STUDY OF ELECTRICAL AND THERMAL TRANSPORT IN LOW-DIMENSIONAL STRUCTURES AIMING FOR IMPROVING THERMOELECTRIC EFFICIENCY

BY

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DISSERTATION

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ABSTRACT

Thermoelectric engineering has been getting much attention anticipating its potential to serve an important role in producing clean energy out of waste heat dissipated from industries, residential processes, and transportation. However, thermoelectric efficiency has been limited to a non-practical range because of the interplay among transport coefficients which measure the efficiency. With widely growing interest in thermoelectrics, understanding the electrical and thermal transport in thermoelectric devices and finding ways to improve the efficiency is critical to develop future thermoelectric applications and to contribute to solving the energy shortage that the world is facing. In this thesis, we present both electron and phonon aspects of the thermoelectric transport employing the Boltzmann transport theory, the Landauer formalism, and the element kinetic theory. We calculate the thermal conductivity of layered bismuth telluride thin films by solving the Boltzmann transport equation in the relaxation-time approximation using full phonon dispersion. The full phonon frequency and gradient are obtained from the framework of the first-principle density functional theory and effectively used to confirm the anisotropic thermal transport arising from the phonon mode softening. In addition, we introduce the phonon scattering due to van der Waals interface in bismuth telluride to fully capture the anisotropy of the material. We also study the thermal conductivity of the rippled graphene which has potential to be used as a future thermoelectric material. The ripple is formed through a deformation process performed in molecular dynamics. We introduce a technique which enables creation of the graphene sheet with evenly distributed ripples and calculate the thermal conductivity using Green-Kubo linear response theory. The study reveals significantly reduced thermal conductivity, which confirms the plausibility of the rippled graphene as a future thermoelectric material. To stimulate the
thermoelectric efficiency, we suggest a strategy that limits the thermal transport with no significant influence on the electrical transport by geometry-engineering. We investigate the Seebeck coefficient, the electrical conductance, and the thermal conductivity of sinusoidally corrugated silicon nanowires as well as an enhancement of the thermoelectric efficiency. A loss in the electronic transport coefficient is calculated with the recursive Green function along with the Landauer formalism, and the thermal transport is simulated with the molecular dynamics. In contrast to a small influence on the thermopower and the electrical conductance of the geometry-modulated nanowires, a large reduction of the thermal conductivity yields an enhancement of the efficiency.
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CHAPTER 1  INTRODUCTION

According to the U.S. energy flow chart for the year 2013 published by Lawrence Livermore National Laboratory, about 80% of primary energy resources used to generate power in a usable form come from fossil fuels that include coal, petroleum, and natural gas. However, if we take a close look at the use ratio of the generated energy being used for actual services compared to that being rejected, only less than 40% of the generated power is used for good, and 60% of the energy is wasted in different forms among which most of the rejected energy is in the form of waste heat. Counting nuclear power plants which also use heat to generate steam and drive turbines to generate electricity would make the amount of waste heat by far greater. Although one should not expect 100% energy conversion rate from any types of power plants, around 40% efficiency seems desperate considering the fossil fuels which are the major energy resources are not at all clean, economical and sustainable. In this matter, there is increasing demand to develop energy which is renewable and sustainable as well as environmentally friendly.

One of the solutions to the waste-energy problem is to utilize thermoelectric-energy-conversion technology that can recover the waste heat in the form of ready-for-use electricity. Among three key thermoelectric theories, Seebeck effect, Peltier effect, and Thompson effect, the Seebeck effect [1], [2] is the one governing the power generation from the temperature gradient built in a system: When there exists temperature difference in the thermoelectric generator, a certain voltage develops along the generator in nearly equilibrium condition, and the voltage is called the Seebeck voltage.
Solid-state thermoelectric materials and devices have drawn much interest in the last couple of decades due to their potential to efficiently harvest wasted heat. The efficiency of a thermoelectric system is measured through a dimensionless quantity, the thermoelectric figure of merit $ZT = S^2\sigma T / \kappa$, where $S$, $\sigma$, and $\kappa$ are the Seebeck coefficient, the electrical conductivity, and the total thermal conductivity (the sum of its electronic, $\kappa_e$, and lattice, $\kappa_L$, contributions), respectively [3].

It is clear from the $ZT$ expression that materials should hold high electrical power factor, $S^2\sigma$, and low $\kappa$ in order to achieve high $ZT$. However, finding the best combination of those thermoelectric properties has been most challenging because of the interplay between $S$ and $\sigma$: $S$ is inversely proportional to the carrier concentration while $\sigma$ is proportional to the carrier concentration. Furthermore, thermoelectric materials in which the lattice contribution dominates the overall thermal conductivity (i.e., $\kappa \approx \kappa_L$) could be potentially engineered to yield improvements in thermoelectric efficiency, through size reduction (i.e., by moving from bulk to low dimensions). In such thermoelectric materials, the phonon confinement effect can be used to reduce $\kappa$ without degrading electron transport due to the large difference between phonon and electron mean-free-paths ($\lambda_{\text{MFP-ph}} > \lambda_{\text{MFP-el}}$) [4], [5]. There have been numerous reports on this demonstrating improved $ZT$ in nanostructured semiconductors such as nanowires, superlattices, thin films, and nanograin ed bulk materials due to drop in $\kappa$, with minimal effect on electrical properties [6]–[11], and those $ZT$ values mostly fell within 0.01 – 1.5 over a wide range of temperatures. Nonetheless, despite such improvements further enhancement is needed since it is widely accepted that $ZT$ value of 3 or above is essential for solid-state based thermoelectric materials to be considered as viable thermoelectric power generators [9]. Among thermoelectric materials, bulk bismuth telluride ($\text{Bi}_2\text{Te}_3$) and its alloys have yielded the highest $ZT \sim 1$ [10], and the $ZT$ has improved up to 2.4 at room temperature when $\text{Bi}_2\text{Te}_3$ formed a thin film superlattice with antimony telluride.
(Sb₂Te₃) [11]. This improvement was attributed to phonon confinement evident in nanostructures as well as the high atomic weight of such telluride materials. High atomic weight leads to low phonon vibrational frequencies and low group velocities which hinder lattice thermal transport and thereby reduce κ without affecting electrical properties [12]. Over the past two decades, a major breakthrough in improving ZT has been achieved by minimizing κ through size-engineering and utilizing high-atomic-weight materials such as Bi₂Te₃, Sb₂Te₃, and bismuth selenide (Bi₂Se₃).

In this thesis, we will walk through the overview of the thermoelectric transport properties in Chapter 1 which includes both electronic and thermal contributions to the thermoelectrics. In Chapter 2, we will investigate bismuth telluride which has been reported to be the most widely used and the most efficient thermoelectric material. A thermal conductivity model for bismuth telluride in in-plane and cross-plane directions accounting for van der Waals forces will be introduced and studied. Chapter 3 will discuss the thermal transport in strain-induced rippled graphene. The techniques used to generate graphene with evenly distributed ripples by molecular dynamics simulation will be introduced and thoroughly explained. In Chapter 4, a strategy to improve thermoelectric efficiency in semiconductor nanowires will be discussed employing various theories and simulation techniques. The method that effectively controls thermal transport in the system will be demonstrated, and the efficiency improvement rate will also be calculated to suggest a guideline for further enhancement.
CHAPTER 2  OVERVIEW OF THERMOELECTRIC TRANSPORT

The measure of the thermoelectric efficiency involves both electrical ($S$, $\sigma$, and $\kappa_e$) and thermal transport properties ($\kappa_L$), and any changes in elements by which the transport coefficients are defined can cause a notable change in the efficiency, $ZT$. In this regard, it is very important to understand the transport coefficients with respect to how they are defined, how one affects the others, and what to tweak to change the coefficients.

For electrons, both electrical ($J$) and thermal ($U$) currents in a system are defined as functions of the electric field ($\mathcal{E}$) and the temperature gradient ($\nabla T$) (i.e. $J = A\mathcal{E} + B\nabla T$ and $U = C\mathcal{E} + D\nabla T$). By setting the temperature gradient in $J$ to be zero in the system, the electrical conductivity is defined by the coefficient $A$ which is the direct ratio between $\mathcal{E}$ and $J$. Now making the system open circuit, meaning that there is no electrical current flowing through the system, the direct relation between $\mathcal{E}$ and $\nabla T$ is established ($\mathcal{E}/\nabla T = -B/A$), and that relation which literally refers to the generated $\mathcal{E}$ upon applied $\nabla T$ is the Seebeck coefficient, also known as the thermopower. Lastly, knowing that the thermal conductivity is the direct relation between $U$ and $\nabla T$, the electronic contribution to the total thermal conductivity can be easily defined as a function of all the coefficients in $J$ and $U$, $\kappa = -\frac{U}{\nabla T} = -\left( D - \frac{B\cdot C}{A} \right)$. 
2.1 Boltzmann Transport Equation

Fundamentally, the definition of the thermoelectric properties can be explained by solving the Boltzmann transport equation (BTE) expressed as

\[
\frac{df(x,v,t)}{dt} = \left[ \frac{\partial f(x,v,t)}{\partial t} \right]_{\text{collisions}} \tag{2-1}
\]

in which the rate of change of the distribution function \( f(x,v,t) \) is the same as the change due to collisions where \( x \) is the position, \( v \) is the particle momentum, and \( t \) is the time [13]. Expanding the left-hand side of Equation (2-1) by the chain rule of differentiation, the BTE becomes

\[
\frac{df(x,v,t)}{dt} = \frac{\partial f}{\partial t} + \frac{dx}{dt} \cdot \frac{\partial f}{\partial x} + \frac{dk}{dt} \cdot \frac{\partial f}{\partial k} \tag{2-2}
\]

and, by the further expansion,

\[
\frac{\partial f}{\partial t} + v \cdot \nabla_x f + \frac{1}{\hbar} \cdot F \cdot \nabla_k f = \left[ \frac{\partial f(x,v,t)}{\partial t} \right]_{\text{collisions}} \tag{2-3}
\]

with the first term on the left-hand side of Equation (2-3) referring to the time variation of the distribution function, the second term accounting for transport induced by spatial variation with \( v = \frac{dx}{dt} = \nabla_k E / \hbar \), and the third term referring to the field induced transport with \( F = \frac{dp}{dt} = \partial hk / \partial t \) [14].

By solving the BTE and adopting the definitions of the transport coefficients described in the introduction of this chapter, the thermoelectric transport coefficients are given as [15]:

\[
\sigma = q^2 \int_{-\infty}^{\infty} \sum(E) \left( -\frac{\partial f}{\partial E} \right) dE, \tag{2-4}
\]
\[ T \sigma S = \int_{-\infty}^{\infty} \Sigma(E) (E - \mu) \left( -\frac{\partial f}{\partial E} \right) dE, \]  

(2-5)

\[ T \kappa_0 = \int_{-\infty}^{\infty} \Sigma(E) (E - \mu)^2 \left( -\frac{\partial f}{\partial E} \right) dE \]  

(2-6)

where \( \mu \) is the chemical potential and \( \Sigma(E) \) is the transport distribution function.

\[ \Sigma(E) = N(E) u(E)^2 \tau(E) \]  

(2-7)

in terms of the density of states \( N(E) \) and the carrier’s lifetime \( \tau(E) \). However, considering the complexity in solving the BTE accounting for the density of states and the difficulty in applying boundary conditions for the small devices, combining the BTE with Landauer transport theorem can be a good approach to study the transport behaviors.

### 2.2 Landauer Transport Formula

Another way of defining the electrical current as well as solving the BTE is to exploit the Landauer formula named after Rolf Landauer [16]. The formula is unique in that it considers the electrical resistance of a quantum conductor as a measure of the scattering of the conductor. The quantized conductance of a system is defined as \( G_0 = \frac{2q^2}{\hbar} \), where \( q \) is electric charge and \( \hbar \) is the Plank constant. The quantum conductance \( G_0 \) is only valid when the transport through the system is ballistic, and otherwise the conductance is defined by the Landauer formula as \( G = G_0 \times T(E) \), where the total conductance \( (G) \) is described by the quantum conductance \( (G_0) \) times the probability of electron transmission \( (T) \) at energy \( E \). The electrical and thermal current expressed with the Landauer formula are
\[ I(E) = \frac{2q}{\hbar} \int_{-\infty}^{\infty} dE [f_1 - f_2] T(E) \] and

\[ I_q = \frac{2}{\hbar} \int_{-\infty}^{\infty} T(E) (E - E_F) (f_1 - f_2) dE \]

where \( f_1 \) and \( f_2 \) are the Fermi-Dirac distributions in the left and the right ends of the system [17].

Unlike the transport distribution function \( \Sigma(E) \) in the BTE, the transmission function \( T(E) \) is not computed based on the \( E - k \) relationship and readily treats small devices with boundary conditions. The difference between \( f_1 \) and \( f_2 \) can be expanded with the Taylor expansion as a function of the voltage \( \Delta V \) and temperature \( \Delta T \) differences,

\[ f_1 - f_2 \approx -\frac{\partial f_0}{\partial E} q \Delta V - \left( -\frac{\partial f_0}{\partial E} \right) \frac{(E - E_F)}{\tau} \Delta T. \]

The rigorous expression \( f_1 - f_2 \) is very useful for defining the thermoelectric transport coefficients as it allows an independent control of the voltage and temperature in the conducting system, and it will be discussed in the next section.

### 2.3 BTE-Landauer Thermoelectric Properties

Utilizing the strength of the Landauer formalism where the carrier transmission is calculated by the relatively simple transmission function \( T(E) \), the transport coefficients given by solutions of the Boltzmann transport equation (BTE) incorporated with the Landauer formalism are [15], [17]–[19]:

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\[ G = \frac{2q^2}{h} \int_{-\infty}^{\infty} T(E) \left(-\frac{\partial f}{\partial E}\right) dE \ (1/\Omega), \quad (2-11) \]

\[ S = -\frac{1}{qT} \int_{-\infty}^{\infty} T(E)(E-E_F) \left(-\frac{\partial f}{\partial E}\right) dE \ (V/K), \quad (2-12) \]

\[ K_0 = \frac{2}{hT} \int_{-\infty}^{\infty} T(E)(E-E_F)^2 \left(-\frac{\partial f}{\partial E}\right) dE \ (W/K), \quad (2-13) \]

where \( K_0 \) is the electronic thermal conductance for zero electric field, \( T(E) \) is the transmission probability of electrons at energy \( E \), and \( E_F \) denotes the Fermi level. The electronic thermal conductance for non-zero electric field is defined as \( K_e = K_0 - T G^2 S \) [15]. The fact that all the thermoelectric coefficients are functions of \( \frac{\partial f}{\partial E} \) reveals that the thermoelectric transports occur mostly in low field because the \( \frac{\partial f}{\partial E} \) term is weighty only near the Fermi level. It is also worth noting that the \( \frac{\partial f}{\partial E} \) which is a function of \( E_F \) makes the coefficients deeply rely on the carrier concentration. This is where the interplay between the Seebeck coefficient and the electrical conductance takes place: the conductance increases with the carrier concentration while the Seebeck coefficient decreases [20]–[22]. Therefore, finding a trade-off between the two properties that achieves the best power factor should take precedence over proceeding with the calculations.

2.4 Lattice Thermal Conductivity Calculation

Thermal energy transport in semiconductors is realized through lattice vibrations whose energy can be quantized via the concept of a quasi-particle, the phonon. The phonon-responsible heat conduction is called the lattice thermal conductivity, and it is dominant in semiconducting
materials over the electronic thermal conductivity. What makes the lattice thermal conductivity vital in the thermoelectric field is the fact that it is relatively easy to manipulate and therefore can realize an enhancement in the thermoelectric efficiency.

The lattice thermal conductivity has been modeled and studied in several different ways. Like electron transport, phonon transport behavior can be modeled by solving BTE for phonons. The well-known Monte Carlo method provides the solution of the phonon BTE considering the phonon semi-classical transport and collisions (scattering) in a system [23]. The use of the Monte Carlo method is very flexible and accurate in that it can account for geometrical variations and accurate phonon behavior based on the encapsulated phonon dispersion data.

Another widely used method for calculating the lattice thermal conductivity is molecular dynamics (MD) [24]–[26]. As the MD simulation considers trajectories of all the particles in a simulated system, the simulation process provides very realistic transport maps of molecular systems. The simulation is however highly dependent on interatomic potentials and environmental conditions of the system. In this respect, this method is rather powerful in exploring variations of simulation results with alterations in the simulation setups.

Despite the accuracy and flexibility of the Monte Carlo and the MD methods, these methods are very slow and computationally expensive because of the levels of included physics and the way they treat the simulated particles or molecules. Instead, the empirical thermal conductivity model constructed from elementary kinetic theory, \( \kappa_l = \frac{1}{3} CV_l \), is very fast and computationally cheap [27]–[29]. The idea of this method is to use of the empirical scattering rates in the calculation that have been determined by solving BTE with phonon relaxation time approximation [20]. The empirical method has been extended by accounting for additional scattering mechanisms in the
calculation [30], [31], which makes the model flexible and extendible with more features. Even though it may still be questioned as to its accuracy in estimating the heat conduction in newly introduced materials, the calculated values have agreed very well with experimental data of known materials once the approximated scattering terms are confirmed.

In this thesis, we employ the MD simulation and the empirical thermal conductivity model to study the heat conduction in various structures and dimensions of materials, and the details will be discussed in the later chapters.
CHAPTER 3  THERMAL TRANSPORT VIA VAN DER WAALS INTERFACE IN LAYERED STRUCTURES

This chapter introduces a new thermal conductivity model that can be used to calculate direction-wise thermal conductivity of materials with layered structures (bismuth telluride in this work). By calculating the phonon scattering rate at van der Waals interfaces in between the repeating layers in addition to considering the full phonon dispersion, this model predicts thermal conductivity of bulk and thin-film bismuth telluride along in-plane and cross-plane directions. This work has been published in *Journal of Applied Physics*, **117**, 015103 (2015) [20].

3.1 Introduction and Motivation

Upon the development of thermoelectric theories and devices, bismuth telluride and its alloys have been the most widely used materials producing the highest record thermoelectric efficiency in history. While heat conduction of well-known materials such as silicon, germanium, and gallium arsenide has been extensively studied [6], [7], [32], [33], fewer theoretical studies of bulk and nanostructured Bi$_2$Te$_3$ have been examined [34]–[38]. In this regard, it is worthwhile to explore the thermal transport of nanostructured Bi$_2$Te$_3$ in order to provide insight into the thermal properties of Bi$_2$Te$_3$ as a potential high-performance thermoelectric material. Theoretical approaches to thermal transport in semiconductors include the mode-dependent thermal conductivity model which focuses on the contributions from each phonon mode along the respective directions [39]–[41], Landauer approach with relaxation-time approximation [42]–[44],...
and BTE based models [45]–[49]. For most materials, theoretical study of the lattice thermal conductivity generally adopts models based on the seminal works of Callaway [28], Klemens [27], Holland [50], and Glassbrenner [29], which relate \( \kappa \) to simplified analytical models for phonon dispersion and lifetimes. Unlike computationally intensive simulation tools such as phonon Monte Carlo [23] and molecular dynamics [51], the empirical thermal conductivity model is relatively simple and cheap as it represents the phonon scattering processes by frequency-dependent relaxation times with the Debye phonon spectrum and several other assumptions. Later work addressed the simple model’s failure to capture anisotropy by solving the relaxation time approximation with full phonon dispersions [31].

### 3.2 Approach to Thermal Transport in Bismuth Telluride

In this chapter, we build on the earlier work on thermal transport [31], [33] and extend the Klemens-Callaway phenomenological theory for thermal conductivity by utilizing directional group velocity from the full phonon dispersions of Bi\(_2\)Te\(_3\) calculated in the framework of density functional perturbation theory (DFPT) [52]–[54] in which the perturbation is the phonon wave at wavevector \( q \). Furthermore, we introduce an additional phonon scattering mechanism, in the \( \kappa \) calculation, to capture the decrease of phonon transmission across the van der Waals interfaces of the adjacent Bi\(_2\)Te\(_3\) layers forming the thin film. The inclusion of the vdW transmission is justified since the phonon mode softening due to the higher order terms of the vdW potential is not captured by the quasi-harmonic dynamical matrix used to compute the full phonon spectra. Taking these higher order terms into account is vital in order to capture important interactions such as the
anharmonic phonon-phonon scattering and van der Waal interactions, and may be captured to some degree by ab-initio methods. In the case of vdW interactions, experimental measurement and theoretical calculation of such higher order coefficients is even more intricate [55], [56]. In this work, our goal is to capture the experimental anisotropy due to the weak vdW interaction between the Bi$_2$Te$_3$ layers through the Klemens-Callaway framework. Our results demonstrate that the group velocity alone (without taking into account the phonon transmission across the vdW interfaces) does not fully capture the experimental anisotropy. As such, we treat the vdW interaction, which results in decrease in phonon transmission at the interface, as a perturbation which shifts phonon frequency through scattering, as happens with other interactions within the Klemens-Callaway framework. We believe that this approach helps extend the applicability of the Klemens-Callaway based models to highly anisotropic materials bonded through vdW interactions and provides better agreement with experimental $\kappa$ data.

### 3.3 Simulation Model (Structure)

Bi$_2$Te$_3$ is a layered semiconductor which crystalizes in a rhombohedral crystal structure with five atoms in one unit cell (Figure 3.1). Atomic weights of bismuth and tellurium are at least seven and four times heavier than silicon, respectively, which makes this compound a good candidate as a thermoelectric material. As shown in the side view of the structure in Figure 3.1, it consists of repeating quintuple layers (where each layer consists of Te'-Bi-Te-Bi-Te') along the z-direction, and quintuple layers are stacked on top of each other.
Parameters defining the Bi$_2$Te$_3$ crystal structure are summarized in Table 3.1 including the lattice parameters that are optimized for this work [57]. The variation in bonding length between the various atoms shown in the table provides some intuition about the strength of the corresponding bonding force, as they are inversely correlated.

<table>
<thead>
<tr>
<th>Bond length (Å)</th>
<th>Bond angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Te'-Bi</td>
<td>91º</td>
</tr>
<tr>
<td>Te-Bi</td>
<td>85º</td>
</tr>
<tr>
<td>Te'-Te'</td>
<td>74º</td>
</tr>
<tr>
<td>Bi-Te'-Bi</td>
<td>3.06</td>
</tr>
<tr>
<td>Bi-Bi-Te</td>
<td>3.23</td>
</tr>
<tr>
<td>Te'-Te'-Te'</td>
<td>3.62</td>
</tr>
</tbody>
</table>

Table 3.1: Parameters used to define Bi$_2$Te$_3$ crystal structure

Although there currently is no consensus on the chemical bonding description, two well-known bonding models worth mentioning are those of Mooser and Pearson [58] – which assumed purely covalent p$^3$d$^3$ hybrid bonding types between Bi and Te atoms – and Drabble and Goodman [59] – which proposed single covalent bonds between Bi and Te atoms by transferring electrons from Te to neighboring Bi atoms, resulting in sp$^3$d$^2$ hybrid orbitals occupied by Bi and Te' and an ionic character between Bi-Te. Nonetheless, regardless of the chemical bonding model employed, it is indisputable that Te'-Te' bonds are predominantly of the vdW type, implying that the electron density between the bonds is effectively zero [60], and as a result, the weak bonding between Te'-Te' connecting two quintuple layers is responsible for the cleavage of Bi$_2$Te$_3$ crystal along the (0001) planes.
Figure 3.1: (Left) Crystal structure of Bi$_2$Te$_3$ with rhombohedral unit cell embedded inside. Bismuth and tellurium atoms are shown as yellow and green circles, respectively. (Top right) A separate rhombohedral unit cell structure, generated from XCrySDen [61]. (Bottom right) Side view of a quintuple layer (Te'-Bi-Te-Bi-Te') with each layer separated from the next by the real-ratio distance. The superscripts are used to distinguish two types of differently bonded Te atoms.
3.4 Calculation Details and Results

3.4.1 DFT phonon frequency calculation

To build a thermal conductivity model of an anisotropic material, exploiting full phonon dispersions within the first Brillouin zone (BZ) is essential considering phonon behaviors in different propagating directions. The first BZ of Bi$_2$Te$_3$ is shown in Figure 3.2 (a). The red-colored area inside the zone represents the irreducible BZ, which makes the calculation computationally more efficient by reducing the area by a factor of twelve. Phonon frequencies at specific q-vectors are calculated by Quantum ESPRESSO [62], which employs density-functional theory (DFT) with a plane-wave basis set and pseudopotentials. The BZ is sampled with $8 \times 8 \times 8$ Monkhorst-pack grid points, and a plane wave cutoff of 80 Ry is chosen from the energy convergence test. For the self-consistent calculation, Hartwigsen-Goedecker-Hutter pseudopotentials are used with local density approximation (LDA).

Based on the phonon data, we observe that the 3 acoustic phonon branches dominate the phonon heat conduction as they show higher group velocities as compared to the 12 slow optical phonon branches. As such, the contribution of the optical branches, which can be approximated by the Einstein model, is negligible in the thermal conductivity calculation [63]. In Figure 3.2(b), in order to provide a visual description of the phonon data beyond the conventional phonon dispersions plot [57], [64], which is typically plotted along the propagating directions from the center to the high symmetry points of the BZ, we utilize a 3D map with color-shaded data planes inserted in the irreducible BZ. It is clearly evident from Figure 3.2(b) that the phonon frequencies are lowest at the center of the BZ and increase toward the edge of the BZ. The corresponding phonon group velocities, $v = |\partial \omega / \partial k|$ for TA1, TA2, and LA modes are displayed in Figure 3.3.
Figure 3.2: (a) Brillouin zone for Bi$_2$Te$_3$ with an embedded irreducible BZ zone (red). (b) Phonon dispersions of transverse and longitudinal acoustic modes in the irreducible BZ where phonon frequencies are mapped to the colors.
Figure 3.3: Phonon group velocities of longitudinal and transverse acoustic modes in the irreducible BZ, where the velocities are mapped to the colors.

Acoustic phonon velocities can be as high as 3500 m/s, and phonons with relatively high velocities are all situated around the center, which implies that heat is carried primarily by small wavevector (large wavelength) phonons, which justifies the use of the Debye approximation in the calculation of the phonon-phonon (umklapp) scattering rates employed in the phenomenological model. The full phonon frequency and group velocity obtained here are used in the calculation of the phonon relaxation time, which plays a critical role in our thermal conductivity model.
3.4.2 Phonon transmissivity through vdW interface

In addition to the phonon-phonon scatterings, the vdW-induced boundary scattering between the adjacent Bi$_2$Te$_3$ quintuple layers forming the thin film significantly contributes to the reduction of thermal transport in nanostructured systems. The gaps between the repeating quintuple layers of Bi$_2$Te$_3$ thin film are connected through weak vdW forces which perturb the thermal transport at these vdW contacts. In fact, short-range potentials between Bi$_2$Te$_3$ atoms have been found as 0.975 eV, 0.582 eV, and 0.076 eV for Bi-Te', Bi-Te, and Te'-Te', respectively [65]. The short-range potentials are proportional to two-body interatomic potentials that describe interactions between a pair of atoms: The higher the two-body potential, the more easily the thermal energy is transported.

To model thermal transport through the vdW interface, Prasher modified the acoustic mismatch model (AMM), which originally assumed perfectly welded contacts, to incorporate the effect of weaker vdW bonding [66]. The spectral phonon transmissivity ($t_\omega$) of the vdW contact between identical materials is expressed by the modified AMM as [67]

$$t_\omega = \frac{1}{1+\omega^2\frac{z^2}{4K_A^2}\cos^2\theta}, \quad (3-1)$$

where $\omega$ is the phonon frequency, $z$ is the acoustic impedance, and $\theta$ is the angle between the interface normal and the propagation direction. $K_A$ (= 6.622 N/m for this work) is the spring constant per unit area. Figure 3.4 shows the phonon transmissivity through the vdW contact of Bi$_2$Te$_3$ as a function of the phonon frequency. In particular, Figure 3.4(a) and (b) compare the transmissivity behaviors with varying the phonon sound velocity, $v_s$, and the equilibrium atomic separation, $r_0$, respectively.
As can be seen in Equation (3-1), phonon transmission reduces at higher phonon frequencies due to more phonon scattering at the vdW interface, whereas the transmission approaches the ballistic limit of welded AMM at the very low frequencies (i.e., $t_{\omega \to 0} = 1$). In both figures, it is evident that phonons tend to transmit less with higher sound velocities and larger equilibrium distances. The relationship between the phonon transmissivity and the atomic equilibrium distance described in Figure 3.4 (b) is plausible since changes in the equilibrium distance between Te'-Te' influence the strength of the spring constant, thereby changing the phonon transmissivity.
3.4.3 Thermal conductivity model for in- and cross-plane directions

The lattice thermal conductivity model used in this chapter has been constructed from the elementary kinetic theory of gases, \( \kappa = \frac{1}{3} C \nu \ell \), where \( C \) is the heat capacity of the phonons, \( \nu \) is the average sound velocity, and \( \ell \) is the phonon mean free path. Expanding each term of the expression and treating each acoustic branch as a distinct thermal transport medium modify \( \kappa \) as \( \kappa(T) = k_B \sum_j \sum_q \frac{x_j(q)^2 e^{x_j(q)}}{\left( e^{x_j(q)} - 1 \right)} v_j^2 \tau_{j,T}(q) / n \), \( (3-2) \)

where \( x_j(q) = \hbar \omega_j(q) / k_B T \), \( n \) is the number of wavevectors \( q \), and \( v_j \) and \( \tau_j(q) \) are the phonon velocity and the relaxation time at wavevector \( q \) in acoustic branch \( j \), respectively. Phonon behaviors acquired from the full phonon dispersions shown in Figure 3.2 are employed in this calculation to capture the full anisotropy of lattice heat conduction as has been reported previously [31]. The phonon relaxation time is given by Metthiessen’s rule: \( \tau_j^{-1} = \tau_{j,I}^{-1} + \tau_{j,U}^{-1} + \tau_{j,B}^{-1} \) where the second subscripted letter of each term on the right-hand side stands for isotope (I), umklapp (U), and boundary (B) scatterings, respectively.

For anisotropic crystals, additional treatments are necessary to capture the directional variation of thermal conductivity. Thermal conductivity is in general a tensor, and the in-plane and cross-plane thermal conductivities are the diagonal entries of the tensor along the corresponding direction. In highly anisotropic materials like Bi\(_2\)Te\(_3\), the difference between the in-plane and cross-plane components of the tensor arises out of two sources: the difference between the in-plane and cross-plane phonon group velocity due to phonon mode softening and the anisotropically anharmonic phonon-phonon scattering rates, which are usually functions of the phonon wavevector.
The original Klemens-Callaway model was derived for isotropic crystals (e.g., silicon and germanium), utilized phenomenological scattering rates with simplified dispersion, and assumed that the anharmonic scattering rates were the same for all phonons with a given vibrational frequency, regardless of the propagation direction (which was given by the group velocity). Our calculations indicate that the anisotropy arising solely out of the full phonon group velocity is not sufficient to explain the experimental data. We demonstrate in this chapter that we are able to capture such anisotropy by taking into account the possibility of phonons being reflected at the van der Waals interfaces between the quintuple layers. The weaker van der Waals bonds have been already shown by Prasher to lead to partial transmission of phonons [66]. In this regard, the phonon
scattering at the vdW interfaces is considered in our thermal conductivity model to account for the diminished phonon transmissivity through the vdW contacts.

The DFT-based phonon dispersion calculation relies on quasi-harmonic approximation, capturing only the harmonic part, which is quadratic in the atomic displacements, and ignoring the higher-order anharmonic terms that cause scattering through small perturbation of the phonon frequencies [68]. We treat the higher order terms of the vdW potential as a perturbation and define a corresponding scattering rate. The vdW scattering is then added to the effective phonon relaxation time, in accordance to Matthiessen’s rule. We believe that this formalism provides a straightforward approach to obtaining a thermal conductivity model that agrees well with experiments. The phonon scattering rate at the vdW interfaces $\tau_{\text{vdW}}^{-1}$ can be defined by assuming Bi$_2$Te$_3$ structure as a superlattice structure as shown in Figure 3.5. Projecting a conventional superlattice structure onto the Bi$_2$Te$_3$ crystal structure provides a good insight into treating it as a superlattice material. Instead of two or more materials periodically repeated, Bi$_2$Te$_3$ forms duplicated quintuple layers connected through the vdW forces between Te' layers that serve as interfaces in the superlattice. The scattering term, $\tau_{\text{vdW}}^{-1}$, can be justified on a fundamental level. Each phonon mode has a direction determined by its velocity vector, which is in turn calculated from the gradient of the dispersion. Hence, phonons cannot be grouped into those that are parallel and perpendicular to the quintuple layers, but instead every phonon mode has both a parallel and perpendicular component to its velocity and contributes both to the parallel and perpendicular heat transfer, which depends on the direction of the temperature gradient rather than the phonons themselves. Therefore, even if phonon umklapp scattering rates can and do depend on the phonon wavevector, the scattering rates for each phonon mode cannot be further decomposed into parallel and perpendicular. The same holds also for the Debye temperature as it is a property of the material.
and does not have in-plane and cross-plane components. For this reason, the Debye temperature
and even scattering rates should not have two separate versions: one for the in-plane and the other
for the cross-plane direction. Although the anisotropy may be captured by using different Debye
temperatures and different Gruneisen parameters in the parallel versus the perpendicular directions
to account for the change in the anharmonic rates in the two directions, this would lead to
complications in dealing with thermal transport in the off directions (say at a 45 degree angle)
since the rates would be mixed. Instead, they should be the same for the parallel and perpendicular
directions, and should depend on the phonon wavevector. The addition of the vdW scattering term
to the cross-plane thermal conductivity model incorporates the anisotropy of the thermal
conductivity that the full phonon dispersion is not able to capture.

Earlier work has demonstrated the lattice thermal conductivity model of Si/Ge superlattice
nanowires based on the phonon Boltzmann transport equation with diffuse mismatch interface
conditions [69], [70]. From the phonon thermal conductivity equation of superlattice nanowires
[69], the phonon interface scattering term can be extracted and expressed as \( \tau_{SL}^{-1} = \frac{4v(1-t)}{3Ht} \), where \( t \) and \( H \) are the phonon transmissivity and the thickness of the layer
between the segment interfaces, respectively. Incorporating it with the earlier defined phonon
transmissivity through vdW interface (Equation (3-1)) yields the phonon scattering rate due to
vdW interfaces, and the total phonon relaxation time should be redefined as

\[
\tau_{j,T}^{-1} = \tau_{j,l}^{-1} + \tau_{j,u}^{-1} + \tau_{j,b}^{-1} + \tau_{j,vdW}^{-1},
\]

where

\[
\tau_{l}^{-1} = \frac{3V_0 \Gamma \omega_j^4}{\pi v^2} \quad [29],
\]

(3-4)
\[ \tau_U^{-1} = \frac{\hbar^2}{m \theta \omega^2} \exp \left( -\frac{\theta}{3T} \right) \omega_j^2 T \quad [29], \]  
(3-5)

\[ \tau_B^{-1} = \frac{\nu_{\perp}}{L} \quad [31], \]  
(3-6)

\[ \tau_{vdW}^{-1} = \frac{4}{3} \frac{\nu_{\perp}}{H} \left( 1 - \frac{t\omega_j}{\omega_j} \right). \]  
(3-7)

Variable names and their values used in this chapter are summarized in Table 3.2. Mainly the scattering terms are functions of the phonon frequency, phonon velocity, and the dimension of the system. Among those different scattering terms, for \( \tau_B^{-1} \) and \( \tau_{vdW}^{-1} \), the velocity component normal to the surface, \( \nu_{\perp} \), is used instead of the averaged phonon sound velocity because both the surface boundary and the vdW interface cause scattering of phonons moving in the direction of the normal to the surface.

Table 3.2: Parameters used in the phonon scattering rate calculations

<table>
<thead>
<tr>
<th>Bi$_2$Te$_3$ scattering parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_0 ) Avg. vol. per atom in the crystal</td>
<td>0.034 nm$^3$</td>
</tr>
<tr>
<td>( \Gamma ) Point impurity scattering parameter</td>
<td>( 2 \times 10^{-4} )</td>
</tr>
<tr>
<td>( \nu ) Sound velocity</td>
<td>980 m/s</td>
</tr>
<tr>
<td>( \gamma ) Grüneisen’s constant</td>
<td>1.04</td>
</tr>
<tr>
<td>( m ) Avg. mass of a single atom</td>
<td>160.152 u</td>
</tr>
<tr>
<td>( \theta ) Debye temperature</td>
<td>45 K</td>
</tr>
<tr>
<td>( H ) Thickness of the repeating layer</td>
<td>1.01 nm</td>
</tr>
<tr>
<td>( L ) Thin film thickness</td>
<td></td>
</tr>
</tbody>
</table>

For phonons bouncing between two surface boundaries or within the quintuple layers, their lifetime will be proportional to the time it takes to cross the confinement sources [31]. The phonon momentum in each direction is interpreted by taking the gradient of the phonon frequency inside BZ.

25
3.4.4 Thermal conductivity of bulk and 2D Bi$_2$Te$_3$

With the full phonon dispersions and gradients, the lattice $\kappa$ of Bi$_2$Te$_3$ is computed from Equation (3-2). Figure 3.6 compares $\kappa$ of bulk crystals with and without taking account of phonon blockade due to vdW interfaces along with the experimental and simulation data reported earlier [34], [38], [71]. The experimental data contains the thermal conductivity measured parallel and perpendicular to the quintuple layers, where the two directions show different rates of heat propagations.

![Thermal conductivity of bulk Bi$_2$Te$_3$](image)

Figure 3.6: Thermal conductivity of bulk Bi$_2$Te$_3$ computed in this chapter with and without considering phonon scattering at the vdW interfaces, presented in the solid line and the dashed line, respectively. Our data is compared to the previously reported experimental and simulation data. Thermal conductivity parallel, $\kappa_{||}$, and perpendicular, $\kappa_{\perp}$, to the quintuple layers is expressed with open and filled markers, respectively.
Qiu and Ruan attributed the directional variation of heat flux to the weaker lattice vibration in the perpendicular direction than in the parallel direction due to the combined nature of vdW interactions across tellurium layers and covalent bonds within the same layers [38]. Goldsmid also emphasized the importance of the anisotropic effect through his experiments but did not discuss it further in the literature [71]. Our result without the vdW effect agrees well with measured $\kappa$ along parallel planes, while the calculated $\kappa$ that considers the vdW effect agrees better with $\kappa$ in the perpendicular direction because the vdW bonding gets involved more in heat propagation along the perpendicular to the quintuple layers. These behaviors support the necessity of the vdW phonon scattering term included in our thermal conductivity model.

In Figure 3.7, predicted $\kappa$ of thin films with thickness of 3.03 nm and 9.09 nm (3-QL and 9-QL) are compared with previously reported experimental data [35]–[37], [72], [73]. The thickness of multiple quintuple layers is chosen because the presence of weak vdW bonds allows the crystal to be easily disassembled into quintuple layers [9]. The reduction of $\kappa$ in thin films is mainly attributed to the phonon-boundary scattering at the film surfaces. As expected, lower $\kappa$ is achieved with the additional phonon scattering at the vdW interface; the thicker the film, the greater the difference between the comparison groups because more Te'-Te' layers are present in thicker films. In addition, vdW scattering has less impact on $\kappa$ in thinner films due to the stronger boundary scattering, which primarily limits thermal conduction. As temperature increases, the difference between the results incorporating vdW scattering and those without it becomes smaller because umklapp scattering dominates at 300 K and above, as evidenced by the $T^{-1}$ behavior of $\kappa$. 
Chiritescu measured $\kappa$ of the nano-scale Bi$_2$Te$_3$ layers in the [(Bi$_2$Te$_3$)$_m$(TiTe$_2$)$_n$] multilayer samples and extracted the effective $\kappa$ of homogeneous Bi$_2$Te$_3$ layers, estimating the conductivity to be slightly lower than our calculation [35]. Another thermal conductivity study on Bi$_2$Te$_3$ thin films was performed with molecular dynamics simulations, which mainly focused on $\kappa$ behaviors of perfect and nanoporous few-quintuple thin films; the nanoporous thin films produced remarkably lower $\kappa$ due to spatial disturbance to thermal transport [37]. As not many $\kappa$
measurements have been conducted on nanostructured Bi$_2$Te$_3$, the reported $\kappa$ does not form a consistent data group, but the predicted $\kappa$ in our model stays within range of those data. Instead, recent work has studied $\kappa$ of Bi$_2$Te$_3$ processed in different forms to achieve lower $\kappa$. A thin film Bi$_2$Te$_3$ with thickness of 1 $\mu$m has been deposited on 25 $\mu$m-thick polyimide film by thermal co-evaporation technique [72]. Even though the sample was a thin film, its thickness of 1 $\mu$m surpasses the phonon mean-free-path, so the measured $\kappa$ is comparable to the bulk $\kappa$. Goyal studied the thermal conductivity of stacks of mechanically exfoliated Bi$_2$Te$_3$ films [73]. The exfoliated films were put on top of each other with annealing to improve structural stability and assembled into a non-periodic “pseudosuperlattice.” Both in-plane and cross-plane thermal measurements showed lower $\kappa$ than bulk samples, mainly due to the large thermal boundary resistance between the exfoliated films. The experiment also exhibited independency of $\kappa$ on thickness, signifying dominance of the phonon scattering at the interfaces between the films over other types of scattering in this type of structure. Another experiment revealed the $\kappa$ reduction from p-type nanocrystalline (NC) Bi$_x$Sb$_{2-x}$Te$_3$, which was made by the ball milling and hot pressing of nanoparticles into bulk ingots [36]. It is worth noting that the small particles forming the bulk in this experiment facilitate grain boundaries and defect scattering, resulting in thermal degradation far worse than that resulting from phonon scattering due to the crystal boundaries of nanostructures. As such, phonon mean-free-path in this case is limited by the grain size. This NC bulk alloy has achieved $\kappa$ as low as that of thin film (ZT of 1.2 at room temperature) while nearly maintaining the electrical transport properties of the composing materials.
3.5 Summary

In summary, we have introduced a novel and straightforward approach of extending the Klemens-Callaway’s model to anisotropic materials with minimal change in the number of empirical parameters. We take a simplified view where the anharmonic phonon scattering rates are estimated to be functions of group velocity and phonon frequency obtained from full phonon dispersions and then reproduce the experimentally measured anisotropy of Bi$_2$Te$_3$, for which one cannot solely rely on the anisotropy in the group velocity alone. Our analysis starts by viewing the various Bi$_2$Te$_3$ quintuple layers forming the thin film as a virtual superlattice bonded by weak vdW forces, and we add a scattering term to capture the phonon transmissivity through the vdW interface. We have shown that the phonon transmissivity across the interface decreases with higher group velocity and greater distance between vdW contacts. Our model captures the anisotropy of Bi$_2$Te$_3$ and agrees well with both in-plane and cross-plane experimental thermal conductivity data. Furthermore, this approach can be easily extended to compute the thermal conductivity of other promising layered semiconductors, such as Bi$_2$Se$_3$, Sb$_2$Te$_3$, and MoS$_2$, that are bonded through vdW interactions.
CHAPTER 4  THERMAL TRANSPORT IN RIPPLED GRAPHENE

This chapter introduces an MD technique to generate rippled graphene sheets with controllable ripple size and periodicity. Benefitting from the periodic boundary condition in the MD, evenly spread textures are realized all over the graphene surface, and their thermal transport behaviors are studied by the Green-Kubo method.

4.1  Introduction

4.1.1  Why graphene?

Upon discovery of a single layer of carbon atoms in a honeycomb lattice in 2004 [74], [75], graphene has been extensively explored experimentally and theoretically owing to its remarkable physical properties and potential to offer great future applications. Graphene has been studied in the form of a single layer, multiple layers, or combined structure with various substrates and has exhibited unique properties such as high carrier mobility [76], high thermal conductivity [77], extraordinary mechanical stiffness and strength [78], [79]. In addition, its exceptional electronic behavior which resembles massless Dirac fermions [75] makes graphene superior for some applications because of its quantum spin Hall effect [80], [81], suppression of weak localization [82], [83], and enhanced Coulomb interaction [84]. At the same time, graphene is inferior for some applications due to its semimetalic behavior with a zero-gap band structure [75].
4.1.2 Graphene as thermoelectric material

Graphene has been exploited for many different electronic applications [85], [86], and it is not surprising that researchers and industries have called upon graphene as a material for thermoelectric devices, expecting it to achieve an enhanced energy conversion ratio [87]–[94]. Thermoelectric energy conversion, by which electrical energy is converted into thermal energy, or vice versa, has attracted great interest in renewable energy development owing to the fact that above all it retrieves heat energy which would otherwise be wasted, and therefore is environmentally friendly. However, due to low energy conversion efficiency governed by a dimensionless thermoelectric figure-of-merit $ZT = S^2\sigma T / \kappa$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, and $\kappa$ is the thermal conductivity [3], [20], thermoelectric devices are still not in common use and their applications have been limited to niche markets. As seen in the figure-of-merit expression, low thermal conductance of a thermoelectric material is essential to achieve high energy conversion rate, and in this regard, the extremely high thermal conductance of graphene has prevented it from being a good candidate for a future thermoelectric material despite its extraordinary electronic transport properties [92], [95].

4.1.3 Previous study and motivation for texturized graphene

Recent studies have revealed the potential of graphene-family nanomaterials with modified structures or orientation for enhanced thermoelectric energy generation. Mazzamuto et al. predicted an enhanced $ZT$ of graphene nanoribbons (GNRs) with optimized pattern employing non-equilibrium Green’s function simulation for both electron and phonon transport [87]. They calculated the thermal conductivity of the structures to be extremely low due to the mismatch of
phonon modes at alternating-chirality intersections. In addition, their electronic thermoelectric properties remained high by introducing the resonant tunneling of electrons through the mixed edged GNRs. Park et al. measured the spatially varying thermopower ($S$) of epitaxial graphene on SiC with defects and wrinkles formed due to thermal expansion of a graphene layer [91]. Their work provided spectroscopy maps of the electronic, thermoelectric, and structural properties of a graphene layer with structural defects and suggested a possibility of atomic-scale control for effective utilization of graphene. Hossain et al. explored thermoelectric properties of GNRs with nanopores to effectively reduce the thermal conductivity with minimized decrease in electrical properties [88]. They comprehensively calculated both electrical and thermal transport behaviors of GNRs with different pore size to find the optimal structure, and eventually achieved a $ZT$ 6 times higher than conventional GNRs of the same dimension. They concluded that precise control of edges of GNRs and advanced fabrication techniques are needed for an experimental realization of the devices. Dollfus et al. recently reviewed and thoroughly summarized previously reported studies on graphene and graphene nanostructures as thermoelectric materials [89]. This work widely covered why graphene has not been the best thermoelectric material, which is mainly due to its gapless electronic characteristic and exceptionally high thermal conductivity, what has been done to make better thermoelectric devices with graphene and its nanostructures, and what remains to be solved in the near future. Above all, it was very well demonstrated in this chapter that the thermoelectric performance of 2D materials consisting of carbon atoms has been definitely improved by nanostructuring and band-gap engineering, and even higher thermoelectric efficiency should be achievable with future development.

In spite of previous extensive study to improve the thermoelectric efficiency of not only carbon-based materials but also materials that have been treated as good candidates for thermoelectric
applications [6], [7], [96], thermoelectric devices are still experiencing difficulty in producing a commercializable-level energy-conversion rate, and continued effort to raise the conversion rate is required to keep up with the current development. It has been very well understood that the best strategy to improve the thermoelectric efficiency is to lower the thermal conductivity without significant loss in the electronic portion of thermoelectric properties [97].

Recent work by Wang et al. has successfully demonstrated a method for controlled crumpling of graphene and graphite via exploiting thermally induced contractile deformation of shape-memory thermoplastics, which eventually formed heterogeneous 3D texturing of graphene [98]. Their unique single-step strategy to form the 3D crumpled graphene enabled creation of large, tunable, and scalable crumpled textures, and the report investigated electrical, morphological, and materials characterizations of the crumpled graphene generated with uni-axial and equi-biaxial strains. Wang also has fabricated crumpled graphene FET arrays and has observed device performance consistent with other graphene FETs reported in earlier literature [98], and this fact suggests feasibility of the 3D textured graphene for future thermoelectric material owing to anticipated thermal conductivity regulation without noticeable variation of electron transport properties; due to the large difference between electron and phonon mean-free-paths, a decrease in thermal conductivity due to structural perturbation is expected to occur ahead of a decrease in electrical conductivity [97].

Another advantage of strained graphene for thermoelectric applications is band-gap opening owing to the modified orbital hybridization [99], [100] and the inversion symmetry breaking [101], [102], which, in turn, makes the graphene a good candidate for other electronic devices as well. Previous study on strained graphene has revealed electrical and mechanical property changes and its plausibility for electronic devices [103]–[107].
However, to the best of our knowledge, study of thermal transport in two-dimensionally strained graphene has never been reported with the molecular dynamics (MD) approach which captures atom-to-atom interactions in a very realistic way. In this chapter, we report the thermal conductivity of strain-induced rippled graphene and its relation to varying ripple size and periodicity. We also discuss a framework used in MD simulation by applying bi-axial compression to the suspended pristine graphene to intentionally create two-dimensional periodic ripples.

4.2 Simulation Details

4.2.1 Strain-induced rippled graphene structure

A strain-induced rippled graphene generated with bi-axial strain which is the structure of our interest is shown in Figure 4.1. The ripples are distributed evenly with fixed amplitude and wavelength, and the way we generate the rippled graphene is as follows: we first create strain-induced ripples with only a quarter size graphene (inset of Figure 4.1) and replicate the inset structure four times in two in-plane directions. Generally, applying strain (compression) to 2D structure in MD produces one large undulation regardless of strain dimensionality, and this phenomenon has made it difficult to explore the suspended graphene with ripples or crumples all over the surface with the MD approach. Even though some MD studies have addressed the wrinkling effect in graphene sheets, the wrinkles were produced by shear stress [93], [108], [109], circular shearing load [110], or nanoindentation on a circular graphene [111], not by the axial strain with which most of the recent experimental studies on texturized graphene have been performed [89].
Figure 4.1: Strain-induced rippled graphene with dimensions 16.2 × 15.8 nm created by linking four identical structures prepared by deforming a small graphene sample (8.1 × 7.9 nm, inset). The degree of strain is 10% and the ripple amplitude is measured to be approximately 1.7 nm. Visualization of the structure is done with OVITO [112].

4.2.2 Ripple generation via molecular dynamics

To create the repeating strained-graphene, deformation of a flat graphene layer is performed using an open source MD simulator, LAMMPS [113]. For the structure in the inset of Figure 4.1, a single layer of carbon atoms with size of 8.1 by 7.9 nm is used for the deformation simulation. Its boundary conditions are set to be periodic in the in-plane directions and non-periodic in the direction orthogonal to the graphene layer. It is essential to set the periodic boundary conditions
in the in-plane directions because the simulated structures can be replicated next to each other only with this setup as the atoms at the edges interact with the atoms across the boundary. Therefore, linking the replicas does not alter the relaxed condition of the original structure while the final structure eventually has the strain-induced recurrent undulations.

Figure 4.2: Bi-axial strain process of a graphene sample (top) to be replicated three times in each in-plane direction to generate to-be-simulated structures (bottom). The numbers on top indicate the degrees of strain applied to the graphene sample. The strain process is performed with the deformation feature in MD simulation.

Before the deformation, the initial structure with 2304 carbon atoms is subjected to MD equilibration under isothermal-isobaric (NPT) ensemble for 0.5 ns and microcanonical (NVT) for another 0.5 ns with the simulation time step of 1.0 fs. We adopted the adaptive intermolecular reactive empirical bond order (AIREBO) potential which captures accurately the bond-bond interaction and bond breaking between carbon atoms [114]. Once it reaches a fully relaxed state, the structure is compressed in both in-plane directions at an engineering strain rate of -0.001 every picosecond until it comes to the desired strain level (%). The deformation process is described in Figure 4.2 with the degree of strain from 0.05 to 0.40. For each strain step in the figure, the top and bottom images are the strained small sample and the final structure that is constructed via
replicating the samples three times in each in-plane direction. The ripple amplitudes for strain of 0.1, 0.2, 0.3, and 0.4 are measured to be about 1.7 nm, 2.4 nm, 2.8 nm, and 3.1 nm. Unlike tensile strain that causes a fracture of graphene at around 0.2 [115], [116], the compressive strain instead creates large undulations by which atoms feel significant pressure in the in-plane directions after a certain level of strain, which could possibly limit the lattice vibration compared to their ambient state.

4.2.3 Green-Kubo thermal conductivity calculation

In this chapter, we employed equilibrium molecular dynamics (EMD) simulation based on the Green-Kubo method [24], [25], [117], which is among the most widely used methods using the equilibrium fluctuations of the heat current vectors. In this method, the thermal conductivity is calculated by integrating the heat current autocorrelation function (HCACF) which was established in the Green-Kubo linear response theory, and the thermal conductivity tensor $\kappa$ is defined as

$$\kappa = \frac{1}{V k_B T^2} \int_0^\infty \langle J(0) \cdot J(t) \rangle \, dt,$$  

where $V$ is the volume of the simulated structure with thickness of 3.4 Å [116], $k_B$ is the Boltzmann constant, and $T$ is the equilibrium temperature. The heat flux $J$ in each direction is expressed as

$$J = \frac{1}{V} \left[ \sum_l e_l \mathbf{v}_l - \sum_i \mathbf{S}_i \mathbf{v}_l \right] \quad (4-2)$$

$$= \frac{1}{V} \left[ \sum_l e_l \mathbf{v}_l - \sum_{ij} (\mathbf{f}_{ij} \cdot \mathbf{v}_j) \mathbf{x}_{ij} \right] \quad (4-3)$$

$$= \frac{1}{V} \left[ \sum_l e_l \mathbf{v}_l - \frac{1}{2} \sum_{ij} (\mathbf{f}_{ij} \cdot (\mathbf{v}_j + \mathbf{v}_j)) \mathbf{x}_{ij} \right] \quad (4-4)$$
where $e_i$ is the total per-atom energy (potential and kinetic), $S_i$ is the per-atom stress tensor, and $v_i$ is the per-atom velocity. The angular bracket in Equation (4-1) denotes an ensemble average, and the term inside the bracket represents HCACF. During the simulation, the heat flux is obtained each step, and the final conductivity tensor is calculated with the integration of the correlation function in Equation (4-1) up to a finite cut-off time, $t$, where the HCACF integral converges. In this work, the cut-off time of 2 ns suffices, and the tensor components of only $\kappa_{xx}$ and $\kappa_{yy}$ have been used to find the thermal conductivity of flat and rippled graphene.

4.3 Results and Discussion

Thermal conductivity values of graphene and GNRs studied with the MD simulations have been reported and lay in a wide range (75-10,000 W/m-K) because the MD results highly rely on interatomic potentials, bonding mechanisms, and the way of defining simulated structures [92]. In this regard, the MD simulation is very useful in studying effects of various simulation setups and therefore needs to be interpreted with respect to the relative changes in the setup.

In this chapter, we generate flat and rippled graphene films made up of two differently sized samples: a small sample referring to $8.1 \times 7.9$ nm and a large sample referring to $16.2 \times 15.8$ nm. Based on the number of replications made along the in-plane directions, three kinds of simulated structures are prepared with sizes of $16.2 \times 15.8$ nm, $24.3 \times 23.7$ nm, and $32.3 \times 31.5$ nm and called FILM16, FILM24, and FILM32, respectively.
The thermal conductivity tensors of the prepared graphene films are calculated with the Green-Kubo MD simulation and compared to analyze its relation to varying structural parameters. For the result comparison, we take the average value of the thermal conductivity tensors in the in-plane directions, $\kappa_{xx}$ and $\kappa_{yy}$. The directional deviation of the thermal conductivity in wrinkled graphene where the wrinkles develop along a specific direction has been reported earlier [93], but, in this chapter, a variation of the calculated conductivity between $\kappa_{xx}$ and $\kappa_{yy}$ is not noticeably significant as the ripples undulate diagonally on the film surface, which does not produce distinctively advantageous thermal transport in one direction over the other.

Figure 4.3: (a) Thermal conductivity of the rippled graphene (FILM32, 32.3 × 31.5 nm) as a function of the degree of strain, normalized by the conductivity of the flat graphene for the quick comparison. (b) Absolute thermal conductivity value comparison of the flat FILM32 and the rippled graphene with 10% and 20% strain. Films in both (a) and (b) are made of the small samples (8.1 × 7.9 nm).
Figure 4.3(a) shows the thermal conductivity of the rippled graphene (FILM32) with strain of up to 0.4, normalized by that of the flat graphene at 300 K for ease of viewing the reduction rate. As expected and obviously, the conductivity decreases with the strain as the structural barrier effectively restrains the lattice movement and accordingly the phonon transport. It is worthwhile noting that the thermal transport gets restricted significantly at the first appearance of ripples, which is about 25% decrease from flat to 5% strain, as a consequence of a rise in the surface-phonon scattering [118].

The thermal conductivity of the graphene FILM32 that are flat, rippled with 10% strain, and rippled with 20% strain is compared in Figure 4.3(b) as a function of temperature. In general, the conductivity decreases with temperature accompanying more phonon scattering. With different strain degrees, larger ripples induce lower thermal conductivity. Interestingly, however, the difference in conductivity among the differently strained graphene structures decreases with higher equilibrium temperature because of the three-phonon scattering outweighing the phonon restriction due to the undulating ripples.
Figure 4.4: (a) Thermal conductivity of FILM16, FILM24, and FILM32 as a function of the degree of strain. The values are normalized with the conductivity of the flat graphene FILM32. (b) Comparison of the thermal conductivity among differently sized films with strain degrees varying from 0 to 20%.

Figure 4.4(a) and (b) compare the thermal conductivity of the rippled graphene films with different dimensions, FILM16, FILM24, and FILM32, normalized by that of the flat graphene FILM32 at 300 K. The larger the dimension, the higher the thermal conductivity the film exhibits, owing to presence of more phonons whose propagation is not limited by the smaller system dimension than their wavelengths. For each film, the conductivity seems to be linearly dependent on the structure size, which agrees with the previous MD thermal conductivity study [119]. It is confirmed that the conductivity changes comparably significantly between flat and 5% strain for all cases as the introduction of the phonon blockade greatly modifies the lattice movement.
Figure 4.5: (a) Thermal conductivity comparison between the rippled graphene sheets with wavelengths (λ) of 8 and 16 nm. The square and circle markers refer to λ of 8 and 16 nm, respectively, and the filled and open markers refer to strain degree of 10 and 20%, respectively. (b) Comparison of the thermal conductivity of the graphene sheets with the ripple wavelengths of 8 and 16 nm. The values are normalized with the conductivity of the flat FILM32 with λ of 8 nm. The simulated structures are also shown in the figure.

The periodicity of the ripples is another element modifying thermal transport in the strained graphene. To investigate the periodicity effect, we also generate the flat and rippled graphene FILM32 by replicating the large sample (16.2 × 15.8 nm) twice in each in-plane direction. As the strain creates one large ripple on the graphene sheet, the wavelength (λ) of the ripples on the graphene FILM32 made out of the large sample (λ = 16 nm) is twice that of the sheets made out of the small sample (λ = 8 nm). Figure 4.5(a) compares the absolute thermal conductivity values of the rippled graphene FILM32 with different ripple periodicity. The long ripple periodicity induces higher thermal conductivity of the graphene than the graphene with the short periodicity but still seemingly not as high as that of the flat graphene. The wavelength-dependent thermal
conductivity of the FILM32 is shown as a function of the degree of strain in Figure 4.5(b). The simulated graphene structures with ripple wavelengths of 8 and 16 nm are also inserted in the figure. For both films, the conductivity drops with the increasing degree of strain at a similar rate.

### 4.4 Summary

To conclude, we have demonstrated the thermal conductivity of the strain-induced rippled graphene calculated with the Green-Kubo method in the framework for the molecular dynamics. To overcome the difficulty that the MD approach has faced in simulating evenly texturized 2D films all over the surface, we have introduced the method that generates thin film structures with regular undulations formed on surfaces by replicating pre-manipulated small samples. In this work, a small graphene sample has been prepared and strained with MD deformation simulation, and the resulting small samples with the desired degree of strain have been reproduced right next to each other in the in-plane directions to finally create the graphene films with evenly distributed ripples. The absolute values of and normalized thermal conductivity for the flat and rippled graphene films are calculated and compared by varying the degree of strain, temperature, the size of the structure, and the periodicity of the ripples. The conductivity drops relatively notably when its structure has changed from flat to the first appearance of ripples due to the promptly introduced interruption to the phonon transport. Our study has revealed that the thermal conductivity of the rippled graphene decreases with increasing temperature and the degree of strain attributed to the predominance of three-phonon scattering over the surface-phonon scattering and the rise in phonon blockade caused by the rippling, respectively.
The results presented in this chapter shed light on the control of thermal conductivity of graphene films by manipulating such characteristics of crystallographic structure as the texture size, the rate of occurrence of the textures, and the surrounding temperature. In addition, this work can be easily extended to investigate various characteristics of the graphene films with wrinkles, ripples, or crumples allocated in a special pattern with the MD techniques introduced in this chapter for potential applications.
CHAPTER 5  GEOMETRY-MODULATED SEMICONDUCTOR NANOWIRES

This chapter introduces a strategy to improve the thermoelectric efficiency by modulating geometry of nanowires. Comprehensive study of both electrical and thermal transport properties predicts an enhancement of the $ZT$ from sinusoidally corrugated silicon nanowires compared to the $ZT$ of straight conventional nanowires. To investigate changes in transport coefficients, the BTE-Landauer formalism, recursive Green function, and the MD simulation are employed. This work has been published in *Nanotechnology*, 27, 035401 (2016) [97].

5.1 Motivation and Strategy for $ZT$ Enhancement

Heavily-doped semiconductors have been known as the most efficient thermoelectric materials owing to electronic contributions to the power generation, the so-called thermoelectric power factor ($S^2\sigma$) that is maximized between a metal and semiconductors [10]. Despite high electronic transport properties of metal-like-semiconductors, high thermal conductivity had limited thermoelectric efficiency to reach a certain level of applicability. It has been discovered, however, that acoustic phonons which have a long mean-free-path and contribute dominantly to the lattice thermal conductivity, can be restrained with system size comparable to or smaller than the mean-free-path, and as a result, a significant drop of the thermal conductivity has been observed in nano-scale structures [120]–[122]. Such nano-scale thermoelectric semiconductors as silicon, germanium, bismuth telluride, and antimony telluride have been extensively studied in the form of thin film [6], [9], [20], nanowire [7], [96], [122], superlattice [69], [70], [123], and
nanostructured bulk materials [6], [8], [36]. The improvement of \( ZT \) in nanostructures with a high surface-to-volume ratio has arisen from the reduction of thermal conductivity attributed to the phonon surface and interface scattering, and accordingly most efforts have been devoted to find means of minimizing thermal conductivity by drawing more scattering of phonons.

Recent studies have suggested solutions for efficient energy conversion from rough surface nanowires as a consequence of phonon scattering at the surface [7], [30], [33]. Hochbaum et al. measured the thermal conductivity of intentionally roughened silicon nanowires that were five to eight orders of magnitude lower than that of typical nanowires, and as a result the \( ZT \) of the nanowire obtained was nearly twice that of optimally doped bulk silicon [7]. Zianni studied geometry-dependent thermoelectric efficiency by modulating the diameter of nanowires and computing corresponding electron transmission coefficients as well as calculating subband energy structures of those nanowires [124], [125]. Jiang et al. reported the MD study of a possible modulation of thermal conductivity in kinked silicon nanowires whose synthesis process has been reported earlier by Lieber’s group at Harvard University [126], [127]. The heat transport in the kinked nanowires revealed reduction of at least 50% compared to that in the straight silicon nanowires at room temperature [126].

In this regard, there is substantial potential in thermoelectric applications for geometrical modification of nanostructures in which thermal transport is restrained by non-uniform surfaces on top of the phonons already confined in nano-scale dimensions. In this chapter, we introduce a comprehensive study of thermoelectric properties of sinusoidally corrugated silicon nanowires as we treat the geometrical undulation as a sole perturbation to the systems. In spite of the previous studies focusing only on the decrease in the lattice thermal conductivity from geometry-modification [7], [30], [33], [126], we must treat both electron and phonon transport on equal
footing in such nanowires whose diameters or widths are comparable to electron mean-free-path (a few nanometers in heavily-doped silicon) because the geometrical fluctuations at nano-scale can impinge on charge carrier transport [6]. In order to extend the advantage of the geometrical variations in nanowires, an investigation of trade-offs to maximize the figure-of-merit is essential. We compute an energy-dependent electron transmission coefficient in silicon nanowires from a Recursive Green Function (RGF) approach [128], [129], and then use the Landauer formalism to calculate the Seebeck coefficient, the electrical conductance, and the electronic thermal conductance [16], [17]. Particularly, the electronic contribution to the thermal transport ignored in most thermoelectric calculations becomes worth considering in such small-scale and heavily-doped semiconductors. For lattice thermal conductivity calculation which is dominant in semiconductors compared to the electronic contribution to the total thermal conductivity [20], the reverse non-equilibrium molecular dynamics (rNEMD) simulation is performed using LAMMPS [26], [113].

5.2 Simulation Details

5.2.1 Structures

The structures under consideration in this chapter are shown in Figure 5.1(a) and (b), a typical straight nanowire (straight NW) and a sinusoidally undulated nanowire (sine NW), respectively, with square cross-sections. We will investigate the nanowires with the length (L) of 108.6 nm in the transport direction and the widths (W) of 4.34 nm and 2.17 nm in the transverse direction. The
sine NW in Figure 5.1(b) has a wavelength ($\lambda$) of half of its length and an undulation height (H) equal to its width (measured with respect to the center of the cross-section plane).

Figure 5.1: Schematics of the (a) straight and (b) sinusoidal silicon nanowires oriented along [100] with square cross-sections. The small spheres residing inside the structures indicate atomic positions. The structural parameters are the length (L), width (W), the undulation height (H), and the wavelength of sinusoidal wave ($\lambda$).

5.2.2 Electrical transport coefficients in thermoelectrics

The electrical transport coefficients of the straight and sine NWs are calculated using the Equations (2-11)-(2-13) defined in the framework for the BTE-Landauer formula. The electrical conductance ($G$) and the Seebeck coefficients ($S$) are obtained as functions of energy ($E$), the transmission function $T(E)$, and the Fermi-Dirac distribution function $f(E)$. In this chapter, we calculate those electrical transport coefficients of silicon nanowires integrated all over the energy levels as
functions of temperature. As mentioned briefly in Chapter 2, finding the maximum power factor ($S^2 G$) is critical to achieve high thermoelectric efficiency, $ZT$, and the adjustable element that influences both $S$ and $G$ is the carrier concentration of the system.

For silicon, it has been reported that the carrier concentration of $10^{19} - 10^{21}$ cm$^{-3}$ has produced the highest power factor, and we calculate the transport coefficients of silicon with the concentration of $10^{20}$ cm$^{-3}$ [3], [7], [130]. The Landauer approach used in the above expressions is robust to disclose the role of dimensionality in the thermoelectric performance and has been used to prove the advantage of lower dimensionality [17]. As it can be observed in Equations (2-11)-(2-13), the electronic transport highly relies on the $T(E)$, and the $T(E)$ plays an important role in evaluating the deviations between the transport coefficients of the straight and sine NWs.

5.2.3 Recursive Green function

To inspect an influence of non-uniformity in geometry on the thermoelectric performance, a thorough and deliberate study of the transmission probability through the system is essential. Assuming such electron scattering mechanisms as electron-electron interactions, impurities, defects, and thermal vibrations are negligible in ultra-thin nanowires, the RGF approach which has been elucidated by Sols et al. and Martin et al. with the details can evaluate an energy transport explicitly with the perturbation by the geometrical fluctuation [128], [129]. The Green function approach is a very rigorous technique especially for studying the transmission coefficient through such systems with geometrical variations, different orientations, or structural barriers [87], [131]–[133], as it considers the propagation of wavefunctions from one to the other end. In Figure 5.2, a sample is discretized with a sufficiently dense nearest-neighbor tight-binding (TB) lattice where a
series of transverse cross-sections is solved by the 2D Schrödinger equation to consider the quantum nature of the carrier transport.

The total transmission coefficient \( T(E) = \sum_{m,n} |t_{mn}|^2 \) at energy \( E \) is computed recursively from the rightmost site to the leftmost site of the system assuming contact with semi-infinite leads, where \( m \) and \( n \) refer to the transverse modes of each site. The transmission probability from the transverse mode \( m \) at the leftmost site \( l \) to \( n \) at the rightmost site \( r \) is expressed as [129]

\[
t_{mn} = -2iV \left( \sin \theta_m \theta_n \right)^{1/2} e^{i(\theta_m l - \theta_n r)} \langle n | G_{rl} | m \rangle,
\]

(5-1)

where \( G_{rl} \) is the Green function operator between sites \( l \) and \( r \). The RGF algorithm begins with calculating the Green function operator between the rightmost site and the adjacent semi-infinite lead, and the new operators at site \( q \) are defined as

\[
G_{r,q}^{L+R} = G_{r,q+1}^R + V_{q+1,q} (I - G_{q,q}^L S_{q,q}^R)^{-1} G_{q,q}^L,
\]

(5-2)

\[
G_{q,q}^{L+R} = G_{q,q}^L + G_{q,q}^L S_{q,q}^R (I - G_{q,q}^L S_{q,q}^R)^{-1} G_{q,q}^L,
\]

(5-3)

where \( S_{q,q}^R = V_{q,q+1} G_{q+1,q+1}^R V_{q+1,q} \) is the self-energy matrix for the transverse chain \( q \) due to the presence of chains to the right. \( G_{r,q}^{L+R} \) is the Green function propagator from \( r \) to \( q \), and \( G_{q,q}^{L+R} \) computed in the general form of Dyson’s equation updates \( G_{q+1,q+1}^R \) at each simulation step in a recursive fashion [134]. The total transmissions calculated with this approach can then be interpolated in the transport equations.
Figure 5.2: Side view of the nearest-neighbor TB lattice structure of a sine NW. Each transverse site is solved by the 2D Schrödinger equation, and the RGF calculates energy transmission probability recursively from the rightmost site \( r \) through the leftmost site \( l \).

5.2.4 Non-equilibrium molecular dynamics

The rNEMD simulation is performed for the lattice thermal conductivity calculation of the isotopically pure silicon (\(^{28}\text{Si}\)) nanowires. The phonon-isotope scattering has been omitted in our calculation because the isotope contribution to the thermal transport in natural silicon (92.2% of \(^{28}\text{Si}\), 4.7% of \(^{29}\text{Si}\), and 3.1% of \(^{30}\text{Si}\)) becomes negligible at \( T > 200 \) K as three-phonon scattering outweighs the isotope scattering [135], [136]. The rNEMD approach which was first carried out by Müller-Plathe imposes a heat flux \( (J_x) \) on the finite system and measures the resulting temperature gradient \( (\partial T / \partial x) \) [26], which is the reverse of the natural simulation procedure where one imposes a temperature gradient first and then calculates the heat flux. This way, the simulation becomes more efficient in terms of simulation time as it avoids large fluctuations of the heat flux.
induced by the imposed temperature gradients. The expression for the thermal conductivity in the transport direction \((x)\) becomes \(\kappa_i = -J_x/(\partial T/\partial x)\) [26]. In this study, the rNEMD simulations are performed with periodic boundary conditions in the longitudinal direction and free boundary conditions in the transverse directions, and the Stillinger-Weber interatomic potential is adopted as it has demonstrated estimations of thermal conductivity of silicon nanowires in good agreement with experimental measurements [137]–[139]. The structures are relaxed through isothermal-isobaric (NPT) and microcanonical ensembles (NVE), each for 1 ns with the simulation time step of 1.0 fs, and then the actual rNEMD simulation is performed for 2 ns. In the MD simulation which follows the classical statistics, the occupation number of phonons below the Debye temperature \((\theta_D, 645 \text{ K for Si})\) needs to be rescaled to take into account unequally associated energy to each mode by the quantum mechanical description of lattice energy [140], [141]. To recover the discrepancy between the classical and quantum mechanics, the quantum correction which remaps the temperature in the MD simulation \((T_{MD})\) to the quantum corrected temperature \((T_{QC})\) is employed, and the expression with zero-point energy is [119]:

\[
T_{MD} = \frac{3}{8} \theta_D + 3T \left(\frac{T_{QC}}{\theta_D}\right)^3 \int_0^{\theta_D/T_{QC}} \frac{x^3}{e^x-1} \, dx.
\]
5.3 Results and Discussion

5.3.1 Quantum transmission

The total transmission probabilities of electrons for the straight and sine NWs computed with the RGF technique discussed in Section 5.2.3 are shown in Figure 5.3. The transmissions of the straight NWs under the ballistic transport assumption exhibit the number of propagating modes at energy $E$ and increase in steps as counting wavevectors available at each energy level [19]. One thing to note here is that the straight nanowires with the same cross-section area hold an identical transmission coefficient at any energy level regardless of their lengths (L): there is no interruption for carriers during transport through the wires other than the geometrical barriers, and the number of conducting channels in the straight NWs relies only on the cross-section area. In that respect, length-dependence of the transmissions of the sine NWs should be explained by the wavelength of the sinusoid rather than the actual length of the wire. As more conducting channels are available within the larger cross-section, the transmission for the wire of $W = 4.34$ nm shows a steeper increase than the wire of $W = 2.17$ nm. While the transmissions of sine NWs at high energy levels tend to weaken compared to those of the straight NWs (see Figure 5.3(b)), the sinusoid has limited impact on the transmissions of the first energy level where most thermoelectric transport occurs. As it has been reported from the carrier transport studies in rough surface nanowires that the surface roughness scattering becomes more significant with more conduction channels at high energy [129], [142], only a minimal influence on the low-field transport in the nanowires is anticipated by a certain degree of geometrical corrugation. Figure 5.3(c)-(f) compare the transmissions of the sine NWs with different $W$, $H$, and $\lambda$, respectively. Specifically, Figure 5.3(c)
and (e) reveal the transmission differences between the wires with different H, and Figure 5.3(d) and (f) exhibit the effect of \( \lambda \) on the transmission coefficients.

Figure 5.3: Comparisons of electron transmission probabilities of (a) the straight NWs with different cross-section widths (\( W \)), (b) the sine NWs with different \( W \) (transmissions of the straight NWs are also shown in dashed lines for comparison), (c, e) the sine NWs with different undulation heights (\( H \)), and (d, f) the sine NWs with different wavelengths (\( \lambda \)). Transmission is computed as a function of energy above the first conduction energy (\( E_c \)). All sample NWs have the same length (\( L \)) of 108.6 nm.
Taking a close look at the comparisons, it becomes very obvious that the more undulations in a sine NW, the less energy transmission occurs through the nanowire. In other words, more geometrical variation brings more electron scattering into play and consequently reduces the transmission through the system, but most importantly, a drop of the transmission is not remarkable at low energy.

5.3.2 $S^2G$ and $K_e$

With the results of the transmission probability calculation, the thermoelectric coefficients of the straight and sine NWs can be computed and compared using Equations (2-11)-(2-13). As shown in Figure 5.4, the electrical conductance obviously decreases with more structural fluctuation while the Seebeck coefficient increases as a consequence of the interplay with the conductance [20]. The power factors of the sine NWs at high temperature range ($T > 250$ K) show only a slight drop compared to that of the straight NW, so an improvement of thermoelectric efficiency can be expected along with a decrease in total thermal conductivity. In contrast, the sine NWs show fairly large differences from the straight NWs at low temperature in both the Seebeck coefficient and the electrical conductance. This can be explained with the transmission coefficient, which is an independent element to the temperature, becoming less influential in the Seebeck coefficient and the electrical conductance calculations with increasing temperature. Besides, a decrease in electronic thermal conductance which becomes non-negligible in highly-doped nanostructures compensates for the reduction of the power factor to some extent in the efficiency calculation.
Figure 5.4: Seebeck coefficient, electrical conductance, power factor, and the electronic contribution to the thermal conductance of the straight (STR) and sine (SIN) NWs with widths of (a) - (d) 2.17 nm and (e) - (h) 4.34 nm. The length of all simulated nanowires is 108.6 nm, and the sine NWs with different structure setups are distinguished with the enclosed numbers.
5.3.3 Lattice thermal conductivity

The lattice thermal conductivities of the straight and sine NWs adjusted with the quantum correction are compared in Figure 5.5. The lower the temperature, the more significant the deviation that is observed between the quantum corrected conductivity and the conductivity predicted with the classical MD simulation, which arises from the low heat capacity of phonons at low temperature accounted for by Bose-Einstein distribution [143]. It is also well shown in Figure 5.5(a)-(d) that the thermal transport through sine NW is indeed limited compared to the transport through straight NW, and the more geometrical corrugation present, the more interruption to the transport: The larger undulation height (H) and the shorter wavelength (λ) of nanowires cause the thermal conductivity to be lower than that in less fluctuating nanowires. We would like to note here that the absolute value of the thermal conductivity estimated by the MD simulation may deviate from experimental data as the results are semi-classical and highly depend on the interatomic potentials. In addition, the thermal conductivity of nanowires calculated with the NEMD method has a strong relationship with a length of the wire: the thermal conductivity of a nanowire keeps increasing with its length until the size becomes comparable to the bulk structure [119]. However, as the MD approach has its strength in analyzing the effect of atomistic changes, the simulation results should be interpreted with respect to the relative changes [92].
Figure 5.5: Lattice thermal conductivity of straight (STR) and sine (SIN) NWs calculated by MD simulation. Blue circles and red squares represent nanowires with widths of 4.34 nm and 2.17 nm, respectively. The conductivity with the quantum correction is displayed with filled markers while the classical simulation results without the quantum correction are shown in open markers.

Based on the calculated thermoelectric properties \((S, G, K_e, \text{ and } \kappa_l)\) calculated above, \(ZT\) of the straight and sine NWs can be evaluated. By definition, conductance \((G, K_e)\) is easily converted to conductivity \((\sigma, \kappa_e)\) by multiplying \(L/A\) where \(A\) is the cross-section area. This work does not encounter all of the known scattering mechanisms; therefore, assuming ballistic transport for electrons except for the geometrical barriers and neglecting phonon scattering due to surface-roughness and point-defects, it is more meaningful to interpret the \(ZT\) of the sine NWs based on
the improvement from that of the straight NWs. We compute the $ZT$ improvement by normalization, expressed as $\overline{ZT} = ZT_{\text{SIN}}/ZT_{\text{STR}}$. The $\overline{ZT}$ of the sine NWs with widths of 2.17 nm and 4.34 nm (see Figure 5.6(a) and (b)) shows around 10 - 35% improvement at room temperature. In the same manner as the thermal conductivity calculation, the nanowires with the shorter $\lambda$ and the large $H$ have resulted in high $ZT$ among the sine NWs studied in this work. However, it is not always the case. If the electron transmission at low energy were more strongly bothered with more sinusoidal corrugations, it would result in a relatively large reduction in the power factor compared to the amount of reduction made in the thermal conductivity with the same degree of the undulation. This is because the electronic contribution to the thermoelectric transport is low-field transport, and therefore the changes in the transmission at low energy have substantial impact on both $S$ and $G$. Although, it is hard to define in general at which point an efficiency improvement of a sine NW becomes ineffective because it is closely related to all structural parameters, we have found that, at least for the structures studied in this work, the $ZT$ of the sine NW has improved little, or even worsened, with the undulation height ($H$) of twice the cross-section width ($W$) and the wavelength ($\lambda$) of a quarter of its length ($L$).

The efficiency tends to increase with increasing sinusoidal undulations in nanowires in Figure 5.6(a), whereas all simulated models have produced quite similar improvement rates at room temperature in Figure 5.6(b). The dissimilarity is attributed to a larger reduction of thermal conductivity caused by the smaller cross-section nanowires while less thermal conductivity reduction and greater power factor loss are observed from the wider nanowires. Both resulting $ZT$ improvements follow the trends in the power factor (see Figure 5.4) of wires with $W$ of 2.17 and 4.34 nm: the less the difference in the power factors between the straight and sine NWs, the less the $ZT$ improvements achieved in the corresponding structures. Especially for low temperature
range, the large deviations in the Seebeck coefficient and the electrical conductance lead to greater
enhancement in $ZT$ compared to the $ZT$ around high temperature range where the enhancement
results mostly from the reduction of the lattice thermal conductivity.

Figure 5.6: $ZT$ of the sine NWs ($L = 108.6$ nm) with widths of (a) 2.17 nm and (b) 4.34 nm, normalized by
the $ZT$ of the straight NWs.

If the sine NWs were fabricated or bent by mechanical stress, the electronic and thermal transport
coefficients would be slightly different from the results reported in this chapter. This anticipation
has been made in the previously reported work: an enhancement in the electrical conductance of a
p-type silicon nanowire has been achieved under the applied bending strain, which resulted from
the modification of the band structure [144], and a reduced thermal conductivity from a silicon
nanowire under the uniform tensile strain was measured due to a disturbance in the phonon
transport [145]. These reports indicate the possibility of enhanced thermoelectric efficiency even
from the strain effect in nanowires. The nanowire structures studied in this work are oriented in the [100] direction instead of accounting for the strain effect. If we were to do the actual fabrication, those nanowires with non-uniform geometry could be synthesized through the meniscus-mask lithography process [146].

5.4 Summary

In summary, we have proposed a possible improvement of the thermoelectric efficiency by introducing geometrical modification to nanowires, exploiting the large difference of electron and phonon mean-free-paths. We have investigated both the electronic and lattice contributions to the thermoelectric coefficients of the straight silicon nanowires and the sinusoidally corrugated nanowires with varying structural parameters, and an enhancement of the thermoelectric efficiency $ZT$ has been demonstrated. The improvement was attributed mainly to the drop of thermal conductivity resulting from interrupted phonon transport by the undulating surface which has shown minimal impact on the electronic transport coefficients. The RGF and Landauer approaches have well-estimated loss in electronic transport, and the reduction of the thermal transport has been well predicted with the MD simulations. As a result, the sine NWs have improved the $ZT$ by 10 - 35% compared to the straight nanowires at room temperature. Since the electron transmission and thermal conductivity variations between the straight and sine nanowires have been evaluated as the geometrical corrugation is the only source of resistance in the systems, the resulting coefficients should be analyzed regarding the relative changes due to the perturbation. Besides, the compared structures are of the same material and dimensions. For that reason, accounting for
electron and phonon scattering mechanisms other than the geometrical variation would have little impact on the efficiency improvement.

Besides the successful enhancement in the thermoelectric efficiency of the sinusoidally corrugated nanowires, the RGF and MD approaches are capable of detecting the changes in the transport coefficients of other types of structures when the size of the structure is comparable to electron and phonon mean-free-paths, respectively. As the electron and phonon mean-free-paths in silicon have been reported to be tens to hundreds of nanometers [20], [121], [147]–[149], these methods can be used to estimate the thermoelectric efficiency improvement not only for nanowires but also for thin films and 2D materials with proper sizes. Furthermore, as the transport coefficients are confined and limited more effectively with smaller system dimensions, the $ZT$ enhancement due to an increase in the power factor and a reduction in thermal transport will be more noticeable in the structures whose dimensions are on the order of tens of nanometers or smaller.
REFERENCES


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