A STUDY OF THERMOELECTRIC PROPERTIES OF GRAPHENE MATERIALS

by

Chris Twombly
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Golden, Colorado

Date ___________________________

Signed: _________________________
Chris Twombly

Signed: _________________________
Dr. Zhigang Wu
Thesis Advisor

Golden, Colorado

Date ___________________________

Signed: _________________________
Jeff Squier
Professor and Head
Department of Physics
ABSTRACT

Graphene has very beneficial charge transport properties which make it an interesting potential thermoelectric material, but its thermoelectric efficiency is limited by large thermal conductivity. Nanostructuring graphene by incorporating periodic holes in the crystal structure produces graphene nanomesh with reduced thermal conductivity due to increased phonon scattering. The goal of this study was to investigate the thermoelectric properties of graphene nanomeshes and defected graphene using Density Functional Theory and semi-classical Boltzmann Transport Theory. We computed the Seebeck coefficient, electrical conductivity, and the electrical component of thermal conductivity from first principles. We first developed and verified the accuracy of our techniques using silicon. We then examined the properties of silicon nanowires in order to study systems with more complex geometry and to show that nanostructuring can improve thermoelectric properties. Our results agreed closely with previous experimental and theoretical studies of silicon systems. We then employed this suite of methods to study graphene, graphene nanomeshes, and periodically defected graphene. Our calculations for pristine graphene agreed closely with experimental measurements, proving that our methods work well with 2D systems. Our calculations suggest that there is up to a one order of magnitude increase in Seebeck coefficient for graphene nanomeshes compared to pristine graphene. This increase was found to be strongly dependent on a previously predicted geometrically based semimetal to semiconductor transition. We estimated a maximum ZT of 0.15-0.4 for graphene nanomeshes based on a simple scaling law for the thermal conductivity in these systems. The ZT value is strongly dependent on the purity and the quality of the graphene crystal lattice, which affects the relaxation time of charge carriers in these systems. We then studied defected graphene with partial hydrogen passivation and boron-nitride (BN) doping to further demonstrate the importance of the semimetal to semiconductor transition. We concluded that the geometrically based semimetal to semiconductor transition in graphene systems is responsible for improved thermoelectric properties, and helps explain strong disorder based reduction in efficiency reported in previous computational studies. Our study suggests that with further optimization nanostructured graphene could be a potential thermoelectric material.
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CHAPTER 1

INTRODUCTION

This chapter introduces thermoelectric materials. Section (1.1) discusses common applications of thermoelectric materials and introduces relevant physical quantities. Section (1.2) briefly reviews the history of thermoelectric materials, current research frontiers, and the beneficial properties of graphene. Section (1.3) introduces graphene nanomesh and its physical properties. Section (1.4) covers previous theoretical studies of the thermoelectric properties of graphene materials. Recent interest in thermoelectric materials comes from theoretical predictions and subsequent experimental observations that nanostructuring can be used to improve thermoelectric properties. Graphene has very beneficial charge transport properties as a potential thermoelectric material, but is limited by very large thermal conductivity. Periodic nanostructures in graphene are therefore an interesting thermoelectric material. The goal of our study was to better understand the physical properties controlling improved thermoelectric efficiency in graphene nanostructures, specifically graphene nanomesh and periodically defected graphene. To accomplish this goal, we first developed and evaluated a new multistep computational method using Density Functional Theory and Boltzmann Transport Theory using silicon as a simple model material. We applied our methods to silicon nanowires, graphene, graphene nanomeshes, and periodically defected graphene. Our study resulted in an improved understanding of some of the key parameters that should be considered in the development of graphene nanomesh as a thermoelectric material. This chapter provides information to place our study in better context.

1.1 Introduction to Thermoelectric Materials

The thermoelectric effect converts heat to electrical current through carrier diffusion along a thermal gradient. Thermoelectric based power systems have several features that make them practical choices under special environmental conditions. They have no moving parts, are very durable, require little maintenance, and can be fueled by waste heat without some of the negative environmental consequences associated with fossil fuels. However, low power output, typically less than 100 W, very high material cost, and physical or manufacturing limitations make thermoelectric devices uncompetitive with current technology. Thermoelectric generators today are limited to special physical conditions where their benefits outweigh costs, such as in deep space or remote research stations. Some typical current applications of thermoelectric materials are shown in figure 1.1.1.
The thermoelectric effect was first observed in the early 19th century by Thomas J. Seebeck. He observed deflection of a compass needle near the junction of two different metals that were unequally heated, although he incorrectly assumed that the deflection was caused by a magnetic effect. A series of descriptive constants were developed by Seebeck and other scientists to quantify the thermoelectric effect. The Seebeck coefficient, also called the thermoelectric potential or thermopower, is defined by

$$\alpha = -\frac{\Delta V}{\Delta T}$$

(1.1.1)

where $\alpha$ is the Seebeck coefficient, $\Delta V$ is the measured electrical voltage difference, and $\Delta T$ is the temperature difference or gradient between the hot and the cold sides of a thermoelectric device. The value of the Seebeck coefficient can be positive or negative, depending on the direction of current flow, and is typically measured in $\mu$V/K. Two different material-specific properties contribute to the Seebeck coefficient: carrier diffusion and phonon drag. The entropy carried by carrier diffusion through a material determines the magnitude of the Seebeck voltage difference ($\Delta V$). Phonon drag decreases the produced voltage difference ($\Delta V$) by increasing the effective mass of charge carriers. The contribution of phonon drag to the Seebeck coefficient from phonon drag is assumed to be important for some materials, but it has not been studied rigorously computationally. The Seebeck coefficient is limited near the melting point of a material because of increased phonon drag, and at extremely low temperatures because of reduced carrier diffusion.

The thermoelectric figure of merit $ZT$, is a dimensionless number that combines the Seebeck coefficient with other key physical parameters to describe the energy conversion efficiency of a material. $ZT$ is defined to be:

![Figure 1.1.1. Some sample applications of thermoelectric materials, including (a) a commercially available 20 W power generator, (b) a wine cooler, and (c) the power module used in the Cassini and New Horizons space probes.](image)
where $ZT$ is the thermoelectric figure of merit, $\sigma$ is the electrical conductivity of a material, $\alpha$ is the Seebeck coefficient, $T$ is the temperature, and $\kappa$ is the thermal conductivity. $ZT$ is the key parameter used in thermoelectric materials science and engineering to describe and compare the relative efficiency of thermoelectric materials. It is estimated that $ZT$ needs to be around 3 to make thermoelectric devices competitive with other existing technology\(^9\). Common materials such as Si and GaAs have very small $ZT$ values, much less than 0.01 at 300 K\(^8\). The two most common thermoelectric materials today, BiTe and PbTe have $ZT \sim 0.4$ at 300 K\(^10\). Recently nanostructured materials such as silicon nanowires with $ZT \sim 0.6$ at 300 K\(^11\), and quantum dot superlattice systems with $ZT \sim 1.6$ at 300 K\(^12\), have shown improved thermoelectric properties. These materials are limited by complicated manufacturing processes.

The complexity of designing efficient thermoelectric materials can be understood by examining the interdependence of key quantities used to define $ZT$. For maximum efficiency, an ideal thermoelectric material needs to have the large electrical conductivity of a metal, the high Seebeck coefficient of a semiconductor, and the low thermal conductivity of a glass\(^10\). An increase in electrical conductivity which improves efficiency, is associated with an increase in thermal conductivity which decreases efficiency. Large thermal conductivity is the key parameter limiting the efficiency in current thermoelectric devices. Current research focuses on lowering lattice thermal conductivity, while still maintaining a sufficiently high electrical conductivity and Seebeck coefficient, to produce efficient thermoelectric devices\(^10\). Thermal conductivity can be modified by material engineering to minimize phonon heat transmission. Some of the most commonly used approaches are applying mechanical strain\(^13\), doping with isotopes\(^14\), forcing complex surface interactions\(^15\), introducing crystallographic defects\(^16\), and surface roughening\(^17\).

The efficiency of thermoelectric devices is compared using $\overline{ZT}$. This is the device specific figure of merit. The efficiency is quantified using a modified Carnot cycle

$$
\eta = \frac{T_H - T_C}{T_H} \sqrt{1 + \overline{ZT}} - 1
\frac{1}{\sqrt{1 + \overline{ZT}} + \frac{T_C}{T_H}}
$$

where $\eta$ is the efficiency of the device, $T_H$ is the temperature on the hot side of a device, $T_C$ is the cold side temperature, and $\overline{ZT}$ is the device-specific figure of merit. $\overline{ZT}$ is obtained from experimental measurements of
composite device efficiency. Figure 1.1.2 shows how the efficiency of a thermoelectric device changes with varying hypothetical $\overline{ZT}$ by plotting equation (1.2.3) in terms of different temperature gradients. $ZT$ is a simplification of $\overline{ZT}$ and ignores device specific loss terms that are not necessary when comparing the relative efficiency of pure materials. $ZT$ is the key parameter used to compare the relative efficiency of a thermoelectric material in our study.

1.2 A Brief Review of Thermoelectric Materials and Current Research

The thermoelectric effect was first discovered by Seebeck in 1821-1823. Jean Peltier discovered thermoelectric cooling in 1834, the inverse of the thermoelectric effect. William Thomson (Lord Kelvin) connected the Seebeck and Peltier experiments using thermodynamics. He predicted a third physical effect (Thomson coefficient) that describes creation or absorption of heat by a material with applied current and temperature gradients. Work by Mangus, Releigh, Kohlrausch, Diesselhorst, Altenkirch, and many others led to the development of practical thermoelectric devices by the 1920s. Improvements in efficiency developed slowly. Thermoelectric devices with $ZT \approx 1$ were first developed by the 1960s. Current devices use bulk thermoelectrics developed during this period such as BiTe, which remain the most widely used materials today. BiTe is an efficient thermoelectric material because of large asymmetries in effective mass leading to improved Seebeck coefficient, lower thermal conductivity compared to other semiconductors, as well as improved electrical conductivity. The high cost and rarity of Tellurium, comparable to platinum, limits widespread use. Modern interest in nanoscale thermoelectric materials began with theoretical predictions by Hicks and Dresselhaus in 1993.
They predicted that quantum confinement of charge carriers caused by lower dimensionality could lead a one to three order of magnitude improvement in ZT using a simple two band model. This improvement was strongly dependent on confinement radius and orientation. Current research in thermoelectric materials is focused on decreasing lattice thermal conductivity to improve ZT.

The interdependence of the other components of ZT can be summarized with the Weidemann-Franz law, which demonstrates the interdependence of electrical and thermal conductivity\textsuperscript{10}

\[ \kappa_e = LT\sigma = nq\mu_e LT \]  

were L is the Lorentz factor of a material, q is the charge, n is the number of electrons, \( \mu_e \) is the carrier mobility \( \kappa_e \) is the electrical part of thermal conductivity. The Lorentz factor is a constant depending on material specifics, but for free electrons\textsuperscript{10} it is 2.4x10\textsuperscript{-8} J/(K\textsuperscript{2}C\textsuperscript{2}). Electrons in a material carry heat as well as causing electrical current. Therefore, increasing the electrical conductivity of a material leads to an increase in thermal conductivity, which have opposing effects on ZT. The interdependence of the heat and electrical current is demonstrated more completely with Onsager’s reciprocal relations:

\[ J_\rho = \sigma E - \sigma a \nabla(T) \]  
\[ J_Q = \sigma a TE - \kappa \nabla(T) \]  

Where \( J_\rho \) is the electrical current, \( J_Q \) is the heat current \( E \) is the electric field, \( \kappa \) is thermal conductivity, and \( \nabla(T) \) is the temperature gradient. Equations (1.2.1) to (1.2.3) show the full interdependence of terms controlling improvements in ZT. The heat and electrical currents in a material are coupled. Better understanding of these relationships have led to current research efforts to improve thermoelectric properties.

Current material science research is focused on lowering lattice thermal conductivity while still maintaining sufficiently high electrical conductivity and Seebeck coefficient to produce efficient thermoelectric devices.

Nanoscale thermoelectric materials are widely studied because of their reduced thermal conductivity. Several areas of active research are nanocomposite systems (BiTe, PbTe, skutterudites, half-heusler compounds, SiGe), thin film quantum wells, quantum dots, quantum dot superlattices, and nanowires, and graphene based systems.

One promising area of active research in thermoelectric materials are nanocomposite systems. Nanocomposite materials are composed of small crystallites combined into a larger structure. Nanocomposite systems have extremely low thermal conductivity. These materials are limited from widespread application by high cost, rarity of component elements, and poor scalability of processing techniques. Bismuth telluride alloys have been
used to produce nanocomposite systems. Poudel et al.\textsuperscript{30} in 2008 were able to produce a bismuth antimony telluride (Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\)) by ball milling pure crystalline ingots and hot pressing the resulting powder to produce loosely fused nanocrystal composites with an average particle diameter of approximately 20 nm. This method produced devices with a maximum ZT of 1.4 at 373 K. These materials have lower thermoelectric efficiency at lower temperatures (<320 K), with ZT=1.1 at 300 K due to low electrical conductivity. Xie et al.\textsuperscript{31} produced thermoelectric devices using Bi\(_{0.52}\)Sb\(_{1.48}\)Te\(_3\) using melt spinning and quick spark plasma sintering, giving a maximum ZT at 300 K of 1.56. Xie et al. found that controlling the grain size and maintaining coherent grain boundaries was critical to improvement of the thermoelectric properties of bismuth based nanocomposites. Maintaining grain boundaries between nano-crystallites was thought to strongly decrease lattice thermal conductivity, while crystallite fusion better maintains the large Seebeck coefficient and electrical conductivity of bulk BiSbTe. This was further supported by Fan et al.\textsuperscript{32} who produced a partial nanocomposite composed of approximately 60% large micron sized crystal fragments and 40% dispersed nanoparticles smaller than 200 nanometers. They were able to observe ZT=1.8 at 316 K. They observed approximately the same electrical conductivity and Seebeck coefficient values as bulk bismuth telluride, while maintaining the low thermal conductivity of traditional nanocomposites.

Nanocomposite materials have been produced using other elements. Lead telluride and lead selenide nanocomposite have been studied as potential high temperature thermoelectric materials. Bulk lead telluride has ZT~0.76 at 740 K. It is widely used in industry for high temperature applications. Industrial AgPbSbTe systems\textsuperscript{8} typically have ZT~1.2 at approximately 800 K. Lead telluride and lead selenide have been used to make several interesting nanocomposite systems. Hsu et al.\textsuperscript{33} in 2004 were able to produce high quality AgPb\(_{18}\)Sb\(_{20}\)Te\(_3\) crystals that have ZT=2.2 at 800 K using a melt growth crystal process. At 300 K lead telluride and lead selenide systems are much less efficient, with ZT=0.4. These nanocrystals act as phonon scattering sites and the lower lattice thermal conductivity of the overall superlattice system. Wang et al. in 2014\textsuperscript{34} achieved similar ZT improvement with sodium doping in PbSe materials, where the sodium dopant acts as a phonon scattering site inside a crystal lattice. Biswas et al.\textsuperscript{35} combined 2-10 nm SrTe monocrystalline inclusions and sodium doping in lead telluride to improve ZT. This produced material with maximum ZT=2.2 at 915 K.

Skutterudites, naturally occurring cobalt arsenide minerals, are potential thermoelectric materials because of low thermal conductivity, have been used to produce nanocomposite thermoelectric devices. The low thermal conductivity measured in bulk skutterudites is believed to be caused by the “open” crystal structure, combined with
“loose” atoms that dramatically increases low frequency phonon scattering\textsuperscript{36–40}. The most efficient nanocomposite skutterudite thermoelectric device was developed by Shi \textit{et al.}\textsuperscript{39} in 2011. They produced a Ba$_{0.08}$La$_{0.05}$Yb$_{0.04}$Co$_4$Sb$_{12}$ nanocomposite using ball milling and hot pressing. This gives a maximum ZT=1.7 at 850 K. At present skutterudites are not efficient enough to be competitive against lead telluride systems in the same temperature range.

Half-heusler compounds are a ferromagnetic alloys that contains a double exchange mechanism between ions. They have very high thermal stability and large Seebeck coefficient, and high thermal conductivity. The high thermal conductivity of half-heusler materials can be reduced by producing nanocomposite systems. Joshi \textit{et al.}\textsuperscript{41} in 2012 studied Hf$_{0.5}$Zr$_{0.25}$Ti$_{0.25}$NiSn$_{0.99}$Sb$_{0.01}$ and produced a nanocomposite using ball milling and hot pressing. Yan \textit{et al.}\textsuperscript{42} was able to produce a Hf$_{0.8}$Ti$_{0.2}$CoSb$_{0.8}$Sn$_{0.2}$ nanocomposite using arc melting, ball milling and hot pressing. Both materials have similar thermoelectric efficiency, with maximum ZT=1 at high temperatures, 773 K and 1073 K. This suggests that half-heusler compounds could make interesting high temperature thermoelectric devices but are not currently competitive with PbTe and PbSe.

Bulk SiGe were used to build thermoelectric generators in spacecraft\textsuperscript{43} such as Voyager 1 and 2. Bulk Si$_{0.8}$Ge$_{0.8}$ has been used to produce devices with ZT between 1 and 0.6 depending on the doping and temperature range. Wider application is limited by high production cost. Bulk Si-Ge alloys have high thermal stability similar to half-heusler materials. There has been interest in using nanocomposite Si-Ge to decrease the thermal conductivity and hopefully produce more efficient devices. This was demonstrated by Wang \textit{et al.}\textsuperscript{44} and Joshi \textit{et al.}\textsuperscript{45} in 2008. They were able to build a nanocomposite using high energy ball milling and hot pressing. This method produced maximum efficiency values at 1173 K of ZT=1.3. These materials could be used to produce very high temperature thermoelectric devices in future.

Thin film thermoelectric materials have been built using periodically aligned quantum dots. Thin film quantum dot structures have low thermal conductivity compared to bulk materials\textsuperscript{46}, leading to improved ZT. The first studies of thin film nanostructures to improve thermoelectric efficiency were carried out by Harman \textit{et al.}\textsuperscript{47} in 1996, who first produced thin film nanostructure thermoelectrics, measured BiTe based devices with ZT=1.23 at 300 K. Custom optimized thin film bismuth telluride nanostructures were built by Venkatasubramanian \textit{et al.}\textsuperscript{12} that show high thermoelectric efficiency at room temperature. They reported ZT=2.4 for small individual structures on the order of 20-40 Å on a side with a thickness of 1.35 μm.
More advanced alignment techniques have been used to produce quantum dot superlattice structures with superior thermoelectric properties. Thin film quantum dot superlattice systems are designed around the lattice mismatch between PbSe and PbTe that promotes the growth of small quantum dots in periodic structures with average diameter between 1-10 nm. The ZT values for quantum dot superlattice thermoelectric materials are competitive on an efficiency basis with existing power generating technology. Böttner et al.\textsuperscript{48} in 2006 reported a measured maximum ZT of 3.6 for a PbSe\(_{0.98}\)Te\(_{0.02}\)/PbTe thin film quantum dot superlattice at 580K. Harman et al.\textsuperscript{49} report maximum ZT values of 3.5 at 300 K for another PbSe\(_{0.98}\)Te\(_{0.02}\)/PbTe quantum dot superlattice structure. The thermal conductivity of quantum dot superlattice structures is thought to be limited by resonant surface phonon scattering\textsuperscript{46}, which is controlled by the lattice spacing between quantum dots. Quantum dot superlattice and thin film thermoelectric materials are limited by their complicated production processes. The complicated production process limits reproducibility and scalability of experimental thermoelectric devices.

Current theoretical predictions suggest that nanowires can be used to produce thermoelectric materials with efficiency comparable to quantum dots\textsuperscript{28}. Nanowire thermoelectric materials have the disadvantage of larger thermal conductivity compared to quantum dots. There have been a number of historical measurements of different thermoelectric properties of nanowire composites, but these studies were unable to measure ZT of individual nanowires. Heremans et al.\textsuperscript{50} in 2003 created a series of different zinc nanowire composites using vapor deposition methods on SiO\(_2\) and Al\(_2\)O\(_3\) porous substrate. They observed Seebeck coefficient values of 130 \(\mu\)V/K at 300K but did not directly measure ZT. Measurements of the thermoelectric properties of nanowire composite materials cannot be used to accurately represent the properties of individual nanowires. Silicon nanowires were the first nanowire thermoelectrics to be directly measured. Li et al.\textsuperscript{51} measured a reduction in the lattice thermal conductivity of silicon nanowires of varying diameters produced using vapor-liquid-solid method\textsuperscript{52,53}. They found that thermal conductivity could be reduced to about 8 W/(m·K) for a nanowire with a diameter of 22 nm, with strong diameter dependence assumed to be related to the surface scattering of phonons. More recently, Hochbaum et al. in 2008\textsuperscript{54,11} used metal assisted chemical etching to produce silicon nanowires with very rough surfaces. They measured larger reductions in lattice thermal conductivity down to approximately 1 W/(m·K) in 50 nm diameter silicon nanowires. The roughened nanowire surface resulted in a substantial two order of magnitude increase in the thermoelectric figure of merit, ZT of 0.6 at 300K, when compared to bulk silicon which has ZT \(-0.017\) at 300 K\textsuperscript{55}. The reduction in thermal conductivity was further supported by Boukai et al.\textsuperscript{56}. They measured a reduction in thermal conductivity down to 1
W/(m·K) for a 10 nm diameter silicon nanowire. They also found a maximum thermoelectric figure of merit of ~1 for a 20 nm diameter nanowire at 200 K. Other materials have been used to produce nanowire thermoelectrics. Kim et al.\textsuperscript{57} in 2015 measured the diameter dependence of the thermoelectric figure of merit for individual BiTe nanowires. They found that ZT is maximized at a value of 0.26 for 109 nm diameter nanowires. The strong radial dependence on the thermoelectric figure of merit is interpreted as competition between drop in thermal conductivity with decreasing radius against a similar drop in Seebeck coefficient and electrical conductivity due to edge states. Yang et al.\textsuperscript{58} in 2015 measured the thermoelectric properties of PbTe capped 28 nm diameter Ag\textsubscript{2}Te nanowire composite, with ZT=0.66 at 390K. The capping was designed to block minority carrier transport, and thus improve Seebeck coefficient. Improved ZT in nanowire systems compared to bulk materials show that physics and material engineering can be used to improve thermoelectric efficiency.

Graphene is a 2D sheet of carbon atoms arranged into a periodic ring structure with unusual physical properties that make it an interesting possible thermoelectric material. The charge transport properties of graphene make it an interesting potential thermoelectric material, and have been the subject of extensive research. Graphene was first theoretically predicted in 1947 by P. R Wallace\textsuperscript{59} and first experimentally produced by A. K. Geim and K. S. Novoselov in 2004 by cleaving highly ordered pyrolytic graphite\textsuperscript{60}. One unusual property of graphene is extremely large electron mobility, which was measured\textsuperscript{1} to be approximately 200,000 cm\textsuperscript{2}/Vs. This compares favorably against the measured mobility of 1300 cm\textsuperscript{2}/Vs for pure silicon. Silicon is a poor thermoelectric material. Graphene has a large electrical conductivity\textsuperscript{61}, measured to be between 0.5 and 2 S/cm. This was confirmed by Zuev, Chang, and Kim\textsuperscript{62} in 2009. They used electron beam lithography to produce a graphene Hall bar on a silicon oxide substrate. Zuev et al.\textsuperscript{62} measured the thermoelectric properties of graphene in terms of gate voltage and temperature. They were able to directly observe integer Seebeck coefficient from changes at low temperatures that was related to the quantum hall effect. They also observed approximately linear electrical conductivity at 300 K, as expected for a 2D system. They further measured the maximum absolute value of Seebeck coefficient to be approximately 80 μV/K. The sign of the Seebeck coefficient was related to the sign of the gate voltage. This is approximately half the expected theoretical value predicted for graphene\textsuperscript{8}, but still sufficiently large for graphene to be an interesting potential thermoelectric material. The decrease in Seebeck coefficient suggests that high levels of disorder are present in the crystal lattice of the measured graphene flake. This suggests that the graphene flake studied by Zuev et al. was strongly interacting with the silicon carbide substrate. Zuev et al. did not directly
calculate $ZT$ for graphene, but we can use their experimental data to find a maximum value that is much less than 0.01 at 300 K. Kim et al.\textsuperscript{63} directly probed how the Fermi energy of graphene changes with the carrier concentration. They were able to accurately predict the Fermi energy changes, and this allowed the exact calculation of the carrier concentration changes in pure graphene as a function of the carrier concentration and gate voltage. The similarity in measurement techniques between both graphene papers allows for the direct comparison of computational predictions against experimentally measured values. The high electron mobility, Seebeck coefficient, and electrical conductivity of graphene are beneficial to increasing $ZT$.

Thermoelectric properties of materials have been traditionally simulated using Boltzmann Transport Theory (BTT). BTT provides a way to accurately and efficiently approximate the thermoelectric properties of materials from first principles. BTT is a statistically based method that calculates properties at the nanoscale and larger, at or close to standard temperatures and pressures. BTT uses the group velocities of charge carriers (obtained from the electronic structure of materials) combined with an occupational probability and shifting chemical potential to approximate charge transport. The first attempts to use BTT with graphene were complicated by its unusual electronic structure. Graphene has zero band gap. The bands touch at the Dirac points in the electronic structure. The derivatives of the dispersion relationship between energy states are not well defined at these Dirac points. This complicates simulation of graphene thermoelectric materials. The group velocity of charge carriers is described by the first derivative of the electronic structure. The group velocity of electrons is infinitely large at the Dirac points. The effective mass of charge carriers is related to the inverse of the second derivative of the energy dispersion relationship, and it has a singularity at the Dirac points. Charge carriers therefore experience zero effective mass at the Dirac points. The theoretical framework adapting BTT for use with graphene systems is briefly discussed in section (1.4). Das Sarma et al.\textsuperscript{64} predicted that the impurity concentration and surface interactions are thought to have a large impact on the thermoelectric properties of graphene. Current BTT can be used to predict the thermoelectric properties of graphene, and we use this framework to calculate thermoelectric properties.

Pristine graphene is a poor thermoelectric material because of large thermal conductivity. The thermal conductivity for graphene has been measured to be around 4000–6000 W/(m·K) at room temperature\textsuperscript{65}, much larger than most materials. Graphene has one of the largest thermal conductivities known, only nanodiamond is larger, at approximately\textsuperscript{66} 6000 W/(m·K). The thermal conductivity is strongly dependent on the purity and quality of the graphene material studied. The large thermal conductivity makes graphene an inefficient thermoelectric material, but
is useful and necessary point of comparison. Graphene nanomesh, introduced in section (1.3), and defected graphene provides a method to limit thermal conductivity while maintaining sufficient charge transport to produce more efficient thermoelectric devices. Graphene nanostructures are therefore interesting potential thermoelectric materials.

In summary, designing thermoelectric materials with improved efficiency is complex. Research has focused on engineered nanostructured thermoelectric materials to reduce thermal conductivity and thereby improve ZT. Nanocomposite materials have produced thermoelectric materials with maximum ZT less than 2. Quantum dot and quantum dot superlattice structures have been used to build devices with maximum ZT greater than 3. Nanowires have been predicted to produce thermoelectric materials with ZT comparable to quantum dot superlattice systems. Nanowire thermoelectric materials have observed maximum ZT values ~1. These materials are all limited by either low ZT or manufacturing constraints. Studies continue to search for more efficient and more reproducible efficient thermoelectric materials. Graphene based thermoelectric materials are promising thermoelectric materials due to superior charge transport properties, but are limited by large thermal conductivity.

1.3 Introducing Graphene Nanomeshes

Graphene nanomesh is pristine graphene which has been modified by incorporation of periodic holes in the crystal lattice. Our present study is inspired by recent improvements in the understanding of the electronic structure and thermal conduction properties of graphene nanomeshes. Semiconducting graphene nanomeshes have been recently synthesized, and their band gaps can be tuned according to hole size, separation and distribution. Molecular Dynamics (MD) simulations have suggested that their thermal conductivity can be substantially reduced compared to that of the pristine graphene. The presence of periodic defects in the graphene lattice is predicted to open a band gap, improving Seebeck coefficient. Graphene nanomesh was first experimentally produced by Bai et al. in 2010 using block copolymer lithography to create hexagonally periodic circular defects with a variable radius as small as approximately 5 nm. Representation of two different graphene nanomesh systems with a vacancy defect is shown in figure 1.3.1. The periodicity of the defect is used to define a sublattice. Each system has a single vacancy defect in a standard graphene lattice that has been repaired with hydrogen termination. Black spheres represent carbon atoms, red represent hydrogen atoms, dashed blue atoms represent bonds, yellow lines highlight the sublattice periodicity of the defects, and the scale of the sublattice is reported in both angstroms and the lattice vectors of standard graphene.
1.4 Theoretical Predictions of Graphene Based Materials

Dvorak, Oswald and Wu recently developed a theoretical model using Tight Binding (TB) that can predict the bandgap opening in graphene nanomeshes based on the symmetry of defects. Dvorak et al. were able to accurately predict the bandgap opening when different types of defects were added to graphene, such as surface adsorbents, boron nitride-doping, and vacancy defects with hydrogen termination. Dvorak and Wu further developed an additional theory that predicts and can be used to control Dirac point shifts in the electronic structure of graphene when the symmetry of the graphene lattice is broken by different defects. Breaking the C$_3$ lattice
symmetry of graphene leads to a transition from semimetal to semiconductor states in graphene nanomesh. Montambaux et al., Wunsch et al., and Hasegawa and Kishigi discuss and develop several parts of the TB theory. Precise control of the electronic structure allows the precise adjustment of important physical parameters needed to improve thermoelectric efficiency. Our study analyzes the thermoelectric properties of nanomesh systems with complex geometry in order to better understand the physics controlling improvement in thermoelectric properties.

The symmetry and spacing of defects have been used in previous studies to minimize lattice thermal conductivity of graphene nanomesh. Gunst et al., and Hu and Maroudas both used MD simulations of defected graphene to develop qualitative predictive trends of thermal conductance and thermal conductivity. Gunst et al. used fitted MD simulations to describe the temperature and defect fraction dependence of lattice thermal conductance in hexagonally periodic graphene nanomesh. They observed a large reduction of lattice thermal conductivity through material optimization, which makes graphene nanomesh a more promising thermoelectric material than standard graphene. Gunst et al. derived an equation to approximate lattice thermal conductance as a function of the defect fraction,

\[ C_{lat}(T) = \left( -\alpha(T) \frac{N_{rem}}{N_{tot}} + \beta \right) C_{0}^{lat}(T) \]  

where \( C \) is the thermal conductance, \( \alpha(T) \) is a temperature-dependent fitting parameter, \( \beta \) is a fixed fitting parameter approximately equal to 0.25, \( N_{rem}/N_{tot} \) is the defect fraction, and \( C_{0}^{lat}(T) \) is the thermal conductance of pristine graphene as a function of temperature. The Gunst et al. equation is useful as a first-order approximation of the temperature dependence of the thermal conductivity of graphene nanomesh. The equation is limited by only accurately describing large defect fraction nanomesh systems. The equation does not describe the important dependence of lattice thermal conductivity on the geometry and symmetry of graphene nanomesh systems.

Hu and Maroudas developed another equation using symmetry-based arguments to describe the relationship between defect spacing and defect fraction, and lattice thermal conductivity. They investigated hexagonal and square periodic defects with different aspect ratios with a fixed spacing of 24 carbon atoms between defects. The authors found that lattice thermal conductivity scales proportional to the spacing between the defects and the fraction of remaining atoms in the lattice. This is described by

\[ \ln \left( \frac{\kappa}{\kappa_0} \right) = f \left( 1 - \frac{n}{n_0} \right)^{1/2} \]  

(1.4.2)
where $\kappa$ is the lattice thermal conductivity, $\kappa_0$ is the lattice thermal conductivity of pure graphene, $f$ is the aspect ratio of the nanomesh, $n$ is the mesh density, and $n_0$ is the density of a pure unit cell without defects. The defect fraction is proportionally related to the spacing between defects. This equation can be used to estimate the thermal conductivity of graphene nanomesh materials with more complex geometry. We adopt Eq. (1.4.2) to predict the thermal conductivity of a graphene-nanomesh systems.

Graphene-based materials have the potential to produce efficient thermoelectric systems due to their excellent transport properties. The accurate prediction of thermoelectric properties of graphene was difficult because of its unusual electronic structure. Several theoretical works have used traditional BTT to predict thermoelectric properties of graphene-based systems. The theoretical framework used to expand BTT to 2D graphene was developed by Adam, Hwang, and Das Sarma\textsuperscript{64,73–76}, and their works suggest that the presence of scattering sites at high concentrations disrupts the smooth movement of charge carriers. This causes charge pooling in smaller regions of the graphene lattice, which disrupts the electronic structure of graphene around the Dirac point, smoothing out the singularities in the electronic structure. The presence of these scattering sites allows the physical properties of graphene to be accurately predicted using BTT, provided that the carrier concentration is sufficiently large. Without charge pooling, thermoelectric properties could not be predicted numerically using standard BTT.

A series of experimental and theoretical works have determined that approximately $10^{11}$ carriers per square centimeter is sufficient for BTT to accurately predict the thermoelectric properties\textsuperscript{64,75,77,78} of graphene. Das Sarma \textit{et al.}\textsuperscript{64} simulated highly localized scattering sites in the graphene lattice. They then assumed an energy-dependent scattering interaction and found good fits between experimental data and theoretical predictions when a Coulomb-like scattering source was assumed to be dominant. These early studies did not attempt to predict all parameters that affect the thermoelectric efficiency of pure graphene.

Some studies have used more complex computational methods to predict the thermoelectric properties of graphene based materials. The standard calculation method uses DFT or tight binding (TB) to first approximate the electronic structure of a material. Next, the electronic structure is used with the 3D Boltzmann transport equation (BTE) to solve for the thermoelectric properties. Lattice thermal conductivity then needs to be independently calculated using molecular dynamics (MD) simulations. This method had been used to study the thermoelectric properties of unrelated materials, such as diamond nanorods\textsuperscript{79}, different nanowires\textsuperscript{8,9,80–82}, and quantum dots\textsuperscript{8,10,83}. These techniques have been adapted to study pure graphene\textsuperscript{77}, but not graphene nanomesh.
Previous studies of graphene nanomesh have used TB with the nonequilibrium Greens functions (NEGF). Sivan et al. discuss the computational method in detail\textsuperscript{84}, which was developed by Landauer in 1957\textsuperscript{85}. This is an independent methodology that does not rely on the BTE to solve for relevant quantities. This method allows for the direct calculation of phonon-related quantities from first principles, skipping the MD step necessary with traditional BTE calculations. The NEGF method has been used to study graphene\textsuperscript{77}, graphene nanoribbons\textsuperscript{86,87}, and graphene nanomesh\textsuperscript{16,88–92}. The thermoelectric properties calculated using NEGF use a transfer or transmission matrix\textsuperscript{93,94} to describe the scattering behavior of both charge carriers and phonons. The thermoelectric properties are proportional to a transverse 2D density of states. NEGF can be used to directly calculate all the components of ZT from first principles. These methods typically approximate the complex scattering dynamics in graphene materials using only electron-phonon, phonon-phonon, and phonon-surface scattering. Finite nonperiodic systems are required to use NEGF techniques to estimate thermoelectric properties. The thermoelectric properties of graphene systems predicted using NEGF are in the ballistic transport regime instead of the true diffusive limit observed in real world thermoelectric devices. Other methods such as deformation potential theory (DPT)\textsuperscript{95,96} are currently being used to study the thermoelectric properties of graphene systems.

Several previous theoretical works have investigated the thermoelectric properties of graphene nanomesh. In these studies Gunst et al.\textsuperscript{16} in 2011 first used TB and NEGF methods to predict the thermoelectric properties of graphene nanomesh with large defects. They studied hexagonally periodic defects that range in diameter from 1.2 to 2.6 nm and used the GULP program\textsuperscript{97} with Brenner potentials\textsuperscript{98} to calculate a maximum ZT~0.25. This maximum ZT was obtained when the defect shape and spacing was optimized to highly localize electron states near the defect edges. Gunst et al.\textsuperscript{16} observed that graphene nanomesh systems had extremely reduced thermal conductivity compared to standard graphene. The thermal conductivity of standard graphene is between 4 – 6 \times 10^3 \text{ W/(m\cdot K)} based on experimental measurements\textsuperscript{65}. Gunst et al. calculated the thermal conductance of their nanomesh system could be as low as 1 nW/(K). This extreme reduction in thermal conductivity is offset by large reductions in electrical conductivity and only causes an approximate three order of magnitude increase in ZT compared to normal unmodified graphene. Seebeck coefficient peaks between 10 and 150 \text{ \mu V/K} for the different nanomesh systems were considered, similar to experimental measurements and theoretical predictions for carbon-based systems\textsuperscript{8}.

Karamithari et al.\textsuperscript{91} in 2011 investigated the thermoelectric properties of graphene and graphene with hexagonally periodic defects. These defects had complex geometric shapes such as squares and triangles.
Karamithari et al.\textsuperscript{91} used the third nearest neighbor TB\textsuperscript{99} to estimate the electronic structure of these nanomesh systems in combination with the same NEGF methods as Gunst et al. They observed that the shape of the defect affected the magnitude of the improvement in the thermoelectric efficiency compared to standard graphene. They found that a triangular-shaped defect that minimized the spacing between defects produced the largest increase in $ZT \sim 0.2$. These studies do not consider the thermoelectric properties of small-defect graphene nanomesh systems or the key physical parameters affecting thermoelectric properties beyond the defect shape and size.

Disorder in the defect lattice strongly decreases the thermoelectric efficiency of graphene nanomesh. Fan et al.\textsuperscript{92} and Power et al.\textsuperscript{88} studied the effect of different types of crystalline disorders on $ZT$ in nanomesh materials. They use a recently developed modified version of the NEGF method\textsuperscript{100} that is optimized to work with GPUs (graphics processor unit). They observed that extremely small amounts of disorder in the periodicity of the defect sublattice substantially reduced the beneficial charge transport properties compared to regularly ordered graphene nanomesh. This suggests that the thermoelectric properties of graphene nanomesh systems are dependent on the sublattice symmetry and periodicity of the defects. The calculation methods used in these studies required relatively large defects, and non-periodic systems. This is problematic because it masks the underlying mechanisms determined by the sublattice periodicity over a large length scales. These calculations were performed in the ballistic transport regime, rather than the diffusive transport regime. Model charge carriers must undergo a sufficient number of scattering events seen in the diffusive transport regime to accurately represent the behavior of real materials. After conducting our study, we believe that they examined a periodicity based effect using a non-periodic method.

The thermoelectric properties of a variety of other graphene-based systems have been investigated. A variety of theoretical methods such as doping\textsuperscript{87}, introducing scattering defects\textsuperscript{101}, and designing complex phonon transmission paths\textsuperscript{86} have been used to limit phonon transmission and decrease thermal conductivity. Several of these methods are combined in Sevinçli et al. from 2013\textsuperscript{87}. Sevinçli et al.\textsuperscript{93,94} used NEGF and TB calculations of the electronic structure to predict the thermoelectric properties of graphene nanoribbons with C\textsubscript{14} doping and shape control. The combination of shape control and doping reduced lattice thermal conductivity by a factor of approximately 100 compared to standard graphene. Doping and shape control did not significantly reduce electrical conductivity that is typically lost with graphene modification. They predicted a $ZT$ of 3.25 at 800 K. This is achieved using C\textsubscript{14} as a doping agent to build the nanoribbon with a 50% dopant concentration. The nanoribbon was approximately 1 μm in length, with a complex zig-zag geometry designed to minimize phonon transmission.
Maximum values of ZT for graphene nanoribbons using a similar geometry, but without doping, are around 0.7 when Fermi energy is displaced by about 1.25 eV\textsuperscript{86}. The C\textsubscript{14} doping is therefore important in decreasing thermal conductivity and thus increasing ZT. The large value of ZT reported by Sevinçli \textit{et al.} is comparable in efficiency to some of the best values found using PbTe quantum dot superlattice systems. Such systems are theoretically interesting and, if similar findings could be reproduced experimentally, would have wide-ranging practical applications. This demonstrates that graphene has the potential to produce efficient thermoelectric systems.

There have been extensive theoretical predictions of the thermoelectric properties of graphene-based materials. The electronic structure of graphene complicates attempts to predict the thermoelectric properties of graphene nanomesh. However, theoretical predictions and experimental measurements indicate that the presence of scattering sites leads to charge pooling. This charge pooling justifies the use of BTT to predict the thermoelectric properties of graphene materials provided that the density of scattering sites is greater than $10^{11}$ per square centimeter. Different forms of BTT have been used to estimate the thermoelectric properties of graphene-based systems, ranging from nonlinear Greens functions to deformation potential theory. Further theoretical and numerical study is necessary to better understand the key physical parameters controlling improvement in thermoelectric efficiency for graphene nanomesh, and is motivation for our work. Previous studies investigated graphene nanomeshes in very different size ranges, and investigated very different physical parameters. We investigated a different material, using a new method.
CHAPTER 2
METHODOLOGY

This chapter focuses on the theoretical basis of the computational methods we used to perform calculations of the thermoelectric properties of materials. Section (2.1) summarizes the important theoretical components of Density Functional Theory. Section (2.2) describes Boltzmann Transport Theory. We used Density Functional Theory to calculate the electronic structure of materials using the ABINIT package\textsuperscript{102-105}. We then used the calculated electronic structure with Boltzmann Transport Theory to compute the thermoelectric properties of materials. Boltzmann Transport theory calculations were performed using the BoltzTraP program\textsuperscript{106}.

2.1 Density Functional Theory

Density functional theory (DFT) is a computational modeling process widely used for predicting the electronic structures and physical properties of materials. The complex electron-electron interactions in the many-particle Schrödinger equation are computationally intensive. DFT reduces the complexity of modeling the properties of materials by representing the same system without these complex interactions. DFT is based on the Hohenberg–Kohn (HK) theorems\textsuperscript{107}. Properties of materials are computed by solving the Kohn–Sham (KS) equation\textsuperscript{108} using functionals of the spatially dependent electron density. DFT provides a way to quickly and efficiently calculate the properties of materials.

The physical properties of materials are determined by the structure and arrangement of valance electrons. The behavior of a single electron at the extremely small length, time, and energy scales of quantum mechanics is represented by the Schrödinger equation

\[ \hat{H} \Psi = E \Psi \]  

(2.1.1)

where \( \hat{H} \) is the Hamiltonian operator, \( \Psi \) is the wave function describing the state of a particle, and \( E \) is the energy of the state. Materials contain many interacting valence electrons. For systems with \( N \) electrons, the Schrödinger equation is expanded to include additional interaction terms

\[
\left( \sum_{i=1}^{N} \left( -\frac{\hbar^2}{2m} \nabla^2 + v(r_i) \right) + \sum_{j \neq i=1}^{N} U(r_i, r_j) \right) \psi(r_1, r_2, ... r_N) = E \psi(r_1, r_2, ... r_N) 
\]

(2.1.2)

where \( N \) is the total number of electrons, \( \hbar \) is Plank’s constant, \( m \) is the mass of an electron, \( U \) is the electron-electron interaction, and \( \Psi \) is the many-body wave function. This is known as the many-particle Schrödinger equation. Direct numerical solutions to the many-particle Schrödinger equation are impossible for any realistic
systems except for the simplest cases because the exponential increase of computational cost with respect to the number of particles involved. DFT overcomes these complications.

DFT uses an effective mean-field approach based on the HK theorems, in which electron density is the basic variable instead of the many-particle wave function. The first HK theorem states that the external potential of a many-electron system is uniquely determined, within a constant value, by the ground-state electron density \( n(r) \) defined by

\[
n(r) = N \int d^3r_1 \int d^3r_2 \ldots \int d^3r_N \psi^*(r, r_1, r_2, \ldots, r_N)\psi(r, r_2, \ldots, r_N)
\]  

(2.1.3)

where \( N \) is the total number of electrons and \( \psi \) is the many-body wave function. This can be used to predict the physical properties of the ground state of materials in terms of the electron density in DFT. The second HK theorem demonstrates that a unique functional of the electron density, within a constant value, can be defined so that it accurately describes any external potential. Therefore, a real interacting system can be mapped to an artificial non-interacting system with the same electron density. The single-particle eigenenergies and eigenfunctions of valance electrons represented by this artificial system can be obtained by solving the KS equation

\[
\left( \frac{\hbar^2}{2m} \nabla^2 + v_{eff}(r) \right) \varphi(r) = \varepsilon \varphi(r)
\]  

(2.1.4)

where \( \varepsilon \) is the single particle eigenenergy, \( \varphi(r) \) is the single particle eigenfunction, and \( v_{eff} \) is the effective potential. The effective potential \( v_{eff} \) has three terms,

\[
v_{eff}(r) = V_{ion}(r) + V_{xc}(r) + V_H(r)
\]  

(2.1.5)

\( V_{ion} \) is the Coulomb potential from ionic cores within the Born–Oppenheimer approximation\(^{109}\). \( V_H \) represents the Hartree potential of the electron distribution resulting from the Coulomb interaction between different electrons. The exchange-correlation potential \( V_{xc} \) increases because of the quantum exchange effect and many-body correlation. The exact analytical form of the exchange-correlation functional for many-electron systems remains unknown. Numerous approximations have been made to represent the exchange-correlation potential in order to better represent material properties with DFT. We used the generalized gradient approximation (GGA) proposed and parametrized by Perdew, Berke, and Ernzerhof\(^{110}\) (PBE) to perform our calculations because it is thought to better refine representations of the exchange-correlation energy. In summary DFT uses the first and second HK theorems to represent the properties of electrons using a mean field approach to avoid the complications of electron-electron interaction. We used DFT to compute the ground state ionic structure and the band structure that are input into BTT.
2.2 Boltzmann Transport Theory

We estimated transport properties of materials using the Boltzmann Transport Equation (BTE) implemented in the BoltzTraP\textsuperscript{106} code. The following is a very brief review of semi-classical transport theory. The dynamic behavior of charge carriers can be described using a distribution function, \( f(r, k, t) \), that represents the occupational probability of an electron state (approximated by the KS state) by three independent variables of position in space \( r \), wave vector \( k \) and time \( t \). The distribution function can be obtained by solving the Boltzmann Transport Equation (BTE)

\[
\frac{\partial f(r, k, t)}{\partial t} \bigg|_{fields} + \frac{\partial f(r, k, t)}{\partial t} \bigg|_{scattering} + \frac{\partial f(r, k, t)}{\partial t} \bigg|_{diffusion} = 0 \tag{2.2.1}
\]

where the only factors assumed to affect the behavior of charge carriers represented by the distribution function are the external fields, scattering between the charge carriers and carrier diffusion. The time derivative term of the distribution function \( \frac{df(r, k, t)}{dt} \) included in the complete BTE is omitted because thermoelectric properties are generally calculated for quasi-static systems near thermodynamic equilibrium. The linearized form of the BTE derived from Eq. (2.2.2) is represented by

\[
\frac{\partial}{\partial \varepsilon_i(k)} \left( \frac{\varepsilon_i(k) - \mu}{T} \nabla \mu + \nabla \mu \right) \cdot v_i(k) = \frac{f^1(r, k, t)}{\tau} \tag{2.2.2}
\]

where \( f^1(r, k, t) \) describes how the distribution function of charge carriers shifts when external forces are applied and \( f^0(\vec{r}, \vec{k}, t) \) represents the distribution of charge carriers at thermodynamic equilibrium. \( \nabla \mu \) is related to the applied external forces in terms of electrochemical potential, and \( \mu \) is the chemical potential. \( v_i(k) \) is the group velocity of charge carriers with band index \( i \) and momentum \( k \), whose eigenenergies are \( \varepsilon_i(k) \). The \( \frac{f(r, k, t)}{\tau} \) term on the right hand side of Eq. (2.2.3) represents the scattering behavior of charge carriers in a material by assuming the relaxation time approximation

\[
\frac{\partial f(r, k, t)}{\partial t} \bigg|_{scattering} = \frac{f^1(r, k, t)}{\tau (\varepsilon_i(k))} = \frac{f(r, k, t) - f^0(r, k, t)}{\tau (\varepsilon_n(k))} \tag{2.2.3}
\]

\( \tau (\varepsilon_n(k)) \) is the relaxation time, describing the average time interval between scattering events for charge carriers with a specific energy \( \varepsilon \) inside the distribution function describing the average time interval between scattering events for charge carriers with band \( n \) and momentum \( k \). Relaxation time is assumed to be energy dependent. In
most simulations the constant relaxation time approximation is adopted. The scattering behavior of charge carriers is fully separate from other components of the BTE.

The relaxation time can be calculated from first principles or obtained through experimental measurement. The different components of the relaxation time can be described by Matthiessen’s rule

\[
\frac{1}{\tau} = \frac{1}{\tau_{cr}} + \frac{1}{\tau_{im}} + \frac{1}{\tau_{p}} + \frac{1}{\tau_{p}} \ldots \ldots
\]  

(2.2.4)

where the total relaxation time \(\tau\) is expressed in proportion to the assumed contributing terms originally developed to describe empirically derived relationships for carrier mobility\(^{111,112}\). Here \(\tau_{cr}\) is the relaxation time that can be described by crystallographic vacancy defects, \(\tau_{im}\) is caused by adsorbed or doped charge impurities, \(\tau_{p}\) represents electron-phonon interactions, and \(\tau_{p}\) is scattering caused by bound or edge states. In graphene nanomeshes, impurity and vacancy relaxation terms are thought to dominate over other contributing factors, and the previous calculations suggest that phonon contributions to the relaxation time are one order of magnitude smaller than the dominant terms\(^{64,75}\). In graphene nanomesh, impurity and vacancy relaxation terms are thought to dominate over other contributing factors, and previous calculations suggest that phonon contributions to the relaxation time are one order of magnitude smaller than the dominant terms\(^{64,75}\).

At thermodynamic equilibrium electrons are represented by the Fermi–Dirac distribution\(^{113-115}\)

\[
f^\alpha(r, \mathbf{k}, t) = \frac{1}{e^{\frac{\mathbf{k}^2}{2k_bT} + 1}}
\]  

(2.2.5)

where \(k_b\) is Boltzmann’s constant\(^{116}\), \(\mu\) is the chemical potential, \(\varepsilon\) the energy, and \(T\) is temperature. The carrier dynamics of a thermoelectric material can be derived from the first law of thermodynamics

\[
dU = TdS + \mu dN
\]  

(2.2.6)

where \(U\) is the total internal energy of the system, \(T\) is temperature, \(dS\) describes the change in entropy of the system, \(\mu\) is the chemical potential, and \(dN\) is the change in particle number. The internal energy is assumed to be isochoric in thermoelectric materials. In this thermodynamic system, entropy and mass are both the conjugate variables to energy. The change in entropy and the change in mass terms in Eq. (2.2.6) are coupled, leading to an equation on the interaction among the heat, electrical, and energy current

\[
J_e = TJ_s + \mu J_N
\]  

(2.2.7)

where \(J_e\) is the energy current, \(J_s\) is the entropic current, and \(J_N\) is the mass or in this case electrical current. Eq.
(2.2.7) creates a set of equations that can be used to independently solve for important thermoelectric properties, such as conductivity and Seebeck coefficient. Thermoelectric materials are assumed to be in quasi-static equilibrium

\[ J_s = \frac{I_q}{T} \quad \rightarrow \quad dS = \frac{dQ}{T} \quad (2.2.8) \]

where \( I_q \) is the heat current and \( dQ \) is the change in heat for a quasi-static system. Eqs. (2.2.7) and (2.2.8) can be used to determine the various contributions to the heat and electrical currents, and lead to Onsager’s reciprocal relations:

\[ J_N = \sigma E - \sigma S \nabla(T) \quad (2.2.9) \]
\[ J_Q = \sigma \alpha T E - \kappa \nabla(T) \quad (2.2.10) \]

where \( \alpha \) is the Seebeck coefficient. These relations can be used to calculate thermoelectric properties such as Seebeck coefficient and electrical conductivity using DFT calculated electronic structure

\[ v_{i\beta}(k) = \frac{1}{\pi \hbar} \frac{\partial \epsilon_{i,k}}{\partial k_{\beta}} \quad (2.2.11) \]
\[ \sigma_{i\beta\gamma}(i,k) = e^2 \tau_{i,k} v_{i\beta}(i,k) v_{i\gamma}(i,k) \quad (2.2.12) \]
\[ \frac{\sigma_{\beta\gamma}(T;\mu)}{\tau} = -\frac{1}{\mu} \int \sigma_{\beta\gamma}(\epsilon) \frac{\partial f(\epsilon,\mu,T)}{\partial \epsilon} d\epsilon \quad (2.2.13) \]
\[ \frac{v_{\beta\gamma}(T;\mu)}{\tau} = -\frac{1}{qT\Omega} \int \sigma_{\beta\gamma}(\epsilon)(\epsilon - \mu) \frac{\partial f(\epsilon,\mu,T)}{\partial \epsilon} d\epsilon \quad (2.2.14) \]
\[ \frac{\kappa_{\beta\gamma}(T;\mu)}{\tau} = -\frac{1}{q^2T\Omega} \int \sigma_{\beta\gamma}(\epsilon)(\epsilon - \mu)^2 \frac{\partial f(\epsilon,\mu,T)}{\partial \epsilon} d\epsilon \quad (2.2.15) \]
\[ \alpha_{kl}(T;\mu) = E_i(\nabla_j T)^{-1} = (\sigma^{-1})_{\delta k} v_{\delta l}(T;\mu) \quad (2.2.16) \]

The BoltzTraP program\textsuperscript{106}, developed by Madsen and Singh in 2006, uses Onsager’s reciprocal relations to numerically solve equations (2.2.13)-(2.2.18). BoltzTraP expands the electronic structure using Fourier interpolation to increase the number of k-points with star functions to maintain symmetry

\[ \epsilon_i(k) = \sum_R c_{R,i} S_R(k) \quad (2.2.12) \]

\[ S_R(k) = \frac{1}{n} \sum_{\{\Lambda\}} e^{ikR} \]

here \( R \) is the real space lattice vector and \( \{\Lambda\} \) are the point group rotations used to describe the symmetry of a periodic lattice. The accuracy of thermoelectric predictions is negatively affected by energy band crossings in the electronic structure. Convergence usually requires between 12,000 to 24,000 \( k \) points in the first Brillouin zone.
BTT is useful for predicting the charge transport properties of materials at the micro scale and larger, at or near standard temperatures and pressures, with medium to large carrier concentrations. BTT has been experimentally verified under these conditions.\textsuperscript{8,10} BTT further requires that deviations from thermodynamic equilibrium remain small, so that Onsager’s reciprocal relations (equations (2.2.9) and (2.2.10)) hold. BoltzTraP uses first order BTT, further restricting calculations to include only electric field effects, no magnetic field effects. BTT fails to accurately predict the properties of materials when more complicated physical processes control transport properties, such as the quantum hall effect, or when the free carrier concentration is extremely small. BTT is appropriate for our study because we examined the thermoelectric properties of materials at the length, temperature, pressure, and time scales where this theory is most accurate. This coincides with the conditions under which experimental measurements can be performed on real world devices. BTT is discussed in greater detail in Appendix B.
CHAPTER 3
THERMOELECTRIC PROPERTIES OF SILICON AND SILICON NANOWIRES

We first developed and tested our computational techniques using silicon (section (3.1)) and silicon nanowires (section (3.2)) as model materials. We used silicon because it has been extensively studied experimentally and theoretically. Silicon nanowires provided an opportunity to test our computational techniques using systems with more complex geometry, and to further demonstrate that nanostructuring can be used to produce a material with improved thermoelectric properties.

3.1 Crystalline Silicon

We first tested the accuracy of our computational methods by predicting the thermoelectric properties of silicon and then comparing our results with previously published studies. Our computations were compared to experimental measurements performed by Weber and Gmelin using a thermocouple setup\(^{117}\), and two published theoretical works that used different computational methods. The first study was performed by Heinz\(^{9}\), using identical theoretical techniques to investigate the thermoelectric properties of silicon as part of a more detailed study of zinc nanowires. The second study was conducted by Wang \textit{et al.}\(^{118}\) and used more complex computational techniques based on deformation potential theory. These studies investigated the thermoelectric properties of silicon at 300 K. Our calculations were further compared to experimental measurements over a wide temperature range. These comparisons demonstrate the accuracy of our computational methods.

Silicon is an abundant element that has a wide range of commercial applications. The thermoelectric properties of crystalline silicon have been well studied. Bulk silicon is found in a diamond face centered cubic crystal structure. Silicon is a semiconductor with an indirect band gap\(^{112}\) of 1.17 eV at 300K. The thermoelectric properties of silicon are highly dependent on dopant concentration. Pure silicon like all semiconductors has large measured Seebeck coefficient, approximately 600 μV/K at 300K\(^{119}\). Thermal conductivity of pure silicon is measured\(^{119}\) to 149 W/(m·K) at 300 K, much smaller than graphene. Weber and Gmelin\(^{55}\) in 1991 investigated the thermoelectric properties of crystalline silicon with doping by 1.7 · 10\(^{19}\) arsenic or 2.8 · 10\(^{16}\) phosphorus atoms measured using a thermocouple setup. They did not directly measure ZT, but it is easily extractable from their measurements. Based on these measurements the maximum observed ZT was ~0.02 for phosphorus doped silicon. Crystalline silicon is a poor thermoelectric material because of low electrical conductivity.
Peter Heinz performed calculations of the thermoelectric properties of bulk silicon in 2010 as part of a larger study of zinc oxide nanowires. This study used VASP within the GGA. Thermoelectric properties were calculated using BoltzTraP. Scattering dynamics of charge carriers in silicon were estimated by numerically fitting electron mobility measurements. These measurements are dependent on carrier concentration. Heinz observed weak resonance in predicted ZT, electrical conductivity, and thermal conductivity of silicon with a local maximum at $10^{18}$ e/cm$^3$. This weak resonance has not been confirmed by experimental measurements or other theoretical predictions, and is probably caused by errors in interpolation of the electronic structure of silicon. We did not observe this resonance effect, and we believe that this was due to our more detailed convergence studies of key computational quantities used by ABINIT and BoltzTraP. We believe that our methods more accurately predict the thermoelectric properties of crystalline silicon. Wang et al. used a slightly modified version of deformation potential theory that incorporates electron-plasmon and ionized impurity scattering. Most studies using deformation potential theory assume that electron-phonon and phonon-phonon interaction are the dominant scattering mechanisms that affect accurate predictions of thermoelectric properties. The extra scattering terms are added to better describe the behavior of real materials. They used Quantum Espresso and the Local Density Approximation (LDA) to calculate the electronic structure of silicon. Thermoelectric properties were estimated by numerically solving the linearized form of the BTE without using the relaxation time approximation. This method directly predicts the electron mobility, Seebeck coefficient, electrical conductivity, and the electrical component of the thermal conductivity from first principles. They did not predict ZT because lattice thermal conductivity was not estimated.

We performed DFT electronic structure calculations using ABINIT within the GGA with norm conserving pseudopotentials. We used a primitive cell of silicon containing two atoms, and converged the total energy within 0.1 eV. BoltzTraP requires a very dense $k$ point grid for accurate prediction of thermoelectric properties, generally require between 12000 to 36000 $k$ points in the first Brillouin zone. BoltzTraP uses Fourier interpolation to expand the electronic structure from $\sim 10^3$ $k$ points to $\sim 10^7$-$10^9$ $k$ points. The number and degeneracy level of band level crossings determines the exact density of $k$ points needed for specific interpolations. More complex materials require finer $k$ grid spacing to maintain prediction accuracy. The accuracy of interpolation can be quantified by examining secondary oscillations in predicted thermoelectric quantities such as Seebeck coefficient. The amplitude of these secondary oscillations decrease exponentially with the number of $k$ points, in the DFT...
electronic structure, as shown in figure 3.1.1. We defined convergence to occur when secondary oscillations in the Seebeck coefficient are less than 1 µV/K in average amplitude. This is two orders of magnitude smaller than primary features in the Seebeck coefficient of crystalline silicon. We used similar BTT convergence methods with all of our calculations in this thesis. We achieved this using a $k$ point grid of 27000 $k$ points (30x30x30 grid, 752 irreducible points in the first Brillouin zone). This is a much larger number of $k$ points compared to traditional density functional theory calculations of the electronic structure that do not use BTT. We also used a lattice parameter of 5.465 Å, a cutoff energy of 436 eV, and Trouiller-Martins\textsuperscript{123} type norm conserving pseudopotentials. Convergence testing and other quantities are discussed in detail in appendix A.

![Figure 3.1.1](image.png)

Figure 3.1.1. Average amplitude of secondary oscillations in the calculated Seebeck coefficient of crystalline silicon as a function of the number of $k$ points in the electronic structure. The present study defines convergence to occur when the average amplitude in secondary oscillation is smaller than 1 µV/K.

We calculate the bandgap of crystalline silicon to be 0.61 eV, almost identical to the 0.616 eV reported by Heinz\textsuperscript{9} using a similar method. This bandgap is approximately 50% smaller than the expected experimentally measured value of 1.17 eV\textsuperscript{9}. The difference between the theoretically derived and the experimentally measured bandgaps is caused by well-known fundamental problems in the current application of DFT, including errors in approximating the exchange correlation energy. Boltzmann transport theory depends mostly on the band width and shape, and the bandgap problem can be remedied by the scissor-shift approach. The band structure and DOS of crystalline silicon is shown in figure 3.1.2. The asymmetric effective mass positively impacts the thermoelectric
properties of silicon.

We estimated the relaxation time in crystalline silicon using

\[ \tau(n) = \tau_o + \left( \frac{\tau_1 - \tau_o}{1 + \alpha n} \right) \]

where \( n \) describes carrier concentration in a sample, \( \tau_o = 1.449913 \times 10^{-16} \) s, \( \tau_1 = 8.03289 \times 10^{-16} \) s, and \( \alpha = 1.89859 \times 10^{-16} n^{-1} \). This equation was used by Heinz to estimate the relaxation time for silicon and silicon nanowires\(^9\), and is based on fitting electron mobility data. We adopted a lattice thermal conductivity of either 100 or 80 W/(m·K), with ZT shown for both cases. These values were taken from previous computational studies of the thermoelectric properties of crystalline silicon. Good agreement is achieved between our estimated Seebeck coefficient, electrical conductivity, electrical thermal conductivity, and ZT, and previously cited studies.

The results of our calculations are first summarized in figure 3.1.3, and larger versions of the same plots are shown in figures 3.1.4, 3.1.5, 3.1.6, and 3.1.7 following the discussion. Figure 3.1.4 shows our calculated Seebeck coefficient of electrons and holes in silicon, along with previous computational studies by Heinz\(^9\), Wang \textit{et al.}\(^{118}\), and experimental measurements by Geballe & Hull\(^{124}\). The sign of the Seebeck coefficient changes for different types of charge carriers (negative for electrons, positive for holes), and a slight asymmetry is observed, caused by

![Figure 3.1.2. Our calculated electronic structure and density of states for bulk crystalline silicon calculated using ABINIT\(^{102}\). The Brillouin zone of a face centered cubic system is shown in appendix (A.1), with high symmetry points and is reproduced from Jochym\(^4\).]
asymmetric effective mass. Heinz used a very similar calculation process to our study, and the close agreement between our calculations and this work demonstrates the overall accuracy of our computational methods. Wang et al. used the more complex DFP based calculation process that goes beyond the relaxation time approximation to calculate thermoelectric properties. These calculations show the complexity of simply using the band structure to make qualitative predictions of thermoelectric properties, since several competing effects such as asymmetric effective mass, degeneracy of bands, and shifting band occupancy combine to complicate direct predictions. Most importantly the close agreement with Geballe & Hull shows that our DFT calculated electronic structure can be used to predict the thermoelectric properties of real world devices. Figure 3.1.5 shows calculated electrical conductivity for our work, Wang et al., and Heinz. As expected electrical conductivity in silicon scales exponentially with the number of free charge carriers. We closely agree with electrical conductivity calculations performed by Heinz. Wang et al. predict an identical exponential relationship between electrical conductivity and
carrier concentration. The difference between Wang et al. and our work are assumed to be caused by their use of the LDA instead of the GGA to calculate electronic structure, and the different process used to approximate relaxation time. Figure 3.1.6 depicts the electrical component of thermal conductivity. This again scales exponentially with the number of free carriers. We believe that weak resonance predicted by Heinz in the middle of the carrier concentration range is caused by insufficient convergence testing. Except for the resonance effect, our results agreed closely with these calculations. Wang et al. predicted similar functional form, but very different magnitude, and we assume this was caused by the differences in the calculation process. Since the electrical component of thermal conductivity is an extremely small contributing factor to ZT in materials, this does not significantly affect thermoelectric efficiency or the usefulness of our comparison. Figure 10 shows our predictions of ZT for crystalline silicon. We predict a maximum ZT of ~0.008 for electrons in standard crystalline silicon. We calculated ZT for lattice thermal conductivity of 100 W/(m·K) and 80 W/(m·K) with the temperature of silicon set to 300 K. We did this to demonstrate the strong lattice thermal conductivity dependence in ZT. Heinz calculated ZT of crystalline silicon using a lattice thermal conductivity of 100 W/(m·K). Wang et al. determined Seebeck coefficient, electrical conductivity, and electrical thermal conductivity. We used their values to extract ZT based on the same assumed lattice thermal conductivity (figure 3.1.7). The weak resonance predicted by Heinz in electrical conductivity and electrical thermal conductivity is assumed to be caused by insufficient convergence testing. Wang et al. calculated the properties of silicon over a narrower carrier concentration range and a different carrier type, but similar functional form. Figure (3.1.8) shows the temperature dependence of our calculated Seebeck coefficient compared to experimental measurements of $1.7 \times 10^{19}$ Arsenic doped crystalline silicon by Weber and Gmelin. The close similarity in the Seebeck coefficient supports the accuracy of our DFT electronic structure calculations compared to crystalline silicon. BTE calculations of Seebeck coefficient do not require knowledge of relaxation time. This further supports the conclusion that the absolute magnitude of the band gap in materials is less important to predicting thermoelectric properties than the shape of the electronic structure, especially close to the Fermi energy which we set to be in the middle of the band gap. We achieved close agreement with these experimental measurements. In conclusion, we confirmed the accuracy of our methods using crystalline silicon as a model material.
Figure 3.1.4 Seebeck coefficient for crystalline silicon (a) (b) calculated as part of our study for different charge carriers (electrons or holes). The calculated values are compared against work by (c) Heinz, (d) Wang et al., and experimental measurements by (e) Geballe & Hull. The jagged behavior is caused by a small dataset.

Figure 3.1.5 Electrical conductivity for crystalline silicon (a) (electrons) (b) (holes) calculated as part of our study. The calculated values are plotted against similar work by (c) Heinz and (d) Wang et al. The primary difference between Wang et al. and our is different assumptions about the scattering behavior.
Figure 3.1.6. Electrical component of thermal conductivity of crystalline silicon (a) (electrons) (b) (holes) calculated as part of our study. These values are compared against work by (c) Heinz\textsuperscript{9}, and (d) Wang \textit{et al.}\textsuperscript{118}.

Figure 3.1.7. Thermoelectric figure of merit (ZT) for crystalline silicon as a function of carrier concentration. Lattice thermal conductivity was assumed to be (a) 100 W/(m·K) (b) 80 W/(m·K) as calculated in our study. These values are compared to work with lattice thermal conductivity of 80 W/(m·K) by (c) Heinz\textsuperscript{9} and (f) Wang \textit{et al.}\textsuperscript{118}. We also show ZT assuming a thermal conductivity of 100 W/(m·K) by (d) Heinz\textsuperscript{9} and (e) Wang \textit{et al.}\textsuperscript{118}.
Silicon nanowires are cylindrical silicon based nanostructures that typically have very large aspect ratios (D/L > 1000). We use silicon nanowires as another method to check the accuracy of our computational techniques with a more complex system, and to show that nanostructuring can improve thermoelectric properties. Silicon nanowires are interesting potential thermoelectric materials. Experimental measurements have been performed of the thermoelectric properties of large diameter silicon nanowire (20-50 nm diameter, see section (1.2)). We considered the thermoelectric properties of small (1 nm) silicon nanowires with simple surface termination and three different crystallographic orientations. There have been no measurements of the thermoelectric properties of such small diameter nanowire systems, but several theoretical works have predicted improved thermoelectric properties compared to bulk silicon. We compared our calculations to one independent theoretical study in order to test predictive accuracy of our computational techniques. The close agreement between our results and sample published work supports the accuracy of our methods for predicting the thermoelectric properties of materials with complex geometry, and that we are able to predict improvement of thermoelectric properties.

Figure 3.1.8. Seebeck coefficient of n-type crystalline silicon as a function of temperature for specific carrier concentrations. (a) $1.7 \cdot 10^{19}$ e/cm$^3$ calculated in our study. (b) Experimental measurements of $1.7 \cdot 10^{19}$ n/cm$^3$ Arsenic doped crystalline silicon conducted by Weber and Gmelin. 

3.2 Silicon Nanowires

Silicon nanowires are cylindrical silicon based nanostructures that typically have very large aspect ratios (D/L > 1000). We use silicon nanowires as another method to check the accuracy of our computational techniques with a more complex system, and to show that nanostructuring can improve thermoelectric properties. Silicon nanowires are interesting potential thermoelectric materials. Experimental measurements have been performed of the thermoelectric properties of large diameter silicon nanowire (20-50 nm diameter, see section (1.2)). We considered the thermoelectric properties of small (1 nm) silicon nanowires with simple surface termination and three different crystallographic orientations. There have been no measurements of the thermoelectric properties of such small diameter nanowire systems, but several theoretical works have predicted improved thermoelectric properties compared to bulk silicon. We compared our calculations to one independent theoretical study in order to test predictive accuracy of our computational techniques. The close agreement between our results and sample published work supports the accuracy of our methods for predicting the thermoelectric properties of materials with complex geometry, and that we are able to predict improvement of thermoelectric properties.
Large diameter (≥20 nm) silicon nanowires are interesting potential thermoelectric materials that have been experimentally studied. Hochbaum et al. in 2008\textsuperscript{54,11} used metal assisted chemical etching to produce silicon nanowires with very rough surfaces and approximately 50 nm in diameter. They measured large reductions in lattice thermal conductivity, approximately 1 W/(m·K) at 300K (~149 W/(m·K) for bulk silicon). The roughened nanowire surface resulted in a two order of magnitude increase in the thermoelectric figure of merit, ZT of 0.6 at 300K, when compared to bulk silicon which has ZT ~0.0017 at 300 K\textsuperscript{55}. The reduction in thermal conductivity was further supported by Boukai et al.\textsuperscript{56}. They measured a reduction in thermal conductivity down to 1 W/(m·K) for a 10 nm diameter silicon nanowire. They also found a maximum thermoelectric figure of merit of ~1 for a 20 nm diameter nanowire at 200 K. Experimental measurements are currently limited by the fabrication techniques to produce silicon nanowire thermoelectric devices. Silicon nanowires are generally produced from photolithographic processes that loose resolution below 20 nm. Smaller diameter nanowire systems were predicted to have large improvement in ZT when compared to larger diameter nanowires, but experimental study of such systems is not yet possible.

Heinz\textsuperscript{9} in 2008 developed a practical method for predicting the thermoelectric properties of silicon nanowires using DFT with PBE-GGA and BoltzTraP. He used numerically fitted electron mobility data for pure silicon to approximate the carrier relaxation time in silicon nanowires. The fitting equation developed by this process is discussed was section (3.1). Heinz used this process to study nanowires with a fixed radius of approximately 1 nm. Heinz estimated a maximum value of ZT~ 0.08, only slightly larger than bulk silicon. Our study adapts these methods to predict the thermoelectric properties of slightly different silicon nanowire systems. The relative difference between our nanowire system and Heinz is highlighted in table 1.

Galli et al. in 2008\textsuperscript{125} used experimental data\textsuperscript{126} to better represent the complex surface termination of silicon nanowires and then thermoelectric properties of systems with varying diameter between 1 to 3.25 nm. Galli used QBOX\textsuperscript{127} along with Quantum Espresso\textsuperscript{122} for electronic structure calculations with the LDA and Hamann pseudopotentials\textsuperscript{128}. Galli et al. directly calculated lattice thermal conductivity using MD simulations\textsuperscript{80}, and found lattice thermal conductivity to be approximately a factor of 50 smaller than crystalline silicon and independent of the crystallographic orientation of the nanowire. They performed BTT calculations by solving the 1D BTE for each system. Galli et al. estimated the relaxation time by numerically fitting electron mobility data for crystalline silicon. Galli et al. predicted strongly improved ZT for silicon nanowires. They found a maximum ZT of approximately 1.12 with $10^{19}$ charge carriers per cubic centimeter. ZT was observed to be dependent on the crystallographic orientation
of the nanowire, and inversely dependent on the diameter. We did not directly compare our calculations to Galli et al. because of the radically different calculation process and surface termination scheme, but include band gap and general information about their nanowire systems in table 3.2.1.

The thermoelectric properties of silicon nanowires are affected by differences in crystallographic orientation. There are three primary crystallographic orientations for silicon nanowires. These orientations are Miller indices (1,0,0), (0,1,1), and (1,1,1), based on the symmetry planes of bulk silicon129. Figure 3.2.1 shows the different nanowire systems we considered. This figure shows a series of images of each silicon nanowire from different view angles to demonstrate the different arrangements of silicon atoms in each nanowire. The first step in our DFT calculations was to estimate the initial position of each atom in the nanowire systems. We calculated the position of each atom by defining a hypothetical cylinder around a volume containing crystalline silicon oriented so that the primary axis of the cylinder is aligned with respect to the Miller index. All atoms outside the cylinder are removed, and the dangling silicon bonds are repaired with hydrogen termination.

![Figure 3.2.1](image)

Figure 3.2.1. Images of the three different orientations of 1 nanometer diameter silicon nanowire produced using VESTA crystal visualization software143. Blue spheres represent silicon atoms, white spheres represent hydrogen atoms. Blue cylinders represent Si-Si single bonds, and blue and white cylinders represent Si-H bonds. (1a), (1b), (1c) shows (0,0,1) orientation, (2a), (2b), (2c) shows (0,1,1) orientation, and (3a), (3b), (3c) shows (1,1,1) orientation.
We included off axis \( \mathbf{k} \) points because of the constraints imposed by the Fourier interpolation subroutine in BoltzTraP. This subroutine requires a minimum of 4 \( \mathbf{k} \) points along any direction in reciprocal space in order to expand the electronic structure for 1D calculations. We performed DFT calculations with a 4x4x32 \( \mathbf{k} \) point grid, a cutoff energy of 544 eV, and an inter-nanowire spacing of 15.4 Å. We then constrained BoltzTraP to use a sparse energy grid along the off-axis directions in reciprocal space. We estimated the band gap of the silicon nanowire systems to be 2.621 eV (0,0,1), 1.595 eV (0,1,1), and 2.242 eV (1,1,1). Table 1 summarizes the differences in our calculated band gap and the values reported by Heinz and Galli \textit{et al.} For example, we calculated a band gap of 2.621 eV for the (0,0,1) nanowires system, while Heinz finds a gap of 2.124 eV, and Galli reported 2.35 eV. We conclude that these differences are likely caused by structural variation in our nanowire systems compared to Heinz and Galli \textit{et al.} Columns 2, 4, and 6 in Table 1 show differences between the number of atoms included in each supercell. Our DFT band gap predictions are similar to values found by Zhao \textit{et al.} who use similar nanowire structures, as seen in Table 3.2.2. We believe that differences in band gap do not alter the validity of comparison with Heinz. The bands in our calculated electronic structures (figure 3.2.2) are very flat near the band gap. This

<table>
<thead>
<tr>
<th>Growth direction</th>
<th># atoms (Diameter)</th>
<th>Band Gap (eV)</th>
<th># atoms (Diameter)</th>
<th>Band Gap (eV)</th>
<th># atoms (Diameter)</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0,0,1)</td>
<td>41 (1.05 nm D)</td>
<td>2.621</td>
<td>65 (1 nm D)</td>
<td>2.124</td>
<td>96 (1.1 nm D)</td>
<td>2.35</td>
</tr>
<tr>
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<td>42 (1 nm D)</td>
<td>1.398</td>
<td>102 (1.2 nm D)</td>
<td>1.72</td>
</tr>
<tr>
<td>(1,1,1)</td>
<td>68 (1.07 nm D)</td>
<td>2.242</td>
<td>102 (1 nm D)</td>
<td>1.849</td>
<td>136 (1.1 nm D)</td>
<td>2.12</td>
</tr>
</tbody>
</table>

Table 3.2.1. Calculated band gaps of different nanowire systems compared against previous studies.

<table>
<thead>
<tr>
<th>Growth direction</th>
<th># atoms (Diameter)</th>
<th>Band Gap (eV)</th>
<th># atoms (Diameter)</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0,1,1)</td>
<td>28 (1.07 nm D)</td>
<td>1.595 eV</td>
<td>28 (1.2 nm D)</td>
<td>1.5 eV</td>
</tr>
<tr>
<td>(1,1,1)</td>
<td>68 (1.07 nm D)</td>
<td>2.242 eV</td>
<td>68 (1 nm D)</td>
<td>2.2 eV</td>
</tr>
</tbody>
</table>

Table 3.2.2. Calculated band gaps of different nanowire systems compared against other studies with similar structural elements. Zhao \textit{et al.} included GW corrections in some calculations, but we did not include the GW corrections in this table.
leads to improved Seebeck coefficient.

We found that it was necessary to increase the maximum number of convergence steps in the BoltzTraP program from 1000 to 5000 in lines 156 and 181 in the Fermiintegrals.F90 subroutine. This increases the number of finite element search cycles used to determine the carrier concentration in terms of the shift in the Fermi energy. We used 40 real space points per k point to minimize interpolation error, a chemical potential and DOS shift resolution of $1.36 \times 10^{-4}$ eV/segment, included 192 individual bands from the DFT electronic structure, and set the chemical potential range to 2.8 eV. DFT and BTT convergence testing is discussed in detail in appendix A.

The relaxation time of all silicon nanowires was estimated using the fitting equation of crystalline silicon shown in section (3.1). Galli et al. performed MD simulations of the lattice thermal conductivity of their nanowire systems. They calculated a lattice thermal conductivity of 2 W/(m·K) at 300K. Heinz used an identical value of lattice thermal conductivity in his study. Li et al. measured the thermal conductivity of (1,1,1) oriented silicon nanowires with diameters between 22 and 115 nm, between 20 and 320K. He found lattice thermal conductivity to be between 10-50 W/(m·K). Based on the MD simulations performed by Galli et al. and experimental measurements by Li et al., we determined that 2 W/(m·K) at 300K was a reasonable approximation of the lattice thermal conductivity of silicon nanowires, and we used this value in our ZT calculations.

The results of our calculations are summarized in figure 3.2.3, and shown in greater detail in figures 3.2.4, 3.2.5, 3.2.6 and 3.2.7 along with similar work by Heinz. Figure 3.2.4 shows calculated Seebeck coefficient for all three silicon nanowire orientations. We predict Seebeck coefficient to be approximately a factor of 2 smaller than
Heinz for all nanowire orientations, but the trends are identical. We assume this difference was caused by a combination of slightly different nanowire structures and our more careful convergence testing that included additional bands in the electronic structure. Seebeck coefficient scales linearly within this range of carrier concentration. Our results correspond to an approximate factor of 8 increase in Seebeck coefficient compared to standard silicon caused by decreased effective mass.

Figure 3.2.5 shows calculated electrical conductivity for the same systems. The nanowire structure does not seem to cause a decrease in electrical conductivity compared to crystalline silicon. We do not know if the calculated electrical conductivity is an artifact of the fitted carrier relaxation time or truly represents physical behavior in silicon nanowires. Combined with experimental measurements of larger diameter nanowire systems which also predict improved Seebeck coefficient and stable electrical conductivity, we believe that our calculations could represent the thermoelectric properties of silicon nanowires. In previous experimental measurements electrons were able to travel through the core of nanowires without encountering increased scattering. Phonons traveling through nanowires are thought to encounter increased surface scattering leading to a decrease in lattice thermal conductivity.

Figure 3.2.3. Summary of our calculations for (a) (0,0,1) (b) (0,1,1), and (c) (1,1,1) silicon nanowires. The corresponding calculations performed by Heinz\textsuperscript{9} are shown for (d) (0,0,1) (e) (0,1,1) and (f) (1,1,1). We calculated the Seebeck coefficient using ABINIT\textsuperscript{103} and BoltzTraP\textsuperscript{106}. Plot references correspond with larger resolution figures that are referenced in the discussion, and show (3.2.4) Seebeck coefficient, (3.2.5) electrical conductivity, (3.2.6) electrical thermal conductivity, and (3.2.7) ZT.
We used identical fitting equations to approximate the relaxation time of charge carriers, and the differences between our calculations and Heinz are assumed to be caused by structural differences between the nanowire systems and electronic structures. Despite these differences, our calculations remain very similar, with almost identical qualitative trends. Figure 3.2.6 shows our calculated electrical component of thermal conductivity. We believe that more careful convergence testing and inclusion of additional bands from the DFT electronic structure strengthen the accuracy of our calculations.

Figure 3.2.7 shows calculated ZT. We estimate at 300K a maximum $ZT=0.015$ (0,0,1), $ZT=0.011$ (0,1,1), and $ZT=0.013$ (1,1,1) for the nanowire systems considered. This corresponds to a factor of 100 improvement compared to bulk silicon. This is caused by predicted reduction in thermal conductivity for these nanowire systems. This is not sufficient to make silicon nanowires an efficient thermoelectric material, but shows that nanoscale confinement can be used to improve thermoelectric efficiency. Heinz estimated larger maximum ZT values (ex. of 0.08 at $10^{19}$ e/cm$^3$ for (0,1,1) orientation). The difference between our calculated ZT and Heinz’s is caused by a factor of 2 lower calculated Seebeck coefficient and lower electrical conductivity. Galli et al. predicted a much higher ZT of 2.5 at $10^{19}$ e/cm$^3$ for a (0,1,1) nanowire with different surface termination. Hochbaum et al. experimentally measured the thermoelectric efficiency of larger diameter roughened silicon nanowires and observed maximum ZT of 0.6 at 300K. Even though Hochbaum et al. considered larger diameter nanowires, the roughened surface dramatically decreases thermal conductivity. This decreased thermal conductivity is most likely representative of smaller smooth nanowire systems. These measurements suggest that smaller diameter silicon nanowire systems are not promising thermoelectric materials, but provide a path for further improvements. We conclude that our methods can be used to predict the thermoelectric properties of more complex systems. In addition, nanostructured materials provide a path toward improved thermoelectric efficiencies because of reduced thermal conductivity and improved ZT.
Figure 3.1.4. Calculated Seebeck coefficient for (a) (0,0,1) (b) (0,1,1), and (c) (1,1,1) silicon nanowires. The corresponding calculations performed by Heinz are shown for (d) (0,0,1) (e) (0,1,1) and (f) (1,1,1). We calculated the Seebeck coefficient using ABINIT and BoltzTraP.

Figure 3.2.5. Calculated electrical conductivity of for (a) (0,0,1) (b) (0,1,1), and (c) (1,1,1) silicon nanowires. The corresponding calculations performed by Heinz are shown for (d) (0,0,1) (e) (0,1,1) and (f) (1,1,1). We calculated the conductivity using ABINIT and BoltzTraP.
Figure 3.2.6. Calculated electrical component of thermal conductivity for (a) (0,0,1) (b) (0,1,1), and (c) (1,1,1) silicon nanowires. The corresponding calculations performed by Heinz\(^9\) are shown for (d) (0,0,1) (e) (0,1,1) and (f) (1,1,1). We calculated the electrical component of thermal conductivity using ABINIT\(^{103}\) and BoltzTraP\(^{106}\).

Figure 3.2.7. Calculated ZT for (a) (0,0,1) (b) (0,1,1), and (c) (1,1,1) silicon nanowires. The corresponding calculations performed by Heinz\(^9\) are shown for (d) (0,0,1) (e) (0,1,1) and (f) (1,1,1). We calculated ZT using ABINIT\(^{103}\) and BoltzTraP\(^{106}\).
CHAPTER 4

THERMOELECTRIC PROPERTIES OF GRAPHENE

We first calculated the thermoelectric properties of pristine graphene in order to better interpret our predictions of graphene nanomesh. Standard graphene has unusual physical properties that show great promise for many electronic applications such as transistors\(^2\) and lighting\(^{131}\), but is a poor thermoelectric material because of large phonon mediated thermal conductivity as discussed in section 1.2. We approximated carrier relaxation time by numerically fitting previously published experimentally measured electron mobility\(^{1,2}\). We then combined fitted electron mobility with other previously published experimental measurements of the carrier properties of graphene systems\(^2,63\). We compared the results of our calculations to previous experimental measurements of the Seebeck coefficient and electrical conductivity of graphene\(^{62}\). We achieved good agreement with these experiments. This provided the foundation for our primary study of the thermoelectric properties of graphene nanomesh.

The calculated band structure and DOS of graphene is shown in figure 4.1. We used a 144x144x1 \(k\) point grid, with 1610 irreducible points to minimize secondary interpolation based oscillations in Seebeck coefficient. This is a much denser in-plane \(k\) grid than we used for silicon. The increased \(k\) point density is required to resolve the electronic structure near the \(K\) points and helped with debugging. The exponential decrease of average amplitude in secondary oscillations with respect to increasing \(k\)-grid density is shown in figure 4.2. This is the same convergence process we developed for crystalline silicon. We defined convergence to occur when secondary interpolation oscillations are two orders of magnitude smaller than primary features in Seebeck coefficient. Such

![Graphene Band Structure and DOS](image)

Figure 4.1. Band structure and DOS of Graphene calculated as part of this work using ABINIT\(^{103}\) with GGA and PBE\(^{144}\) based Trouiller-Martins\(^{123}\) type norm conserving pseudopotentials.
dense k grids are not necessary when calculating the thermoelectric properties of materials with a true band gap. In addition, we used a cutoff energy of 1197 eV, a graphene spacing of 12.7 Å, a lattice parameter of 2.458 Å, the GGA with PBE based Trouiller-Martins\textsuperscript{123} type norm-conserving pseudopotentials, 40 real space points per k point in expanding the electronic structure, and used 40 individual bands in our BTT calculations. Details of the convergence process and other quantities are discussed in appendix A.3.

We determined after extensive testing that BoltzTraP version 1.2.5 did not accurately predict the thermoelectric properties of graphene without modification. Three different modifications were necessary to the BoltzTraP program. These modifications included the imposition of a sparse interpolation along the Z direction in the electronic structure, a slight modification of the calculation process for tensor traces, and hardcoding some of the preconditioning settings needed for Fourier interpolation. Imposing a sparse interpolation along the Z direction in the electronic structure was required in order to minimize effects from interpolation oscillation along the unused direction in reciprocal space. The dependence of the chemical potential shift due to carrier concentration is determined by lines 155-183 in Fermiintegrals.f90 subroutine using a finite element search. We know from published experimental data\textsuperscript{2,63} that the chemical potential shift resulting from changes in carrier concentration should scale proportionally with $\sqrt{n}$. This calculation format does not accurately determine the carrier concentration.

![Figure 4.2. Average oscillation amplitude in the calculated Seebeck coefficient vs. number of total k points included in the DFT calculation of the electronic structure of pure graphene.](image)
for 2D systems, and needed to be modified. Tensor traces of the respective thermoelectric properties are calculated at lines 342-346 in the same subroutine. It was necessary to remove references to the unused dimension in 2D systems. Settings used to start the Fourier interpolation are in the bandana.f90 subroutine. When performing convergence testing with low density k-grids, it was necessary to hardcode zero band gap into the interpolation process. Without this modifications, BoltzTraP falsely assumes that there is a band gap in the electronic structure of graphene. The CBM and VBM are then set equal to the Fermi energy using the variables vbm and cbm. With these modifications we were able to accurately calculate the thermoelectric properties of graphene. The effects of our modifications on calculated Seebeck coefficient is shown in figure 4.3. The red line (a) shows results of the unmodified BoltzTraP program, with large oscillations caused by transverse interpolation errors from the unused dimension in reciprocal space. The green line (b) shows the effect of imposing a sparse k grid in the transverse dimension with incorrect functional form. The blue line (c) shows the cumulative effect of all our modifications with

Figure 4.3. Seebeck coefficient for graphene calculated using BoltzTraP, showing the effects of modifications applied to the BoltzTraP program. The red line (a) is from unmodified BoltzTraP program. The green line (b) shows the effect of imposing a sparse k grid in the transverse dimension. The blue line (c) shows the cumulative effect of all our modifications.
The relaxation time of graphene was estimated by numerically fitting mobility measurements performed by Bolotin et al. and Das et al. Bolotin et al. in 2008 measured the mobility of high purity suspended graphene produced by mechanically exfoliating Highly Ordered Pyrolytic Graphite (HPOG). The graphene was then deposited on a clean 300 nm thick silicon oxide substrate. Electron beam lithography was used to build electrodes on the graphene flake into a Hall bar configuration. Selective oxide etching is used to remove the SiO$_2$ substrate from underneath the graphene flake. The flake was then annealed in a cryostat chamber at 400K to remove surface adsorbents. Graphene suspension was confirmed by quantum Hall effect measurements, conductivity measurements, and AFM observation. Bolotin et al. measured extremely large electron mobility in annealed graphene, on the order of 200,000 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. Das et al. in 2008 used polymer based electrochemically gated graphene transistor system to measure electron mobility. Graphene flakes were again mechanically exfoliated from HPOG, and then deposited on a 300 nm thick SiO$_2$ layer. Platinum electrodes and a polymer based top gating material were deposited on the graphene flake using photolithography. They measured slightly lower electron mobilities on the order of 70,000 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for their system. Experimentally measured values from both papers are incorporated into figure 4.4. The difference between the two measurements is probably due to complex surface interactions. We estimated the relaxation time using both measurements, in order to predict the thermoelectric properties of both freely suspended and surface interacting graphene systems.

The next step in calculation process was to convert the experimental carrier mobility measurements into useful predictions of the relaxation time using numerical fitting. The electron mobility of graphene can be represented using a fitted equation:

$$
\mu_m(n) = \mu_0n + \frac{\mu_1n}{\alpha + \beta n}
$$

(4.1)

where $\mu_m$ is the electron mobility, $\mu_0$, $\mu_1$, $\alpha$, and $\beta$ are numerically fitted parameters, and $n$ is the carrier concentration. Experimentally measured and numerically fitted electron mobility are shown in figure 4.4. Soft annealing of graphene systems by heating graphene flakes in vacuum removes a significant proportion of surface adsorbents that act as carrier scattering sites. This leads to increased electron mobility and decreased surface interaction. The exact fitting parameters we used for each system are shown in table 4.1.
Table 4.1. Numerical fitting parameters used to fit electron mobility data using equation (4.1)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bolotin et al annealed</th>
<th>Bolotin et al unannealed</th>
<th>Das et al top gating</th>
<th>Das et al back gated</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_a$ (m$^2$V$^{-1}$s$^{-1}$)</td>
<td>28.15</td>
<td>2.12</td>
<td>8.07</td>
<td>1.54</td>
</tr>
<tr>
<td>$\mu_1$ (m$^2$V$^{-1}$s$^{-1}$)</td>
<td>152.60</td>
<td>14.16</td>
<td>2757</td>
<td>57.61</td>
</tr>
<tr>
<td>$\alpha$ (unitless)</td>
<td>0.15</td>
<td>0.031</td>
<td>396.2</td>
<td>28.28</td>
</tr>
<tr>
<td>$\beta$ (1/n*, (n*=n/10^{11})</td>
<td>47.83</td>
<td>5.065</td>
<td>2099</td>
<td>94.15</td>
</tr>
</tbody>
</table>

Figure 4.4. Electron mobility measured by Bolotin et al.\(^1\) where freely suspended (a) annealed and (b) unannealed graphene. Numerical fits using equation (4.4) is shown with dashed lines (c) and (d). Das et al.\(^2\) measured the electron mobility of (e) top and (f) back gated graphene based device. Numerical fits using equation (4.4) is shown with (f) and (g). Values for the fitting parameters are shown in Table (4.1).
The relationship between the shift in the Fermi energy and the carrier concentration is well understood. A series of theoretical predictions and experimental measurements\(^2,^6,^3\) has firmly established the relationship between carrier concentration and the shift in Fermi energy

\[ E_f = \hbar v_f \sqrt{\pi n} \]  \hspace{1cm} (4.2)

Where \( E_f \) is the Fermi energy and \( v_f \) is the Fermi velocity measured\(^6,^3\) to be \( v_f = 1.15 \times 10^8 \) cm/s in graphene. The relationship between the relaxation time and the electron mobility can be defined by:

\[ \tau = \frac{\mu m E_f}{e v_f^2} \]  \hspace{1cm} (4.3)

Where \( \tau \) is the relaxation time and \( e \) is the charge of the electron. Based on equation (4.2) and (4.3) we developed approximations to relaxation time in terms of either the Fermi energy shift or the net free carrier concentration

\[ \tau = \frac{\hbar \sqrt{\pi n}}{e v_f} \left( \mu_{on} + \frac{\mu_{in}}{\alpha + \beta n} \right) \]  \hspace{1cm} (4.4)

\[ \tau = \frac{E_f}{e v_f^2} \left( \mu_{on} + \frac{\mu_{in}}{\alpha + \beta \left( \frac{E_f}{\hbar v_f} \right)^2} \right) \]  \hspace{1cm} (4.5)

We used equation (4.4) to estimate the relaxation time of unmodified graphene, while equation (4.5) was used to

![Figure 4.5](image)

Figure 4.5. Our estimated relaxation time as a function of carrier concentration using equation (4.4). Estimated relaxation time based on fitting electron mobility measurements from (a) un-annealed, (b) annealed graphene flakes by Bolotin \textit{et al} \(^1\), and (c) un-annealed or (d) annealed top gated graphene transistor by Das \textit{et al} \(^2\).
approximate the relaxation time of graphene nanomesh (chapter 5). Extracted carrier relaxation is shown in figure 4.5 in terms of free carrier concentration. Figure 4.6 shows how the relaxation time scales with respect to Fermi energy shift. These figures confirm the functional form and correct order of magnitude for the relaxation time for graphene based systems, and show effects of charge pooling and screening predicted by Das Sarma et al.\textsuperscript{75}. We did not know before completing our calculations which fitted equation would most accurately predict transport properties. We include plots of all fitted equations to demonstrate how transport properties scale with variable relaxation time.

The final step in our calculation process was to estimate the lattice thermal conductivity of graphene using values determined by previously published experimental measurements\textsuperscript{65,132}. The large phonon mean free path predicted for 2D materials (~775 nm for graphene\textsuperscript{133} and 300K) compared to 3D materials (~30 nm for Silicon\textsuperscript{55} at 300 K as an example) complicates accurate prediction and measurement of thermal properties. NEGF techniques cannot use periodic boundary conditions to calculate the thermoelectric properties of materials. As a result, these methods are limited by finite system size that force calculation into the ballistic transport regime. Real world thermoelectric devices operate in the diffusive limit. In contrast, our calculation technique used periodic boundary conditions to estimate the thermoelectric properties of materials. Our calculations were therefore performed in the diffusive limit. This allows us to rely on previous calculations of lattice thermal conductivity in graphene nanomesh.

Figure 4.6. Relaxation time of graphene as a function of chemical potential shift away from the fermi energy. Estimated relaxation time based on fitting electron mobility measurements from (a) un-annealed, (b) annealed graphene flakes by Bolotin et al\textsuperscript{1}, and (c) un-annealed or (d) annealed top gated graphene transistor by Das et al\textsuperscript{2}. 

- (a)
- (b)
- (c)
- (d)
A series of experimental measurements summarized by Balandin\textsuperscript{65} estimated the lattice thermal conductivity of graphene to be between 4000 and 6000 W/(m·K) at 300 K. These experiments measured the shift in the Raman spectrum of graphene, especially around the G peak, after laser heating. Lattice thermal conductivity in graphene is strongly affected by purity and quality of measured samples. Theoretical studies summarized by Nika and Balandin\textsuperscript{132} estimated the thermal conductivity of graphene to be between 500 and 11000 W/(m·K). It has been suggested\textsuperscript{132} that the thermal conductivity of graphene is finite in experimental measurements because of disorder and impurities in the crystal lattice. Fourier’s heat conduction law predicts infinite lattice thermal conductivity if disorder is not present. These theoretical works used a variety of techniques ranging from MD simulation to solving the phonon form of the BTE. As a result of these measurements and theoretical predictions, we used a value of 4000 W/(m·K) to approximate the lattice thermal conductivity of graphene.

We determined the thermoelectric properties of graphene using our multi-step BTT and DFT based computational process. Figure 4.7 summarizes the results of our calculations, while larger versions of the same graphs are provided following the discussion. We were required to modify the BoltzTraP program to accurately predict thermoelectric properties. Carrier relaxation time was approximated using experimentally measured electron mobility as discussed earlier. Figure 4.8 shows our calculated Seebeck coefficient compared to experimental measurements by Zuev \textit{et al.}\textsuperscript{62}. We concluded that the difference in Seebeck coefficient is probably due to surface interaction and the overall complexity of measuring carrier concentration in materials. Zuev \textit{et al.} measured the thermoelectric properties of graphene located on a SiO\textsubscript{2} substrate, which causes strong surface interaction effects. Our calculations have identical trends to these experimental measurements, but over a narrower carrier concentration range. Our calculated maximum Seebeck coefficient is approximately 150 µV/K at 300 K. This is located very close to the Fermi energy, accessible by very low free carrier concentrations. This strengthens our conclusion that graphene has properties that could be used to develop useful thermoelectric devices given minimization of lattice thermal conductivity. Figure 4.9 shows our calculated electrical conductivity compared to experimental measurements. Our calculated electrical conductivity scales linearly with carrier concentration, as expected for 2D systems. The accuracy of our calculations compared to experimental measurement strongly decrease as carrier concentration approaches $10^{11}$ e/cm\textsuperscript{2}. This is consistent with previous theoretical predictions by Das Sarma \textit{et al.}\textsuperscript{64}. As carrier concentration decreases, the probability of sufficient charge carriers undergoing scattering decreases. When this occurs more complex quantum effects dominate over standard charge scattering leading to finite nonzero
electrical conductivity with extremely low carrier concentration. These effects cannot be incorporated into standard semi-classical BTT. We predict identical trends and very similar values to experimental measurements by Zuev et al.\textsuperscript{62} when carrier concentration is sufficiently large. The slight differences between our calculations and these experimental measurements can be accounted for by differences in carrier relaxation time and electronic structure. We relied on experimental measurements of systems with differing purity and quality. Surface interaction effects in the electronic structure of graphene were not included in our calculations. Increases in electrical conductivity near the Fermi energy are artifacts of our numerical fitting of relaxation time, and do not represent true physical trends.

Figure 4.10 shows our calculated electrical component of thermal conductivity. As expected this is a linear function in terms of carrier concentration. This further shows the extremely small electrical contribution to thermal conductivity in graphene, many orders of magnitude smaller than the 4000 W/(m·K) measured in experiment. Figure 4.11 shows our predicted ZT values for standard graphene. As expected, this is extremely low, even compared to...
bulk materials such as crystalline silicon. The primary cause of low ZT is large lattice thermal conductivity. We estimated a maximum ZT of $2.15 \times 10^{-4}$ at 300K with a carrier concentration of $10^{12}$ for annealed freely suspended graphene. As expected increasing disorder lowers ZT by decreasing beneficial charge transport properties. We show ZT in terms of chemical potential shift of the Fermi energy since this is more useful in direct comparison to later calculations of graphene nanomesh and defected graphene.

We conclude that the beneficial charge transport properties of graphene could be used to produce more efficient thermoelectric materials with careful minimization of lattice thermal conductivity. We further conclude that we were able to accurately predict the thermoelectric properties of pristine graphene using a relatively simple calculation methodology. This required modification of the standard BTT calculation process to more accurately represent 2D systems. Our computed results are supported by experimental measurements of the thermoelectric properties of graphene conducted by Zuev et al$^{62}$ shown in figures 4.7, 4.8 and 4.9.

![Graph](image)

**Figure 4.8.** Calculated Seebeck coefficient performed using ABINIT$^{103}$, GGA, norm conserving pseudopotentials, and BoltzTraP$^{106}$. (a) Depicts our calculated values, (b) are measured values reported by Zuev et al$^{62}$. 
Figure 4.9. Estimated electrical conductivity of graphene with relaxation times fitted from experimental measurements of (a) un-annealed freely suspended graphene\textsuperscript{100} (b) annealed freely suspended graphene\textsuperscript{100} (c) surface interacting un-annealed graphene\textsuperscript{138} (d) surface interacting annealed graphene\textsuperscript{138} This was based on electron mobility data shown in figure (4.4). These calculations are compared to experimental measurements by (e) Zuev \textit{et al}\textsuperscript{62} on an interacting SiO\textsubscript{2} substrate.

Figure 4.10. Electrical part of thermal conductivity for graphene with relaxation times fitted from experimental measurements of (a) un-annealed freely suspended graphene\textsuperscript{100} (b) annealed freely suspended graphene\textsuperscript{100} (c) surface interacting un-annealed graphene\textsuperscript{138} (d) surface interacting annealed graphene\textsuperscript{138} This was based on electron mobility data shown in figure (4.4).
Figure 4.11. ZT of graphene calculated using ABINIT\textsuperscript{103} with GGA, norm conserving pseudopotentials, and BoltzTraP\textsuperscript{106}. This used relaxation times fitted from experimental measurements of (a) un-annealed freely suspended graphene\textsuperscript{100} (b) surface interacting un-annealed graphene\textsuperscript{138} (c) surface interacting annealed graphene\textsuperscript{138} and (d) annealed freely suspended graphene\textsuperscript{100}. This was based on electron mobility data shown in figure (4.4).
CHAPTER 5
THERMOELECTRIC PROPERTIES OF GRAPHENE NANOMESH

The goal of this study was to better understand the properties affecting improvement of the electronic component of thermoelectric efficiency. We hypothesized that graphene nanomesh would be a significantly improved thermoelectric material compared to standard graphene. Comparison with experiment and other theoretical studies showed the accuracy of our methods for standard silicon (section 3.1). Our calculations involving silicon nanowires showed that decreasing dimensionality could be used to improve thermoelectric properties (section 3.2). We were then able to predict the thermoelectric properties of standard graphene (chapter 4). This showed that graphene has beneficial transport properties which could be used to produce more efficient thermoelectric materials if lattice thermal conductivity could be reduced. This chapter discusses our calculations of simple nanomesh (section 5.1), nanomesh with variable defect spacing (section 5.2), hydrogen passivation, and boron nitride doping (section 5.3). Our studies indicate that graphene nanomesh has great potential as a thermoelectric material given careful optimization of the electronic structure.

5.1 Simple Nanomesh Systems

The first graphene nanomesh systems we investigated were simple hexagonally periodic and square periodic with a single hydrogen terminated ring vacancy defect first shown in figure (1.3.1). We hypothesized that hexagonally periodic and square periodic graphene nanomesh would have improved ZT compared to standard graphene. Previous theoretical studies of graphene nanomesh\textsuperscript{67-69} have predicted band gap opening under special symmetry conditions. The relaxation time of graphene nanomesh was then approximated using previous experimental measurements of electron mobility in graphene (chapter 4). The lattice thermal conductivity of the graphene nanomesh systems was approximated using previously published fitting equations\textsuperscript{3,16} developed using MD simulations (section 1.3). We then predicted the thermoelectric properties of hexagonally periodic and square periodic graphene nanomeshes. Our results predict a substantial improvement in ZT of graphene nanomesh compared to standard graphene. This is partly due to an increase in the Seebeck coefficient resulting from opening up a band gap in the nanomesh electronic structure. The additional improvement in ZT was due to substantial reduction in thermal conductivity. We concluded that graphene nanomesh is a promising thermoelectric material based on our calculations.
We considered two different periodic arrangements of graphene nanomesh based on previous studies of graphene nanomesh by Dvorak et al.\textsuperscript{67-69}. The graphene supercell was aligned so that a hexagonal hydrogen terminated ring defect (figure 1.3.1) was centered at the origin of each supercell and then formed a graphene mesh.
around the defect. Both systems have a total of 72 atoms, 6 hydrogen and 66 carbon. We used a very similar convergence process to our previous studies. The electronic structure of both systems is shown in figure 5.1.1. The band structures are shown along different high symmetry paths through the Brillouin zone because of the different sublattice periodicities. We calculated a band gap of 0.778 eV for the hexagonally periodic system and 0.693 eV for the square periodic system. Our calculated band gap values, and the overall shape of the bands, especially close to the Fermi energy, match previously published values of 0.78 eV (hexagonally periodic) and 0.69 eV (square periodic) nanomesh systems reported by Dvorak and Wu\textsuperscript{67} who used VASP with GGA. We used a 24x24x1 gamma centered un-shifted \textbf{k} point grid in our BTT calculations. This is sufficient to minimize secondary interpolation based oscillations in Seebeck coefficient to be two orders of magnitude smaller than primary features, as shown in figure 5.1.2. These oscillations decrease exponentially with increasing \textbf{k} point density. We found that a band gap in graphene nanomesh decreased the number of \textbf{k}-points required for interpolation compared to standard graphene. Sharply increasing, decreasing, degenerate, or crossing bands increase the number of required \textbf{k} points. We used a cutoff energy of 1360 eV, an inter-layer spacing of 15 Å, 40 real space points per \textbf{k} point, and energy range of 13.6 eV, an energy resolution of $1.36 \cdot 10^{-4}$ eV, and used 192 individually resolved bands in the electronic structure. Convergence testing and other details of our calculation process are discussed in appendix A.4.

Figure 5.1.2. Average amplitude of secondary oscillations in the Seebeck coefficient far away from the Fermi level. These oscillations are a qualitative measure of BTT convergence. These oscillations are two orders of magnitude smaller than primary features in the Seebeck coefficient. (a) Shows oscillations in hexagonally periodic graphene nanomesh, and (b) square periodic graphene nanomesh.
We relied on a fitting equation that we developed to describe carrier relaxation times for pure graphene (chapter 4). We elected to use the fitted equation from the graphene system with lowest mobility, that was measured from a graphene flake located between a silicon oxide surface and a long chain polymer based coating material. This maximizes the probability of strong surface interaction that more closely resembles the scattering effects of graphene nanomesh. We are limited by the lack of published experimental measurements or theoretical study of carrier relaxation in similar graphene nanomesh systems. The very low defect fractions considered in this section of our study (0.083), along with the functional form of the calculated Seebeck coefficient results, suggest that our system exhibits strong graphene-like behavior away from the band gap. We believe that this approximation method can be used to qualitatively predict overall trends in the thermoelectric properties of graphene nanomesh related to electronic structure effects.

The thermal conductivity of graphene nanomesh was approximated using previously developed fitting equations (chapter 1 section 4). Hu and Maroudas\(^3\) developed another descriptive equation using symmetry based arguments to describe the relationship between defect spacing, defect fraction, and lattice thermal conductivity:

\[
\ln \left( \frac{\kappa}{\kappa_0} \right) = f \left( 1 - \frac{n}{n_0} \right)^{1/2}
\]  

(5.1.1)

where \(\kappa\) is the lattice thermal conductivity, \(\kappa_0\) is the lattice thermal conductivity of pure graphene, \(f\) is an effective

![Graph showing calculated thermal conductivity values predicted by Hu and Maroudas\(^3\) for (a) hexagonally periodic and (b) square periodic graphene nanomesh systems as a function of mesh density \(n\) compared to pristine graphene \(n_0\). These values were calculated using MD simulations.](image)

Figure 5.1.3. The graph shows calculated thermal conductivity values predicted by Hu and Maroudas\(^3\) for (a) hexagonally periodic and (b) square periodic graphene nanomesh systems as a function of mesh density \(n\) compared to pristine graphene \(n_0\). These values were calculated using MD simulations.
aspect ratio, \( n \) is mesh density, and \( n_0 \) is the density of a pure unit cell without defects. The defect fraction is proportionally related to the spacing between defects. We predicted the thermal conductivity of each graphene nanomesh system using equation (5.1.1). Figure 5.1.3 shows how the thermal conductivity scales with hexagonally periodic and square periodic graphene nanomesh. We assumed an initial thermal conductivity of 5000 W/(m·K) in order to stay consistent with Hu and Maroudas. Based on this scaling law, we assume a thermal conductivity of 57.5 W/(m·K) for the hexagonally periodic graphene nanomesh at 300 K, and a thermal conductivity of 50.4 W/(m·K) for the simple square periodic graphene nanomesh system at 300 K. This corresponds to a 2 order of magnitude decrease in thermal conductivity compared to pure graphene. This reduction in thermal conductivity was expected to cause a large 2 order of magnitude increase in ZT. This strengthens our initial hypothesis that graphene nanomesh could be a much more efficient thermoelectric material compared to pure graphene.

We hypothesized that hexagonally periodic and square periodic graphene nanomesh would have an improved ZT when compared to standard graphene. The results of our calculations are summarized in figure 5.1.4, and shown with higher resolution in the figures following the discussion. Figure 5.1.5 shows calculated Seebeck coefficient, electrical conductivity, electrical thermal conductivity, and ZT. In each plot, we show our calculations for (a) hexagonally periodic graphene nanomesh, (b) square periodic graphene nanomesh, and (c) unmodified graphene for comparison calculated using BoltzTraP\textsuperscript{106} and ABINIT\textsuperscript{103}.

![Figure 5.1.5](image-url)

Figure 5.1.4. Summary of our calculations for simple nanomesh systems. The plot references correspond with figure numbers that follow the discussion. These plots show (5.1.5) Seebeck coefficient, (5.1.6) electrical conductivity, (5.1.7) electrical thermal conductivity, and (5.1.8) ZT. In each plot, we show our calculations for (a) hexagonally periodic graphene nanomesh, (b) square periodic graphene nanomesh, and (c) unmodified graphene for comparison calculated using BoltzTraP\textsuperscript{106} and ABINIT\textsuperscript{103}.

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coefficient of the nanomesh systems compared to standard graphene. We predict a substantial increase in Seebeck coefficient for graphene nanomesh, showing a transition from the semimetal behavior of standard graphene to that of a semiconductor. This extremely large Seebeck coefficient is approximately a factor of two larger than pure crystalline silicon (chapter 3 section 1) and comparable to values we predicted for silicon nanowires (chapter 3 section 2). Hexagonally periodic graphene nanomesh has slightly larger Seebeck coefficient than square periodic system. This is caused by slight differences in relative flatness of the bands close to the Fermi energy of the two band structures shown in figure 5.1.1. The energy spacing between the maximum peaks corresponds with the band gap, the trends are very similar for electrons and holes because of almost identical effective masses and direct band gap. Figure 5.1.6 shows calculated electrical conductivity of the two nanomeshes over a wider energy range compared to standard graphene. We predict a decrease in electrical conductivity compared to standard graphene. Conductivity scales quadratically with changing Fermi energy in standard graphene. Calculated conductivity scales exponentially close to the Fermi energy, but returns to quadratic scaling approximately 0.4 eV with oscillations on either side of the Fermi energy for both systems. This is again consistent with a semiconductor with a band gap of approximately 0.8 eV. Figure 5.1.7 shows similar trends in the electrical component of thermal conductivity. Figure 5.1.8 shows our calculated ZT values. The maximum ZT of the hexagonally periodic graphene nanomesh system is 0.15 with a chemical potential shift of 0.5 eV. The maximum ZT for the square periodic system was 0.145 with a chemical potential shift of 0.5 eV. The differences between the symmetry of each system only slightly affected the predicted thermoelectric properties.

These improved ZT values compared to standard graphene suggest that graphene nanomesh is a promising thermoelectric material. In conclusion we predict that graphene nanomesh is a promising thermoelectric material, but our calculations raise a question about the true cause of the increase in thermoelectric efficiency. We used a simple scaling law to predict lattice thermal conductivity. Improvements in Seebeck coefficient and the electrical component of thermal conductivity are compensated by a decrease in electrical conductivity. We assumed that the electronic structure of graphene nanomesh is the cause of improved thermoelectric efficiency, thus requiring further work to test this assumption.
Figure 5.1.5. Calculated Seebeck coefficient of (a) hexagonally periodic graphene nanomesh, (b) square periodic graphene nanomesh, and (c) unmodified graphene for comparison calculated using BoltzTraP\textsuperscript{106} and ABINIT\textsuperscript{103}. 
Figure 5.1.6. Conductivity of (a) hexagonally periodic and (b) square periodic graphene nanomesh calculated using BoltzTraP\textsuperscript{106} and ABINIT\textsuperscript{103} (c) pure graphene for reference.
Figure 5.1.7. Calculated electrical component of thermal conductivity for (a) hexagonally periodic (b) square periodic graphene nanomesh, and (c) standard graphene. These calculations were performed using BoltzTraP\textsuperscript{106} and ABINIT\textsuperscript{103}. 

\footnotesize {61}
5.2 Defect Spacing Dependence

We next investigated how the thermoelectric properties of graphene nanomesh change when the spacing between defects is varied. We hypothesized that changing the spacing between ring vacancy defects in the graphene lattice would change the band gap. We examined how changing the electronic structure improved ZT and related quantities. If the improvement in thermoelectric efficiency was caused solely by decreased lattice thermal conductivity, then improvement in ZT should scale proportionally with defect spacing. This involved performing complete calculations with hexagonally periodic graphene nanomeshes with a single ring vacancy defect of fixed size and variable spacing. The relaxation time for charge carriers in these systems was approximated using the same fitting equation used in section (5.1). The lattice thermal conductivity of each system was approximated using previously published MD simulations by Hu and Maroudas (section (5.1)). We observed a strong defect spacing and sublattice symmetry dependence in Seebeck coefficient, electrical conductivity, the electrical component of thermal conductivity, and ZT. Controlling the distance between defects strongly influences the thermoelectric efficiency of graphene nanomesh. Increasing the band gap improves the Seebeck coefficient, while also causing a decrease in the electrical conductivity. These improvements combine to increase ZT to a maximum value of 0.42, a four order of
magnitude increase relative to standard graphene. This suggests that it may be possible to design efficient graphene nanomesh thermoelectric devices once the symmetry dependence is better understood.

We studied 5 different graphene nanomeshes. The initial atomic positions for the ring defect and surrounding graphene were based on our previous study of simple nanomesh systems. Key structural differences between each nanomesh are shown in table (5.2.1). Each supercell contains one identical ring vacancy defect, and the size of the supercell determines the defect fraction. A larger lattice parameter corresponds to a larger distance between defects and decreased defect fraction. Models of each nanowire system are shown in figure 5.2.1, further illustrating the increasing number of atoms in each supercell. We performed calculations using an un-shifted gamma centered 24x24x1 k point grid. Complete information on the converged values we used in our BTT calculations is

![Models of nanomesh systems](image)

Figure 5.2.1. Model representations of different systems considered during our study. (a) 3-3 system (b) 4-4 system (c) 5-5 system (d) 6-6 system (e) 7-7 system. Carbon atoms are represented using brown spheres, hydrogen atoms are represented using white spheres. These representations were produced using VESTA.\(^{143}\)
The calculated band gap for all graphene nanomesh systems is shown in Table 5.2.2. Our calculations show that the band gap of graphene nanomesh systems is strongly symmetry dependent. Hexagonally periodic graphene nanomesh has 6-fold symmetry across the graphene plane. We oriented the hexagonally periodic graphene nanomesh system to force a 3-fold symmetry of the supercell with respect to defect orientation. Systems that follow this forced 3-fold symmetry with respect to defect spacing (3x3 and 6x6 systems) and meet specific scattering conditions open a band gap in graphene and cause a transition from semi-metal to a semiconducting state. Decrease or increase in cell size does not necessarily lead to an increase or decrease in band gap unless the symmetry of the defects meets key scattering conditions. These observations are corroborated by previous calculations by Dvorak and Wu. Band structures and DOS of sample system are shown in Figure 5.2.2 to demonstrate when these nanomesh systems have a band gap. We include the DOS since changing the sublattice symmetry modifies the electronic structure and could cause the location of K points to shift. The DOS is therefore a better predictor of band gap, while the band structure can provide qualitative information about the shape of the bands. The overall symmetry of the sublattice has substantial impact on electronic structure of graphene nanomesh.

### Table 5.2.1. Key structural differences between various hexagonally periodic nanomesh systems

<table>
<thead>
<tr>
<th>Supercell (number of rings along the primary axis)</th>
<th>Lattice Parameter</th>
<th># of atoms</th>
<th># of C</th>
<th>Defect fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>3x3</td>
<td>7.437 Å</td>
<td>18</td>
<td>12</td>
<td>0.33</td>
</tr>
<tr>
<td>4x4</td>
<td>9.878 Å</td>
<td>32</td>
<td>24</td>
<td>0.25</td>
</tr>
<tr>
<td>5x5</td>
<td>12.322 Å</td>
<td>50</td>
<td>44</td>
<td>0.12</td>
</tr>
<tr>
<td>6x6</td>
<td>14.788 Å</td>
<td>72</td>
<td>66</td>
<td>0.08</td>
</tr>
<tr>
<td>7x7</td>
<td>17.253 Å</td>
<td>98</td>
<td>92</td>
<td>0.06</td>
</tr>
</tbody>
</table>

### Table 5.2.2. Calculated band gaps of each nanomesh system

<table>
<thead>
<tr>
<th>Hexagonal Periodic</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3x3</td>
<td>2.42 eV</td>
</tr>
<tr>
<td>4x4</td>
<td>0.01 eV</td>
</tr>
<tr>
<td>5x5</td>
<td>0.00 eV</td>
</tr>
<tr>
<td>6x6</td>
<td>0.78 eV</td>
</tr>
<tr>
<td>7x7</td>
<td>0.00 eV</td>
</tr>
</tbody>
</table>

shown in appendix A. The calculated band gap for all graphene nanomesh systems is shown in Table 5.2.2. Our calculations show that the band gap of graphene nanomesh systems is strongly symmetry dependent. Hexagonally periodic graphene nanomesh has 6-fold symmetry across the graphene plane. We oriented the hexagonally periodic graphene nanomesh system to force a 3-fold symmetry of the supercell with respect to defect orientation. Systems that follow this forced 3-fold symmetry with respect to defect spacing (3x3 and 6x6 systems) and meet specific scattering conditions open a band gap in graphene and cause a transition from semi-metal to a semiconducting state. Decrease or increase in cell size does not necessarily lead to an increase or decrease in band gap unless the symmetry of the defects meets key scattering conditions. These observations are corroborated by previous calculations by Dvorak and Wu. Band structures and DOS of sample system are shown in Figure 5.2.2 to demonstrate when these nanomesh systems have a band gap. We include the DOS since changing the sublattice symmetry modifies the electronic structure and could cause the location of K points to shift. The DOS is therefore a better predictor of band gap, while the band structure can provide qualitative information about the shape of the bands. The overall symmetry of the sublattice has substantial impact on electronic structure of graphene nanomesh.
Figure 5.2.2. Calculated band structure and DOS for different graphene systems (a) 3-3 (b) 4-4 (c) 5-5 and on the following page (d) 6-6. The same symmetry directions are chosen for all band structures along the K-Γ-M-K path for hexagonally periodic systems.
We approximated the relaxation time of charge carriers by using experimentally measured electron
mobility for standard graphene\textsuperscript{1,2}. The approximation process is detailed in chapter 4, and chapter 5 section 1.
Accurate BTT based models have been developed for graphene that assume a fixed minimum level of
crystallographic disorder\textsuperscript{73–75,134,135}. This crystallographic disorder limits the electrical conductivity of graphene to a
large but finite value. We developed and evaluated 4 functionally similar fitted equations to predict relaxation time
in pure graphene (chapter 4). We assumed that the fitting equation for the graphene system with highest disorder
(lowest mobility) would best represent the thermoelectric properties of graphene nanomesh. Since we used the same
equation to estimate the relaxation time for all nanomesh systems, quantitative differences in the calculated
thermoelectric properties were the result of changes in the electronic structure.

The final term that we used to estimate ZT as a measure of thermoelectric efficiency was thermal
conductivity. The thermal conductivity of graphene is the major limiting factor to thermoelectric based applications.
Large thermal conductivity limits thermoelectric efficiency because of the relationship shown with Onsager’s
reciprocal relations (equations 2.2.10, 2.2.11) and ZT (equation 1.1.2). Increasing thermal conductivity reduces the
relative efficiency of carrier diffusion. Previous MD simulations have predicted a strong defect spacing dependence
in the thermal conductivity\textsuperscript{3}. The aspect ratio of the defect and the defect fraction also influence the lattice thermal
conductivity (chapter 1 section 4, chapter 5 section 1). The values of thermal conductivity used in this section are
shown in table 5.2.3, and scale with defect fraction. We assumed that the thermal conductivity of our nanomesh
systems ranged between 14 to 71 W/(m·K) based on previous md simulations. These values are substantially smaller than those observed in standard graphene (~4000-6000 W/(m·K)). The reduced thermal conductivity resulted in a substantial 2-3 order of magnitude improvement in ZT for graphene nanomesh when compared to standard graphene (chapter 4).

We hypothesized that manipulating the spacing between ring vacancy defects in the graphene lattice would change the band gap and modify the thermoelectric properties of graphene nanomesh systems. We tested our hypothesis by varying the spacing between ring vacancy defects. We confirmed our hypothesis and observed change in the calculated electronic structure for graphene nanomesh that showed semiconducting behavior. These changes substantially improved key thermoelectric properties of graphene nanomesh systems. Simply having a vacancy defect present in the supercell was however not sufficient but itself to guarantee improvement in thermoelectric properties. When we forced the symmetry of the defects to match specific scattering conditions that caused band gap opening, then the thermoelectric properties of graphene nanomesh were substantially improved. This suggests that the geometrically based semimetal to semiconductor transition is important in improved thermoelectric properties. These trends are summarized in figure 5.2.3 and shown in greater detail in figures 5.2.4-5.2.7. Figure 5.2.4 shows how the Seebeck coefficient is modified with defect spacing. Substantial improvement in in Seebeck coefficient occurs when a band gap is opened in graphene nanomesh. The 3x3 and 6x6 systems ((a) and (b)) have substantially larger Seebeck coefficient than standard graphene ((c)). This is consistent with the semi-metal to semiconductor transition first predicted by Dvorak et al. More interestingly, the presence of the defect weakens the Seebeck coefficient for nanomesh systems that do not show semiconducting behavior. The presence of the defect seems to weaken Seebeck coefficient by an approximate factor of 2. The calculated Seebeck coefficient of nanomesh systems without a band gap is very similar over a wide range of chemical potential shift. This corresponds

<table>
<thead>
<tr>
<th>Hexagonal Periodic</th>
<th>$K_t$ (W/(m·K))</th>
</tr>
</thead>
<tbody>
<tr>
<td>3x3</td>
<td>13.7 W/(m·K)</td>
</tr>
<tr>
<td>4x4</td>
<td>28.1 W/(m·K)</td>
</tr>
<tr>
<td>5x5</td>
<td>43.1 W/(m·K)</td>
</tr>
<tr>
<td>6x6</td>
<td>57.5 W/(m·K)</td>
</tr>
<tr>
<td>7x7</td>
<td>70.6 W/(m·K)</td>
</tr>
</tbody>
</table>

Table 5.2.3. Thermal conductivity values used to predict the thermoelectric figure of merit for hexagonally periodic graphene nanomesh systems.
closely with experimental measurements of the thermoelectric properties of graphene interacting with a silicon oxide substrate performed by Zuev et al.\textsuperscript{62}. Improvement in Seebeck coefficient is partially compensated by a decrease in electrical conductivity (figure 5.2.5) and the electrical component of thermal conductivity (figure 5.2.6) for these systems as expected by Onsager’s reciprocal relations. Regions with improved Seebeck coefficient for semiconducting graphene nanomesh correspond with decrease electrical conductivity. Improved graphene nanomesh show electrical conductivity with exponential dependence on chemical potential shift, a trait of a semiconductor. Figure 5.2.7 shows predicted ZT values for these nanomesh systems. We predict that the 6x6 hexagonally periodic graphene nanomesh system has the best thermoelectric efficiency, with maximum ZT of 0.42.

We met the goal of this portion of our research, and show that the scaling law predicting decrease in lattice thermal conductivity is by itself insufficient to improve ZT. The semimetal to semiconductor transition is therefore important, as well as the shape of the electronic structure, especially close to the fermi energy. This raised another question that we wished to investigate. The semimetal to semiconductor transition is geometrically based, and if it is the primary property controlling improvement in ZT, the improvement should remain if the type of the defect is
modified. The strong periodicity dependence could explain why small amounts of disorder in graphene nanomesh systems could lead to weakening of ZT. Physical systems would need to guarantee few error in periodicity semiconducting graphene nanomesh and to force diffusive behavior from free charge carriers.

Figure 5.2.4. Calculated Seebeck coefficient of graphene nanomesh systems with different spacing between vacancy defects. (a) 6-6 (b) 3-3 (c) 4-4 (d) 5-5 (e) 7-7 (f) Shows the calculated Seebeck coefficient of pure graphene as a reference.

Figure 5.2.5. Calculated electrical conductivity of graphene nanomesh systems with different spacing between vacancy defects. (a) 6-6 (b) 3-3 (c) 4-4 (d) 5-5 (e) 7-7.
Figure 5.2.6. Calculated electrical component of thermal conductivity of graphene nanomesh systems with different spacing between vacancy defects. (a) 6-6 (b) 3-3 (c) 4-4 (d) 5-5 (e) 7-7.

Figure 5.2.7. Calculated ZT of graphene nanomesh systems with different spacing between vacancy defects. (a) 6-6 (b) 3-3 (c) 4-4 (d) 5-5 (e) 7-7.
5.3 Surface Adsorbents and Doping

After observing improvement in the thermoelectric properties of graphene nanomesh systems (especially the 6x6 system in section (5.2)), we wanted to further investigate the relative importance of the semimetal to semiconductor transition. We assumed that the nanomesh transition would have a substantial impact, but did not know the relative importance of defect type. In order to test this, we investigated the thermoelectric properties of the 6x6 periodically modified graphene and replaced the ring vacancy defect with partial hydrogen passivation and boron nitride doping. We fixed the symmetry of the defect, all the systems shown in this section have a ring shaped defect located in the middle of the supercell. Boron nitride doping and partial hydrogen passivation have been previously shown to open a band gap in graphene\textsuperscript{68}. We then estimated the carrier relaxation time using experimental electron mobility data (chapter 4). We further relied on previous MD simulations by Hu and Maroudas\textsuperscript{3}. We determined that there is substantial improvement in the thermoelectric properties of all three 6x6 systems, suggesting strong symmetry dependence. The relative differences in the magnitude of the improvement suggest that there is also some type of dependence on the type of defect. Further study is necessary to quantify the relative strength of improvement specifically caused by changing defect type and investigate other graphene materials.

The hydrogen terminated system has 78 atoms, while the Boron Nitride ring defect system has 72 atoms in the unit cell. A model representation of each new system considered in this section is shown in figure 5.3.1. We

Figure 5.3.1. Models representing the two different types of graphene systems considered in this section. (a) Overhead view of 6-6 graphene nanomesh system with partial hydrogen passivation. (b) Side view of the same system. (c) Top down view of the boron nitride doped 6-6 graphene nanomesh system. (d). Brown dots represents the position of carbon atoms in the lattice, white hydrogen, blue boron, and green nitrogen.
calculated a band gap of 0.731 eV for the hydrogen passivated system, and a gap of 0.337 eV for boron nitride doped system. The electronic structure of both materials is shown in figure 5.3.2 showing the magnitude of changes to the electronic structure by changing defect type. We found that a 24x24x1 un-shifted gamma centered \( k \) point grid was generally sufficient to minimize secondary interpolation error bases oscillations in Seebeck coefficient (section (5.1)). We also used a cutoff energy of 1687 eV (hydrogen passivation), 1360 eV (boron nitride doping), an inter-layer spacing of 17 Å (hydrogen passivation), 15 Å (boron nitride doping, 20 real space points per \( k \) point, an energy

Figure 5.3.2. Calculated band structure and DOS of symmetric 6x6 graphene systems with (a) partial hydrogen passivation and (b) boron nitride doping. Both systems have band gaps. We calculated a band gap of 0.731 eV for the hydrogen passivated system, and a gap of 0.337 eV for boron nitride doped system.
range of 14 eV around the Fermi level, and utilized 192 individual bands in the electronic structure. Fine points of
convergence testing are discussed in appendix A.

We approximated the relaxation time of charge carriers by using experimentally measured electron
mobility for standard graphene. We used the same fitting equation to approximate the relaxation time in these
systems, so relative changes in the thermoelectric properties are solely the result of modifications to the electronic
structure. This process is detailed in chapter 4, and chapter 5 section 1. In our study we relied on MD simulations by
Hu and Maroudas\(^3\) (chapter 5 section 1). We assume a thermal conductivity of 57.5 W/(m∙K) for both hexagonally
periodic graphene nanomesh systems at 300 K. These methods are sufficient to test the relative importance of
symmetry in the thermoelectric properties of graphene nanomesh.

The results of our calculations are summarized in figure 5.3.3 and shown in greater detail in figures 5.3.4-
5.3.7. We calculated substantial improvement in the thermoelectric efficiency for the partial hydrogen passivation
and boron nitride doped system when compared to standard graphene. However, the improvement was
approximately half of what we calculated with the 6x6 ring vacancy system. The type of defect does affect the

![Figure 5.3.3](image)

**Figure 5.3.3.** Summary of the thermoelectric properties of graphene nanomesh and defected graphene. The
individual plot references correspond with larger figures that accompany the discussion. The plots show \((5.3.4)\)
Seebeck coefficient, \((5.3.5)\) electrical conductivity, \((5.3.6)\) electrical thermal conductivity, and \((5.3.7)\) \(ZT\). The
plots show (a) standard 6x6 nanomesh with a hydrogen terminated vacancy defect, (b) ring defected graphene
with partial hydrogen passivation, and (c) boron nitride doped defected graphene. (d) Standard graphene is
shown as a reference.
overall relative level of improvement in the thermoelectric properties of 6x6 graphene nanomesh systems. Figure 5.3.4 shows calculated Seebeck coefficient for all 3 6x6 systems and standard graphene. All 6x6 systems have improved Seebeck coefficient compared to standard graphene. The vacancy defect system has the largest band gap, visible in the electronic structure with flattest bands close to the Fermi level. This results in the largest improvement in Seebeck coefficient. The hydrogen passivated system has the second largest band gap, and the second most improved Seebeck coefficient. Boron nitride doping was the weakest perturbation to the graphene lattice, resulting in the smallest band gap, sharpest bands close to the fermi energy, and least improved Seebeck coefficient. The Seebeck coefficient of the boron nitride doped system was approximately a factor of 2 smaller than the ring vacancy system. The different electronic structures of each system is further shown in shifting edge modes farther from the Fermi energy. The close symmetry similarity of the graphene systems is reflected in the electronic structure. This is shown with regions of improved Seebeck coefficient farther from the fermi energy. These modes correspond to regions in the electronic structure where there is very little band overlap, and the bands simply touch somewhere in the Brillouin zone. Changing the strength of the perturbation to the graphene lattice shifted the relative position of these improved modes. Figure 5.3.5 shows our calculated electrical conductivity for these systems. All the 6x6 systems have a band gap, and show semiconducting behavior in electrical conductivity. This appears as exponential dependence of electrical conductivity with respect to chemical potential shift over the band gap regions. Farther away from the band gap region the electrical conductivity returns to graphene-like quadratic dependence with oscillations. These oscillations correspond to regions with improved Seebeck coefficient. The 6x6 vacancy defected system has the largest conductivity farther away from the fermi energy. The same trends are shown with figure 5.3.6 with electrical thermal conductivity. Electrical thermal conductivity is a small contributing factor to ZT. Figure 5.3.7 shows ZT, with ZT maximized with the 6x6 vacancy system. All the 6x6 periodic graphene systems had improved ZT compared to pristine graphene, but that the magnitude of improvement was modified. We conclude that changing the defect type affects the thermoelectric properties of graphene systems, but that the semimetal to semiconductor transition is a more important controlling factor.
Figure 5.3.4. Calculated Seebeck coefficient of 6-6 hexagonally periodic graphene nanomesh systems. (a) Standard 6x6 nanomesh with a hydrogen terminated vacancy defect. (b) Ring partial hydrogen passivation. (c) Boron nitride doping. (d) Standard graphene as a reference.

Figure 5.3.5. Calculated electrical conductivity of 6-6 hexagonally periodic graphene nanomesh systems. (a) Standard nanomesh with a hydrogen terminated vacancy defect. (b) Partial hydrogen passivation. (c) Boron nitride doping.
Figure 5.3.6. Calculated electrical component of thermal conductivity of 6-6 hexagonally periodic graphene nanomesh systems. (a) Standard nanomesh with a hydrogen terminated vacancy defect. (b) Boron nitride doping. (c) Ring of partial hydrogen passivation.

Figure 5.3.7. Calculated electrical component of thermal conductivity of 6-6 hexagonally periodic graphene nanomesh systems. (a) Standard nanomesh with a hydrogen terminated vacancy defect. (b) Partial hydrogen passivation. (c) Ring of boron nitride doping.
CHAPTER 6
DISCUSSION AND CONCLUSIONS

Thermoelectric materials provide a method to efficiently generate an electrical current using a thermal gradient. Thermoelectric devices have the potential to limit the environmental impact of power generation for small scale applications. The goal of this study was to determine and better understand the key physical parameters necessary to improve thermoelectric efficiency in graphene nanomesh. We first developed and tested our computational methods by examining the thermoelectric properties of silicon. We then examined the thermoelectric properties of silicon nanowires in order to test our methods on a well-studied system with more complex geometry, and to further demonstrate that nanostructuring can produce materials with improved properties. Next we studied the properties of graphene to test the accuracy of our methods with 2D systems, and as a point of comparison with our later studies of periodically modified graphene structures. Finally, we examined the thermoelectric properties of graphene nanomesh, graphene nanomesh with variable defect spacing, periodic partial hydrogen passivation, and boron nitride doping. We determined, based on first principles calculations, that the geometrically based semimetal to semiconductor transition first reported by Dvorak and Wu is critically important to improving the thermoelectric efficiency of graphene systems. This has not been fully investigated by previous studies of graphene systems.

Previous computational studies of the thermoelectric properties of graphene nanomeshes used non-equilibrium Green’s functions with tight binding calculations of the electronic structure. They showed substantial improvement in the thermoelectric efficiency of graphene nanomesh (ZT~0.2). There were several limitations to these studies. First, the thermoelectric properties of graphene nanomesh were calculated in the ballistic transport regime, not the diffusive transport regime seen in real world devices. Second, highest thermoelectric efficiency is found when the chemical potential is shifted sufficiently to include extra allowed energy states farther from the Fermi energy. Tight binding formalism is less accurate farther from the fermi energy. Most importantly, these studies examined the thermoelectric properties of graphene nanomesh with very different defect size ranges, and investigated very different physical parameters. We therefore wanted to use a method that addressed these limitations. We performed density functional theory calculations of the electronic structure using the ABINIT computational package to overcome the limitations of tight binding. We then used the calculated electronic structure with Boltzmann transport theory with the BoltzTraP program to calculate the thermoelectric properties of
materials in the true diffusive limit with periodic boundary conditions. This involved using the relaxation time approximation with Boltzmann transport theory. We approximated carrier relaxation time in materials using numerical fitting of experimental measurements of electron mobility in different materials. We did this to better represent scattering conditions in graphene materials where exact representation of scattering behavior remains an area of active research. In order to estimate ZT, a key measure efficiency in thermoelectric materials, we relied on previous computational studies and experimental measurements of lattice thermal conductivity. With nanostructured graphene materials, we incorporated geometrical dependencies in the lattice thermal conductivity calculated by Hu and Maroudas\textsuperscript{3}.

We first examined the thermoelectric properties of pure silicon (chapter 3 section 1) a model material to test the accuracy of our computational techniques. We estimated the relaxation time of charge carriers in silicon using a previously developed fitted equation of electron mobility\textsuperscript{9}. We found close agreement between our calculated thermoelectric properties and previous theoretical studies by Heinz\textsuperscript{9} and Wang \textit{et al.}\textsuperscript{118}. Heinz used very similar calculation techniques, and developed the fitting equation we used to approximate relaxation time. Wang \textit{et al.} used the more complex deformation potential theory based calculation process that goes beyond the relaxation time approximation to calculate thermoelectric properties from first principles. Wang \textit{et al.} calculated the properties of silicon over a narrower carrier concentration range and a different carrier type, but observed similar functional forms. We further compared our results to experimental measurements by Gabelle & Hull\textsuperscript{124} and Weber and Gmelin\textsuperscript{55}. The close similarity between our results and previous studies shows the accuracy of our computational techniques.

The sign of the Seebeck coefficient changes for different types of charge carriers (negative for electrons, positive for holes), and a slight asymmetry is observed, caused by asymmetric effective mass. As expected electrical conductivity in silicon scales exponentially with the number of free charge carriers. We closely agree with electrical conductivity calculations performed by Heinz. Wang \textit{et al.} predict an identical exponential relationship between electrical conductivity and carrier concentration. The difference between Wang \textit{et al.} and our work are assumed to be caused by their use of the LDA instead of the GGA to calculate electronic structure, and the different process used to approximate relaxation time. The electrical component of thermal conductivity scales exponentially with the number of free carriers. The weak resonance predicted by Heinz in the middle of the carrier concentration range is caused by insufficient convergence testing. We then assumed a lattice thermal conductivity is approximately\textsuperscript{9} \textsuperscript{100}
W/(m·K) at 300 K. Based on these assumptions, we estimate the maximum ZT of crystalline silicon to be approximately 0.009 with a carrier concentration of $10^{20}$ e/cm$^2$. We further compared our calculated Seebeck coefficient to experimental measurements of $1.7 \times 10^{19}$ Arsenic doped crystalline silicon by Weber and Gmelin. The close similarity in the Seebeck coefficient supports the accuracy of our DFT electronic structure calculations compared to crystalline silicon. Calculations of Seebeck coefficient do not require knowledge of relaxation time. This further supports the conclusion that the absolute magnitude of the band gap in materials is less important to predicting thermoelectric properties than the shape of the electronic structure, especially close to the Fermi energy. We achieved close agreement with these experimental measurements. In conclusion, we confirmed the accuracy of our methods using crystalline silicon as a model material.

We then estimated the thermoelectric properties of 1 nm diameter hydrogen terminated silicon nanowires with three different growth orientations ((0,0,1), (0,1,1), and (1,1,1)) in order to test our methods using a system with more complex geometry, and to show that nanostructuring can improve thermoelectric properties. We compared our results to previous work by Heinz. The nanowire systems contained between 28 and 72 atoms. We estimated the band gap of the silicon nanowire systems to be 2.62 eV (0,0,1), 1.59 eV (0,1,1), and 2.24 eV (1,1,1). These band gaps corresponded closely with values reported by Zhao et al.

We predict Seebeck coefficient to be approximately a factor of 2 smaller than Heinz for all nanowire orientations, but the trends are identical, and strongly dependent on orientation. We assume this difference was caused by a combination of slightly different nanowire structures and our more careful convergence testing that included additional bands in the electronic structure. Seebeck coefficient scales linearly within this range of carrier concentration. Our results correspond to an approximate factor of 8 increase in Seebeck coefficient compared to standard silicon. Nanowire confinement does not seem to cause a decrease in electrical conductivity compared to crystalline silicon. Combined with experimental measurements of larger diameter nanowire systems which also predict improved Seebeck coefficient and stable electrical conductivity, we believe that our calculations represent the thermoelectric properties of silicon. Differences between our calculations and Heinz are assumed to be caused by structural differences between the nanowire systems and electronic structures. Despite these differences, our calculations remain very similar, with almost identical qualitative trends.

Based on the MD simulations performed by Galli et al. and experimental measurements by Li et al. we determined that 2 W/(m·K) at 300K was a reasonable approximation of the lattice thermal conductivity of such
We estimated the thermoelectric properties of graphene (chapter 4). This required modification of the BoltzTraP program. We compared our calculations to experimental measurements of the thermoelectric properties of graphene performed by Zuev et al.\textsuperscript{62}. We approximated the relaxation time of graphene by numerically fitting of mobility measurements performed by Bolotin \textit{et al.}\textsuperscript{1} and Das \textit{et al.}\textsuperscript{2}. We concluded that the difference in Seebeck coefficient is probably due to surface interaction and the overall complexity of measuring carrier concentration in materials. Zuev \textit{et al.} measured the thermoelectric properties of graphene located on a SiO\textsubscript{2} substrate, which causes strong surface interaction effects. Our calculations have identical trends to these experimental measurements, but over a narrower carrier concentration range. Our calculated maximum Seebeck coefficient is approximately 150 µV/K at 300 K. We were able to calculate the Seebeck coefficient with remarkable accuracy to these experimental measurements given the differences in the system we considered. Our calculated electrical conductivity scales linearly with carrier concentration, as expected for 2D systems. The accuracy of our calculations compared to experimental measurement strongly decrease as carrier concentration approaches $10^{11}$ e/cm\textsuperscript{2}. This is consistent with previous theoretical predictions by Das Sarma \textit{et al.}\textsuperscript{64}, who showed that complex quantum effects dominate over standard charge scattering leading to finite nonzero electrical conductivity with extremely low carrier concentration. These effects cannot be incorporated into standard semi-classical BTT. We predict identical trends and very similar values to Zuev \textit{et al.}\textsuperscript{62} when carrier concentration is sufficiently large. The slight differences between our
calculations and these experimental measurements can be accounted for by differences in carrier relaxation time and electronic structure caused by surface interaction and differing quality. Increases in electrical conductivity near the Fermi energy are artifacts of our numerical fitting of relaxation time, and do not represent true physical trends. We were able to compute the electrical conductivity of graphene with remarkable accuracy given the simple fitting model we used to approximate relaxation time. We further demonstrate that the electrical component of thermal conductivity in graphene is extremely small, many orders of magnitude smaller than the lattice component. We assumed the thermal conductivity of 4000 W/(m∙K) at 300 K. As expected ZT in graphene is extremely low even compared to bulk materials such as crystalline silicon. Graphene systems with larger electron mobility have improved ZT. We conclude that the beneficial charge transport properties of graphene could be used to produce more efficient thermoelectric materials with careful minimization of lattice thermal conductivity. We further conclude that we were able to accurately predict the thermoelectric properties of pristine graphene using a relatively simple calculation methodology. We demonstrate that graphene is a poor thermoelectric material, but the transport properties are sufficient for thermoelectric applications if thermal conductivity could be reduced.

We then examined the thermoelectric properties of simple hexagonally periodic graphene nanomesh (section (5.1)), in order to determine if we could predict improved efficiency. We used the same fitted relaxation time equation for all subsequent studies of periodic graphene systems, taken from the graphene material with highest disorder and lowest mobility. Relative differences in the thermoelectric properties of graphene systems are caused by changes to the electronic structure. We predict a substantial increase in Seebeck coefficient for simple graphene nanomesh, showing a transition from the semimetal behavior of standard graphene to that of a semiconductor. This extremely large Seebeck coefficient is approximately a factor of two larger than pure crystalline silicon (chapter 3 section 1) and comparable to values we predicted for silicon nanowires (chapter 3 section 2). Hexagonally periodic graphene nanomesh has slightly larger Seebeck coefficient than square periodic system. This is caused by slight differences in relative flatness of the bands close to the Fermi energy of the two materials. We predict a decrease in the electrical conductivity of graphene nanomesh compared to standard graphene. Calculated electrical conductivity scales exponentially close to the Fermi energy, but returns to graphene quadratic dependence approximately 0.4 eV with oscillations on either side of the Fermi energy for both systems. This is consistent with a semiconductor with a band gap of approximately 0.8 eV. We approximated the thermal conductivity of graphene nanomesh using a simple scaling law developed by Hu and Maroudas3.
The maximum predicted ZT of the hexagonally periodic graphene nanomesh system was 0.15, and 0.145 for the square periodic system, with a chemical potential shift of 0.5 eV. The differences between the sublattice symmetry of each system only slightly affected the predicted thermoelectric properties. These improved ZT values compared to standard graphene suggest that graphene nanomesh is a promising thermoelectric material. The improved thermoelectric efficiency is strongly dependent on the quality of the graphene lattice, based changes in relaxation time. Graphene nanomesh which better maintain the periodicity of pristine graphene have improved ZT. Our calculations raise a question about the true cause of the increase in thermoelectric efficiency. We used a simple scaling law to predict lattice thermal conductivity. Improvements in Seebeck coefficient are compensated by a decrease in electrical conductivity. We assumed that the electronic structure of graphene nanomesh is the cause of improved thermoelectric efficiency, thus requiring further work to test this assumption.

We therefore investigated the thermoelectric properties of graphene nanomesh with variable defect spacing. We hypothesized that manipulating the spacing between simple ring vacancy defects in the graphene lattice would change the band gap and modify the thermoelectric properties of graphene nanomesh systems. If reduced thermal conductivity was the primary process improving thermoelectric efficiency, then it should scale exponentially with decreased inter-defect spacing. We confirmed our hypothesis and observed change in the calculated electronic structure. These changes substantially improved key thermoelectric properties of graphene nanomesh systems. Simply having a vacancy defect present in the supercell was not sufficient to beneficially alter the electronic structure, and thereby improve the thermoelectric properties of nanomesh systems. When we forced the symmetry of the defects to match specific scattering conditions that caused band gap opening, then the thermoelectric properties of graphene nanomesh were substantially improved. We observed an approximate one order of magnitude increase in Seebeck coefficient compared to pristine graphene. This is consistent with the semi-metal to semiconductor transition first predicted by Dvorak et al. More interestingly, the presence of the defect weakens the Seebeck coefficient for nanomesh systems that do not show semiconducting behavior by an approximate factor of 2. The calculated Seebeck coefficient of nanomesh systems without a band gap is very similar over a wide range of chemical potential shift, and correspond closely with experimental measurements of graphene interacting with a silicon oxide substrate conducted by Zuev et al. Improvement in Seebeck coefficient is partially compensated by a decrease in electrical conductivity and the electrical component of thermal conductivity for these systems. This is expected by Onsager’s reciprocal relations. Regions with decreased electrical conductivity compared to chemical
potential shift correspond with increased Seebeck coefficient. We predict that the 6x6 hexagonally periodic graphene nanomesh system has the best thermoelectric efficiency, with maximum $ZT$ of 0.42. This is insufficient to make graphene nanomesh a potential thermoelectric material, but these values are strongly dependent on approximated relaxation taken from a very disordered graphene material. With relaxation time taken from a higher quality graphene material, $ZT$ could be improved so that graphene nanomesh is a very useful thermoelectric material. We concluded that the semimetal to semiconductor transition is important in causing improved thermoelectric efficiency. This required additional investigation. If improved thermoelectric properties are dependent on the semimetal to semiconductor transition, then the improvement should remain if the type of defect is varied.

We finally investigated the relative importance of defect type and the semimetal to semiconductor transition by studying the thermoelectric properties of 6x6 periodically modified graphene with partial hydrogen passivation and boron nitride doping. We fixed the symmetry of the defect by confining our examination to ring shaped defects in the middle of the supercell. We calculated substantial improvement in the thermoelectric efficiency for all the systems considered compared to standard graphene. All 6x6 graphene nanomesh systems had a band gap (vacancy ~0.78 eV hydrogen passivation ~0.73 eV, BN doped 0.34 eV). The type of defect does seem to affect the overall magnitude of improvement in thermoelectric properties of 6x6 graphene nanomesh systems, but is of secondary importance compared to the semimetal to semiconductor transition. The relative strength of the perturbation to the graphene lattice determined the magnitude of improvement in thermoelectric properties. This can be seen in the relative change in the electronic structure. The 6x6 vacancy system has the largest band gap, and more importantly the flattest bands around the fermi energy. This translates into largest improvement in Seebeck coefficient. The partial hydrogen passivated system has the second largest improvement in Seebeck coefficient. The boron nitride doped system is the weakest perturbation to the graphene lattice, and the lowest improvement in Seebeck coefficient. The black dashed line shows our calculation for pristine graphene as a reference. Another interesting effect tied to the electronic structure is the shifting position of edge modes. These modes correspond to regions in the electronic structure where there is very little band overlap, and the band simply touch somewhere in the Brillouin zone. With improved Seebeck coefficient comes decreased electrical conductivity. Oscillations in the electrical conductivity correspond to regions with improved Seebeck coefficient, and provide an interesting opportunity to tune the properties of periodically modified graphene by varying the chemical potential shift.
We conclude that the semimetal to semiconductor transition is responsible for improved thermoelectric efficiency in graphene nanomeshes and defected graphene. Simply having a defect in a graphene lattice is insufficient to maximize thermoelectric efficiency, even with strongly decreased thermal conductivity. Further optimization is possible to improve thermoelectric efficiency. More complex semiconducting graphene nanomeshes could be used to improve ZT further, as well as the relative purity and quality of the graphene lattice. Periodic graphene systems which better maintain the crystal periodicity have improved electron mobility, and as a result improved thermoelectric properties. Periodically modified graphene nanostructures are interesting potential thermoelectric materials. This would require a significant degree of control over the periodicity of the graphene system over length scales so that the semimetal to semiconducting transition, and confinement of charge carriers into the diffusive limit. Some interesting areas of further research could involve directly calculating lattice thermal conductivity or carrier relaxation time from first principles.
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APPENDIX A

DENSITY FUNCTIONAL THEORY CONVERGENCE STUDIES

This appendix contains information on exact convergence parameters, conditions, and values used in our calculations. This appendix is broken into sections corresponding to the different materials investigated during our study. The sections discuss silicon (section 1), silicon nanowires (section 2), graphene (section 3), simple graphene nanomesh (section 4), and defected graphene (section 5). Key quantities are summarized at the end of each section with a table.

A.1 Silicon

Density functional theory calculations in our study were performed using ABINIT and adjusting the input parameters to minimize the calculated total energy of crystalline silicon. We used PBE pseudopotentials and GGA in DFT calculations of the electronic structure. The electronic structure calculations of bulk silicon were performed using two atoms in the primitive unit cell. Our methods, based on Heinz (see above), use careful convergence studies to predict the thermoelectric properties of crystalline silicon. The electronic structure and the total energy of silicon are minimized with respect to lattice parameter, cutoff energy, and size of the k point grid. The atomic positions in crystalline silicon and stress tensor of the crystalline silicon unit cell do not need to be minimized. Atoms in the crystalline silicon lattice are already located on high symmetry points. Atoms at high symmetry points in a crystal lattice fully minimize the atomic forces and stresses. Lattice parameter determines the spacing between silicon atoms. The cutoff energy sets the number of plane waves used to represent the wave functions of electrons in the ABINIT software. The size of the k point grid determines the number of calculated points used to describe the electronic structure and calculate the thermoelectric properties using BoltzTraP. We use an un-shifted energy grid centered on the gamma point (origin in reciprocal space). A dense k point grid is required for convergence of Boltzmann transport equations using BoltzTraP. The goal of DFT calculations is to minimize the total energy within 0.1 eV/atom so that the ground state electron density can be accurately approximated. The initial conditions used to start convergence testing of the DFT and BTT calculations of the thermoelectric properties of crystalline silicon were a lattice parameter of 5.47 Å, 10x10x10 k point grid, a cutoff energy of 10 Hartree (~272 eV). These parameters were selected because of close similarity with computational values used in general DFT calculations.
We use three important quantities to determine total energy convergence. The first important quantity is lattice parameter. The minimum of the parabola results in a lattice parameter of 5.465 Å which is within 0.65% of the experimentally measured value of 5.43 Å\textsuperscript{129}. The second convergence parameter we investigated was cutoff energy. DFT convergence requires a cutoff energy larger than 7.23 Hartree (196.5 eV). Due to the high k point grid required, we actually use a cutoff energy of 16 Hartree (436 eV) in our BTT calculations. Finally, we need to check the convergence with respect to the number of k points. BoltzTraP requires a very dense k point grid for accurate prediction of thermoelectric properties. The number and degeneracy level of band crossings determines the density of k points needed. Convergence generally starts around 12000 k points for very simple systems. The Fourier interpolation routine used in BoltzTraP to increase the density of the k point grid introduces oscillations in predicted thermoelectric quantities as a function of Fermi energy displacement represented by a chemical potential shift. We defined convergence to occur when oscillations in the Seebeck coefficient are less than 1 µV/K in average amplitude. In silicon this is achieved with a k point grid of 27000 k points (30x30x30 grid, 752 irreducible points in the first Brillouin zone). This is a much larger number of k points compared to traditional density functional theory calculations of the electronic structure that do not use BTT. When conducting a standard DFT calculation, convergence tested using similar techniques as cutoff energy, was achieved with 90 k points (rounded up this is a 5x5x5 grid). More complex materials require finer k grid spacing to maintain prediction accuracy. Key quantities are summarized in table A.1.1. The brillouin zone face centered cubic system is shown in figure A.1.

Figure (A.1). Brillouin zone of a face centered cubic system showing high symmetry points, reproduced from the PhD thesis by Jochym\textsuperscript{4}.  

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Defining accurate initial conditions for DFT and BTT calculation is essential to establishing predictive accuracy. We base our choice of initial parameters for DFT and BTT calculation on the values described in Galli et al. and Heinz cited above. In our study DFT calculated total energy of each system was converged in terms of intern-nanowire spacing, relaxing the relative position of atoms, cutoff energy, and number of k-points in the electronic structure. Off axis k points are needed to estimate the thermoelectric properties of nanowires because of the constraints imposed by the Fourier interpolation subroutine in BoltzTraP. This subroutine requires a minimum of 4 k points along any direction in reciprocal space in order to expand the electronic structure for 1D calculations. The program was modified to impose a sparse k-mesh so that a 1D or 2D k-grid along off axis directions. Considerable effort was needed to modify the BoltzTraP program so that we could compare the effects of a sparse 3D k-point grid on calculation compared to exact modification to a 1D calculation process. These two different methods produced identical computed values for the desired thermoelectric properties of materials and gave us confidence that the simpler method resulted in accurate predictions. We therefore elected to use the simpler imposed sparse energy grid instead of the more complex modification to allow for a more direct comparison with Heinz and Galli et al. We set the initial inter-wire spacing to be 30 Bohr (15.8 Å). We used a gamma centered, un-shifted k-point grid of 4x4x24 k points. The energy cutoff was set to 18 Hartree (489 eV). Converged values for each of these quantities are shown in table A.2.1. These initial conditions were used in DFT and BTT calculation of the thermoelectric properties of each of the three silicon nanowire systems.

### Table A.1.1. Some key quantities used or calculated in our Density Functional Theory Calculations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice Parameter</td>
<td>5.465 Å</td>
</tr>
<tr>
<td>Cutoff Energy</td>
<td>16 Hartree (436 eV)</td>
</tr>
<tr>
<td>K point grid size</td>
<td>30x30x30 grid, 752 irreducible points</td>
</tr>
<tr>
<td>K point grid shift</td>
<td>None, gamma centered</td>
</tr>
<tr>
<td>Exchange Correlation Energy Approximation</td>
<td>GGA, PBE</td>
</tr>
<tr>
<td>Pseudopotential</td>
<td>Norm-conserving, Trouiller-Martins type</td>
</tr>
<tr>
<td>Calculated Band Gap</td>
<td>0.61 eV</td>
</tr>
</tbody>
</table>

### A.2 Silicon nanowires

Defining accurate initial conditions for DFT and BTT calculation is essential to establishing predictive accuracy. We base our choice of initial parameters for DFT and BTT calculation on the values described in Galli et al. and Heinz cited above. In our study DFT calculated total energy of each system was converged in terms of intern-nanowire spacing, relaxing the relative position of atoms, cutoff energy, and number of k-points in the electronic structure. Off axis k points are needed to estimate the thermoelectric properties of nanowires because of the constraints imposed by the Fourier interpolation subroutine in BoltzTraP. This subroutine requires a minimum of 4 k points along any direction in reciprocal space in order to expand the electronic structure for 1D calculations. The program was modified to impose a sparse k-mesh so that a 1D or 2D k-grid along off axis directions. Considerable effort was needed to modify the BoltzTraP program so that we could compare the effects of a sparse 3D k-point grid on calculation compared to exact modification to a 1D calculation process. These two different methods produced identical computed values for the desired thermoelectric properties of materials and gave us confidence that the simpler method resulted in accurate predictions. We therefore elected to use the simpler imposed sparse energy grid instead of the more complex modification to allow for a more direct comparison with Heinz and Galli et al. We set the initial inter-wire spacing to be 30 Bohr (15.8 Å). We used a gamma centered, un-shifted k-point grid of 4x4x24 k points. The energy cutoff was set to 18 Hartree (489 eV). Converged values for each of these quantities are shown in table A.2.1. These initial conditions were used in DFT and BTT calculation of the thermoelectric properties of each of the three silicon nanowire systems.
Following the establishment of initial conditions, our next step was to fully minimize the DFT total energy. The calculated inter-atomic forces acting on each atom were first minimized by relaxation. This was done by fixing the cell parameters, and then minimizing the net forces and stresses acting on each atom. Since we are specifically using the ABINT software, this process was performed using the Broyden-Fletcher-Goldfarb-Shanno minimization process\textsuperscript{136-140}. The calculated DFT total energy was found to converge with inter-nanowire spacing of approximately 10 Å for all growth orientations, or 1.5 times the diameter of the nanowire. In our calculations we used an inter-nanowire spacing of 15.4 Å in order to minimize interaction effects in our BTT calculations. Total energy convergence was found to occur at 496.5 eV is required (0,0,1), 439.3 eV (0,1,1) and 495.8 eV (1,1,1). In our calculations we used a cutoff energy of 544 eV. These values are larger than the cutoff energy used by Heinz (245.3 eV) and Galli \textit{et al}. (476.2 eV) independent of nanowire orientation. DFT energy convergence was achieved for all the nanowire systems using a 1x1x4 k point grid. This small energy grid is insufficient for BTT calculations.

After careful calculation of the electronic structure, the next step in our methodology was convergence of the BTT calculations. BTT calculations using BoltzTraP were converged with respect to the number of k points in the calculated electronic structure, the energy grid spacing, and the energy range considered around the Fermi level. The first parameter was convergence with respect to the number of k points included in the electronic structure. BoltzTraP expands and interpolates the electronic structure of materials in order to efficiently calculate thermoelectric properties from a sparse DFT calculations. As a consequence of the interpolation, oscillations are observable in the calculated Seebeck coefficient of silicon nanowires. The smoothness and accuracy of the interpolation process is dependent on the density of the k-points. The oscillations are most noticeable in regions where the chemical potential is shifted farthest from the Fermi energy. After converging the BTT calculations, we concluded that a 4x4x30 k point grid was sufficient. The interpolation process is also dependent on the number of real space points used to expand each k point in the electronic structure. The number of real space points per k point was set to 40 for all nanowire systems. This improves interpolation accuracy with larger k-point density. The next factor to consider in convergence is the energy grid segmentation. The energy grid segmentation controls the accuracy of the shift in chemical potential with carrier concentration. Higher segmentation decreases computational speed while increasing accuracy. We found that a minimum grid density of 6.8 \texttimes 10^4 eV/bin was required for convergence for calculation of the carrier concentration dependence of the nanowire systems. In final calculation we used an energy grid density of 1.36 \texttimes 10^4 eV/bin for all nanowires to improve accuracy. The segmentation of the
density of states is dependent on the energy grid segmentation. The final quantity converged in our calculation process was the energy range considered around the Fermi level. The energy range around the Fermi level determines the number of bands included in the BTT calculation. Bands not within the Fermi energy range are removed by BoltzTraP from the electronic structure by a simple scissor operation. We calculated 192 individual bands in the electronic structure of each silicon nanowire system. In order to include all but the very lowest valance bands in the (0,0,1) system, we set the energy range to be 13.6 eV. The exact values used in our final BTT calculations are again highlighted in table (A.2.1).

Table A.2.1. Key quantities used in our calculations. The values we used are listed first, followed by the converged values shown in brackets for each quantity.

<table>
<thead>
<tr>
<th>Crystallographic orientation</th>
<th>(0,0,1)</th>
<th>(0,1,1)</th>
<th>(1,1,1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>k-grid</td>
<td>4x4x32 (1x1x4)</td>
<td>4x4x32 (1x1x4)</td>
<td>4x4x32 (1x1x4)</td>
</tr>
<tr>
<td>cutoff energy (eV)</td>
<td>544 eV (496.5 eV)</td>
<td>544 eV (439.3 eV)</td>
<td>544 eV (495.8 eV)</td>
</tr>
<tr>
<td>inter-nanowire spacing (Å)</td>
<td>15.4 Å (10 Å)</td>
<td>15.4 Å (10 Å)</td>
<td>15.4 Å (10 Å)</td>
</tr>
<tr>
<td>real space points/k point</td>
<td>40 (5)</td>
<td>40 (4)</td>
<td>40 (6)</td>
</tr>
<tr>
<td>off axis k points</td>
<td>4 (4)</td>
<td>4 (4)</td>
<td>4 (4)</td>
</tr>
<tr>
<td>energy grid density</td>
<td>1.36·10^{-4} eV/bin (6.8·10^{-4} eV/bin)</td>
<td>1.36·10^{-4} eV/bin (9.5·10^{-4} eV/bin)</td>
<td>1.36·10^{-4} eV/bin (4.1·10^{-4} eV/bin)</td>
</tr>
<tr>
<td>energy range around Fermi level</td>
<td>13.6 eV (10.8 eV)</td>
<td>13.6 eV (10.8 eV)</td>
<td>13.6 eV (10.8 eV)</td>
</tr>
<tr>
<td>number of bands used</td>
<td>189</td>
<td>192</td>
<td>192</td>
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<tr>
<td>chemical potential range (eV)</td>
<td>2.8 eV (2.62 eV)</td>
<td>1.86 eV (1.60 eV)</td>
<td>2.5 eV (2.24 eV)</td>
</tr>
</tbody>
</table>

A.3 Graphene

We defined initial conditions based on previous DFT studies of graphene systems\textsuperscript{67-69}. These initial conditions included atomic position, lattice parameter, k-grid density, cutoff energy for the plane wave basis, and inter-layer graphene spacing. For the position of carbon atoms, we used the standard primitive unit cell of graphene, with atoms located at:

\[
\mathbf{a}_1 = \left( \frac{2}{3}, \frac{1}{3}, 0 \right) \quad \mathbf{a}_2 = \left( \frac{1}{3}, \frac{2}{3}, 0 \right) \quad (A.3.1)
\]

With the non-orthogonal primitive vectors defined in terms of standard Cartesian unit vectors:

\[
\mathbf{n}_1 = \left( 1 \quad 0 \quad 0 \right) \quad \mathbf{n}_2 = \left( \frac{1}{2} \quad \frac{\sqrt{3}}{2} \quad 0 \right) \quad \mathbf{n}_3 = \left( 0 \quad 0 \quad 1 \right) \quad (A.3.2)
\]

This forms the standard hexagonally periodic 2D graphene lattice. The atoms are located on high symmetry points within the primitive cell. The forces acting on atoms in this primitive cell are already fully minimized, so
convergence with respect to atomic position is not necessary. The initial lattice parameter values used to test total energy convergence were:

\[ r_1 = 2.458 \text{ Å} \quad r_2 = 2.458 \text{ Å} \quad r_3 = 12.682 \text{ Å} \]  

For initial convergence testing, we use a 24x24x1 energy grid, and a cutoff energy of 20 Hartree (544 eV). We used an un-shifted gamma centered k point grid through all our DFT calculations. For convergence testing we used an inter-layer graphene spacing of 15 Å. The total energy of the graphene system is next converged in terms of lattice parameter, cutoff energy, energy grid spacing, and inter-layer graphene spacing.

The next step in our methodology was detailed DFT convergence testing. We first converged the DFT total energy with respect to the lattice parameter, followed by cutoff energy, inter-layer spacing, and finally k-grid density. DFT total energy convergence was found with a lattice parameter of 2.4582 Å, which shows close agreement with the experimentally measured value of 2.46 Å\textsuperscript{60}. Cutoff energy convergence was observed to occur at 620 eV. The extremely large k-point grid necessary for BTT calculations required us to use a much larger cutoff energy of 1197 eV in order to increase the number of plane waves in our calculation basis and as a result more accurately predict energy values with higher k-grid density. Next the total energy was converged within 10\textsuperscript{-5} eV in terms of the inter-layer graphene spacing. We found the convergence condition was met with inter-layer spacing of 10.295 Å. This lattice parameter corresponded to an interlayer spacing approximately 6.7 times larger than the measured carbon-carbon bond length of 1.54 Å\textsuperscript{129}, or 1.5 times the expected interlayer spacing between planes of graphite\textsuperscript{129}. In our calculations we used an interlayer spacing of 12.7 Å. This reduced graphene interaction effects in our calculated electronic structure, thereby better representing the electron dynamics of graphene. We found that DFT convergence with respect to k-grid density occurred with a 4x4x1 k-point grid, which is insufficient for BTT calculations. This low number of k-points leads to large oscillations in the thermoelectric properties of graphene because of the interpolation process used by BoltzTraP to expand the electronic structure. Converged values are shown in table 3.

After DFT convergence, the next step in our calculation process was BTT convergence testing. Based on convergence testing we found that some modification was necessary to the BoltzTraP program in order to accurately predict the thermoelectric properties of graphene. We converged our BoltzTraP calculations based on the k-grid density, and energy range around the Fermi level. The k-grid density determines the accuracy of the interpolation process used by BoltzTraP to expand the electronic structure and then calculate physical properties. The number of
k-points included in the electronic structure influences the average amplitude of oscillations in the interpolation process observable in the calculated Seebeck coefficient of graphene. These oscillations are most observable far away from the Fermi level. The amplitude of oscillation is a rough measure of the accuracy of the interpolation process. Therefore, we minimized the average amplitude of oscillation with respect to the number of k-points in the electronic structure of graphene. We used a 144x144x1 k point grid, with 1610 irreducible points. The large number of k points needed to represent the thermoelectric properties of graphene was necessary to better represent the electronic structure near the Dirac points. The number of expansion real space points per k point was set to 40 to more smoothly interpolate the electronic structure with higher k-grid density. We calculated 40 individual bands in the electronic structure of graphene. In order to include a higher number of bands, we set the energy range around the Fermi level to be 10 eV. The chemical potential range considered in our BTT calculations was also set to 10 eV.

The exact values for key quantities used in our calculations are shown in table A.3.1.

Table A.3.1. Key quantities used in our DFT and BTT calculations of the thermoelectric properties of pure graphene. Values we used are shown first, while convergence values are shown in brackets.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Lattice Parameter</td>
<td>2.4582 Å (2.4582 Å)</td>
</tr>
<tr>
<td>Cutoff energy</td>
<td>1197 eV (620 eV)</td>
</tr>
<tr>
<td>Energy grid size</td>
<td>144x144x1, (4x4x1 grid)</td>
</tr>
<tr>
<td>Inter-layer spacing</td>
<td>12.7 Å (10.29529 Å)</td>
</tr>
<tr>
<td>Atomic relaxation</td>
<td>None, atoms on symmetry points</td>
</tr>
<tr>
<td>Real Space Points/k point</td>
<td>40 (6)</td>
</tr>
<tr>
<td>Number of bands</td>
<td>40</td>
</tr>
<tr>
<td>Exchange correlation approximation</td>
<td>GGA, PBE</td>
</tr>
<tr>
<td>Pseudopotentials</td>
<td>Norm-conserving, Trouiller-Martins type</td>
</tr>
</tbody>
</table>

A.4 Simple Graphene nanomesh

The first step in our calculation process was to establish initial conditions for calculation. We started with normal graphene, with two atoms in the primitive cell (chapter 4). We considered two different periodic arrangements of graphene nanomesh. DFT related initial testing parameters were based on previous studies of graphene nanomesh by Dvorak, Oswald, and Wu. The primitive lattice vectors for the hexagonally periodic nanomesh system were the same as standard graphene:
\begin{align*}
    v_1 &= \left(\frac{\sqrt{3}}{2}, -\frac{1}{2}, 0\right) \quad v_2 = \left(\frac{\sqrt{3}}{2}, \frac{1}{2}, 0\right) \quad v_3 = (0,0,1) \tag{A.4.1}
\end{align*}

The lattice parameters we used for the hexagonally periodic nanomesh system were:

\begin{align*}
    a_1 &= a_2 = 14.788 \text{ Å} \quad a_3 = 15 \text{ Å} \tag{A.4.2}
\end{align*}

The square periodic system was slightly different, we used standard Cartesian primitive lattice vectors:

\begin{align*}
    v_1 &= (1,0,0) \quad v_2 = (0,1,0) \quad v_3 = (0,0,1) \tag{A.4.3}
\end{align*}

With cell parameters for the square periodic system given by:

\begin{align*}
    a_1 &= 12.798 \text{ Å} \quad a_2 = 14.7887 \text{ Å} \quad a_3 = 15 \text{ Å} \tag{A.4.4}
\end{align*}

The graphene supercell was aligned so that a hexagonal hydrogen terminated ring defect was centered at the origin. We formed a graphene mesh around the defect. Both systems have a total of 72 atoms, 6 hydrogen and 66 carbon.

For the both the hexagonally periodic and square periodic nanomesh system, we used an initial cutoff energy of 1633 eV, an 8x8x1 k point grid, and an initial inter-layer spacing of 15 Å. These initial conditions were used to investigate DFT convergence.

We then performed detailed DFT convergence studies of the key input parameters in order to minimize the calculated total energy. We first relaxed the initial position of atoms in the nanomesh system, using subroutines included in the ABINIT \textsuperscript{103} software package based on the Broyden-Fletcher-Goldfarb-Shanno minimization process \textsuperscript{136-140}. This minimizes the forces and stresses acting on each atom in the graphene lattice. The calculated total energy was then minimized with respect to the cutoff energy, k-point grid size, and inter-layer spacing. Cutoff energy convergence was observed to occur at 1320 eV for the hexagonally periodic system, and 1333 eV for the square periodic system. We used a cutoff energy of 1360 eV for both nanomesh systems. DFT convergence was observed with a 2x2x1 k point grid for both systems. This is clearly insufficient, and further BTT testing was necessary. We found the convergence condition was met with inter-layer spacing of 13.23 Å. An inter-layer spacing of 15 Å was used in our thermoelectric calculations. Converged values are shown in table 6.

After calculation of the electronic structure, we next performed a series of BTT convergence tests. We relied on the modifications to the BoltzTraP program that we first developed to predict the thermoelectric properties of pure graphene (chapter 4) and similar convergence conditions. We converged our BoltzTraP calculations based on the k-grid density, and energy range around the Fermi level. The k-grid density determines the accuracy of the interpolation process used by BoltzTraP to expand the electronic structure and then calculate physical properties.
The number of k-points included in the electronic structure influences the average amplitude of oscillations in the interpolation process observable in the calculated Seebeck coefficient of graphene nanomesh. The amplitude of oscillation is inversely proportional to the accuracy of the interpolation process. Therefore, we minimized the average amplitude of oscillation with respect to the number of k-points in the electronic structure of graphene. We used a 24x24x1 k point grid. We found that a band gap in graphene nanomesh decreased the number of k-points required for interpolation. Sharply increasing, decreasing, or crossing bands increased the number of required points. The number of expansion real space points per k point was set to 40. We calculated 192 individual bands in the electronic structure of both graphene nanomesh systems. In order to include a higher number of bands, we set the energy range around the Fermi level to be 15 eV. The chemical potential range considered in our BTT calculations was set to 4 eV. The values we used in our calculations are shown in table A.4.1. Detailed convergence testing increased the accuracy of our calculations because of improvement in interpolation of the electronic structure of graphene nanomesh.

Table A.4.1. Key input parameters used in our calculations. Converged values are shown in parenthesis.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Hexagonally Periodic</th>
<th>Square Periodic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cutoff energy</td>
<td>1360 eV (1320 eV)</td>
<td>1360 eV (1333 eV)</td>
</tr>
<tr>
<td>Energy grid size</td>
<td>24x24x1, (2x2x1 grid)</td>
<td>24x24x1, (2x2x1 grid)</td>
</tr>
<tr>
<td>Inter-layer spacing</td>
<td>15 Å (13.23 Å)</td>
<td>15 Å (13.23 Å)</td>
</tr>
<tr>
<td>Atomic relaxation</td>
<td>Yes, Broyden-Fletcher-Goldfarb-Shanno minimization</td>
<td>Yes, Broyden-Fletcher-Goldfarb-Shanno minimization</td>
</tr>
<tr>
<td>Real Space Points/k point</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Energy range</td>
<td>13.6 eV (10.8 eV)</td>
<td>13.6 eV (10.8 eV)</td>
</tr>
<tr>
<td>energy grid density</td>
<td>1.36\cdot10^{-4} eV/bin (6.8\cdot10^{-4} eV/bin)</td>
<td>1.36\cdot10^{-4} eV/bin (6.8\cdot10^{-4} eV/bin)</td>
</tr>
<tr>
<td>Number of bands</td>
<td>192</td>
<td>192</td>
</tr>
</tbody>
</table>

A.5 Periodically Defected Graphene

Initial conditions for our DFT convergence testing were based on the values used in chapter 5 section 1. We investigated the effects of a single ring defect caused by partial hydrogen passivation or boron nitride replacement of carbon atoms in the graphene lattice. The hydrogen terminated system has 78 atoms, while the Boron Nitride ring defect system has 72 atoms in the unit cell. Initial lattice parameter values were identical to those used in chapter 5 section 1 for hexagonally periodic graphene nanomesh systems, a$_1$=a$_2$=14.788 Å, a$_3$=15 Å. We used an initial cutoff energy of 1360.6 eV for both defect systems. We used an initial 8x8x1 un-shifted gamma centered k point grid for
both systems. These initial values were adjusted based on DFT convergence studies.

We found slight differences in specific converged parameters between the different systems considered. We first minimized the total energy with respect to lattice parameter, and found that the initial value of 14.788 Å for the primary lattice vectors was sufficient. We then relaxed the atomic positions using subroutines included in the ABINIT software package based on the Broyden-Fletcher-Goldfarb-Shanno minimization process. We then found that a cutoff energy of 1687 eV (hydrogen passivation) or 1360 eV (boron nitride doping) was sufficient to converge the total energy. There was a slight deviation in converged interlayer spacing between the two systems considered (15.5 Å for the hydrogen passivated system, compared to 13.4 Å for boron nitride doping), caused by the additional hydrogen atoms on the graphene substrate. Next we observed that a 4x4x1 k-point grid was more than sufficient to converge the total energy of the system within 0.1 eV. A total of 192 individual bands were calculated in the electronic structure of both graphene systems. We calculated a band gap of 0.731 eV for the hydrogen passivated system, and a gap of 0.337 eV for boron nitride doped system.

We then performed a series of BTT convergence tests to minimize interpolation based error contributions to calculated thermoelectric properties. We performed a series of tests to minimize error sources from the number of k-points, real space points per k-point, and the energy span around the Fermi level. We found that a 24x24x1 k point grid was generally sufficient to minimize secondary interpolation error bases oscillations in Seebeck coefficient (chapter 5 section 1). We found that using a larger number of real space points per k-point (40 for both systems) further minimized interpolation error. The energy range around the Fermi level was set as large as possible (~14 eV) to include as many bands in the electronic structure as possible. Quantities are summarized in table (A.5.1).

Table A.5.1: Key input parameters used in our calculations. Converged values are shown in parenthesis.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Hydrogen Passivation</th>
<th>Boron Nitride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cutoff energy</td>
<td>1687 eV (1320 eV)</td>
<td>1360 eV (1333 eV)</td>
</tr>
<tr>
<td>Energy grid size</td>
<td>24x24x1, (2x2x1 grid)</td>
<td>24x24x1, (2x2x1 grid)</td>
</tr>
<tr>
<td>Inter-layer spacing</td>
<td>17 Å (13.23 Å)</td>
<td>15 Å (13.23 Å)</td>
</tr>
<tr>
<td>Atomic relaxation</td>
<td>Yes, Broyden-Fletcher-Goldfarb-Shanno minimization process</td>
<td>Yes, Broyden-Fletcher-Goldfarb-Shanno minimization process</td>
</tr>
<tr>
<td>Real Space Points/k point</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td>Energy range</td>
<td>14 eV (10.8 eV)</td>
<td>12 eV (10.8 eV)</td>
</tr>
<tr>
<td>energy grid density</td>
<td>1.36·10^-4 eV/bin (6.8·10^-4 eV/bin)</td>
<td>1.36·10^-4 eV/bin (6.8·10^-4 eV/bin)</td>
</tr>
<tr>
<td>Number of bands</td>
<td>192</td>
<td>192</td>
</tr>
</tbody>
</table>
APPENDIX B

BOLTZMANN TRANSPORT THEORY

The purpose of this appendix is to briefly summarize important components of BTT not mentioned in chapters 1 and 2. This was designed to give some greater context to our study of graphene nanomesh. This appendix will discuss the theoretical framework of BTT (Boltzmann Transport Theory) (section 1), summarize the derivation of the BTE (Boltzmann Transport Equation) (section 1), explain the thermodynamic origins of key quantities that can be calculated using BTT (section 2), derive thermoelectric properties we calculated using BoltzTraP$^{106}$ (section 2), and discuss some ideal properties of thermoelectric materials (section 3). Many excellent references exist on the subject, and we recommend consulting works such as *Nanoscale Thermoelectrics* by Wang and Wang$^8$ or *Thermodynamics of Thermoelectric Phenomena and Applications* by Goupil et al.$^{26}$ for a more complete discussion of these topics. We relied heavily on these references when preparing this appendix. This section is intended as a condensed summary of chapter 1 in *Nanoscale Thermoelectrics* and sections 1 and 2 of *Thermodynamics of Thermoelectric Phenomena and Applications*.

B.1 BTT and BTE

The key theoretical framework for current understanding of the thermoelectric effect was developed over a long period by many people, but contains large contributions by Boltzmann and Onsager. Current understanding focuses on trying to describe the statistical behavior of a collection of charge carriers defined by a distribution function:

$$f(r, k, t)$$  \hspace{1cm} (B.1)

that defines the probability of finding a charge carrier at a specific position in space $r$, with specific energy $k$, and at a specific time $t$. In this form the distribution function has 7 dimensions. The BTE is used to describe how this distribution of charge carriers changes with time. In its most basic form the BTE is:

$$\frac{\partial f(r, k, t)}{\partial t}_{\text{fields}} + \frac{\partial f(r, k, t)}{\partial t}_{\text{scattering}} + \frac{\partial f(r, k, t)}{\partial t}_{\text{diffusion}} + \frac{\partial f(r, k, t)}{\partial t}_{\text{distribution function}} = 0$$  \hspace{1cm} (B.2)

where first term represents contributions due to external fields, the second term represents scattering of charge carriers, the third term represents carrier diffusion, and the last term represents time dependence of the distribution function. The last term is irrelevant under steady state conditions when the distribution function does not change with time. Figure B.1.1 shows the contributing factors that change in the distribution function used to represent...
charge carriers in materials. This form of the BTE is valid only for electrons and holes where particle number is conserved. A different form of BTE can also be used to represent phonons, this requires the addition of an extra term to represent change in particle number. We used equation (2) without the time dependence of the distribution function to calculate thermoelectric materials in our study.

BoltzTraP uses a form of equation (2) to calculate thermoelectric properties of materials. A brief mathematical derivation of the fully simplified version of equation (2) is necessary in order to better understand this process. Two derivatives are needed to complete the derivation. Background information about these derivatives can be explored in more detail in such books as *Solid State Physics* by Ashcroft and Mermin. The first derivative relationship, which relates velocity and energy:

\[
\frac{dr}{dt} = v_i(k) = \frac{1}{h} \frac{\partial \varepsilon_i(k)}{\partial k}
\]

Where \(i\) represents a band index, \(v\) is the velocity of a charge carrier, and \(\varepsilon\) the electronic structure. This equation establishes the direct relationship between velocity and energy, and is an expression of Newton’s laws of motion.

The second derivative relationship is an expression of the Lorentz force law (equation 5). This relationship is simplified by ignoring magnetic field effects. This is possible because the form of the BTE used by BoltzTraP is a first order linearization, and magnetic field effects are of second order in the BTE (equation 4). These two important relationships can be summarized with:

\[
v_i(k) \cdot (v_i(k) \times B) = 0
\]

\[
\frac{dk}{dt} = F = \frac{q}{h} (E + v_i(k) \times B) = \frac{q}{h} (E)
\]

Where \(F\) is the force acting on a charge carrier, \(q\) is the carrier charge, \(E\) is the external electric field, \(B\) is the external magnetic field, and \(v_i(k)\) is the velocity of a charge carrier. BoltzTraP is designed to only investigate the electric field contributions to the thermoelectric properties of materials. This approach assumes that magnetic field contributions to the thermoelectric properties of materials are very small, and can therefore be ignored.
Equation (2) is a general statement of the physical effects included in the BTE. Each term in equation (2) has significance. The diffusion term in equation (2) can be represented with:

$$ f_i(r, k, t + \delta t) = f_n(r - v_i \delta t, k, t) $$  \hspace{1cm} (B.6)

Where $f_i$ represents the distribution function of charge carriers, $r$ describes a coordinate in 3D space, $k$ is a reciprocal lattice vector, $t$ is a specific time, and $\delta t$ is a small time difference. The difference between the same particles at different times is simply a function of velocity and time. No energy is added or subtracted from the diffusion of a particle. Equation (6) is more useful when rewritten using a chain rule:

$$ f_i(r, k, t) + \frac{\partial f_i(r, k, t)}{\partial t} \cdot \delta t = f_i(r, k, t) - \frac{\partial f_i(r, k, t)}{\partial r} \cdot \delta t \cdot v_i(k) $$  \hspace{1cm} (B.7)

$$ \frac{\partial f_i(r, k, t)}{\partial t} \cdot \delta t = -\frac{\partial f_i(r, k, t)}{\partial r} \cdot \delta t \cdot v_i(k) $$

$$ \frac{\partial f_i(r, k, t)}{\partial t} \bigg|_{\text{diffusion}} = -\frac{\partial f_i(r, k, t)}{\partial r} \cdot v_i(k) $$  \hspace{1cm} (B.8)

This assumes no change in $\vec{k}$ dependence on diffusion of particles represented by the distribution function. Equation (8) is used to represent the diffusion of charge carriers in the BTE used by BoltzTraP in our study.

The second term in equation (2) describes the external field contribution to the BTE, and can be represented in a similar form to equation (6):

$$ f_i(r, k, t + \delta t) = f_i(r, k - F \delta t, t) $$  \hspace{1cm} (B.9)

Where $F$ is the external force applied to a particle by a field. Equation (9) demonstrates that the only way to change the net energy of a particle from external sources is by application of an external field. Equation (9) is more usefully expressed using a chain rule:

$$ f_i(r, k, t) + \frac{\partial f_i(r, k, t)}{\partial t} \cdot \delta t = f_i(r, k, t) - \frac{\partial f_i(r, k, t)}{\partial k} \cdot \delta t \cdot F $$  \hspace{1cm} (B.10)

$$ \frac{\partial f_i(r, k, t)}{\partial t} \cdot \delta t = -\frac{q}{\hbar} (E) \cdot \delta t \cdot \frac{\partial f_i(r, k, t)}{\partial k} $$

$$ \frac{\partial f_i(r, k, t)}{\partial t} \bigg|_{\text{field}} = -\frac{q}{\hbar} (E) \cdot \frac{\partial f_i(r, k, t)}{\partial k} $$  \hspace{1cm} (B.11)

A modified version of equation (11) is used by BoltzTraP to calculate thermoelectric properties.

The scattering term in equation (2) is the most difficult to represent mathematically. There are a wide range of approaches to estimating the scattering contribution to the BTE. Deformation potential theory is currently the
most commonly used technique to approximating the scattering term from first principles. BoltzTraP relies on the relaxation time approximation to solve the BTE. The relaxation time approximation uses a first order linearization to account for changes to the distribution function from thermal equilibrium. This requires that the corrections to the distribution function away from thermal equilibrium remain small relative to the magnitude of the distribution function at any point in r, k and t space. The distribution function after linearization can be described using:

\[ f(r, k, t) = f^0(r, k, t) + f^1(r, k, t) \rightarrow f^1(r, k, t) = f(r, k, t) - f^0(r, k, t) \quad \text{(B.12)} \]

Where \( f^0 \) is the distribution of charge carriers that solves the BTE at thermal equilibrium, and \( f^1 \) are first order corrections to the distribution function caused by external fields and scattering. Equation (12) allows us to rewrite the scattering term in equation (2) into a much easier form for mathematical manipulation:

\[
\frac{\partial f(r, k, t)}{\partial t} \bigg|_{\text{scattering}} = \frac{f^1(r, k, t)}{\tau(e_i(k))} = \frac{f(r, k, t) - f^0(r, k, t)}{\tau(e_i(k))} \quad \text{(B.13)}
\]

This is the relaxation time approximation, where \( \tau(e_i(k)) \) is known as the relaxation time. All scattering effects in a material are represented using the relaxation time. The relaxation time can be generally represented using Matthiessen’s rule, originally developed to find empirical relationships for carrier mobility:111,112

\[
\frac{1}{\tau} = \frac{1}{\tau_{cr}} + \frac{1}{\tau_{im}} + \frac{1}{\tau_p} + \frac{1}{\tau_b} + \ldots \quad \text{(B.14)}
\]

Where the total relaxation time \( \tau \) is expressed in proportion to assumed contributing factors. Some common examples shown in equation (14) are scattering effects caused by crystal defects \( \tau_{cr} \), charge impurities \( \tau_{im} \), electron-phonon scattering \( \tau_p \), and bound or edge states \( \tau_b \). These terms are qualitatively ranked from the most important to least important in common materials. Das Sarma et al.74,76 have suggested that impurity or defect scattering is the dominant contributing factor to the relaxation time in graphene based systems. As a result, Das Sarma et al. were able to accurately calculate the conductivity of graphene with varying carrier concentration. The important assumption in equation (13) is included in thermoelectric calculations by BoltzTraP.

To make use of equation (2) to calculate thermoelectric properties, it is necessary to assume a functional form of the distribution function. We assume that at equilibrium the charge carriers in a material can be represented using the Fermi-Dirac distribution:113–115

\[
f^0_i(r, k, t) = \frac{1}{e^{\frac{e_i(k) - \mu}{k_B T}} + 1} \quad \text{(B.15)}
\]
Where \( k_b \) is Boltzmann’s constant, \( \mu \) is the chemical potential, \( \varepsilon(k) \) describes the energy, and \( T \) is temperature.

This distribution is extensively used to predict the properties of electrons.

In order to calculate thermoelectric properties, equation (2) can be rewritten using the terms outlined in equations (8), (11) and (13):

\[
F \cdot \frac{\partial f_i^o(r, k, t)}{\partial k} + \frac{\partial f_i^o(r, k, t)}{\partial r} \cdot v_i(k) = -\frac{f_i^o(r, k, t) - f_i^o(r, k, t)}{\tau} \tag{B.16}
\]

Because of equation (15), no direct time dependence is necessary in equation (2). We assume that temperature and chemical potential in equation (15) are functions of position, as stated with:

\[
\mu \rightarrow \mu(r) \quad T \rightarrow T(r) \tag{B.17}
\]

For practical application such as BoltZTraP, removing higher order terms from equation (16) simplifies the calculation process:

\[
F \cdot \frac{\partial f_i^o(r, k, t)}{\partial k} + \frac{\partial f_i^o(r, k, t)}{\partial r} \cdot v_i(k) = -\frac{f_i^o(r, k, t)}{\tau} \tag{B.18}
\]

We can evaluate the derivatives in equation (18):

\[
\frac{\partial (f_i^o(r, k, t))}{\partial \varepsilon_k} = \nabla_r \left( \frac{1}{e^{\frac{\varepsilon(k) - \mu(r)}{k_b T(r)}} + 1} \right) = -e^{\frac{\varepsilon(k) - \mu(r)}{k_b T(r)}} \nabla_r \left( \frac{\varepsilon(k) - \mu(r)}{k_b T(r)} \right) \tag{B.19}
\]
\[
\frac{\partial (f_i^a(r, k, t))}{\partial \varepsilon_i(k)} = \frac{\hbar v_i(k)}{\epsilon(k)} \tag{B.20}
\]

These equations rely on the definition of the derivative:

\[
\frac{\partial (f_i^a(r, k, t))}{\partial \varepsilon_i(k)} = \frac{e(k) - \mu(r)}{e(k) - \mu(r) + k_BT(r)} \tag{B.21}
\]

Equation (18) to first order simplifies to:

\[
\frac{\partial (f_i^a(r, k, t))}{\partial \varepsilon_i(k)} \left( -\nabla_i(\mu(r)) - \frac{\epsilon_i(k) - \mu(r)}{T(r)} \nabla_i(T(r)) \right) \cdot F = -\frac{f_i^a(r, k, t)}{\tau} \tag{B.22}
\]

It is standard to incorporate the electric field contribution to the BTE by incorporating it into the full electrochemical potential:

\[
\mu_e = \mu + qV \tag{B.23}
\]

So that

\[
\frac{\partial \mu_e}{\partial \vec{r}} = \nabla_e \mu_e = \nabla(\mu + qV) = \nabla_e(\mu(\vec{r})) + q\nabla(V) = \nabla_e(\mu(\vec{r})) - q\vec{E} \tag{B.24}
\]

When this is applied to the BTE, the equation can be rewritten to:

\[
\frac{\partial (f_i^a(r, k, t))}{\partial \varepsilon_i(k)} \left( \frac{\epsilon_i(k) - \mu(r)}{T} \nabla T + \nabla \mu \right) \cdot \vec{v}_n(k) = \frac{f_i^a(r, k, t)}{\tau} \tag{B.25}
\]

This is the form of the BTE solved by BoltzTraP\textsuperscript{106} to predict the properties of materials.

**B.2 Thermodynamics and Properties**

Equation (25) is used to solve for the thermoelectric properties of materials. These equations assume an understanding of thermodynamics of thermoelectric materials. The fundamental thermodynamic equation used to represent the BTE is based on the grand canonical ensemble. The key variables for thermodynamic systems described by the grand canonical ensemble are entropy, particle number, and volume. The volume enclosed by the BTE distribution function remains fixed. The fundamental thermodynamic equation simplifies to:

\[
dS = \frac{1}{T} dU + \frac{\mu}{T} d\rho \tag{B.26}
\]
Where $S$ is entropy, $T$ is temperature, $U$ is the total energy, $\mu$ is the chemical potential, and $\rho$ is particle number. The derivatives in equation (26) each satisfy a continuity equation:

$$\frac{\partial U}{\partial t} + \nabla \cdot J_e = 0 \quad \text{(B.27)}$$

$$\frac{\partial S}{\partial t} + \nabla \cdot J_s = 0 \quad \text{(B.28)}$$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot J_\rho = 0 \quad \text{(B.29)}$$

Where $J$ represents a current or flux in the distribution function. In this system entropy and mass are the conjugate variables to energy. The currents are thus coupled, and the relationship is described by:

$$J_e = TJ_s + \mu J_\rho \quad \text{(B.30)}$$

We assume that the thermodynamic system is quasi-static. This allows us to rewrite equation (30):

$$JS = \frac{J_s}{T} \quad \rightarrow \quad dS = \frac{dQ}{T} \quad \text{(B.31)}$$

Where $J_s$ is the heat current, and $dQ$ is the change in heat. This leads to the coupled equation:

$$\begin{pmatrix} J_\rho \\ J_Q \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} -q \frac{1}{T} \nabla (\mu_e) \\ \frac{1}{T} \end{pmatrix} \quad \text{(B.32)}$$

To satisfy Onsager’s theory of minimal entropy production it is necessary that $L_{12} = L_{21}$. Each $L$ term is a coupling factor. These transport coefficients are key to understanding the thermoelectric effect, and lead directly to Onsager’s reciprocal relations. Further analysis reveals the relationships between the coupling terms in equation (32) and commonly described physical properties. When equation (32) is fully decoupled, the first term can show:

$$J_\rho = -q \frac{L_{11}}{T} \nabla (\mu_e) = q^2 \frac{L_{11}}{T^2} \hat{E} \quad \rightarrow \quad \sigma_{\eta T=0} = \frac{q^2 L_{11}}{T} \quad \text{(B.33)}$$

Where $\sigma_{\eta T=0}$ is the isothermal conductivity. The second term is:

$$J_\rho = 0 \rightarrow 0 = -L_{11} \frac{\nabla (\mu_e)}{T} + L_{12} \nabla \left( \frac{1}{T} \right) \rightarrow J_Q = \frac{(L_{21}L_{12} - L_{11}L_{12})}{T^2 L_{11}} \nabla T \rightarrow \kappa_{\rho=0} = \frac{(L_{21}L_{12} - L_{11}L_{12})}{T^2 L_{11}} \quad \text{(B.34)}$$

Where $\kappa_{\rho=0}$ is thermal conductivity with zero electric field. We further find:

$$J_Q = \frac{L_{22}}{T^2} \nabla (T) \quad \rightarrow \quad \kappa_{\mu e=0} = \frac{L_{22}}{T^2} \quad \text{(B.35)}$$
Where $\kappa_{\mu=0}$ is the thermal conductivity with no electrochemical gradient. When the equations are coupled, the Seebeck coefficient can be defined by:

$$S_{\nu\mu=0} = \frac{L_{21}}{qTL_{11}}$$  \hspace{1cm} (B.36)

We calculate the Seebeck coefficient of materials extensively in our study. The fundamental relationship between Seebeck coefficient and entropy can be illustrated with the quantity:

$$S_{en} = \frac{L_{21}}{TL_{11}} \quad qS = S_{en}$$  \hspace{1cm} (B.37)

We can use this quantity to define an entropy loss per charge carrier. This helps to represent the fundamentally different source of electrical current compared to standard electrical systems where entropy is a small factor. Further based on equation (32) the relationship between different sources of thermal conductivity:

$$\kappa_{\mu=0} = \kappa_{\mu=0} + \sigma_{T=0} S^2 T$$  \hspace{1cm} (B.38)

And with the relationship:

$$\nabla \left( \frac{1}{T} \right) = \frac{1}{T^2} \nabla (T)$$  \hspace{1cm} (B.39)

Combining equations (33), (34), (35), (36), and (39) with the rewritten form of equation (32):

$$J_p = -\frac{\sigma_{T=0} S_{en}}{q} \nabla (\mu_e) + \frac{\sigma_{T=0} S_{en} T^2}{q^2} \nabla \left( \frac{1}{T} \right)$$  \hspace{1cm} (B.40)

$$J_q = -\sigma_{T=0} S_{en} T \nabla (\mu_e) + \left( \frac{T^3}{q^2} \sigma_{T=0} S_{en}^2 + T^2 \kappa_{\mu=0} \right) \nabla \left( \frac{1}{T} \right)$$  \hspace{1cm} (B.41)

Equations (40) and (41) are forms of Onsager’s reciprocal relations, which are generally expressed by:

$$J_p = \sigma \bar{E} - \sigma S \nabla (T)$$  \hspace{1cm} (B.42)

$$J_q = \sigma ST \bar{E} - \kappa \nabla (T)$$  \hspace{1cm} (B.43)

Onsager’s reciprocal relationships are the equations used to calculate physical properties with BTT. BoltzTraP uses these relationships to calculate thermoelectric properties. Equations (42) and (43) are fundamental to our study of the thermoelectric properties of graphene nanomesh.

Thermoelectric properties can be calculated using Onsager’s reciprocal relations. At thermal equilibrium there is no net current flowing in a thermoelectric system. Using equations (42) and (43) the heat and electrical currents can be defined by:
\[
J_{\rho} = \frac{q}{4\pi^3} \int \mathbf{v}(\mathbf{k}) f(\mathbf{r}, \mathbf{k}, t) d\mathbf{k} = \frac{1}{4\pi^3} \int \mathbf{v}(\mathbf{k}) f^i_1(\mathbf{r}, \mathbf{k}, t) d\mathbf{k}
\]
(B.44)

\[
J_{\theta} = \frac{1}{4\pi^3} \int \varepsilon(\mathbf{k}) \mathbf{v}(\mathbf{k}) f(\mathbf{r}, \mathbf{k}, t) d\mathbf{k} = \frac{1}{4\pi^3} \int \varepsilon(\mathbf{k}) \mathbf{v}(\mathbf{k}) f^i_1(\mathbf{r}, \mathbf{k}, t) d\mathbf{k}
\]
(B.45)

Thermoelectric quantities can then be calculated using equations (44) and (45):

\[
\mathbf{v}_{i,\beta}(\mathbf{k}) = \frac{1}{\pi \hbar} \frac{\partial \varepsilon_{\mathbf{k}}}{\partial k_\beta}
\]
(B.46)

\[
\sigma_{i,\beta\gamma}(i, \mathbf{k}) = e^2 \tau_{i,\mathbf{k}} \mathbf{v}_{\beta}(i, \mathbf{k}) \mathbf{v}_{\gamma}(i, \mathbf{k})
\]
(B.47)

\[
\frac{\sigma_{\beta\gamma}(T; \mu)}{\tau} = -\frac{1}{\Omega} \int \sigma_{\beta\gamma}(\varepsilon) \frac{\partial f(\varepsilon, \mu, T)}{\partial \varepsilon} d\varepsilon
\]
(B.48)

\[
\frac{\nu_{\beta\gamma}(T; \mu)}{\tau} = \frac{-1}{q^2 \Omega} \int \sigma_{\beta\gamma}(\varepsilon)(\varepsilon - \mu) \frac{\partial f(\varepsilon, \mu, T)}{\partial \varepsilon} d\varepsilon
\]
(B.49)

\[
\frac{\kappa_{\beta\gamma}(T; \mu)}{\tau} = \frac{-1}{q^2 T \Omega} \int \sigma_{\beta\gamma}(\varepsilon)(\varepsilon - \mu)^2 \frac{\partial f(\varepsilon, \mu, T)}{\partial \varepsilon} d\varepsilon
\]
(B.50)

\[
S_{\beta\gamma}(T; \mu) = \frac{1}{\varepsilon_i(T) \Delta \varepsilon} = (\sigma^{-1})_{\beta\gamma} \nu_{\beta\gamma}(T; \mu)
\]
(B.51)

Where \(i\) is a band index. These integrals are solved by BoltzTraP to estimate the thermoelectric properties of materials.

**B.3 Ideal Thermoelectric Materials**

Ideal thermoelectric materials are assumed under current theory to have a very specific set of electronic properties. These properties can be estimated using equations (46)-(51). Ideal thermoelectric materials need large electrical conductivity, large Seebeck coefficient, and low thermal conductivity. The relative thermoelectric efficiency of materials can be estimated with the quantity \(ZT\) (equation 1.1.2) which is called the thermoelectric figure of merit. The direct and indirect relationships between the terms in \(ZT\) complicate design of efficient thermoelectric materials. Careful material engineering is necessary to improve thermoelectric efficiency.

Researchers are actively searching for materials with improved \(ZT\) because of the large number of potential applications for efficient thermoelectric materials. Graphene nanomesh is one such possible material.

Ideal thermoelectric materials must have large electrical conductivity to maximize generated electrical current and large Seebeck coefficient to maximize the entropy per charge carrier. Electrical conductivity is directly related to carrier mobility and carrier concentration in materials:
\[ \sigma = n q \mu_c \]  

(B.52)

Where \( \sigma \) is electrical conductivity, \( n \) is the free carrier concentration, \( q \) is the charge, and \( \mu_c \) is the carrier mobility. An efficient thermoelectric material therefore has a large free carrier concentration and a large carrier mobility. In contrast to electrical conductivity, the Seebeck coefficient is directly related to carrier diffusion. The Seebeck coefficient is improved by asymmetries in carrier concentration. Carrier diffusion is a random process that is affected by thermal gradients. If there is no asymmetry in free carrier population, an equal number of holes and electrons will propagate through a material, resulting in no net thermoelectric based electrical current. Population asymmetries require a reasonably large band gap, and either a difference in carrier concentration caused by doping or large asymmetry in the effective mass of different charge carriers. Bismuth telluride is a strong thermoelectric bulk material because it has a high Seebeck coefficient caused by asymmetry in the effective mass tensor.

The direct and indirect relationships between the terms in ZT complicate design of efficient thermoelectric materials. For example, the large Seebeck coefficient needed for efficient thermoelectric materials is associated with a relative decrease in free carrier concentration because of the band gap. This shows how electrical conductivity and Seebeck coefficient must be balanced to maximize ZT. The inverse relationship between electrical conductivity and Seebeck coefficient was shown in our study of graphene nanomesh. When a band gap was opened in graphene nanomesh, we observed a large increase in Seebeck coefficient and a corresponding decrease in electrical conductivity (chapter 5 section 1). Therefore, a band gap by itself did not result in net improvement in ZT for graphene nanomesh systems. Design of efficient thermoelectric materials must take into account these complex relationships.

The physical properties of thermoelectric materials need to be carefully balanced to maximize efficiency using material engineering. A large Seebeck coefficient is necessary to maximize ZT, while the resulting band gap limits free carrier concentration. The occupation of states near the valance band maximum should be maximized. This increases the chance that thermal excitation of exciting the electron across the band gap and into the conduction band minimum. The density of possible unoccupied states needs to be maximized as close to the conduction band minimum to increase the probability of successful thermal excitation. In order to maximize the contribution to conductivity from each electron and have a higher Seebeck voltage, the effective mass of each electron needs to be as small as possible, while the group velocity needs to be as high as possible to maximize carrier mobility. We can describe the effective mass and group velocity of charge carriers in terms of the first and second derivatives of the
electronic structure of a material:

\[ \nu_n(k) = \frac{1}{\hbar} \frac{\partial \varepsilon_n(k)}{\partial k} \quad m^*_{(l),j,k} = \frac{1}{\hbar^2} \frac{\partial^2 \varepsilon_n(k)}{\partial k_j \partial k_k} \]  

Where \( \nu_n \) is the group velocity, \( n \) is the band index, \( \varepsilon_n \) is the electronic structure of a material, and \( \vec{k} \) is a reciprocal space vector describing the momentum of an electron. Here effective mass is represented as a tensor. This has two competing effects on the electronic structure of an ideal thermoelectric material. We want the first derivative to be as large as possible in order to maximize the group velocity, and thus how far the carriers can travel through a material under an applied thermal or chemical potential gradient. The second derivative needs to be as large as possible, in order to minimize the effective mass and maximize the acceleration caused to each electron by any external force.

Quantum confinement has beneficial effects on the band structure and density of states of materials. Quantum confinement opens band gaps in materials, and has the effect of fundamentally altering the density of states. Figure (B.3.1) illustrates the band structure of an ideal thermoelectric material, and further shows how the electronic structure of an ideal material is positively affected in terms of thermoelectric transport, by quantum confinement. As mentioned previously, efficient thermoelectric materials require low thermal conductivity. Careful material design can weaken lattice thermal conductivity while still maintaining sufficiently high electrical conductivity and Seebeck coefficient. Some previous studies of ZT are shown in table B.3.1. This table is far from complete, but demonstrates some typical measured ZT values for different materials.
Figure B.3.1 Two level qualitative band structure and occupied density of states for (a) n type and (b) p type idealized thermoelectric material. Quantum confinement fundamentally alters the density of states of materials. (c) Density of states of a 3D material, which is proportional to $\sqrt{\epsilon}$. (d) Density of states of a 2D system, proportional to $\sum_m \theta(\epsilon - \epsilon_m)$ where $\Theta$ is the step function. (e) Density of states for a 1D system, proportional to $\sum_{l_x,m_y} \theta(\epsilon - \epsilon_{l_x,m_y})/\sqrt{\epsilon - \epsilon_{l_x,m_y}}$. (f) Density of states of a fully confined 0D system, proportional to $\sum_m \delta(\epsilon - \epsilon_m)$. 
Table B.3.1. Some typical measured ZT values reported in literature for different materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>maximum ZT</th>
<th>Temperature (C)</th>
<th>ZT at 300K</th>
<th>Year</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(BiSb)3Te3</td>
<td>1.47</td>
<td>167</td>
<td>0.6</td>
<td>2008</td>
<td>Cao et al.145</td>
</tr>
<tr>
<td>Bi0.48Sb1.52Te3</td>
<td>1.5</td>
<td>117</td>
<td>1.4</td>
<td>2010</td>
<td>Xie et al.146</td>
</tr>
<tr>
<td>Al2O3/Bi0.5Sb1.5Te3</td>
<td>1.5</td>
<td>50</td>
<td>1.3</td>
<td>2013</td>
<td>Kim et al.147</td>
</tr>
<tr>
<td>PbTe bulk</td>
<td>0.7</td>
<td>151</td>
<td>0.4</td>
<td>2005</td>
<td>Caylor et al.148</td>
</tr>
<tr>
<td>Ag0.5PbSnSb0.2Te10</td>
<td>1.45</td>
<td>357</td>
<td>0.1</td>
<td>2006</td>
<td>Androu. et al.149</td>
</tr>
<tr>
<td>NaNb0.95PbTe22</td>
<td>1.7</td>
<td>427</td>
<td>0.28</td>
<td>2006</td>
<td>Poudeu et al.150</td>
</tr>
<tr>
<td>(Pb0.95Sn0.05Te)0.92(PbS)0.08</td>
<td>1.5</td>
<td>369</td>
<td>0.4</td>
<td>2007</td>
<td>Androu. et al.151</td>
</tr>
<tr>
<td>Tl0.02Pb0.98Te</td>
<td>1.5</td>
<td>500</td>
<td>0.1</td>
<td>2008</td>
<td>Herem. et al.152</td>
</tr>
<tr>
<td>Na/PbTe–PbS</td>
<td>1.8</td>
<td>527</td>
<td>0.1</td>
<td>2011</td>
<td>Girard et al.153</td>
</tr>
<tr>
<td>Na/PbTe–SrTe</td>
<td>2.2</td>
<td>642</td>
<td>0.05</td>
<td>2012</td>
<td>Biswas et al.155</td>
</tr>
<tr>
<td>In/SnTe</td>
<td>1.1</td>
<td>602</td>
<td>0.1</td>
<td>2013</td>
<td>Zhang et al.154</td>
</tr>
<tr>
<td>Na/PbTe</td>
<td>2</td>
<td>500</td>
<td>0.2</td>
<td>2014</td>
<td>Wang et al.156</td>
</tr>
<tr>
<td>Al0.01/PbSe</td>
<td>1.3</td>
<td>577</td>
<td>0.2</td>
<td>2012</td>
<td>Zhang et al.155</td>
</tr>
<tr>
<td>Pb0.92Sb0.08Se</td>
<td>1.5</td>
<td>657</td>
<td>0.01</td>
<td>2014</td>
<td>Wang et al.156</td>
</tr>
<tr>
<td>Yb0.19CoSb12</td>
<td>1</td>
<td>327</td>
<td>0.3</td>
<td>2000</td>
<td>Nolas et al.156</td>
</tr>
<tr>
<td>Yb0.02CoSb12.3</td>
<td>1.3</td>
<td>527</td>
<td>0.35</td>
<td>2008</td>
<td>Li et al.157</td>
</tr>
<tr>
<td>NaNb0.48CoSb12</td>
<td>1.25</td>
<td>577</td>
<td>0.2</td>
<td>2009</td>
<td>Pei et al.158</td>
</tr>
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<td>Ba0.14In0.23CoSb11.84</td>
<td>1.34</td>
<td>577</td>
<td>0.35</td>
<td>2009</td>
<td>Zhao et al.159</td>
</tr>
<tr>
<td>Sr0.12Ba0.18DD0.39Fe2CoSb12</td>
<td>1.3</td>
<td>527</td>
<td>0.3</td>
<td>2010</td>
<td>Rogl et al.160</td>
</tr>
<tr>
<td>Ba0.08La0.05Yb0.04CoSb12</td>
<td>1.7</td>
<td>577</td>
<td>0.4</td>
<td>2011</td>
<td>Shi et al.159</td>
</tr>
<tr>
<td>Hf0.2Zr0.25Te25NiSn0.95Sb0.05</td>
<td>1</td>
<td>500</td>
<td>0.1</td>
<td>2012</td>
<td>Joshi et al.161</td>
</tr>
<tr>
<td>Hf0.8Pb0.2CoSb0.8Sn0.2</td>
<td>1</td>
<td>800</td>
<td>0.1</td>
<td>2012</td>
<td>Yan et al.162</td>
</tr>
<tr>
<td>Si0.6Ge0.40</td>
<td>1.3</td>
<td>900</td>
<td>0.1</td>
<td>2008</td>
<td>Wang et al.154</td>
</tr>
<tr>
<td>PbEuTe/PbTe thin film quantum well structure</td>
<td>1.23</td>
<td>27</td>
<td>1.23</td>
<td>1996</td>
<td>Harman et al.163</td>
</tr>
<tr>
<td>PbTe/PbSe0.20Te0.80 thin film superlattice</td>
<td>1.2</td>
<td>327</td>
<td>0.5</td>
<td>2002</td>
<td>Beyer et al.164</td>
</tr>
<tr>
<td>PbTe/PbTeSe Single layer nanostructure</td>
<td>1.75</td>
<td>151</td>
<td>1.75</td>
<td>2005</td>
<td>Caylor et al.165</td>
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<tr>
<td>PbSe0.96Te0.04/PbTe Quantum dot superlattice</td>
<td>3.5</td>
<td>302</td>
<td>1.4</td>
<td>2005</td>
<td>Harman et al.166</td>
</tr>
<tr>
<td>Bi2Te5/Sb2Te3 thin film superlattice structure</td>
<td>2.5</td>
<td>27</td>
<td>2.5</td>
<td>2006</td>
<td>Böttner et al.167</td>
</tr>
<tr>
<td>PbSe0.98Te0.02/PbTe thin film quantum dot superlattice</td>
<td>3.6</td>
<td>306</td>
<td>1.6</td>
<td>2006</td>
<td>Böttner et al.168</td>
</tr>
<tr>
<td>Bi2Te5 Thin film nanostructure</td>
<td>2.4</td>
<td>27</td>
<td>2.4</td>
<td>2001</td>
<td>Venka. et al.169</td>
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<tr>
<td>PbSe quantum dot superlattice</td>
<td>1.6</td>
<td>27</td>
<td>1.6</td>
<td>2002</td>
<td>Harman et al.170</td>
</tr>
<tr>
<td>In0.5Ga0.47As/ErAs thin film embedded nanoparticles</td>
<td>2</td>
<td>27</td>
<td>2</td>
<td>2006</td>
<td>Kim et al.171</td>
</tr>
<tr>
<td>Si 50 nm diameter nanowire</td>
<td>0.6</td>
<td>27</td>
<td>0.6</td>
<td>2008</td>
<td>Hochb. et al.172</td>
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<td>Si 20 nm diameter nanowire</td>
<td>~1</td>
<td>-7.3</td>
<td>0.1</td>
<td>2008</td>
<td>Boukai et al.173</td>
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<td>PbTe tipped Ag2Te nanowire nanocomposite</td>
<td>0.66</td>
<td>97</td>
<td>0.05</td>
<td>2015</td>
<td>Yang et al.174</td>
</tr>
<tr>
<td>Single Walled Carbon Nanotube bundle 10 nm diameter</td>
<td>0.002</td>
<td>27</td>
<td>0.002</td>
<td>2003</td>
<td>Shi et al.175</td>
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<td>Bi0.5Sb1.5Te3 bound platelets</td>
<td>1.8</td>
<td>57</td>
<td>1.6</td>
<td>2015</td>
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