributions from phase change heat transfer which may occur when the local THV temperature exceeds its melting temperature. The phase change process is a volumetric process that is assumed to proceed in an isothermal manner:

\[
q = \dot{m} h_{f,g}
\]  
(2.2)

Here \( q \) is the heat transfer rate in watts, \( \dot{m} \) is the rate of mass converted from solid to liquid, and \( h_{f,g} \) is the latent heat of melting.

For Joule heating, the heating is a direct result of current flow within an object, which is input from the electromagnetic waves interface. The electromagnetic wave equation is considered within the irradiated region. This module is used to solve for time-harmonic electromagnetic field distributions. For the purposes of our work, we use the module to implement an electric field map into our model and couple the module with the heat transfer in solids module.

\[
\nabla \times \mu_r^{-1}(\nabla \times E) - k^2 \left( \varepsilon_r - \frac{j \sigma}{\omega \varepsilon_0} \right) E = 0
\]  
(2.3)

Here \( \varepsilon_r \) is the relative permittivity, \( \sigma \) is electrical conductivity, \( \varepsilon_0 \) is vacuum permittivity, \( \mu_r \) is relative permeability, \( k_0 \) is wave number, and \( E \) is the electric field strength.

### 2.1.4 Initial Values

The Initial Values node adds an initial value for the electric field that can serve as an initial guess for a nonlinear solver. All domains as required. INITIAL VALUES Enter values or expressions for the initial values of the components of the electric field, \( E \) (V/m).
The default values are 0 V/m [20]. For the initial temperature, we assume ambient room temperature, which in the case of the simulations conducted in this thesis was 20 °C.

Boundary conditions are not straightforward when attempting to simulate a many-particle system by simulating just one “representative” particle. Various boundary condition schemes were used for various different simulation approaches. Frequently, a semi-infinite THV boundary conditions were assumed, with exterior boundary temperatures held constant. To simulate the effects of neighboring particles without physically simulated a many-body problem, we assumed adiabatic boundary conditions. These boundary conditions followed from the assumption that neighboring particles produced identical heat loads as the particle of interest. Later in the thesis we will discuss the adding of modified sides to the model.

2.1.5 COMSOL Overview

In this section, a brief overview of the COMSOL Multiphysics program was introduced. If one were to have other inquiries regarding the inner workings of COMSOL, a link to a manual is provided [27]. The next section will go over the initial stages of modeling the Al/THV polymer system and do various simulation analyses.

2.2 Initial Stages of Modeling Nanoparticle Heating

To ensure our COMSOL simulations are responding correctly, isolated particles heated in liquid water were simulated. The resulting steady state temperature profile could be determined analytically and compared to previously published results. Volumetric heat generation was first computed using the electrical and optical properties of both gold and
water. The equations used to calculate the volumetric heating rate are shown in Eqs. 2.4 to 2.6. The definitions of the variables were defined in Chapter 1[16].

\[
E_0 = \sqrt{\frac{2I_0}{c_0 n}}
\]  

(2.4)

\[
Q = \frac{\omega}{8\pi} E_0^2 \left[ \left| \frac{3\varepsilon_{\text{medium}}}{2\varepsilon_{\text{medium}} + \varepsilon_{\text{particle}}} \right|^2 \right] \text{Im}_{\varepsilon_{\text{particle}}}
\]  

(2.5)

\[
\Delta T_{\text{max}}(E_0^2) = \frac{R_{np}}{3k_0} \text{Re} \left[ i\omega \left( 1 - \frac{\varepsilon(r)}{8\pi} \right) \left| \frac{3\varepsilon_{\text{medium}}}{2\varepsilon_{\text{medium}} + \varepsilon_{\text{particle}}} \right|^2 \right] E_0^2
\]  

(2.6)

For the purposes of our COMSOL simulations, one used two types of models and simulations. The first simulation uses Eqs. 2.4 to 2.5 to calculate the volumetric heat rate with respect to light intensity [16]. This approach only requires the COMSOL HT module. The second simulation approach uses the Joule Heating package. Using the HT module standalone simulation allows us to analyze the simple case of laser heating of a nanoparticle, but the coupling of both modules (Joule Heating Package) allows us to investigate more complicated cases such as our case of an aluminum nanoparticle embedded in a THV polymer with a silver grating. The geometry for the COMSOL model is shown in Fig. 2.3 where the medium is a 10 x 10 x 10 µm cube, and an 80-nm diameter aluminum nanoparticle is positioned in the center of the medium.

Figure 2. 3 The geometric model for the initial stages of simulation analysis. (A) Water medium cube (B) the isolated aluminum nanoparticle
The temperature profiles from the simulation are shown in Fig. 2.4 to 2.5 at different heating times. From the simulations in Fig. 2.4 to 2.5 the parameters regarding light intensity, nanoparticle size, temperature boundaries, and time duration used were described in the paper by Govorov [16] and shown in Tables 2.1 to 2.3. However, for Fig. 2.4, an applied volumetric heat source applied to the gold nanoparticle and an applied a temperature boundary condition of 293.15K on to the water boundary medium. For Fig. 2.5, a coupling of both EM and HT was used because this is more directly tied into to our research and simulation endeavors. The simulation results from both cases are very similar to published results.

Table 2. 1 Validation parameters for Gold NP in water medium

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold Nanoparticle ($R_{np}$)</td>
<td>30 nm</td>
</tr>
<tr>
<td>Light Intensity ($I_0$)</td>
<td>$1 \times 10^5$ W/m$^2$</td>
</tr>
<tr>
<td>Wavelength ($\lambda$)</td>
<td>520 nm</td>
</tr>
<tr>
<td>Volumetric Heat Source ($Q$)</td>
<td>$9.998 \times 10^{15}$ W/m$^3$</td>
</tr>
<tr>
<td>Initial Temperature</td>
<td>20 °C</td>
</tr>
<tr>
<td>Time Frame</td>
<td>0 to 1000 ns</td>
</tr>
</tbody>
</table>

Table 2. 2 Validation parameters for Gold NP in water medium

<table>
<thead>
<tr>
<th>Gold Material Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>thermal conductivity</td>
<td>317 W/mK</td>
</tr>
<tr>
<td>density</td>
<td>19300 kg/m$^3$</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>129 J/kgK</td>
</tr>
<tr>
<td>relative permittivity ($\varepsilon_r$)</td>
<td>$(-3.6381) + 2.6241i$</td>
</tr>
</tbody>
</table>

Table 2. 3 Water material properties used for COMSOL simulations

<table>
<thead>
<tr>
<th>Water Material Parameters (At 20 °C)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity</td>
<td>0.6 W/mK</td>
</tr>
<tr>
<td>Density</td>
<td>998.3 kg/m$^3$</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>4182 J/kgK</td>
</tr>
<tr>
<td>Relative Permittivity ($\varepsilon_0$)</td>
<td>1.8</td>
</tr>
</tbody>
</table>
Figure 2. 4 Temperature increase of an 80-nm gold nanoparticle embedded in water from (A) reference [21] and (B) from the COMSOL simulation.

Figure 2. 5 ΔT v. Distance graph from (A) the paper [21] and (B) from the COMSOL simulation using coupling of both electromagnetic and heat transfer modules.

After validating that COMSOL was accurately interpreting input electric fields and converting the electric fields into appropriate heating rates, a similar simulation was performed using different materials and parameters. The materials and parameters were changed to match experimental work for this project – namely an 80-nm diameter Al NP embedded in a THV matrix. The parameters are shown in Table 2.4 to 2.6.
Table 2. 4 Essential parameters for the case of Aluminum nanoparticle in THV

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al Nanoparticle (R_{np})</td>
<td>40 nm</td>
</tr>
<tr>
<td>Light Intensity (I_0)</td>
<td>1.35 x 10^8 W/m²</td>
</tr>
<tr>
<td>Wavelength (\lambda)</td>
<td>446 nm</td>
</tr>
<tr>
<td>Volumetric Heat Source (Q)</td>
<td>4.40 x 10^{15} W/m³</td>
</tr>
<tr>
<td>Initial Temperature</td>
<td>20 °C</td>
</tr>
<tr>
<td>Time Frame</td>
<td>0 to 1000 ns</td>
</tr>
</tbody>
</table>

Table 2. 5 Aluminum material properties used for COMSOL simulations

<table>
<thead>
<tr>
<th>Aluminum Material Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>thermal conductivity</td>
<td>238 W/mK</td>
</tr>
<tr>
<td>density</td>
<td>2700 kg/m³</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>900 J/kgK</td>
</tr>
<tr>
<td>relative permittivity (\varepsilon)</td>
<td>(-29.655) + 7.3553i</td>
</tr>
</tbody>
</table>

Table 2. 6 THV material properties used for COMSOL simulations

<table>
<thead>
<tr>
<th>THV Material Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>thermal conductivity</td>
<td>2.424 W/mK</td>
</tr>
<tr>
<td>density</td>
<td>1980 kg/m³</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>1200 J/kgK</td>
</tr>
<tr>
<td>relative permittivity (\varepsilon)</td>
<td>1.8495</td>
</tr>
</tbody>
</table>

The purpose of this simulation is not for validation of the COMSOL model with respect to thermal transient response as it is already accomplished, but rather see simulation results as it pertains to the experimental parameters for this project. Before doing so, the projected \( \Delta T_{\text{max}} \) value was computed using Eq. 2.4 and 2.6 and was found to be approximately 1.01K. To validate this calculation, two COMSOL simulations were conducted like before, one with direct heat transfer analysis using the equations from the paper and the coupling of modules.
The maximum $\Delta T$ values obtained for the simulations were 0.9 K and 1.1 K, respectively, as shown in Fig. 2.6. So, the value from both simulations are well within the range of the calculated result. In addition, from these simulations, one managed to get the behavior of the electromagnetic and the heat transfer module to work together correctly again to produce favorable results. This will be important when using the grating structure to simulate photothermal heating on a plasmonic grating system.

![Figure 2.6 $\Delta T$ v. Distance graph from (left) direct heat transfer analysis and (right) from the COMSOL simulation using coupling of both electromagnetic and heat transfer modules](image)

### 2.3 Phase Change Analysis

When the nanoparticle is generating heat from photothermal excitation, the particle may induce a THV melt zone around its perimeter. The THV melting temperature is relatively low – approximately 120 °C, and particles residing in melted THV may tend to aggregate into large clusters. In turn, the clusters will exhibit decreased absorption and reactivity. Therefore, the evolution of the melting front is important to understand the behavior of polymer and fuel nanoenergetic systems.

To estimate the behavior of an isolated Al nanoparticle embedded in THV, a cubic THV polymer domain with lengths of 10 μm was assumed to accommodate thermal diffusion
with extended simulation times. The model is initially at 25 °C to model room temperature conditions on all sides of the THV faces. The nanoparticle resides within the center of the THV polymer. Instead of keeping the aluminum nanoparticle at an 80-nm diameter, the simulation ran with different particle size variations. The purpose of the particle size variations is to simulate an agglomeration and see the effects on melting front distance and speed with respect to phase change.

For simplicity of simulating an agglomeration of nanoparticles, one increased the diameter of the nanoparticle and treated it as a condensed, close packed agglomeration. The nanoparticle underwent three different diameter changes, each with their own analysis and the different diameters are: 300, 500, and 700 nm. The nanoparticle contains both an aluminum core and an alumina shell, where the thickness for each case of the different simulations each had 1 nm thickness between the shell and core.

Using an analytical function feature in COMSOL allows one to model the laser pulse/behavior to closely match the experimental temporal irradiation. The laser irradiation is pulsed with a 31 ms duty cycle. The laser is applied for 1 ms duration, and is then off for 30 ms. Fig. 2.7 (left) shows the laser duty cycle in a graphical manner. The COMSOL analytical function tool was used to couple both the temporal and spatial distribution of the laser. Fig. 2.7 (right) shows the 3D graphical profile of the pulse intensity. Because the system returned to a constant equilibrium temperature between pulses in this simulation, the thermal response for each pulse is identical.
Additionally, using the laser fluence parameter provided by the experiment, one is able to calculate the heat flux needed to use for the COMSOL model. The maximum laser fluence value was 135 J/cm$^2$, which was converted to an energy flux rate for COMSOL simulation. Eq. 2.7 shows a dimensional analysis used for converting the laser fluence value to heat flux value. In the simulation, we applied temperature boundaries of $T = 20^\circ$C at each of the faces of the THV polymer.

$$135 \frac{J}{cm^2} \times \frac{10,000 \, cm^2}{m^2} \times \frac{1 \, ms}{1 \, s} \times \frac{1000 \, ms}{1 \, s} = 1.35 \times 10^9 \frac{W}{m^2}$$ (2.7)

Fig. 2.8 represent temperature change contour plots at 500 µs and 1000 µs, and Fig. 2.9 represent phase change contour plots at 500 µs and 1000 µs. The laser pulse follows a Gaussian temporal distribution, and at 500 µs the model showed its maximum the temperature change, phase change melting front, and speed. After 500 µs, the melting front regressed back to its original position following a gaussian pulse. Greater particle area resulted in greater energy absorption and a greater temperature increase, as expected. At
300 nm diameter, the maximum temperature is 123 °C, while at 700 nm diameter, the maximum temperature is 155 °C.

Figure 2. 8 (A) 300 nm (B) 500 nm (C) 700 nm temperature change contour plots at 500 (Top row) and 1000 (Bottom row) µs

Fig. 2.9 shows the phase change ratio of solid to liquid for the simulations corresponding to the temperature change graphs shown in Fig. 2.8. The phase change is presented as a ratio ranging from 0 to 1, where 0 indicates solid and 1 indicates fully melted material. Note, multiphase change module was not used because the COMSOL license in use for this work did not possess the module. From the figures, we see that the temperature a phase change melting front increased as the particle size increases. THV polymer undergoes phase change at 125 °C, and a phase change ratio of 0.5 is the assumed critical point between liquid and solid phases.
Figure 2. 9 (A) 300 nm (B) 500 nm (C) 700 nm phase change contour plots at 500 (Top row) and 1000 (Bottom row) µs

The melting front distance (from particle edge) and speed for each of the particle size case was analyzed to quantify the expanding melt front. Fig. 2.10 shows melting front distance and speed v. time. As the particle size increases, the melting front and speed of the melting front also increase. Note the melting front and melting speed regresses because it follows a Gaussian temporal profile with a maximum flux at 500 µs. In short, the larger the agglomeration, the bigger the temperature difference. With a larger temperature difference, one will expect to see an increase in melting front and speed accordingly.
Figure 2. 10 (A) Melting Front Distance v. Time Graph (B) Melting Front Speed v. Time Graph

Table 2. 7 Melting front distance and speed at 300 nm particle size

<table>
<thead>
<tr>
<th>Time (μs)</th>
<th>Phase Change Ratio</th>
<th>Distance (nm)</th>
<th>Speed (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>500</td>
<td>0.516253191</td>
<td>197.0791544</td>
<td>0.000394158</td>
</tr>
<tr>
<td>1000</td>
<td>0.30992691</td>
<td>149.5</td>
<td>0.0001495</td>
</tr>
</tbody>
</table>

Table 2. 8 Melting front distance and speed at 500 nm particle size

<table>
<thead>
<tr>
<th>Time (μs)</th>
<th>Phase Change Ratio</th>
<th>Distance (nm)</th>
<th>Speed (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>500</td>
<td>0.500792532</td>
<td>538.678303</td>
<td>0.001077357</td>
</tr>
<tr>
<td>1000</td>
<td>0.500810585</td>
<td>484.1567964</td>
<td>0.000484157</td>
</tr>
</tbody>
</table>
Table 2. 9 Melting front distance and speed at 700 nm particle size

<table>
<thead>
<tr>
<th>Time (µs)</th>
<th>Phase Change Ratio</th>
<th>Distance (nm)</th>
<th>Speed (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>500</td>
<td>0.503828522</td>
<td>994.5202313</td>
<td>0.00198904</td>
</tr>
<tr>
<td>1000</td>
<td>0.501574611</td>
<td>791.544973</td>
<td>0.000791545</td>
</tr>
</tbody>
</table>

2.4 Boundary Resistance

In this section we will utilize a simple study of the interfacial thermal resistance between an Al NP and surrounding THV. Interfacial thermal resistance, also known as thermal boundary resistance (TBR), is the measure of an interface’s resistance to thermal energy flow arising from dissimilar material properties [29]. Because of the differences in electronic and vibrational properties in dissimilar materials, when an energy carrier (phonon or electron) attempts to cross the interface, it may be impeded and scatter at the interface [30]. The probability of transmission after scattering is dependent on the material properties on both sides of the interface.

The thermal resistance at the interface between the Al NP and THV is of interest because a relatively high heat flux is generated by the Al NP heating and because the material mismatch between Al, Al₂O₃, and THV is substantial. The Acoustic Mismatch Model (AMM) was utilized to examine the effects of TBR. The model is based only on phonon transport, so contributions from electrical transport are neglected in the current analysis. Also in AMM, we assume the interface to be perfect, resulting in no scattering and this allows phonons to travel with ease across the interface.

For the AMM, a thermal resistance simulation consisting of an isolated Al nanoparticle (40 nm in radius) with an aluminum oxide thickness of 1 nm, which was
embedded within a THV polymer domain (10 x 10 x 10 µm). The model is shown in Fig. 2.11. The goal of this simulation ultimately is to see the effects of temperature differences ($\Delta T$) between dissimilar materials as a result of varied thermal boundary resistance ($R_b''$) with a fixed heat flux value ($q''$). The relationship is represented by Fourier’s law:

$$q'' = \frac{\Delta T}{R_b''} \quad (2.8)$$

Figure 2.11 The geometric model for the initial stages of simulation analysis. (A) THV polymer cube (B) the nanoparticle (C) The Alumina Shell and Aluminum Particle distinguished

In our model, the TBR can be estimated between the materials of aluminum, aluminum oxide, and the THV polymer. Teflon properties were assumed to represent THV polymer because the properties are very similar to each other, and Teflon properties are much more readily available. The acoustic mismatch model, outlined in Eqs. 2.9 to 2.14, predicts the thermal boundary resistance between dissimilar materials.

$$t_{12} = 1 - \frac{4v_1 v_2}{(v_1 + v_2)^2} \quad (2.9)$$

Here $v_1$ and $v_2$ are speed of sound for two different materials, and $t_{12}$ is the transmittance between materials. The transmittance represents the fraction of energy transmitted from material 1 to material 2 at the interface and is used to compute the boundary resistance below.
\[ R_b'' = \left( \frac{1}{2\pi} \sum_p \int_0^\infty M_{dd}(\omega) \frac{k\omega}{2\pi} t_{12}(\omega) \frac{\partial f_{BE}}{\partial T} d\omega \right)^{-1} \]  

Equation 2.10

Here \( R_b'' \) is the thermal boundary resistance, \( M_{dd}(\omega) \) is the mode density function, \( \hbar \) is the reduced Plank’s constant, \( f_{BE} \) is the Bose – Einstein distribution, and \( T \) is temperature. The phonon mode density is a term that incorporates phonon density of states, group velocity, and area and physically represent the number of phonon modes that may fit within the cross section of a material.

\[ M_{dd}(\omega) = A\pi \left( \frac{v_g(\omega)}{2} D(\omega) \right) \]  

Equation 2.11

Here \( A \) is area at the interface between materials one and two, \( v_g(\omega) \) is the group velocity, and \( D(\omega) \) is the density of states, which is represented in Eq. 2.12

\[ D(\omega) = \frac{3\omega^2}{2\pi^2 v_d^3} \]  

Equation 2.12

Here \( \omega \) is the angular frequency, and \( v_d \) is the Debye velocity. Eq. 2.13 represents the volumetric heat capacity.

\[ C_v(\omega) = \sum_p \int_0^\infty \frac{\hbar \omega}{2\pi} D(\omega) \frac{\partial f_{BE}}{\partial T} d\omega \]  

Equation 2.13

Here \( C_v(\omega) \) is the volumetric heat capacity. Substituting Eqs. 2.9, 2.11 - 2.13 into Eq. 2.10 leads to Eq. 2.14

\[ R_b'' = \frac{4}{t_{12}} \left( \frac{1}{\rho_1 C_{v1} v_1} + \frac{1}{\rho_2 C_{v2} v_2} \right) \]  

Equation 2.14

Now, using Eq. 2.15 we can calculate temperature difference with a given heat flux (\( q'' \)).

\[ \Delta T = q'' R_b'' \]  

Equation 2.15

Table 2. 10 Material properties for thermal boundary resistance calculations

<table>
<thead>
<tr>
<th>Property</th>
<th>Aluminum</th>
<th>Alumina</th>
<th>Teflon</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_p ) (J/kgK)</td>
<td>900</td>
<td>880</td>
<td>1200</td>
</tr>
<tr>
<td>density (kg/m(^3))</td>
<td>2700</td>
<td>3950</td>
<td>2200</td>
</tr>
<tr>
<td>speed of sound (m/s)</td>
<td>6320</td>
<td>9900</td>
<td>1400</td>
</tr>
</tbody>
</table>
To calculate the temperature difference between the aluminum nanoparticle and the surrounding medium, we may consider this problem as a thermal resistance circuit in which the materials are in series with each other. Since the particle is generating heat, the heat flux is directed from the Al to Al$_2$O$_3$ to Teflon sequentially. The circuit shown on the right side of Fig. 2.12 considers only the thermal boundary resistance from Al to Al$_2$O$_3$ and then Al$_2$O$_3$ to Teflon and neglects the thermal resistance due to conduction. Utilizing the properties provided in Table 2.10, the boundary resistance from Al to Al$_2$O$_3$ and from Al$_2$O$_3$ to Teflon are $7.73 \times 10^{-9}$ and $2.12 \times 10^{-9} \frac{m^2K}{W}$ respectively.

![Diagram of thermal resistance circuit](image)

**Figure 2.12 Diagram of thermal resistance circuit**

In a series circuit, the equivalent resistance is equal to the sum of all resistances within the circuit. Therefore, it is appropriate to add the boundary resistances together to obtain an equivalent resistance of approximately $9.85 \times 10^{-9} \frac{m^2K}{W}$. Finally, to calculate the temperature difference from aluminum to Teflon, Eq. 2.15 is utilized with $q''$ equal to the laser heat flux of the experiment, which is $1.35 \times 10^9$ W/m$^2$. After calculating the temperature difference, a temperature drop of approximately 13.3 K is computed as a result of the boundary resistance alone.
Figure 2. 13 Temperature v. Distance Simulation with varying thermal resistances at 1000 µs, which is the time interval at which the experimental laser used for this project ended.

The computed boundary resistances were input into COMSOL to run a more robust simulation. The COMSOL model predicted a temperature difference of 11.83 K, similar to the analytical hand calculations. Note that hand calculations assumed Teflon properties, while THV properties were utilized in COMSOL. Because the acoustic mismatch model is an idealized model that is utilized as an approximation, values of TBR that are an order of magnitude greater and lower than the calculated value were examined. If the experimental TBR is an order of magnitude greater, the temperature difference across the interface rose to greater than 60K. We conclude that thermal boundary resistance has a modest effect on the thermal transport on the Al/THV polymer system.

Table 2. 11 Simulation Outputs for different Thermal Boundary Resistances

<table>
<thead>
<tr>
<th>TBR (m²K/W)</th>
<th>ΔT (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00E-07</td>
<td>60.37</td>
</tr>
<tr>
<td>9.85E-09</td>
<td>11.83</td>
</tr>
<tr>
<td>1.00E-11</td>
<td>6.524</td>
</tr>
</tbody>
</table>
CHAPTER THREE

Photothermal Heating COMSOL Model

3.1 Introduction

After performing validation, phase change, and thermal resistance simulations, we move to actually designing the COMSOL model for comparison to the experimental work. In the new model, we incorporate the plasmonic grating to the geometry as well as the electric field map to go along with the model. With respect to the new model, we will conduct a validation of the thermal model by comparing a flat substrate geometry with our silver grating model. Further, the COMSOL will demonstrate its broad functionality for transient thermal analysis for composite polymer nanoenergetic systems.

3.2 Implementation of Electric Field into COMSOL Model

To simulate the temperature response of Al nanoparticles irradiated by an external laser, the resultant electric field experienced by the Al nanoparticle was imported from an external software package. To obtain the electric field response of an Al nanoparticle to external laser irradiation, RSoft Finite-difference Time-domain (FDTD) analysis using FullWave was used. Based on the Rsoft simulations, the light intensity enhancement of a particle residing on the groove of the grating compared to a particle residing on a flat substrate is found to be $\left| \frac{E_{\text{grating}}}{E_{\text{flat}}} \right|^2 = \left( \frac{8.1}{6} \right)^2 = 2$ times greater than that produced by an Al NP residing on a flat silver substrate. This E-field enhancement results in the enhancement of photothermal heating of Al NPs.
After computing an electric field using the RSoft simulation, the data was then converted to a 3D matrix of dimensions 241 x 241 x 109. To assign coordinates to the electric field produced in RSoft, a MATLAB code was generated. Placement was validated using an interactive slice plot of the RSoft data. This can be shown in Fig. 3.2A and B shows a single plane showing the electric field around the nanoparticle from the RSoft simulation.
If we compare to electric field generated in the RSoft simulation, which is shown in Fig. 3.1, we see that Figs. 3.2 show the same features as Fig. 3.1. So, we have confidence that MATLAB structured the data right for exporting the values into COMSOL. The validation was needed to ensure we can import and export data into MATLAB and COMSOL correctly.

### 3.3 Plasmonic Grating v. Flat Silver Substrate Comparison

After importing the electric field into COMSOL, the electric field was imprinted onto a fixed geometry. The settings for the model are shown below and the geometry of the models are represented in Fig. 3.3. To get a baseline of our model and prove the theoretical hypothesis that the plasmonic grating should enhance the heat generated by the nanoparticle, two models were created. The first was a flat silver substrate model and the second was a plasmonic grating model. The electric fields were imposed on both respectively and the geometry for both matches the respected electric field map.

**Electric Field Coordinate Settings based on RSoft FDTD specifications**
- X coordinates = (-0.6) to 0.6 um with 0.005 um spacing
- Y coordinates = (-0.6) to 0.6 um with 0.005 um spacing
- Z coordinates = (-0.12) to 0.42 um with 0.005 um spacing

**Geometry and Material Settings**
- Silver Grating = 100 nm thickness, 1.2 µm width
- Flat Silver Substrate = 100 nm thickness, 1.2 µm width
- Alumina Layer = 10 nm thickness, 1.2 µm width
- THV Polymer Layer = 420 nm thickness and 1.2 µm width
- Aluminum Nanoparticle (0, -0.2, 0.06) µm
**Thermal Boundary Conditions**
- All vertical faces are at initial temperature = 20°C
- Top face experiences convection with $h = 10 \text{ W/m}^2\text{K}$ and temperature = 20°C
- Bottom face is insulated

**Power Density and Light Intensity Applied**
- Laser Power = 1150 mW
- Light Intensity = $1.35 \times 10^9 \text{ W/m}^2$

Figure 3. COMSOL Geometry (A) Flat Silver Model (B) Plasmonic Grating Model

To match the experimental setup as close as possible, the time frame for this transient analysis was 1 ms. After running the simulation for 1000 µs for both models, the results are shown in Fig. 3.4 – 3.5. The maximum temperature of the nanoparticle was 25.9°C and 137°C for the flat silver and plasmonic grating, respectively. The initial temperature was 20°C for both. Additionally, a temperature v. power graph and table are shown in Fig. 3.5 and Table 3.1. The trends show that the plasmonic grating does enhance the overall heating of the nanoparticle.
Figure 3. 4 Surface Temperature Map (A) Flat Silver Substrate (B) Plasmonic Grating Substrate.

Table 3. 1 Temperature v. Power Single Isolated Particle with different substrates in steady state

<table>
<thead>
<tr>
<th>Power (mW)</th>
<th>Flat Silver Temperature (°C)</th>
<th>Plasmonic Grating Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>255</td>
<td>21.3</td>
<td>70</td>
</tr>
<tr>
<td>1150</td>
<td>25.9</td>
<td>137.41</td>
</tr>
<tr>
<td>1500</td>
<td>27.73</td>
<td>146</td>
</tr>
</tbody>
</table>

Figure 3. 5 Isolated Particle Temperature v. Power Graph Flat Silver v. Plasmonic Grating in steady state
3.4 Single v. Two Particle Simulation

The next simulation involves simulating the temperature response of single, two, and six-particle systems. The settings for the model are shown below and the geometry of the models is shown in Figure 3.6. To simulate significantly larger physical boundaries, anisotropic THV media was considered.

**Electric Field Coordinate Settings based on RSoft FDTD specifications**
- X coordinates = (-0.6) to 0.6 um with 0.005 um spacing
- Y coordinates = (-0.6) to 0.6 um with 0.005 um spacing
- Z coordinates = (-0.12) to 0.42 um with 0.005 um spacing

**Geometry and Material Settings**
- Silver Grating = 100 nm thickness, 1.2 µm width
- Alumina Layer = 10 nm thickness, 1.2 µm width
- THV Polymer Layer = 420 nm thickness and 1.2 µm width
- Aluminum Nanoparticles = 80 nm in diameter

**Thermal Boundary Conditions**
- All vertical faces are at initial temperature = 20°C
- Top face experiences convection with h = 10 W/m²K and temperature = 20°C
- Bottom face is insulated

**Power Input and Light Intensity Applied**
- Laser Power = 1150 mW
- Light Intensity = 1.35E9 W/m²

**Time Interval**
- 0 to 100 µs with 1µs increments
Figure 3.6 (A) Geometry. Anisotropic properties applied in (B) X direction (C) Y direction

The front, back, left, and right faces join with materials with altered “effective” properties to simulate a material with a thickness that is 100x the physical thickness. For example, if one wanted to impose a 10-μm system onto a 1-μm system, one takes the original thermal conductivity of the THV polymer and divide it by 10. Moreover, one had to also multiply the density of the material by 10 to capture an equivalent transient response.

To calculate the modified values for thermal conductivity and density, we consider equivalating the thermal resistance and thermal capacitance. Assuming the thermal resistance is pure conduction, we equivalate the actual resistance with a simulated resistance. The actual resistance in the model of interest in this simulation is 100 μm in length and our simulated resistance is 1 μm in length. Eq.’s 3.1 to 3.3 show the derivation for the simulated thermal conductivity value.

\[
R_{actual} = R_{sim} \quad (3.1)
\]

\[
\left(\frac{L}{kA}\right)_{actual} = \left(\frac{L}{kA}\right)_{sim} \quad (3.2)
\]
\[ k_{\text{sim}} = k_{\text{actual}} \left( \frac{L_{\text{sim}}}{L_{\text{actual}}} \right) \] (3.3)

Here \( R_{\text{actual}} \) is the actual resistance, \( R_{\text{sim}} \) is the simulated resistance, \( L \) is the length, \( k \) is the thermal conductivity, and \( A \) is the cross-sectional area. After considering the equivalent resistance, we also consider the equivalent capacitance to find the equivalent density for this simulation. Eq.’s 3.4 to 3.6 show the derivation.

\[ C_{\text{actual}} = C_{\text{sim}} \] (3.4)

\[ (c\rho V)_{\text{actual}} = (c\rho V)_{\text{sim}} \] (3.5)

\[ \rho_{\text{sim}} = \rho_{\text{actual}} \left( \frac{L_{\text{actual}}}{L_{\text{sim}}} \right) \] (3.6)

Here \( C_{\text{actual}} \) is the actual capacitance, \( C_{\text{sim}} \) is the simulated capacitance, \( L \) is the length, \( V \) is the volume, and \( p \) is the density.

The temperature response of a one- and two-particle system are shown in Figs. 3.7 – 3.8, respectively, after 100 \( \mu \)s (when the system reaches steady state) of a laser power irradiation of 1150 mW. Again, an electric field was generated from the Rsoft program for the two-particle system. The maximum temperature for this time frame for the 1 and 2 particle systems was approximately 280 and 340 °C, respectively. Based on thermogravimetric analysis (TGA) data, this temperature is insufficient to react the particles and initiate combustion. Note, the phase change module simulating solid to liquid was used in these simulations.
Figure 3. 7 One Particle Surface Temperature plots at 250 µs A) Full map B) Close up of particle

Figure 3. 8 Two Particles Surface Temperature plots at 250 µs A) Full map B) Close up of particles

The temperature v. time graphs for each system is described in Fig. 3.9, which the time interval ran from 0 to 100 µs. Due to the lack of resolution of being able to see the time interval at which the simulations behaved before reaching steady state, a second simulation was performed to show this time interval (0.1 to 0.5µs). The single and double particle systems level out and become steady state after a few microseconds. Reducing the
time scale from microscale (Fig. 3.9A) to nanoscale (Fig. 3.9B) increased temporal resolution; however, the temperature ramp rate is unphysical and seemingly incorrect.

![Figure 3.9 Left) Temperature v. Time for 1, 2, and 6 particle systems with a maximum time of 100 µs Right) Temperature v. Time for 1 and 2 particle systems with a maximum time of 0.2 µs](image)

Previous users of COMSOL have experienced unrealistic transient response when simulating nanoparticles heating. One such group used a continuous xenon light source is used for photonic sintering of nanoparticles [39]. Their simulation was similar to the current simulation in that they used an electromagnetic coupling of the Wave Optics module and the Heat Transfer in Solids module to simulate the effects of photo sintering on silver nanoparticles in a transient response. Taking a figure from their paper, which is shown in Fig. 3.10, their constant heating model or temperature v. time trend reacted in the same manner as the temperature v. time trend shown in Figs. 3.8 – 3.9. Their particles reached steady state much faster than anticipated in comparison to experimental work, similar to results in the current nanoenergetic study.
Figure 3. 10 Temperature v. Time Graph from the paper, On the self-damping nature of densification in photonic sintering of nanoparticles [39]

If we consider the Eq. 3.7, and assume a fixed heat energy input (Q) with fixed specific heat ($c_p$) and a mass proportional to an 80-nm diameter, we can then rearrange the equation and solve for the change in temperature ($ΔT$).

\[ Q = mc_p ΔT \]  

(3.7)

Based on Eq. 3.7, a smaller mass will lead to a larger temperature difference. Putting this into context with heat rate, with the nanoparticles mass being so light due it being nanoscale, the nanoparticles will achieve steady state temperature faster than it would with a larger mass or bulk system. In addition, we assume there must be a numerical flaw in the COMSOL program, as the program should ultimately be able to recognize these changes in material properties in the nanoscale and account for these changes in calculations. Nevertheless, the COMSOL technical flaw along with the light mass affecting temperature change are explanation of why the heat rates were magnitudes higher
in the simulation with the one and two particle systems and the heating of the silver nanoparticles with respect to Fig. 3.10.

3.5 Theoretical Calculation for Achieving the Ignition Temperature

Aside from running a one and two particle system, the ultimate goal is to find the minimum number of nanoparticles needed to reach combustion temperature within the Al NP and THV system described above. A mathematical model is necessary before running more COMSOL simulations. Though one can run simulations through a trial and error system to get the values relating to the experimental work, it is not an effective method. We desired an analytical model that would help estimate how many particles will reach ignition temperature based on the incident laser fluence. If we wanted to vary the system for scientific inquiries, a mathematical model would help relay a guideline prediction based on material properties and laser fluence. This section will primarily refer to the experimental work relating to this project as a guide to how the mathematical model takes shape.

In the experiment, Al NPs are assumed to reside near the plasmonic grating. The plasmonic microchip used in this study is made of a 100-nm silver thin film covered with 10 nm layer of alumina, and the silver is deposited on a 100 nm PMSSQ grating structure which resides on a 1 mm thick glass slide. From experimental TGA results, the ignition temperature was approximately 470 °C. In ignition experiments, the laser beam is distributed as an ellipse with the fluence in the central region, \( J_c \), represented by

\[
J_c (J/m^2) = 1.25 \times 10^6 \cdot P (mW) \cdot t (s) \tag{3.8}
\]
where \( P \) is the laser power, and \( t \) is a pulse time. The absorbed energy absorbed by a nanoparticle \( (E_{np}) \) may then be expressed as

\[
E_{np} = J_c \sigma_{abs}
\]  

(3.9)

Here \( \sigma_{abs} \) is the absorption cross-section of Al nanoparticle. For and 80 nm diameter Al NP in THV under 446 nm irradiation, \( \sigma_{abs} = 1.51 \times 10^{-15} \text{m}^2 \) based on COMSOL simulation.

Because the ignition temperature is dependent upon laser fluence, obtaining the threshold laser fluence is critical in determining number of particles necessary to achieve ignition temperature. A transient thermal model is considered to understand the behavior between threshold fluence \( (J_{th}) \) based upon an embedded particle and laser pulse duration.

A list of assumptions for the model may be found below.

**Assumptions:**

- Thermal diffusion through the alumina and silver is neglected because the thermal diffusivity of silver \((D = 1.66 \times 10^{-4} \text{m}^2/\text{s})\) is magnitudes larger than the THV polymer \((D = 3.4 \times 10^{-7} \text{m}^2/\text{s})\) and glass substrate \((D = 0.95 \times 10^{-7} \text{m}^2/\text{s})\).

- Due to the first assumption, the thermal diffusion is prevalent with glass and THV. For simplicity, a composite average thermal diffusivity can be representative of glass and THV, which the value is \((D = 1.5 \times 10^{-7} \text{m}^2/\text{s})\).

- An Al NP is both embedded in an infinite conductive media and undergoing a constant heat loading, the temperature response can be found in a Green’s function approach shown in Eq. 3.10

\[
T(r,t) = \frac{a}{4\pi kr} erf c \left( \frac{r}{\sqrt{4Dt}} \right) - T_0
\]  

(3.10)
where \( q \) is constant heat absorption rate, \( k \) is thermal conductivity of THV, \( r \) is the distance away from Al nanoparticle center, \( D \) is average thermal diffusivity, \( t \) is pulse time and \( T_0 \) = initial temperature.

Now if we assume that the Al NP is subjected to a constant heating rate, we can calculate the total energy and derive the threshold fluence. The steps are outlined below.

\[
Q = Pt \tag{3.11}
\]

\[
Q = \alpha J (\pi r_0^2) E^2 \tag{3.12}
\]

\[
E^2 = \left( \frac{E_{\text{grating}}}{E_{\text{background}}} \right)^2 \tag{3.13}
\]

where \( Q \) is total heat energy, \( P \) is power, \( t \) is pulse time, \( J \) is laser fluence, \( r_0 \) is radius of Al NP, \( E \) is the electric field calculated from the ratio between \( E \)– field grating and \( E \)– field background of system. Combining the above equations into the Green’s function \( T(r, t) \), we can solve the threshold fluence needed for ignition temperature and this is expressed below.

\[
J_{th} = \frac{4k(T_{reaction} - T_0)}{\alpha r_0 E^2} \frac{t_p}{t_p} \frac{1}{erfc\left( \frac{r_0}{\sqrt{4Dt_p}} \right)} \tag{3.14}
\]

where \( J_{th} \) is the threshold laser fluence, \( T_{reaction} \) is the temperature at which combustion occurs, \( t_p \) is the pulse time require to initiate reaction, and \( r_0 \) is the outer radius of the Al NP. With the threshold fluence derived, we can make a relationship between pulse duration, laser fluence, and electric field enhancement needed for combustion temperature. Because the incident of light interacts with the grating, the electric field ultimately is enhanced due to SPR as mentioned before. Fig. 3.11 displays the relationship. The figure on the left is threshold fluence v. pulse time for an individual particle, while the figure on
the right is the threshold fluence v. pulse time for a six-particle system in contact with each other (configuration is on the graph).

Figure 3. 11 Laser Fluence v. Pulse Time (Left) Single Particle (Right) Six particle System

For brevity, the dashed lines shown on the graph and the legend represent the laser fluences used for experimental work, while the solid lines represent the calculated threshold fluence as a function of electric field enhancement and pulse time. As one can see, an increase in electric field enhancement from 1 to 4 or 1 to 9, the necessary threshold fluence and pulse time decreases for ignition temperature. However, a single particle not experience the experimental fluence overlap the threshold fluence. This means the laser fluence used in the experiments is not enough to ignite the Al nanoparticle. On the other hand, if we look at the six-particle graph, the threshold fluence and the experimental fluence do overlap each other at 1080 mW. This indicates that six particles are sufficient to reach ignition temperature. To further validate this rough model a COMSOL simulation of the six-particle system was examined.
3.6 Six Particle Simulation

To support the theoretical calculation for reaching ignition temperature, a COMSOL simulation for six particles was provided. The settings for the model are shown below. The geometry of the models is shown in Fig. 3.12, and how one applied the electric field data as shown in Fig. 3.13. Also, one applied anisotropic properties by adding modified sides in the x and y direction as color coated in Fig. 3.12. Explanation of how the modified sides were carried out is explained in Sec 3.4, so not necessary to outline the steps again. For calculations up to the readers to do on their own, the simulated length \( (L_{\text{sim}}) \) is 1\( \mu \text{m} \) and the actual length of interest \( (L_{\text{actual}}) \) is 100 \( \mu \text{m} \).

**Electric Field Coordinate Settings based on RSoft FDTD specifications**
- X coordinates = (-0.6) to 0.6 um with 0.005 um spacing
- Y coordinates = (-0.6) to 0.6 um with 0.005 um spacing
- Z coordinates = (-0.12) to 0.42 um with 0.005 um spacing

**Geometry and Material Settings**
- Silver Grating = 100 nm thickness, 1.2 \( \mu \text{m} \) width
- Alumina Layer = 10 nm thickness, 1.2 \( \mu \text{m} \) width
- THV Polymer Layer = 10 \( \mu \text{m} \) thickness and width
- Aluminum Nanoparticle \((0, -0.2, 0.06) \mu \text{m}\)

**Thermal Boundary Conditions**
- All faces except the bottom face are at initial temperature = 20\(^{\circ}\)C
- Bottom face is insulated

**Power Density and Light Intensity Applied**
- Power Density = 1150 mW
- Light Intensity = 1.35E9 W/m\(^2\)
Results obtained after 100 μs of heating are shown in Fig 3.14. The maximum average temperature for this time frame was for the six-particle system was approximately 704 °C. From observing the trends on the temperature v. time graph in Fig. 3.14(B) the heat rate calculated for the six-particle system $dT/dt = 1100 \, ^\circ C/\mu s$ or $1.1 \times 10^9 \, K/s$. Compared to value the heat rate found within the Gangopadhyay group, the value is magnitudes larger than it should be. With accordance to experimental work, the value was in the order of $10^4 \, K/s$. As explained earlier, due to the mass of the nanoparticle system being so light
compared to bulk material, it will reach steady state temperature faster than it would with bulk materials.

Figure 3.14 (A) Isometric surface temperature. (B) Nanoparticle Temperature v. Time

In addition to doing these simulations, one also simulated different power densities for all three (single, double, and six particle system). The results are shown below in Table 3.2 and Fig. 3.15. It is apparent that temperature increases with power input and temperature increases with number of particles. With respect to the mathematical model of relating threshold fluence to number of particles needed to reach ignition temperature, one and two Al NP systems were not enough to reach reaction temperature of 470°C with a 1500 mW laser power as can be seen from Fig. 3.15. However, with six Al NPs in contact with each other, the cluster could be ignited to reach reaction temperature with a laser power of 1080 mW. The simulated results match correlate well with the theoretical predictions from the transient heat transfer model using a Green’s function approach.
Table 3. 2 Temperature v. Power Table

<table>
<thead>
<tr>
<th></th>
<th>1 Particle System</th>
<th>Two Particle System</th>
<th>Six Particle System</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Power (mW)</strong></td>
<td><strong>ΔTmax (°C)</strong></td>
<td><strong>Power (mW)</strong></td>
<td><strong>ΔTmax (°C)</strong></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>255</td>
<td>104.7</td>
<td>255</td>
<td>121</td>
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<td>1080</td>
<td>254.5</td>
<td>1080</td>
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<td>1150</td>
<td>684</td>
<td>1150</td>
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</table>

Figure 3.15 Temperature v. Power for a 1, 2, and 6 particle systems after reaching steady state Graph

3.7. Applying Simulation Method to other Al/Polymer Projects

Because the method of implementation for simulating photothermal heating for an Al/polymer system described in this work is adaptable, another simulation was performed for another project. Here, a plasmonic grating platform is used as a fluorescence-based temperature sensor and was developed for in-situ dynamic mapping of temperature in the nanoscale due to photothermal heating of aluminum nanoparticles (Al NPs). In the work, the experimental results showed a measured temperature v. time for Al NP’s embedded in a THV polymer as shown in Fig. 3.16.
For validation purposes, an isolated 80 nm diameter aluminum nanoparticle photothermally heated on a plasmonic grating pattern was simulated using the COMSOL package for joule heating. Since the model is considering an isolated particle only, we evaluated a small area (716 nm in width, length, and height) of the experimental model so that the particle spacing was consistent with the Al nanoparticle loading density observed experimentally. The calculations and material properties can be found within the Appendix. In addition, when evaluating the simulation, we again used anisotropic properties to simulate a large-scale model with a small modeling domain. The method was described above in Sec. 3.3.

Figure 3.17 illustrates the idea of using anisotropic properties to simulate a larger physical domain. The gray material is a small domain that contains the physical THV properties. The x and z directions of the model are thermally insulated, while in the y direction the faces are at a constant temperature bound of 20°C. The insulated boundary conditions are considered because identical heating from neighboring particles is assumed.
Considering these boundary conditions, the left and right faces (in purple) of the model are joined with altered “effective” properties that are scaled to represent a boundary that is significantly larger. Doing so will allow the model to be simulated at a large-scale simulation using a smaller domain. The convenience provides a reduction in numerical calculation time from days to a couple of hours as well as providing accurate results.

Figure 3. 17 Diagram of altered and unaltered properties. (A) Close up (B) Physical Domain Model

Figure 3. 18 MATLAB (A) volumetric Slice Plot of RSoft Data (B) Single Slice Plane Plot of RSoft Data

In the model, we imposed an electrical field map simulated by FDTD, shown in Fig. 3.18. The electric field map was imported into COMSOL as a means of coupling the
electric field results into the COMSOL geometry. The simulated time for the model was 100 ms, with power inputs of 33, 60 and 200 mW. Simulation and experimental results are shown in Fig. 3.19. Note that the simulation and experimental observations are in good agreement for both the grating substrate and the flat glass substrate.

![Figure 3.19 Left) Surface temperature map at 100 ms with power 60 mW. Right) Temperature v. Power graph of an isolated particle on two different platforms and comparing them against simulation and experimental results](image)

<table>
<thead>
<tr>
<th>Power (mW)</th>
<th>Experimental Results</th>
<th>Simulation Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>ΔT_max (°C)</td>
</tr>
<tr>
<td>0</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>33</td>
<td>60</td>
<td>40</td>
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<td>58</td>
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<tr>
<td>200</td>
<td>150</td>
<td>130</td>
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</tbody>
</table>

The simulated data, which can be seen in Fig. 3.19, match experimental results very well. The maximum difference between experiment and simulation (25 °C) occurs at the greatest laser power of 200 mW. Data at lower powers is in agreement within 6 °C. Based on the simplifying assumptions provided to the simulation (an isolated nanoparticle with uniformly-spaced neighbors), the simulation provides excellent agreement to experiments.
The methodology presented in this chapter is generally applicable to polymer nanoenergetic composites. Diverse material systems may be examined by simply altering the material properties of the constituents. In its current form, the electric field experienced by the Al nanoparticles must be determined externally and imported into COMSOL. A fully integrated simulation using only COMSOL (without RSoft) was sought, however, the COMSOL EM package did not successfully generate electric fields in a similar manner as FDTD simulations. Nevertheless, the current COMSOL simulation is expected to have broad functionality for the transient thermal analysis of polymer nanoenergetic composite materials.
CHAPTER FOUR

Determining the Thermal Conductivity of Graphene and Future Work

4.1 Introduction

Exploiting a graphene substrate to rapidly spread thermal energy between Al and oxidizer nanoparticles is potentially beneficial to initiate and sustain rapid combustion. However, the potential thermal conductivity degradation of graphene by surface nanoparticle decoration is still unclear. It is anticipated that the contact points between surface particles and graphene will serve as phonon scattering sites, decreasing the phonon mean free path and conductivity. To experimentally investigate the effect, large-grain monolayer graphene will be suspended between measurement electrodes.

The thermal conductivity of Al nanoparticle-decorated graphene will be experimentally investigated using isolated graphene strips with various particles loading from 0–10% particle loading by area. Graphene flakes will be suspended on lithographically defined SOI (silicon on insulator) trenches for isolation. Platinum resistance temperature detectors (RTDs) will be deposited to the top surface of the regions between trenches to monitor graphene temperature. A resistive heater will supply a known heat load to the suspended graphene sample, while pre-calibrated RTDs will detect temperature differences across the graphene flake during heating. Although the thermal conductivity of graphene will be a function of temperature, measurements will initially be conducted near room temperature to attain the magnitude of conductivity change due to particle loading alone.
4.2 Design Parameters for the thermal conductivity experiment

Material selection for the microfabrication of the heating and temperature sense device is important to note for this endeavor. For the substrate, a silicon (Si) wafer was selected as the base substrate due to its widespread use in manufacturing processes and compatibility with microfabrication processes. An insulating layer is necessary as it is vital in terms of sensor feasibility, stability, and sensitivity. So, a thin film of silicon oxide (SiO$_2$), which is used widely in semiconductor device applications, exhibits a low thermal conductivity (1.4 W/mK) and provides the required insulation between the various temperature sensing elements and the heater as well as reduces the heat loss from the microheater to substrate.

For the microheater fabrication, platinum (Pt) is used because of its appropriate characteristics such as good mechanical properties, good linear temperature dependence, excellent long-term stability, and a confirmed manufacturing process [40]. Graphene flakes will be transferred to the substrate for testing. The graphene itself is synthesized via chemical vapor deposition (CVD) and is a commercialized graphene as provided by the Graphene Supermarket [41]. To implement the mask, the mask will be applied to the commercialized graphene substrate via photolithography because this is one of the simplest
approaches for getting our design and establishing our goals. Lastly, the geometric parameters are listed below as well as the geometric diagrams represented in Fig. 4.2 – 4.3.

**Geometry**

- Silicon layer dimensions 1 cm x 1 cm x 525 um)
- SiO$_2$ layer dimensions (1 cm x 1 cm x 285 nm)
- Graphene layer dimensions (1 cm x 1 cm x 5 Å)
- Pt Contact Pad dimensions (2 mm x 2 mm x 200 nm)
- Pt Microheater thickness (200 nm)

![Figure 4.2 Geometry for Microheater]

**Figure 4.2 Geometry for Microheater**
Figure 4. 3 Overall design of the MEMS system. Labels and dimensions are on the diagram.

Figure 4. 4 A 3D image of the MEMS system on top of the commercialized graphene

For the metal temperature sensors, the total resistance is a strong function of temperature, as shown below. R is the electrical resistance, $\alpha$ is the temperature coefficient of designated material, $\rho$ is the resistivity of designated material, L is length, t is thickness, W is width and T is temperature to be measured [42].

$$R = \frac{\rho L}{Wt} \left(1 + \alpha(T - T_0)\right)$$  \hspace{1cm} (4.1)
Heater power can be related to the length (L), thickness (t), and width (b) of these heater channels to the electrical resistivity coefficient (γ) of a certain material [42]. After considering all these equations, we derive Eq. 4.4, which is the overall equation determining, L, t, and b of our heater design. Electrical resistance is first defined as

\[ R = \frac{\gamma}{A} L = \frac{\gamma}{tb} L \]  

(4.2)

Relating this resistance to the heat power consumption, \( P \)

\[ P = \frac{V^2}{R} = \frac{V^2 tb}{\gamma L} \]  

(4.3)

where V represents the applied voltage crop across the heater. Finally, to determine the final cross section of the heater trace, the following equation is solved.

\[ tb = \frac{\gamma L P}{V^2} \]  

(4.4)

Eq. 4.4 represents the overall equation to calculate the desired geometrical design parameters for our heater. Previous experiments utilized a voltage range from 0 to 5 Volts, and used a heater power input ranging from 0 to 0.8 mW. Here we assume for platinum \( \gamma = 10.5 \times 10^{-8} \Omega m \) [43]. Assuming that one the geometric parameters (L, t or b) is to be a fixed value in regards with the experiment, we can then calculate the area of the heater and determine the appropriate dimensions from there.

For the contact pads used in the experiment, the minimum size that could be used to connect with resistive electrodes is 2 x 2 mm in size. A heat sink was added to the design to direct the heat flow through the graphene and to regulate the microchip temperature. The heat sink occupies a fairly large area in comparison to the heater and chip itself to optimize convection heat transfer. Furthermore, the minimum resolution reliably achieved by the mask aligner as approximately 20 µm in width. The entire device geometry is 2.5 cm x 2.5 cm.
4.3 Experimental Setup

For upcoming experiments, the measurement of the thermal conductivity of graphene will be completed in two parts. The first experiments will measure thermal conductivity of isolated graphene suspended on SOI trenches with measurement electrodes. After a baseline thermal conductivity is determined, with the graphene will be scarcely decorated with 80 nm aluminum nanoparticles, with a 0 to 10% loading by area. Electrical current will be supplied to the microchip heater using a precision current source. The platinum wires will act as RTDs and to sense the temperature change across the suspended graphene.

Measurements will be conducted with the intent of determining the influence of surface-decorated Al nanoparticles with respect to the effective thermal conductivity of the graphene ribbon. By applying up to ~1mW from the resistance heater, the temperature along the graphene ribbon’s length will be measured by the Pt RTD electrodes. The RTDs will be first calibrated using a closed-loop temperature controller. The spatially-resolved temperature response for different applied heat loads will be converted to a thermal conductivity using Fourier’s law (Eq. 4.5).

\[
\frac{P}{w} = k \frac{\Delta T}{\Delta x}
\]  

(4.5)

where P represents the power input to the resistance heater, w is the width of the graphene ribbon, k is the graphene effective thermal conductivity, ΔT is the temperature difference between adjacent measurement electrodes, and Δx is the linear displacement between RTD measurement electrodes. Because three measurement electrodes exist in the measurement
system, the thermal conductivity variation as a function of length because of variable particle loading may be measured.

The thermal conductivity of the as-deposited graphene will first be measured at various power inputs to provide a baseline. A low concentration (~1 wt.%) of 80 nm diameter Al nanoparticles dispersed in isopropyl alcohol will then be applied to the suspended graphene and allowed to dry. The position and size of Al nanoparticles will then be determined using SEM. The thermal conductivity measurements will then be repeated. If nanoparticle loading is not balanced between the three measurement electrodes, then variable thermal conductivity may be observed. Particle loading may be further increased by re-applying the Al nanoparticle suspension.

4.4 Microfabrication Instrumentation

To fabricate microstructures, a sequence of microfabrication processes must be performed. These processes require strenuous clean operating conditions because we want to reduce the effects of particle contaminations that can potentially compromise the functionality and performance of microfabricated devices. Microfabrication is carried out in cleanrooms to control contamination, temperature, humidity, and other external parameters [44].

4.5 Spin Coating Basics

Spin coating is commonly used in microfabrication as a method to apply precise uniform thin films to flat substrates. Fig 4.5 demonstrates the working principles for a spin coater [45]. The substrate to be coated, usually Si or SiO₂, is placed onto the chuck. Once placed onto the chuck, the sample must be secured using a vacuum. This is to immobilize
the substrate from movement. Next, a small amount of coating material on or near the center of the substrate which is either spinning at low speed (typically around 3000 rpm) or remaining static (not spinning). When the chuck rotates at high speeds, the centrifugal forces created due to rotation, usually ranges from 1500 - 6000 rpm and from seconds to several minutes.

![Spincoater diagram and schematics](image)

**Figure 4.5 Spincoater diagram and schematics [45]**

This process allows for the dispensed coating material to uniformly space out upon the substrate of interest. The thickness of the deposited film on substrate strongly depends on the balance between centrifugal forces controlled by spin speed and viscous forces determined by liquid viscosity, surface tension, and evaporation rate [46]. The use of spin coating is frequently used and essential in photolithography as it is used to deposit photoresists on substrates of interest.

### 4.6 Photolithography Summary

Photolithography is a microfabrication process in which ultraviolet (UV) light is used to transfer a desired geometric pattern onto a photomask to a light - sensitive chemical coated bulk substrate [47]. This microfabrication involves substrate cleaning,
photoresist coating, soft baking, mask alignment, exposure, and pattern development. To begin, chemical cleaning of the substrate is required to remove all traces of contamination as well as organic, ionic, and metallic impurities on the substrate surface. Next, a light-sensitive material called photoresist is applied to the surface of the substrate via a spin coater.

Following spincoating, the thin film photoresist is soft baked to remove some excess solvent from the photoresist and increase its rigidity. Note, oversoft and undersoft baking affect photolithography negatively because it degrades the resist’s photosensitivity [47]. In the current experiments, laser printed masks on transparent polymer substrates are utilized. These masks are taped to a square glass plate of 5 x 5” to ensure proper flatness. A wafer with photoresist is then placed on to the mask aligner’s vacuum chuck and positioned under the mask. Figure 4.6 shows a schematic diagram of the alignment fixture.

![Figure 4.6 Mask Aligner Schematic [48]](image)

In the current experiment, a positive mask was the most effective. With positive photoresists, UV light strategically strikes the material in the areas in which photoresist
will be removed. When the photoresist is exposed to UV light, the chemical structure changes and becomes more soluble in the photoresist developer. These exposed areas are then washed away with a photoresist developer solvent, leaving the underlying material exposed [49]. Fig. 4.7 depicts pattern formation using darkfield mask with a positive photoresist.

**Figure 4.7 Darkfield mask and positive photoresist schematic diagram [50]**

After precise alignment, the substrate with the photoresist of interest is then exposed through the pattern on the mask with an intense UV light for 8 – 15s, leading to localized chemical changes within the photoresist layer. The exposure methods are illustrated in Fig. 4.8. In the contact lithography method shown in Fig. 4.8A, the photoresist coated substrate is placed on the vacuum chuck, and the whole assembly rises
until the substrate makes contact with the mask. Due to the contact to contact interaction, high resolution is reached. However, contamination and damage of both mask and substrate are the main disadvantages of this kind of lithography.

Figure 4.8 Three Exposure Methods. A) Contact Aligner, B) Proximity Aligner and C) Projection Aligner [51]

As shown in Fig. 4.8B there is a small gap of approximately 10 µm between the mask and substrate. This is known as the proximity method and using this method results in a lower resolution and decreases the possibility of defects. In projection printing, shown in Fig. 4.8C, there is a large gap between the mask and substrate. In this method, the mask design patterns onto the mask and there is no substrate damage or mask contamination. Following the UV exposure, the sample is then placed into a developer solution. The developer used in the current study was MF-TM-319, and it was used to remove exposed or unexposed regions of the positive or negative photoresist, respectively. Finally, the
coated substrate is then washed with distilled water to remove any possible contaminants and dried with N₂ gas.

4.7 Procedure Used for Photolithography Setup

Turning on/ Equipment Setup
- Turn on blower in back of alignment machine (Power strip button)
- Turn on power supply to mask aligner (Switch power up and hit start) (must warm up for 15 minutes)
- Turn on hotplate set to 115 °C (Should read 110 °C with thermocouple)
- Turn timer on mask aligner on and set to 8 seconds
- Place UV meter on mask aligner (can be found in black case in drawer)
- Bring scope to forward position and hit cycle twice to UV Expose
- Record UV reading and log UV reading + voltage reading on power supply (Should be ≈14W/cm² and ≈74V respectively)
- Screw photo-mask into place on mask holder and screw mask holder into alignment machine and connect vacuum line to holder
- Use Acetone, Methanol, and Distilled water to wash all substrates (Piranha cleaning recommended for glass substrates)

PROCEDURE for 2µm S1813 Positive PR:
- Drop cast S1813 photoresist and spin coat at 3000rpsms for 30s (1.6µm thick)
- Heat on hotplate at 110°C for 1 minute
- Load photoresist coated sample into mask aligner and hit sub-vacuum then close the mask frame and align the sample
• Calculate exposure time from UV Power reading where time = E/P and E = 150mJ/cm² for this resist) Set this time on alignment machine (usually 11s)

• When ready, bring sample as close to photomask as possible and hit cycle twice to expose

• Place exposed sample in MF-TM-319 developer for 1 minute while agitating lightly

• Wash substrate with distilled water and blow dry with N₂

4.8 Sputtering Overview

In this work, deposition of metal thin films is needed to create the Pt micro-heater and contact pad structures. Deposition of the metal is performed using a magnetron sputtering system. In the basic sputtering process, energetic particles bombard a solid target material. These ions are generated in a glow discharge plasma, usually a noble gas such as Argon, that is situated in the proximity of the target interest. The collision between the rapidly moving ions and the targeted material result in the ejection of atoms from the target. These ejected atoms then deposit on the surface of a substrate as a thin film in the vacuum chamber [52]. Because the sputtering system is under a vacuum, the interaction between the ejected atoms and reactive gases is avoided, and the deposited material is pure and unreacted.

Magnetron sputtering is used to overcome drawbacks of basic sputtering such as unwanted substrate heating effects, low deposition rates, and low ionization rates [52]. The secondary electron motion is controlled to the proximity of the target of interest by applying a magnetic field parallel to the targeted surface. Afterwards, the magnet poles are formed so that one is positioned in the central axis of the target and another at the outer
edge of the target in the form of a ring shape pattern [52]. Fig. 4.9 shows the schematic view of the sputter chamber as described in this section.

Figure 4. 9 Magnetron Sputtering Schematic Overview [53]

4.9 Molecular Dynamics Simulation Introduction

To compliment experimental results, molecular dynamics (MD) simulations were investigated to simulate thermal transport on the nanoscale. To give an overview of Molecular dynamics (MD) simulations, they provide the ability to understand materials at a length scale where direct measurement is often difficult. It is a method of analyzing the behavior of a material at the atomistic scales and the MD simulations are numerical computations of the estimated path of an atom or molecule. Results of the simulation can be used to determine material properties, such as the case of thermal conductivity.

By definition the thermal conductivity of $k$ is defined as

$$q^" = (-k)\nabla T$$  \hspace{1cm} (4.6)
where \( k \) is the thermal conductivity, \( \mathbf{q}'' \) is the heat flux vector, and \( T \) is the temperature. The heat flux vector is defined by the amount of energy transferred in a given time through a surface of a given area which is perpendicular to the flux direction. In general, the thermal conductivity is considered a \( 3 \times 3 \) tensor because the temperature gradient is dependent upon direction.

If we take the \( z \) direction as the direction of the temperature gradient, we can define the thermal conductivity microscopically in terms of time averages [54].

\[
\lambda = \lim_{\frac{dz}{\Delta z} \to 0} \lim_{t \to \infty} \left( -\frac{\mathbf{q}''(t)}{\frac{\partial T}{\partial z}} \right)
\]  

(4.7)

Normally to calculate the thermal conductivity, all one would have to do would be to impose a temperature gradient on the simulated system, to calculate the heat flux parallel to the gradient, and to obtain the thermal conductivity through Eq. 4.7. Such calculations have been done. However, \( \mathbf{q}'' (t) \) is a quantity with large fluctuations so its averages converges slowly and large temperature gradients are needed to induce a heat flow distinguishable from the noise [54].

Therefore, a different approach is considered. Instead of solving for heat flux, we instead solve for the temperature gradient, this is otherwise known as the Muller Plathe Method. In this method, a heat flux is imposed on the system and the resulting temperature gradient is measured. The advantage is that the slow converging quantity (heat flux) is known exactly and does not need to be calculated. The temperature and its gradient on the other hand, are averages calculated over time as well as over many particles so they are better defined and converge rapidly.
To generate a heat flux, we begin by dividing our system into two regions: A hot region and a cold region. The heat flux is generated by exchanging hottest atom in the cold region with the coldest atom in the hot region. By doing so, we are periodically swapping the momenta between the coldest atom in the hot region with the hottest atom in the cold region. This increases the temperature in the hot region and decreases in the cold region over a period of time [55]. Linear momentum and kinetic energy is conserved in this process; however, the angular momentum is not conserved, but can be ignored with respect to periodic boundaries.

![Diagram of the Muller Plathe Method](image)

**Figure 4. 10 Diagram of the Muller Plathe Method**

The hottest atom in the cold section is assumed to undergo an elastic collision with the coldest atom in the hot section at regular intervals. The velocities assigned to the atoms, before collision and post-collision, are determined in the simulation. The post collision velocity of the atom in the cold section is calculated as [55]

\[
v_c' = (-v_c) + 2 \left( \frac{m_c v_c + m_h v_h}{m_c + m_h} \right)
\]

(4.8)

The velocity of the atom in the hot section is calculated as
\[ v'_h = (-v_h) + 2 \left( \frac{m_c v_c + m_h v_h}{m_c + m_h} \right) \]  
\[ (4.9) \]

where, \( m_c \) is the mass of the atom in the cold section, \( m_h \) is the mass of the atom in the hot section and \( v_c, v_h \) are the velocities of the atoms in the hot section and cold section before collision and \( v'_c, v'_h \) is the velocity of the atom after collisions. The average heat flux is determined from

\[ q'' = \frac{1}{2AN_k \Delta t} \sum_{k=1}^{N_k} \frac{1}{2} (m_h) \left( v'_h (kv_t^2 - v_h (kv_t^2)) \right) \]  
\[ (4.10) \]

where, \( q'' \) is the average heat flux flowing in the \( k \) direction, \( A \) is the cross-sectional area which is perpendicular to \( k \), \( N_k \) is the total number of time steps, \( v_t \) is the frequency of transfers in time steps. In the above equation, heat flows from both sides of the hot section to both sides of the cold section and the average of half of the exchanged. Heat flowing in each of the two directions is considered. The magnitude of heat flux and the corresponding temperature gradient can be controlled by varying the frequency of heat transfers [54]. In addition, we can calculate the local kinetic temperature between the hot and cold regions of the system as shown in Eq. 4.11.

\[ T_k = \frac{1}{3N_k k_B} \sum_{i=k}^{N_k} m_i v_i^2 \]  
\[ (4.11) \]

Here \( N_k \) is the number of timesteps, \( m \) is mass, \( v \) is velocity of the atom, \( k_B \) is the Boltzmann constant, and \( T_k \) is the kinetic temperature. Once the system is at steady state the temperature gradient can be calculated by time averaging the kinetic temperature found within the system [56].
\[ k = \left( -\sum_{\text{transfers}} \frac{m}{2} \left( \frac{v_h^2}{2} - \frac{v_c^2}{2} \right) \right) \frac{2t}{2t \left( L_x L_y \frac{\partial T}{\partial z} \right)} \]  

(4.12)

The thermal conductivity is calculated in Eq. 4.12. The sum is taken over all transfer events during the simulation time \( t \). In the orthorhombic periodic geometry of the work, the area through which heat transport takes place is the product of \( L_x \) and \( L_y \), the box lengths in x and y respectively. The factor 2 in the denominator arises from the periodicity of the arrangement. Energy can flow from the hot slab to the cold slab in two directions, effectively double the area available for the flux.

With the concepts of the Muller – Plathe method understood, a thermal simulation to determine the thermal conductivity of graphene was sought. A simulation domain of 3 x 5 nm was employed with different time steps reaching to 1,000,000 fs. The averages shown in Table 4.1 show the thermal conductivity of graphene is consistent with the work of others, with an average value of 5118.3 W/mK after 1000 ps. Fig. 4.11 and Table 4.1 shows the outputs of the MD simulation and compares to the value (5030 W/mK) to a referenced source found in literature [19]. So, there is confidence that the value from the MD code used by LAMMPS is calculating the thermal conductivity of graphene comparable to other works.
Table 4. 1 Thermal Conductivity of Graphene with different Time Steps

<table>
<thead>
<tr>
<th>Time (ps)</th>
<th>Thermal Conductivity (W/mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>4769.9</td>
</tr>
<tr>
<td>200</td>
<td>5310.2</td>
</tr>
<tr>
<td>300</td>
<td>5388.1</td>
</tr>
<tr>
<td>400</td>
<td>5362.8</td>
</tr>
<tr>
<td>500</td>
<td>5048.9</td>
</tr>
<tr>
<td>600</td>
<td>4869.7</td>
</tr>
<tr>
<td>700</td>
<td>4971.9</td>
</tr>
<tr>
<td>800</td>
<td>5371.2</td>
</tr>
<tr>
<td>900</td>
<td>5229.8</td>
</tr>
<tr>
<td>1000</td>
<td>5118.3</td>
</tr>
</tbody>
</table>

For the simulation regarding measuring the thermal conductivity of graphene with Al nanoparticles decorated on it one attempted to try to apply particles on the nanosheet at first and run a simulation for it. However, the interatomic potential between alumina and graphene is not readily available from literature. The interatomic potential is a vital
piece of information needed when running LAMMPS in order to simulate the forces acting between atoms. To get around this, a ‘Force’ command was implemented to the LAMMPS code to simulate a foreign alumina particle. If we imagine that the forces only act in the $z$ – direction, it would be similar to mass being placed on top of the graphene sheet. A visualization is given in Fig. 4.12.

![Force in z – direction (F_z)](image)

**Figure 4.12 Visualization of a force being added to a graphene sheet in the z direction**

To simulate a mass on graphene, the graphene sheet experienced a force ($F_z$) in a 0.1 x 0.1 nm area. The applied force was varied from 0 - 160 pN. The theoretical mass of a single Al NP with a diameter of 80 nm, is equal to the density ($2700 \text{ kg/m}^3$) times its volume, which is equal to $7.23 \times 10^{-19} \text{ kg}$. For the purposes of seeing changes in thermal conductivity of graphene with respect to the adding force on the sheet, one added more force than the calculated weight of a single Al NP to see the effects on the sheet. Before running the simulation, one hypothesized the constant average force added in the simulation would decrease the thermal conductivity with increasing force. The results are shown in Fig. 4.13 and Table 4.2. As hypothesized, the thermal conductivity does degrade with increasing force. Though these results are promising, they do not realistically simulate the desired system. The next step would be to simulate the van der Waals forces.
between the graphene sheet and Al NP. By doing this, we can better simulate scattering from a point particle or mass on top of the graphene sheet and measure thermal conductivity change thoroughly.

<table>
<thead>
<tr>
<th>Force (pN)</th>
<th>Thermal Conductivity (W/mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5048.9</td>
</tr>
<tr>
<td>16</td>
<td>4788.2</td>
</tr>
<tr>
<td>8</td>
<td>4715.4</td>
</tr>
<tr>
<td>16</td>
<td>3672.7</td>
</tr>
<tr>
<td>80</td>
<td>1085.7</td>
</tr>
<tr>
<td>160</td>
<td>532.5</td>
</tr>
</tbody>
</table>

Table 4. 2 Thermal Conductivity of Graphene with different Forces added

![Figure 4. 13 Thermal Conductivity v. Force for Graphene](image)

**4.10 Experiment: Two Point – Probe Measurement**

In this work, we used two-point probe measurement to characterize the electrical and thermal properties of the thin film Pt microheater and contact pads. Resistance of a uniform thin metal film is defined in Eq. 4.13.

$$R = \frac{\rho L}{A} = \frac{\rho L}{Wt}$$

(4.13)
where $\rho$ is the material resistivity, $L$ is length, $W$ is width, and $t$ is thickness of the thin film. We can also represent Eq. 4.13 as a function of sheet resistance ($R_s$) as shown in Eq. 4.14.

$$R = \frac{\rho L}{W t} = R_s \frac{L}{W}$$ (4.14)

In this work, two-point probe method is used for measuring a material’s resistance, as two voltage probes are in contact with the surface of the test material separated at a fixed distance. As shown in Fig. 4.14, current is sent by a power supply through one probe and leaves through the other probe. Further, a voltmeter is used to determine the voltage drop between the two probes. The overall material surface resistance between the probes can be calculated by combining both the voltage and current measurements as shown in Eq. 4.15 [56].

![Two-point probe arrangement for measuring the effective surface resistance.](image)

$$R_{total} = \frac{V}{I} = 2(R_w + R_c) + R_s$$ (4.15)
Here $R_{\text{total}}$ is total resistance, $V$ is voltage, $I$ is current, $R_w$ is wire resistance, and $R_c$ is contact resistance. The relationship of electrical resistance of a material and temperature can be written as

$$R(T) = R(T_0)(1 + \alpha(T - T_0))$$  \hspace{1cm} (4.16)

where $T_0$ is the ambient temperature and $\alpha$ is the temperature coefficient of resistivity, which is equal to $3.93 \times 10^{-3}$ per °C [57]. To characterize the sputtered Pt micro-heater and contact pads, the resistance was measured by gradually increasing the temperature on a hot plate using the two–point probe method in which the DC power supply is provided by the Lakeshore 336 Temperature Controller and the probes are made of gold. Furthermore, the Keithley 4200 Semiconductor Characterization System (SCS) was used to quantify the resistance with a change in temperature variation. The measured resistance for the contact pads with respect to varying temperature is shown in Fig. 4.15. Note, the microheater design had a 200-nm thickness for Pt. Additionally, Fig. 4.16 to 4.18 show the correlations between the theoretical resistance v. the measured resistance for each of the contact pads.

![Figure 4.15 Temperature v. Resistance Calibration for the contact pads](image_url)
Figure 4. 16 T v. R Theoretical and Experimental Calibration for the first contact pad

Figure 4. 17 T v. R Theoretical and Experimental Calibration for the second contact pad
Comparing the theoretical with experimental temperature dependent resistance values, the linear relationships are quite similar, though not exactly one to one correlation. The magnitudes of both theoretical and experimental correlations are within range of each of other and does not show drastic differences between the two. Moreover, the theoretical microheater resistance was calculated to be 37Ω, while the measured microheater was approximately 45Ω. Both were measured at room temperature.

4.11 Conclusions and Future Work

From this work, we simulated photothermal heating of nanoenergetic particles on plasmonic gratings. In addition, we found that the number of nanoparticles needed to reach ignition temperature of 470 °C was approximately six particles. The number of particles was found from the mathematical model derived from Chapter 3. In the COMSOL simulation’s current setup, it is expected to have broad functionality for the transient thermal analysis of polymer nanoenergetic composite materials. As shown in the end of Chapter 3, we used a similar COMSOL setup with respect to the Al/Polymer transient
system and found our simulated results were comparable to experimental results within a 6 °C difference between experimental and simulation data at lower laser powers.

For the second part of this thesis, we showed preliminary results with respect to the thermal conductivity of graphene with decorated aluminum nanoparticles. We hypothesize that with decorated Al particles, we believe the thermal conductivity of graphene will decrease. From our MD simulations, we did get thermal conductivity values that were comparable to literature work. In addition, although we did not apply Al nanoparticles onto the graphene sheet, but rather simulated a force in the z direction to represent a mass being applied to the graphene sheet. We found that with an increase in force, we decrease the thermal conductivity of graphene. Furthermore, we have designed a microheater MEMS design to experimentally find the thermal conductivity of graphene and a graphene – Al particle system.

For future work, it is hoped that we can resolve the COMSOL issue to find the heat rate of the Al particles during photothermal heating to better solidify the experimental results and confidence for published work. In addition, we hope to get more MD simulation work to show the thermal conductivity of a graphene – Al particle system. Adding to the MD simulation work, experimental data from our microheater setup is to further complement the simulation work and provide confidence in our hypothesis of the degradation of the thermal conductivity of graphene with decorated Al particles.
REFERENCES


LIST OF PUBLICATIONS

Journal Publications


Conference Proceedings

APPENDIX

A.1 Supplemental Data for Chapter 3.7

Shown in Fig. A.1, are surface temperature and temperature v. time results for a glass substrate system with respect to Chapter 3.3.7.

![Figure A.1 (Left) Surface Temperature Plot after 100 ms for Flat Glass Substrate Geometry (Right) Temperature v. Time Plot for Flat Glass Substrate Geometry](image)

Table A.1 Material Properties for Al and THV

<table>
<thead>
<tr>
<th>Property</th>
<th>Aluminum</th>
<th>THV</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass (kg)</td>
<td>0.0001</td>
<td>0.1</td>
</tr>
<tr>
<td>density (kg/m³)</td>
<td>2700</td>
<td>1970</td>
</tr>
<tr>
<td>radius (m)</td>
<td>4.00E-08</td>
<td>N/A</td>
</tr>
</tbody>
</table>

\[
volume_{np} = \frac{4}{3}\pi r^3 \tag{A.1}
\]

\[
volume_{Al} = \frac{m_{Al}}{\rho_{Al}} \tag{A.2}
\]

\[
volume_{THV} = \frac{m_{THV}}{\rho_{THV}} \tag{A.3}
\]

\[
THV_L = \sqrt{\frac{(volume_{THV} \times volume_{np})}{volume_{Al}}} + volume_{np} \tag{A.4}
\]
Here $\text{Volume}_{\text{np}}$ is the volume of the isolated nanoparticle, $\text{Volume}_{\text{Al}}$ is the volume of the Aluminum material, $\text{Volume}_{\text{THV}}$ is the volume of the THV material, $m_{\text{Al}}$ is the mass of Aluminum, $p_{\text{Al}}$ is the density of Aluminum, $m_{\text{THV}}$ is the mass of THV, $p_{\text{THV}}$ is the density of THV, and $\text{THV}_L$ is the calculated length of THV based on particle loading density.

**A.2 Supplemental Data for Chapter 4. 10**

Shown in Tables A.1 to A.3 are numerical values for the contact pad resistance values as represented from the Figs. 4.16 to 4.18.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Experimental (Ω)</th>
<th>Theoretical (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>100</td>
<td>75</td>
</tr>
<tr>
<td>310</td>
<td>104</td>
<td>78</td>
</tr>
<tr>
<td>320</td>
<td>109</td>
<td>80</td>
</tr>
<tr>
<td>330</td>
<td>110</td>
<td>83.8</td>
</tr>
<tr>
<td>340</td>
<td>110</td>
<td>86.7</td>
</tr>
<tr>
<td>350</td>
<td>112</td>
<td>89.5</td>
</tr>
<tr>
<td>360</td>
<td>114</td>
<td>92.23</td>
</tr>
<tr>
<td>370</td>
<td>116</td>
<td>95.05</td>
</tr>
</tbody>
</table>

**Table A. 2 First Contact Pad Resistance Values**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Experimental (Ω)</th>
<th>Theoretical (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>111</td>
<td>86</td>
</tr>
<tr>
<td>310</td>
<td>115</td>
<td>89</td>
</tr>
<tr>
<td>320</td>
<td>116</td>
<td>92.42</td>
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<tr>
<td>330</td>
<td>119</td>
<td>95.63</td>
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<tr>
<td>340</td>
<td>121</td>
<td>98.83</td>
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<tr>
<td>350</td>
<td>124</td>
<td>102.04</td>
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<tr>
<td>360</td>
<td>127</td>
<td>105.25</td>
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<tr>
<td>370</td>
<td>129</td>
<td>108.46</td>
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</table>
### Table A. 4 Third Contact Pad Resistance Values

<table>
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<th>Temperature (K)</th>
<th>Experimental (Ω)</th>
<th>Theoretical (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
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<tr>
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<tr>
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<td>164.55</td>
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