Thermal Transport in Semiconductors and Metals from First-Principles

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Abstract

Thermal Transport in Semiconductors and Metals from First-Principles by Ankit Jain

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The objective of this work is to study thermal transport in bulk, nano-structured, and two-dimensional semiconductors, and metals. While phonons (i.e., atomic vibrations) dominate the thermal transport in crystalline semiconductors, electrons are the major thermal and charge carriers in metals.

We predict the phonon and electron transport properties from first-principles calculations by considering phonon-phonon, electron-phonon, phonon-boundary, and phononisotopes scattering and using the Boltzmann transport equation. The phonon-phonon scattering rates are obtained from harmonic and anharmonic lattice dynamics calculations. Harmonic and cubic force constants, which are required as an input for harmonic and anharmonic lattice dynamics calculations, are obtained from density functional theory and density functional perturbation theory calculations. For electron-phonon scattering, we used density functional perturbation theory to calculate mode-dependent electron-phonon coupling coefficients on coarse grids and Wannier functions to interpolate them to finer grids.

At a temperature of 300 K, for porous silicon thin films with minimum feature sizes greater than 100 nm, we find that our particle-based phonon-boundary scattering model can capture the experimental trend and magnitude (within 6%) for the in-plane thermal conductivity. These results suggest the absence of coherent (i.e., wave) phonon transport phenomenon.

In compound semiconductors (i.e., semiconductors with more than one atomic species), we find that thermal conductivity depends on the frequency-gap between acoustic and optical phonons and the maximum acoustic phonon frequency. For model compound semiconductors with the zinc-blende structure, the maximum thermal conductivity occurs when the frequency-gap between acoustic-optical phonons equals the maximum acoustic phonon frequency.

We characterize the phonon thermal transport in black and blue phosphorene, which are two-dimensional arrangements of phosphorus atoms and for which there is no experimental thermal characterization. We find that black phosphorene has an unprecedented thermal conductivity anisotropy ratio of three, with predicted values of 110 W/m-K and 36 W/m-K along the two perpendicular in-plane directions at a temperature of 300 K.

We study the effect of electron exchange-correlation and pseudopotential types on the thermal conductivity of isotopically pure silicon. We find that, with the exception of BYLP, all XCs (LDA, PBE, PBEsol, PW91) predict a thermal conductivity between 127 and 148 W/m-K at a temperature of 300 K, which is an under-prediction of the experimental value of 153 W/m-K by 3-17%.

In metals, we find that the phonon contribution towards the thermal conductivity can be as high as 5.5% for aluminum at a temperature of 100 K. We also find that while the phonon mean free paths exhibit a larger range (2-22, 2-62, and 1-64 nm in aluminum, silver, and gold) than electron mean free paths (9-19, 30-53, and 21-38 nm for aluminum, silver, and gold), the gray phonon mean free paths are smaller than gray electron mean free paths in aluminum, silver, and gold at a temperature of 300 K. On comparing the phonon thermal transport in aluminum with silicon, we find that the phonon thermal conductivity is a factor of 15 smaller in aluminum at a temperature of 300 K, which is a result of (i) smaller phonon group velocities, (ii) large anharmonicity, and (iii) higher three-phonon phase space for low-frequency phonons in aluminum.

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"Dream is not that which you see while sleeping it is something that does not let you sleep." - Dr. A. P. J. Abdul Kalam, Wings of Fire: An Autobiography.

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Nomenclature

Abbreviations

Δ	.+ I	Lagrangian	multiplier	for	svmmetrv-re	duced	force	constants
	ı		···· 1					

- 2D Two-Dimensional
- 3D Three-Dimensional
- a Acoustic
- ALD Anharmonic Lattice Dynamics
- BTE Boltzmann Transport Equation
- DFPT Density Functional Perturbation Theory
- DFT Density Functional Theory
- e-p electron-phonon
- EPW Electron-phonon Wannier
- GGA Generalized Gradient Approximation
- HLD Harmonic Lattice Dynamics
- LDA Local Density Approximation
- LED Light Emitting Diode
- mfp Mean Free Path

NC Norm Conserving

- o Optical
- p-p Phonon-phonon
- PAW Projected Augmented Wave
- RTA Relaxation Time Approximation
- SMRT Single Mode Relaxation Time
- TI Translational Invariance
- US Ultrasoft
- XC Exchange-Correlation

Subscripts

- α, β, γ Cartesian directions (x, y, or z)
- b Atom index in unit cell
- *i* Labels phonon wavevector \boldsymbol{q} and polarization ν
- i, j, k Atom index in crystal
- s Isotope s of a given atom

Constants

- \hbar Reduced Plank constant
- $k_{\rm B}$ Boltzmann constant

Superscripts

- * Complex conjugate
- T Transpose

Variables

- κ Electron wavevector
- ∇T Temperature gradient
- Φ Force constant vector containing both harmonic and cubic force constants
- Φ Harmonic force constant
- Ψ Cubic force constant
- \underline{k} Thermal conductivity tensor
- **F** Force-vector
- G Reciprocal lattice vector
- Q Heat flux density
- \boldsymbol{R} Real lattice vector
- r Position vector of atom
- \boldsymbol{u} Atomic displacement from equilibrium position
- **u** Displacement matrix
- ϵ Broadening parameter
- $\epsilon_{\kappa m}$ Electron energy
- $\frac{\partial n_{q\nu}^{iso}}{\partial t}$ ~ Phonon-isotope scattering rate
- $\frac{\partial n_{q\nu}^{pp}}{\partial t}$ Three-phonon scattering rate
- $\frac{\partial n_{\boldsymbol{q}\nu}}{\partial t}$ Phonon scattering rate
- $\Lambda_{ij}^{\alpha\beta\gamma}$ Lagrangian multiplier
- μ Chemical potential
- ν Phonon polarization
- Ω Phonon transition rate

- $\omega_{\boldsymbol{q}\nu}$ Phonon frequency
- $\overline{\Lambda_i}$ Phonon effective mean free path in a nanostructure
- $\overline{\Lambda_{pb,i}}$ Phonon-boundary scattering mean free path
- $\overline{\Lambda_{pp,i}}$ Phonon mean free path due to phonon-phonon scattering
- $\overline{l_i}$ Average distance phonon travels before hitting a boundary in a nanostructure
- \overline{m} Average mass of atoms in a compound semiconductor

 ϕ Porosity

- Ψ^r Symmetry-reduced list of independent cubic force constants
- $\Psi_{ijk}^{\alpha\beta\gamma,a}$ Analytical cubic force constant element
- $\Psi_{ijk}^{\alpha\beta\gamma,c}$ Correction to numerically extracted cubic force constant element
- $\Psi_{ijk}^{\alpha\beta\gamma,n}$ Numerically extracted cubic force constant element
- $\tau_{\kappa m}$ Electron transport relaxation time
- $\tau^{eff}_{a\nu}$ Effective relaxation time of phonons in metals
- $\tau_{a\nu}^{ep}$ Electron-phonon interactions limited phonon relaxation time
- $\tau_{\boldsymbol{q}\nu}, \alpha$ Phonon scattering time
- θ_D Debye temperature
- θ_i Angle between the cross-plane direction and the group velocity vector
- $\Theta_{q\nu}$ Measure of deviation from the equilibrium distribution
- $\underline{\sigma}$ Electrical conductivity tensor
- \underline{K} Related to the electron thermal conductivity as $\underline{k}^e = \underline{K} \underline{S\sigma S}T$
- \underline{k}^e Electron thermal conductivity tensor
- \underline{S} Seeback coefficient tensor

 $\xi_{q\nu}$ Fourier coordinate

a Lattice constant

 $a^{\dagger}_{a\nu}$ Phonon creation operator

- $a_{\boldsymbol{q}\nu}$ Phonon annihilation operator
- $B_{ij}^{\alpha\beta\gamma}$ Numerical value of translational invariance constraint (should be zero theoretically)

C Cost function

 $c_{\boldsymbol{q}\nu}$ Phonon specific heat

e Electron charge

 $\begin{array}{l} F_i^{\alpha} & \text{Force on atom } i \text{ in the } \alpha \text{ direction} \\ F_i^{\alpha} \begin{pmatrix} u_j^{\beta} = h \\ u_k^{\gamma} = h \end{pmatrix} & \text{Force on atom } i \text{ in the } \alpha \text{ direction when atoms } j, k \text{ are displaced in the } \beta, \\ \gamma \text{ direction by small amount } h \end{array}$

- $f_s(b)$ Mass-fraction of isotope s of atom b
- $f_{\kappa m}$ Fermi-Dirac distribution
- $g_2(b)$ Mass-variance parameter of atom b

 $g_{mn}^{\nu}(\boldsymbol{\kappa},\boldsymbol{\kappa}',\boldsymbol{q})$ Electron-phonon coupling matrix element

- *h* Small displacement amount in finite-difference
- k_{α} Thermal conductivity for heat flow in the α direction

L Film thickness

m Electron band-index

 m_2/m_1 Mass-ratio of atoms in a compound semiconductor

- m_b Mass of atom b in the unit cell
- $m_{b,s}$ Mass of isotope s of b atom

- m_{bl} Mass of atom b in the l unit-cell
- N Number of unit-cells
- N Total number of phonon q-points in a system
- n Number of atoms in the unit-cell
- $n^o_{\boldsymbol{q}\nu}$ Bose-Einstein distribution
- $n_{q\nu}^1$ Deviation from the Bose-Einstein distribution
- $n_{a\nu}$ Phonon distribution function
- N_a Number of atoms in a supercell for which forces can be calculated without including the effect of periodic neighbor
- N_o Number of uniformly space phonon q-points in each direction
- N_s Number of displaced supercell
- n_s Number of electron per state
- N_q Number of phonon wavevectors
- N_{ν} Number of phonon polarizations
- p_i Mode-dependent specularity parameter

r Anisotropy ratio

 r_i^{alpha} alpha coordinate of the position of the atom i

- $S^{\alpha\alpha'}$ rotation matrix in symmetry operation
- ST Crystal symmetry operation

T Temperature

- t Time
- T^{α} Translational vector in symmetry operation

- U Potential energy
- V Crystal volume
- $v_{\kappa m}$ α component of electron velocity
- $v^{lpha}_{m{q}
 u}$ α component of phonon group velocity vector $m{v}_{m{q}
 u}$
- w_{κ} Weight of κ -point normalized to two for non-magnetic calculations in metals
- **D** Dynamical Matrix
- $e_{q\nu}$ Eigenvector
- \boldsymbol{q} Phonon wavevector
- $\boldsymbol{v}_{\boldsymbol{\kappa} m}$ Electron velocity
- $oldsymbol{v}_{oldsymbol{q}
 u}$ Phonon group velocity
- A_{tq} Coefficient matrix in translational invariance constraint using symmetry-reduced cubic force constants
- k Thermal conductivity
- \overline{m}_b Average mass of an atom b

Introduction

1.1 Motivation

Nanotechnology has enabled the design and fabrication of hybrid devices in which semiconductors and/or metals are nanostructured and fused together in an intricate fashion to obtain superior device functionality. These resulting nano-engineered devices are at the heart of the current technological boom and are used in applications varying from electronics, heat dissipators, and sensors to light emitting diodes (LEDs), thermoelectrics, and solar cells. These devices offer new possibilities for optical, thermal, and charge transport manipulation. For instance, the wavelength of emitted light in LEDs can be tuned by controlling the dopant concentration [1]. Similarly, the wavelength of adsorbed light in plasmonic solar cells can be tuned by varying the grating period [2].

The performance and efficiency of most of these semiconductor- and/or metal-based nano-engineered devices depend on the operating temperature and material thermal transport properties. For example, the figure of merit for semiconductor-metal superlatticebased thermoelectric materials depends on the thermal carrier properties mismatch between the semiconductor and the metal [3]. Similarly, the number density of transistors and hence performance of current microprocessor chips are limited by the rate of heat dissipation in order to maintain the allowed operating temperature [4]. It is, therefore, imperative to study the fundamental thermal carrier properties in semiconductors and metals.

1.2 Objective

The thermal conductivity, k, in materials is defined using the Fourier law as $\mathbf{Q} = -k\nabla T$, where \mathbf{Q} is the heat flux density and ∇T is the temperature gradient, and is a cumulative result of contributions from different fundamental heat carriers. In semiconductors, with few free electrons, the heat carriers are atomic vibrations, i.e., phonons. In metals, with a lot of free electrons, the heat and charge transport is dominated by electrons.

The objective of this work is to study and understand the thermal transport in a broad range of crystalline materials. We will apply first-principles based density functional theory-driven lattice dynamics calculations to predict phonon properties and thermal conductivity in (i) conventional three-dimensional (3D) semiconductors, (ii) two-dimensional (2D) semiconductors, and (iii) metals. We will also predict the electron thermal and electrical conductivities in metals. Our calculations will provide insight for understanding the underlying physics of thermal transport in semiconductors and metals and will provide guidance for interpreting cutting-edge experiments.

1.2.1 Conventional 3D Semiconductors

With miniaturization in size, thermal transport is becoming increasingly important in the design and realization of semiconductor-based devices. Due to additional scattering of heat carriers at boundaries, the thermal conductivity of semiconductors is reduced in these devices [5, 6, 7, 8]. While the reduced thermal conductivity deteriorates device performance and could result in device failure for applications such as microprocessors, it is advantageous for thermoelectric energy conversion, where the thermoelectric figure of merit is inversely proportional to the thermal conductivity.

We will investigate the thermal transport in conventional semiconductor nanostructures. We will also identify the origin of high thermal conductivity in some bulk conven-
tional compound semiconductors.

1.2.2 2D Semiconductors

Two dimensional materials such as graphene, silicene, and MoS_2 have been a focus of intense research over the past decade because of their new and rich physics [9, 10, 11, 12]. For instance graphene, because of its planar structure, has a quadratic phonon dispersion close to the gamma point as opposed to linear dispersion in conventional 3D materials. This unique dispersion reduces phonon-phonon scattering and results in an ultrahigh thermal conductivity (3000-5000 W/m-K at a temperature of 300 K) [13]. We will study phonon thermal transport in a new and recently fabricated 2D semiconductor, phosphorene [14, 15], which, similar to graphene, has a honeycomb-like structure but is non-planar.

1.2.3 Metals

Metals are different from semiconductors and insulators as they have a large number of free electrons. Phonons in metals, apart from scattering from other phonons and impurities, are also scattered from these free electrons. We will investigate the contribution of phonons towards the total thermal conductivity of metals by considering phonon-phonon and phonon-electron scattering. Even though small, this phonon contribution towards thermal transport in metals plays a crucial role in the analysis of laser-based thermal conductivity measurement experiments such as time-domain thermoreflectance (TDTR) and frequency-domain thermoreflectance (FDTR), where a metal layer is deposited as a transducer on the sample [16, 17, 18]. We will also investigate the mode-dependent contribution of electrons towards the thermal and electrical conductivities in metals.

	Molecular Dynamics Simulations	Lattice Dynamics Calculations
System	F = ma	
Approach	Time-evolution of trajectories of particles	Eigenvalue problem for coupled spring-mass system
Statistics	Classical (inherent)	Classical and quantum
Force-fields	Empirical (typical)	Empirical and first-principles

Table 1.1: Comparison of molecular dynamics simulations and lattice dynamics calculations for studying thermal transport in crystalline solids.

1.3 Methods

The materials to be studied in this work are all crystalline. Crystalline materials are different from amorphous materials as they have long-range order and are characterized by the periodic arrangement of groups of atoms. While experiments can be used to study the thermal transport in crystalline materials, they typically are difficult to set up, trickier to analyze [17, 19, 20, 21], and require phenomenological models for interpretation. Computational methods, on the other hand, can elucidate thermal transport physics but require experiments for validation. The objective of this work is to complement experiments in the understanding of thermal transport physics in crystalline materials using computational methods. Computationally, thermal transport in crystalline materials can be studied by using molecular dynamics simulations and/or lattice dynamics calculations [22, 23].

In molecular dynamics simulations, macroscopic material properties such as thermal

conductivity, Young's modulus, coefficient of diffusion are obtained by solving the timeevolution of trajectories of atoms which are moving under the influence of Newton's laws of motion. Molecular dynamics simulations have been used by researchers in the past to study the temperature [23, 24] and strain dependence [25] of thermal conductivity of argon, spectral phonon transport properties of silicon [26], interface roughness dependence of thermal conductivities of semiconductor superlattices [27], thermal interface conductance of the silicon/germanium interface [28], length dependence of thermal conductivity of single polymer chains [29], and many more systems. Molecular dynamics simulations are inherently classical in nature and their predictive power depends on the accuracy of the inter-atomic force-fields.

In lattice dynamics calculations, on the other hand, atoms/masses are connected to each other through harmonic/anharmonic springs and the mode-dependent phonon transport properties are obtained by solving the eigenvalue problem for this coupled spring mass system. Lattice dynamics calculations have been used by researchers to study a variety of systems varying from simple semiconductors such as bulk argon [30], krypton [30], silicon [30, 31, 32, 33, 34], germanium [32], and diamond [35] to compound [36, 37] and two-dimensional semiconductors [38]. Unlike molecular dynamics simulations, lattice dynamics calculations can be used with both classical as well as quantum statistics. The predictive power of lattice dynamics calculations, similar to molecular dynamics simulations, also depends on the inter-atomic force-fields.

The force-fields governing the interactions between different atoms in molecular dynamics simulations and lattice dynamics calculations can be either obtained from empirical potentials or from first-principles calculations. Empirical potentials are limited in their capacity due to their relatively simple design and lack true predictive power. While first-principles driven molecular dynamics simulations are computationally expensive, use of first-principles based force constants for lattice dynamics calculations is now routine [32, 33, 34, 39].

We will apply lattice dynamics calculations to predict phonon thermal transport properties in semiconductors by considering three-phonon scattering processes. The force constants required as an input for lattice dynamics calculations will be obtained from firstprinciples driven density functional theory (DFT) and density functional perturbation theory (DFPT). The phonon scattering rates and thermal conductivity will be calculated using an iterative solution of the Boltzmann transport equation (BTE) [30]. In metals, where phonons can scatter from electrons as well, we will use DFPT and Wannier functions to calculate the electron-phonon coupling coefficients [40, 41, 42]. We will predict electron thermal and electrical conductivities by using the relaxation time approximation (RTA) of the BTE in metals.

1.4 Overview and Scope

The tools and framework necessary for predicting thermal transport properties in semiconductors and metals are discussed in Chapter 2. Theoretical derivations are presented for calculation of phonon dispersion from harmonic lattice dynamics (HLD), three-phonon scattering rates from anharmonic lattice dynamics (ALD) [43], phonon-isotope scattering rates from the Tamura theory [44], and thermal conductivity prediction from the iterative solution of the BTE [30]. The predicted thermal conductivities of silicon and germanium using the developed tools are compared against experimental measurements. The importance of crystal symmetries in the extraction of force constants from DFT is analyzed. The framework for the calculation of electron-phonon coupling coefficients and electronic transport properties using DFPT [40] and Wannier functions [41, 42] is presented.

In Chapter 3, the thermal transport properties of phonons in nanostructured semicon-

ductors are investigated and compared against experimental measurements. A framework is developed for the calculation of scattering rates of phonons from nanostructure boundaries. The framework is compared with existing phonon-boundary scattering models and available experimental data for simple silicon nanostructures. Phonon transport properties and thermal conductivity predictions are made and compared with the experimental data from El-Kady et al. [45] and Hopkins et al. [46] for silicon nanoporous thin films at a temperature of 300 K.

Chapter 4 is focused on the phonon thermal transport in compound semiconductors, i.e., semiconductors with more than one atomic species. The thermal conductivities of model compound semiconductors, which differ only in the mass-ratio of the atomic species, are presented and analyzed. The effect of harmonic phonon properties on the phonon scattering rates and thermal conductivity is studied. By normalizing the model system thermal conductivities with the Slack group of parameters [47], a comparison is made between the model system and IV, III-V, and II-VI real compound semiconductors.

In Chapter 5, the thermal transport properties of black and blue phosphorene are investigated. The thermal conductivities are compared with the other 2D materials and the factors affecting the thermal transport are analyzed. The possibility of strain tuning the thermal transport through the application of uni-axial and bi-axial strain is discussed.

In Chapter 6, the effect of the choice of DFT electron exchange-correlations (XCs) and pseudopotential types on the thermal conductivity of isotopically pure silicon is examined. The local density approximation (LDA) and generalized gradient approximation (GGA) (PBE [48], PBEsol [49], BYLP [50, 51], and PW91 [52]) XC-based ultrasoft (US), normconserving (NC), and projected augmented wave (PAW) pseudopotentials are employed for the thermal conductivity prediction. The predicted thermal conductivities are compared with experimental measurements and causes of discrepancies between them are discussed at the phonon mode level. Recommendations are made for strategies of how to choose the DFT parameters for the study of new materials.

Chapter 7 focuses on phonon and electron transport in metals (aluminum, silver, and gold). The phonon thermal conductivity, electron thermal conductivity, and electrical conductivity are predicted from first-principles calculations by considering phonon-phonon and electron-phonon scattering. A comparison is made between the phonon thermal transport in metals and semiconductors.

In Chapter 8, the major contributions of this work are presented and suggestions for future study are discussed.

Thermal Transport Theory

In this chapter, we describe the theoretical and computational framework needed for thermal conductivity prediction in semiconductors and metals. The prediction of phonon scattering rates, by considering three-phonon and electron-phonon scattering processes from lattice dynamics and first-principles calculations, is discussed. Two different techniques are presented for the extraction of harmonic and cubic force constants from the DFT calculations. The iterative solution of the BTE for the calculation of lattice thermal conductivity in semiconductors and the RTA solution of the BTE for the calculation of thermal and electrical conductivities in metals are discussed. The derivations presented in this chapter are adopted from Refs. 43, 44, 53, 54, 55, 56.

2.1 Thermal Transport in Semiconductors

In semiconductors, thermal transport is dominated by phonons. The heat flux due to the flow of phonons when a finite temperature gradient is applied across a material is given by

$$\boldsymbol{Q} = \frac{1}{V} \sum_{\boldsymbol{q}} \sum_{\nu} \hbar \omega_{\boldsymbol{q}\nu} \boldsymbol{v}_{\boldsymbol{q}\nu} n_{\boldsymbol{q}\nu}.$$
(2.1)

The summation in the above equation is over all the phonon wavevectors, \boldsymbol{q} , and polarizations, ν , V is the crystal volume, \hbar is the reduced Planck constant, $\omega_{\boldsymbol{q}\nu}$ is the phonon frequency, $\boldsymbol{v}_{\boldsymbol{q}\nu}$ is the phonon group velocity, and $n_{\boldsymbol{q}\nu}$ is the phonon distribution function. The heat flux is also related to the temperature gradient through the Fourier law:

$$\boldsymbol{Q} = -\underline{\boldsymbol{k}}\boldsymbol{\nabla}T,\tag{2.2}$$

where \underline{k} is the thermal conductivity tensor. On equating the heat flux from Eqns. 2.1 and 2.2, we get:

$$-\underline{k}\nabla T = \frac{1}{V}\sum_{q}\sum_{\nu}\hbar\omega_{q\nu}v_{q\nu}n_{q\nu}.$$
(2.3)

 \underline{k} is a rank-two symmetric tensor with zero non-diagonal elements. The non-zero diagonal elements of \underline{k} are represented as k_x , k_y , and k_z in this work and denote thermal conductivity for the x, y, and z direction of heat flow. For cubically isotropic materials, $k_x = k_y = k_z$.

The evolution of the phonon distribution function $(n_{q\nu} \text{ in Eqn. 2.3})$ at any given time, when a temperature gradient ∇T is applied across a material, is governed by the BTE. At steady state with no external forces, the BTE is a balance between changes in the phonon distribution due to drift and scattering,

$$\boldsymbol{v}_{\boldsymbol{q}\nu} \cdot \boldsymbol{\nabla} n_{\boldsymbol{q}\nu} = \left(\frac{\partial n_{\boldsymbol{q}\nu}}{\partial t}\right)_{coll}.$$
(2.4)

The phonons in a material can scatter from other phonons, isotopes, defects, impurities, grain/system boundaries, etc. and $(\partial n_{q\nu}/\partial t)_{coll}$ denotes the total change in phonon distribution due to all scattering mechanisms. As will be shown in Sec. 2.1.4, Eqns. 2.3 and 2.4 can be solved together to obtain an expression for the thermal conductivity in the α direction,

$$k_{\alpha} = \sum_{\boldsymbol{q}} \sum_{\nu} c_{\boldsymbol{q}\nu} v_{\boldsymbol{q}\nu,\alpha}^2 \tau_{\boldsymbol{q}\nu,\alpha}, \qquad (2.5)$$

where $c_{\boldsymbol{q}\nu}$ is the phonon specific heat, $v_{\boldsymbol{q}\nu,\alpha}$ is the α component of phonon group velocity vector, and $\tau_{\boldsymbol{q}\nu,\alpha}$ is the phonon scattering time. Phonons are bosons and follow the Bose-Einstein distribution, when in equilibrium. The phonon specific heat can be obtained from the phonon vibrational frequencies as:

$$c_{\boldsymbol{q}\nu} = \frac{\hbar\omega_{\boldsymbol{q}\nu}}{V} \frac{\partial n^o_{\boldsymbol{q}\nu}}{\partial T} = \frac{k_{\rm B}x^2 e^x}{(e^x - 1)^2}.$$
(2.6)

The $n_{q\nu}^{o}$ in Eqn. 2.6 is the Bose-Einstein distribution $(n_{q\nu}^{o} = \frac{1}{e^{x}-1})$, $k_{\rm B}$ is the Boltzmann constant, and $x = \frac{\hbar\omega_{q\nu}}{k_{\rm B}T}$.

2.1.1 Lattice Dynamics

The calculation of lattice thermal conductivity from Eqn. 2.5 requires phonon specific heats, group velocities, and scattering times. Here, we discuss calculation of these phonon properties from harmonic and anharmonic lattice dynamics calculations.

2.1.1.1 Harmonic Lattice Dynamics

The potential energy portion of the system Hamiltonian can be expanded using a Taylor series as:

$$U = U_0 + \sum_i \prod_i^{\alpha} u_i^{\alpha} + \frac{1}{2!} \sum_{ij} \Phi_{ij}^{\alpha\beta} u_i^{\alpha} u_j^{\beta} + \frac{1}{3!} \sum_{ijk} \Psi_{ijk}^{\alpha\beta\gamma} u_i^{\alpha} u_j^{\beta} u_k^{\gamma} + \mathcal{O}\left(u^4\right), \qquad (2.7)$$

where,

$$\Phi_{ij}^{\alpha\beta} = \frac{\partial^2 U}{\partial u_i^{\alpha} \partial u_j^{\beta}}, \qquad (2.8a)$$

$$\Psi_{ijk}^{\alpha\beta\gamma} = \frac{\partial^3 U}{\partial u_i^{\alpha} \partial u_j^{\beta} \partial u_k^{\gamma}}.$$
(2.8b)

 U_0 in Eqn. 2.7 represents the reference energy, Π represents the forces acting on atoms, u_i labels a small displacement of atom i in the α direction, and Φ and Ψ are the harmonic and cubic force constants. In equilibrium, the sum of forces acting on all atoms are zero.

Therefore, by taking the reference potential energy as zero and by expanding potential energy Taylor series about the equilibrium positions of atoms, the first two terms on the right hand side of Eqn. 2.7 can be ignored. The harmonic and cubic force constants are the second- and third-order derivatives of the potential energy.

Using the first non-zero term on the right side of Eqn. 2.7, the equations of motion for each atom under the harmonic approximation can be written as

$$m_b \ddot{u}^{\alpha}_{bl}(t) = -\sum_{b'l'} \Phi^{\alpha\beta}_{bl;b'l'} u^{\beta}_{b'l'}(t).$$
(2.9)

Here m_b is the mass of atom b in the unit-cell and $u_{bl}(t)$ is the displacement of atom b in the l^{th} unit-cell from its equilibrium position at time t. The solution of Eqn. 2.9 can be obtained by doing a Fourier coordinate transformation by assuming the following form for the atomic displacements [43]:

$$\boldsymbol{u}_{bl}(t) = \frac{1}{\sqrt{m_b}} \sum_{\boldsymbol{q}} \sum_{\nu} \xi_{\boldsymbol{q}\nu} \boldsymbol{e}_{b,\boldsymbol{q}\nu} \exp\left\{i(\boldsymbol{q}\cdot\boldsymbol{r}_{bl}-\omega_{\boldsymbol{q}\nu}t)\right\},\tag{2.10}$$

where $\xi_{q\nu}$ is the transformed coordinate, r_{bl} is the equilibrium position of atom b in the l unit-cell, and $e_{b,q\nu}$ is the eigenvector of atom b. Substituting Eqn. 2.10 into Eqn. 2.9 results in an eigenvalue problem:

$$\omega_{\boldsymbol{q}\nu}^2 \boldsymbol{e}_{\boldsymbol{q}\nu} = \boldsymbol{D}_{\boldsymbol{q}} \cdot \boldsymbol{e}_{\boldsymbol{q}\nu}, \qquad (2.11)$$

where $e_{q\nu}$ is the eigenvector and D_q is the Dynamical matrix whose elements, $D_q^{3(b-1)+\alpha,3(b'-1)+\beta}$, are given by:

$$D_{\boldsymbol{q}}^{3(b-1)+\alpha,3(b'-1)+\beta} = \frac{1}{\sqrt{m_b m_{b'}}} \sum_{l'} \Phi_{b0;b'l'}^{\alpha\beta} \exp\left\{i[\boldsymbol{q}.(\boldsymbol{r}_{b'l'} - \boldsymbol{r}_{b0})]\right\},\tag{2.12}$$

where the summation is over all unit-cells in the lattice. With n atoms in the unit-cell, the Dynamical matrix is a $3n \times 3n$ Hermitian matrix with all real eigenvalues and orthogonal eigenvectors. The square root of the eigenvalues of D_q are the phonon vibrational frequencies ($\omega_{q\nu}$) and the eigenvectors of D_q are the phonon mode shapes (polarization vectors). Due to the Hermitian nature of D_q , the polarization vectors are normalized such that $e_{q\nu}^T \cdot e_{q\nu}^* = 1$.

2.1.1.2 Anharmonic Lattice Dynamics

Within the harmonic approximation for a perfect crystal, phonons do not interact with each other and have infinite lifetime. The higher-order terms in the system Hamiltonian results in interactions between phonons and hence finite intrinsic lifetime. The expression for phonon scattering rates by considering the three-phonon scattering processes can be obtained by treating the cubic term (the fourth term on the right side of Eqn. 2.7) as a perturbation to the harmonic phonons.

It is convenient to introduce the phonon creation and annihilation operators defined by [43]:

$$a^{\dagger} |n_{\boldsymbol{q}\nu}\rangle = (n_{\boldsymbol{q}\nu} + 1)^{\frac{1}{2}} |n_{\boldsymbol{q}\nu} + 1\rangle,$$
 (2.13a)

$$a |n_{q\nu}\rangle = n_{q\nu}^{\frac{1}{2}} |n_{q\nu} - 1\rangle.$$
 (2.13b)

The transformed Fourier coordinate (introduced in Eqn. 2.10) can be written in terms of these phonon creation and annihilation operators as:

$$\xi_{\boldsymbol{q}\nu} = \left[\frac{\hbar}{2\omega_{\boldsymbol{q}\nu}}\right]^{\frac{1}{2}} (a_{\boldsymbol{q}\nu} + a_{\boldsymbol{q}\nu}^{\dagger}).$$
(2.14)

By combining Eqns. 2.10 and 2.14, the atomic displacements can be expressed in terms of

the creation and annihilation operators to give

$$\boldsymbol{u}_{bl} = \left(\frac{\hbar}{2Nm_b}\right)^{\frac{1}{2}} \sum_{\boldsymbol{q}} \sum_{\nu} \omega_{\boldsymbol{q}\nu}^{-1/2} \tilde{\boldsymbol{e}}_{b,\boldsymbol{q}\nu} \exp\left\{i(\boldsymbol{q}\cdot\boldsymbol{r}_{0l})\right\} (a_{\boldsymbol{q}\nu} + a_{-\boldsymbol{q}\nu}^{\dagger}), \quad (2.15)$$

where N is the number of unit-cells and $\tilde{\boldsymbol{e}}_{b,\boldsymbol{q}\nu} = \boldsymbol{e}_{b,\boldsymbol{q}\nu} \exp\{i(\boldsymbol{q}\cdot\boldsymbol{r}_{b0})\}$. Using Eqn. 2.14, the cubic term in the system Hamiltonian (the fourth term in Eqn. 2.7) can be rewritten as:

$$U_{3} = \frac{1}{3!} \left(\frac{\hbar}{2N}\right)^{\frac{3}{2}} \sum_{bl} \sum_{b'l'} \sum_{b''l'} \sum_{b''l''} \sum_{\alpha\beta\gamma} \Psi^{\alpha\beta\gamma}_{bl;b'l';b''l''} \sum_{qq'q''} \sum_{\nu\nu'\nu''} e^{[i(q\cdot r_{0l} + q'\cdot r_{0l'} + q''\cdot r_{0l''})]} \times \frac{\tilde{e}^{\alpha}_{b,q\nu} \tilde{e}^{\beta}_{b',q'\nu'} \tilde{e}^{\gamma}_{b'',q''\nu''}}{\sqrt{m_{b}\omega_{q\nu}m_{b'}\omega_{q'\nu'}m_{b''}\omega_{q''\nu''}}} (a_{q\nu} + a^{\dagger}_{-q\nu}) (a_{q'\nu'} + a^{\dagger}_{-q'\nu'}) (a_{q''\nu''} + a^{\dagger}_{-q''\nu''}).$$

$$(2.16)$$

Due to the translational invariance of the crystal, shifting all three of \mathbf{r}_{0l} , $\mathbf{r}_{0l'}$, and $\mathbf{r}_{0l''}$ by a lattice vector \mathbf{R} should leave the Hamiltonian unchanged. This invariance leads to the following constraint on the exponential:

$$e^{i\{(\boldsymbol{q}+\boldsymbol{q}'+\boldsymbol{q}'').\boldsymbol{R}\}} = 1,$$
 (2.17)

or, equivalently,

$$q + q' + q'' = G,$$
 (2.18)

where G is a reciprocal lattice vector. Further, in a crystal, only the relative positions of the unit-cells, l' - l and l'' - l, affect the Hamiltonian. Therefore, by taking the origin of the coordinate system at l = 0, the first term in the exponential can be ignored and the summation over l can be evaluated to result in a constant prefactor of N. With these simplifications, the cubic term in the Hamiltonian reduces to

$$U_{3} = \frac{1}{3!} \left(\frac{\hbar}{2N}\right)^{\frac{3}{2}} N \sum_{b} \sum_{b'l'} \sum_{b''l''} \sum_{a'' l''} \sum_{\alpha \beta \gamma} \Psi_{bl;b'l';b''l''}^{\alpha \beta \gamma} \sum_{qq'q''} \Delta(q+q'+q'') \sum_{\nu\nu'\nu''} e^{[i(q'\cdot r_{0l'}+q''\cdot r_{0l''})]} \times \frac{\tilde{e}_{b,q\nu}^{\alpha} \tilde{e}_{b',q'\nu'}^{\beta} \tilde{e}_{b',q'\nu'}^{\beta} \tilde{e}_{b',q'\nu''}^{\gamma}}{\sqrt{m_{b}\omega_{q\nu}m_{b'}\omega_{q'\nu'}m_{b''}\omega_{q''\nu''}}} (a_{q\nu} + a^{\dagger}_{-q\nu}) (a_{q'\nu'} + a^{\dagger}_{-q'\nu'}) (a_{q''\nu''} + a^{\dagger}_{-q''\nu''}),$$

$$(2.19)$$

where $\Delta(\boldsymbol{q})$ is defined as

$$\Delta(\boldsymbol{q}) \equiv \begin{cases} 1 & \text{if } \boldsymbol{q} = \boldsymbol{G} \text{ (reciprocal lattice vector)} \\ 0 & \text{otherwise} \end{cases}$$
(2.20)

2.1.2 Phonon Scattering Mechanisms

2.1.2.1 Phonon-Phonon Scattering

The scattering rate of phonons due to three-phonon scattering processes can be calculated using the Fermi's golden rule, according to which the transition rate, Ω , of three phonons scattering from initial state $|i\rangle$ to final state $|f\rangle$ is given by

$$\Omega = \frac{2\pi}{\hbar} \left| \langle f | U_3 | i \rangle \right|^2 \delta(E_i - E_f), \qquad (2.21)$$

where $\langle f | U_3 | i \rangle$ is the matrix element of the cubic Hamiltonian between initial and final states and $\delta(E_i - E_f)$ is the delta function ensuring conservation of energy.

For the three-phonon scattering mechanism (i) in Fig. 2.1, the initial and final states

	Three-phonon Process	Final State	Contribution to Transition Rate
(i)		$ \begin{vmatrix} n_{\boldsymbol{q}\nu} & -1 \\ n_{\boldsymbol{q}'\nu'} +1 \\ n_{\boldsymbol{q}''\nu''} +1 \end{vmatrix} $	$\left[n_{{\bm{q}}\nu}(n_{{\bm{q}}'\nu'}+1)(n_{{\bm{q}}''\nu''}+1)\right]^{\frac{1}{2}}$
(ii)-a	$q'\nu'$ $q'\nu'$ $q''\nu''$	$ \begin{vmatrix} n_{\boldsymbol{q}\nu} & +1 \\ n_{\boldsymbol{q}'\nu'} & -1 \\ n_{\boldsymbol{q}''\nu''} +1 \end{vmatrix} $	$\left[\left(n_{\bm{q}\nu} + 1 \right) n_{\bm{q}'\nu'} \left(n_{\bm{q}''\nu''} + 1 \right) \right]^{\frac{1}{2}}$
(ii)-b	$q''\nu''$	$ \begin{vmatrix} n_{\boldsymbol{q}\nu} & +1 \\ n_{\boldsymbol{q}'\nu'} & +1 \\ n_{\boldsymbol{q}''\nu''} & -1 \end{vmatrix} $	$\left[(n_{{\bm{q}}\nu}\!+\!1)(n_{{\bm{q}}'\nu'}\!+\!1)n_{{\bm{q}}''\nu''}\right]^{\!\!\frac{1}{2}}$
(iii)-a	$ \begin{array}{c} $	$ \begin{vmatrix} n_{\boldsymbol{q}\nu} & -1 \\ n_{\boldsymbol{q}'\nu'} & -1 \\ n_{\boldsymbol{q}''\nu''} +1 \end{vmatrix} $	$\left[n_{{\bm{q}}\nu} n_{{\bm{q}}'\nu'} (n_{{\bm{q}}''\nu''} + 1) \right]^{\frac{1}{2}}$
(iii)-b	$ \begin{array}{c} q\nu \\ q'\nu' \\ q'\nu'' \end{array} $	$ \begin{vmatrix} n_{\boldsymbol{q}\nu} & -1 \\ n_{\boldsymbol{q}'\nu'} +1 \\ n_{\boldsymbol{q}''\nu''} -1 \end{vmatrix} $	$\left[n_{{\bm{q}}\nu} \left(n_{{\bm{q}}'\nu'} + 1 \right) n_{{\bm{q}}''\nu''} \right]^{\frac{1}{2}}$
(iv)	$ \begin{array}{c} $	$ \begin{vmatrix} n_{\boldsymbol{q}\nu} & +1 \\ n_{\boldsymbol{q}'\nu'} & -1 \\ n_{\boldsymbol{q}''\nu''} & -1 \end{vmatrix} $	$\left[\left(n_{{\bm{q}}\nu}\!+\!1 \right) n_{{\bm{q}}'\nu'} n_{{\bm{q}}''\nu''} \right]^{\!\!\frac{1}{2}}$

Figure 2.1: All possible three-phonon scattering processes. In processes (i), (ii)-a, and (ii)-b one phonon gets annihilated to create two new phonons, and in (iii)-a, (iii)-b, and (iv) two phonons scatter together to make one new phonon. All of these phonon scattering processes are required to satisfy energy conservation.

of the three phonons are:

$$|i\rangle = |n_{\boldsymbol{q}\nu}; n_{\boldsymbol{q}'\nu'}; n_{\boldsymbol{q}''\nu''}\rangle, \qquad (2.22a)$$

$$|f\rangle = |n_{\boldsymbol{q}\nu} - 1; n_{\boldsymbol{q}'\nu'} + 1; n_{\boldsymbol{q}''\nu''} + 1\rangle.$$
 (2.22b)

Accordingly, from Eqns. 2.21 and 2.16, the matrix element of the cubic Hamiltonian between these states is

$$\langle f | U_{3} | i \rangle_{(i)} = \langle n_{\boldsymbol{q}\nu} - 1; n_{\boldsymbol{q}'\nu'} + 1; n_{\boldsymbol{q}''\nu''} + 1 | \Psi_{\boldsymbol{q}\boldsymbol{q}'\boldsymbol{q}''}^{\nu\nu'\nu''} \Delta(\boldsymbol{q} - \boldsymbol{q}' - \boldsymbol{q}'') \times (a_{\boldsymbol{q}\nu} + a_{-\boldsymbol{q}\nu}^{\dagger}) (a_{\boldsymbol{q}'\nu'} + a_{-\boldsymbol{q}'\nu'}^{\dagger}) (a_{\boldsymbol{q}''\nu''} + a_{-\boldsymbol{q}''\nu''}^{\dagger}) | n_{\boldsymbol{q}\nu}; n_{\boldsymbol{q}'\nu'}; n_{\boldsymbol{q}''\nu''} \rangle ,$$

$$(2.23)$$

where $\Psi_{qq'q''}^{\nu\nu'\nu''}$ is defined for convenience as:

$$\Psi_{qq'q''}^{\nu\nu'\nu''} = N\left(\frac{\hbar}{2N}\right)^{\frac{3}{2}} \sum_{b} \sum_{b'l'} \sum_{b''l''} \sum_{\alpha\beta\gamma} \Psi_{bl;b'l';b''l''}^{\alpha\beta\gamma} \times \frac{\tilde{e}_{b,q\nu}^{\alpha}\tilde{e}_{b',q'\nu'}^{\beta}\tilde{e}_{b'',q''\nu''}^{\gamma}}{\sqrt{m_{b}\omega_{q\nu}m_{b'}\omega_{q'}\nu''m_{b''}\omega_{q''\nu''}}} e^{[i(q'\cdot r_{0l'}+q''\cdot r_{0l''})]}.$$
(2.24)

The effect of the creation and annihilation operators on $|i\rangle$ and $|f\rangle$ can be calculated by using Eqns. 2.13a and 2.13b to give

$$\langle n_{\boldsymbol{q}\nu} - 1; n_{\boldsymbol{q}'\nu'} + 1; n_{\boldsymbol{q}''\nu''} + 1 | (a_{\boldsymbol{q}\nu} + a^{\dagger}_{-\boldsymbol{q}\nu})(a_{\boldsymbol{q}'\nu'} + a^{\dagger}_{-\boldsymbol{q}'\nu'})(a_{\boldsymbol{q}''\nu''} + a^{\dagger}_{-\boldsymbol{q}''\nu''}) | n_{\boldsymbol{q}\nu}; n_{\boldsymbol{q}'\nu'}; n_{\boldsymbol{q}''\nu''} \rangle = n_{\boldsymbol{q}\nu}^{1/2} (n_{\boldsymbol{q}'\nu'} + 1)^{1/2} (n_{\boldsymbol{q}''\nu''} + 1)^{1/2}.$$

$$(2.25)$$

Thus, using Eqns. 2.21, 2.66, 2.24, and 2.25, the transition rate for process (i) of Fig. 2.1 is

$$\Omega_{(i)} = \frac{2\pi}{\hbar^2} \left| \Psi_{qq'q''}^{\nu\nu'\nu''} \right|^2 n_{q\nu} (n_{q'\nu'} + 1) (n_{q''\nu''} + 1) \Delta (q - q' - q'') \delta(\omega_{q\nu} - \omega_{q'\nu'} - \omega_{q'\nu''}).$$
(2.26)

If we consider a particular phonon, $q\nu$, and wish to calculate its total scattering rate, we need to sum over contributions from all the three-phonon processes shown in Fig. 2.1 that includes the phonon under investigation. From the point of view of phonon $q\nu$, processes (ii)-a and (ii)-b are equivalent, so we need to include only one of them. Similarly, we need to include only one of the processes (iii)-a and (iii)-b. Processes (i) and (iv) will be counted twice while performing the summation over all possible $q'\nu'$ and $q''\nu''$, and as such we need to multiply them by 1/2. Thus, the total scattering rate of phonon $q\nu$ due to three-phonon scattering, $\frac{\partial n_{q\nu}^{q\nu}}{\partial t}$, is

$$\frac{\partial n_{\boldsymbol{q}\nu}^{pp}}{\partial t} = \sum_{\boldsymbol{q}'\nu'} \sum_{\boldsymbol{q}''\nu''} \left[\left(\Omega_{(ii)} - \Omega_{(iii)} \right) + \frac{1}{2} \left(\Omega_{(iv)} - \Omega_{(i)} \right) \right].$$
(2.27)

By substituting Eqn. 2.26 and likewise into Eqn. 2.27, we get the final expression for the total scattering rate of phonon, $q\nu$, to be

$$\frac{\partial n_{\boldsymbol{q}\nu}^{pp}}{\partial t} = \frac{2\pi}{\hbar^2} \sum_{\boldsymbol{q}'\nu'} \sum_{\boldsymbol{\nu}''} \left\{ \left\{ \left| \Psi_{\boldsymbol{q}\boldsymbol{q}'\boldsymbol{q}''}^{\nu\nu'\nu''} \right|^2 \left[(n_{\boldsymbol{q}\nu}+1)(n_{\boldsymbol{q}'\nu'}+1)n_{\boldsymbol{q}''\nu''}^2 - n_{\boldsymbol{q}\nu}n_{\boldsymbol{q}'\nu'}(n_{\boldsymbol{q}''\nu''}+1) \right] \times \right. \\ \left. \delta(\omega_{\boldsymbol{q}\nu} + \omega_{\boldsymbol{q}'\nu'} - \omega_{\boldsymbol{q}''\nu''}) \right\} + \frac{1}{2} \left\{ \left| \Psi_{\boldsymbol{q}\boldsymbol{q}'\boldsymbol{q}''}^{\nu\nu'\nu''} \right|^2 \left[(n_{\boldsymbol{q}\nu}+1)n_{\boldsymbol{q}'\nu'}n_{\boldsymbol{q}''\nu''}^2 - n_{\boldsymbol{q}\nu}(n_{\boldsymbol{q}'\nu'}+1)(n_{\boldsymbol{q}''\nu''}+1) \right] \right\} \right\},$$

$$\left. - n_{\boldsymbol{q}\nu}(n_{\boldsymbol{q}'\nu'}+1)(n_{\boldsymbol{q}''\nu''}+1) \right] \delta(\omega_{\boldsymbol{q}\nu} - \omega_{\boldsymbol{q}'\nu'} - \omega_{\boldsymbol{q}''\nu''}) \right\} \right\},$$

$$(2.28)$$

with $q_{1}^{''} = q + q^{'} + G$ and $q_{2}^{''} = q - q^{'} + G$.

2.1.2.2 Phonon-Isotope Scattering

The scattering rate of phonons due to scattering from isotopes can also be calculated using the Fermi's golden rule (Eqn. 2.21). Assuming that the presence of isotopes of an atom does not alter the electronic environment, the modified total Hamiltonian of a system with isotope can be written as [44]:

$$H = \frac{1}{2} \sum_{bl} \overline{m}_b \dot{\boldsymbol{u}}_{bl}^2 + \frac{1}{2} \sum_{bl} \left(m_{bl} - \overline{m}_b \right) \dot{\boldsymbol{u}}_{bl}^2 + U, \qquad (2.29)$$

where \overline{m}_b is the average mass of atom b defined as

$$\overline{m}_b = \frac{1}{N} \sum_l m_{bl} = \sum_s f_s(b) m_{b,s}, \qquad (2.30)$$

where $f_s(b)$ is the mass-fraction of isotope s of atom b with mass $m_{b,s}$. By rewriting the perturbed Hamiltonian (second term in Eqn. 2.29) using Eqn. 2.15, substituting it into the Fermi's golden rule (Eqn. 2.21), and carrying out the algebra, the expression for the scattering rate of phonon $q\nu$ due to presence of isotopes can be written as [44]

$$\frac{\partial n_{\boldsymbol{q}\nu}^{iso}}{\partial t} = \frac{\pi}{2N} \sum_{\boldsymbol{q}'\nu'} \omega_{\boldsymbol{q}\nu} \omega_{\boldsymbol{q}'\nu'} \sum_{\boldsymbol{b}} g_2(\boldsymbol{b}) n_{\boldsymbol{q}\nu} (n_{\boldsymbol{q}'\nu'} + 1) \left| \boldsymbol{e}_{\boldsymbol{b},\boldsymbol{q}\nu}^* \cdot \boldsymbol{e}_{\boldsymbol{b},\boldsymbol{q}'\nu'}^* \right|^2 \delta \left(\omega_{\boldsymbol{q}\nu} - \omega_{\boldsymbol{q}'\nu'} \right), \quad (2.31)$$

where $g_2(b)$,

$$g_2(b) = \sum_s f_s(b) \left(1 - \frac{m_{b,s}}{\overline{m}_b}\right)^2,$$
 (2.32)

is the mass-variance parameter.

Please note that Eqn. 2.31 has been arrived at by using the second-order perturbation theory (i.e., by ignoring the higher-order terms). See Ref. 44 for details.

2.1.2.3 Other Phonon Scattering Mechanisms

Apart from scattering with other phonons and isotopes, a phonon can also scatter from grain and system boundaries, electrons, and defects. For a defect free semiconductor with no free electrons, phonon-electron scatterings are negligible as compared to phononphonon and phonon-isotope scatterings. The phonon-boundary scattering is significant in poly-crystalline and nanostructured semiconductors and is discussed in Ch. 3.

2.1.3 Linearized Boltzmann Transport Equation

As can be seen from Eqn. 2.28, the three-phonon scattering rate of phonon $q\nu$ depends on the distribution function of all other phonons in the system. Equation 2.28, therefore, represents $N_q N_{\nu}$ number of non-linear coupled equations, where N_q and N_{ν} are the number of phonon wavevectors and polarizations. In this section, we discuss the linearization of Eqn. 2.28, which can then be solved iteratively, along with Eqns. 2.31 and 2.4, to obtain the converged scattering rate of all phonons in a material.

In equilibrium, the rate of change of population of phonon $q\nu$ is zero. This statement leads to the following conditions from Eqn. 2.28:

$$(n^{o}_{\boldsymbol{q}\nu}+1)(n^{o}_{\boldsymbol{q}'\nu'}+1)n^{o}_{\boldsymbol{q}''\nu''} = n^{o}_{\boldsymbol{q}\nu}n^{o}_{\boldsymbol{q}'\nu'}(n^{o}_{\boldsymbol{q}''\nu''}+1)$$
(2.33)

$$(n^{o}_{\boldsymbol{q}\nu}+1)n^{o}_{\boldsymbol{q}'\nu'}n^{o}_{\boldsymbol{q}''\nu''} = n^{o}_{\boldsymbol{q}\nu}(n^{o}_{\boldsymbol{q}'\nu'}+1)(n^{o}_{\boldsymbol{q}''\nu''}+1).$$
(2.34)

When a small temperature gradient, $\partial T/\partial \alpha$, is applied across a material in the α direction, the non-equilibrium phonon distribution can be written as

$$n_{q\nu} = n^{o}_{q\nu} + n^{1}_{q\nu}, \qquad (2.35)$$

where $n_{q\nu}^1$ is a small deviation from the equilibrium Bose-Einstein distribution. Without the loss of generality, the deviation distribution can be assumed to be of the form

$$n_{\boldsymbol{q}\nu}^{1} = \frac{\partial n_{\boldsymbol{q}\nu}^{o}}{\partial (\hbar \omega_{\boldsymbol{q}\nu})} \frac{\partial T}{\partial \alpha} \Theta_{\boldsymbol{q}\nu},$$

$$= -\frac{n_{\boldsymbol{q}\nu}^{o} (n_{\boldsymbol{q}\nu}^{o} + 1)}{k_{B}T} \frac{\partial T}{\partial \alpha} \Theta_{\boldsymbol{q}\nu},$$
(2.36)

with $\Theta_{q\nu}$ as the measure of deviation from the equilibrium distribution. By substituting Eqn. 2.36 into Eqn. 2.28 and ignoring second- and higher-order terms and using Eqns. 2.33 and 2.34, the expression for the scattering rate of phonon $q\nu$ can be linearized as [57]:

$$\frac{\partial n_{\boldsymbol{q}\nu}^{pp}}{\partial t} = \frac{1}{k_B T} \frac{\partial T}{\partial \alpha} \sum_{\boldsymbol{q}'\nu'} \sum_{\nu''} \left\{ \Upsilon_{\boldsymbol{q}\boldsymbol{q}'\boldsymbol{q}_1''}^{\nu\nu'\nu''} \left(\Theta_{\boldsymbol{q}\nu} + \Theta_{\boldsymbol{q}'\nu'} - \Theta_{\boldsymbol{q}''\nu''} \right) + \frac{1}{2} \Upsilon_{\boldsymbol{q}\boldsymbol{q}'\boldsymbol{q}_2''}^{\nu\nu'\nu''} \left(\Theta_{\boldsymbol{q}\nu} - \Theta_{\boldsymbol{q}'\nu'} - \Theta_{\boldsymbol{q}''\nu''} \right) \right\},$$
(2.37)

where $\Upsilon_{qq'q_1'}^{\nu\nu'\nu''}$ and $\Upsilon_{qq'q_2'}^{\nu\nu'\nu''}$ are defined for convenience as

$$\Upsilon_{\boldsymbol{qq'q''}}^{\nu\nu'\nu''} = \frac{2\pi}{\hbar^2} \left| \Psi_{\boldsymbol{qq'q''}}^{\nu\nu'\nu''} \right|^2 n_{\boldsymbol{q}\nu}^o n_{\boldsymbol{q'\nu'}}^o (n_{\boldsymbol{q}_1'\nu''}^o + 1) \delta(\omega_{\boldsymbol{q}\nu} + \omega_{\boldsymbol{q'\nu'}} - \omega_{\boldsymbol{q}_1'\nu''}), \quad (2.38)$$

$$\Gamma_{\boldsymbol{q}\boldsymbol{q}'\boldsymbol{q}_{2}''}^{\nu\nu\nu'\nu''} = \frac{2\pi}{\hbar^{2}} \left| \Psi_{\boldsymbol{q}\boldsymbol{q}'\boldsymbol{q}_{2}'}^{\nu\nu'\nu'} \right|^{2} (n_{\boldsymbol{q}\nu}^{o}+1) n_{\boldsymbol{q}'\nu'}^{o} n_{\boldsymbol{q}_{2}'\nu''}^{o} \delta(\omega_{\boldsymbol{q}\nu}-\omega_{\boldsymbol{q}'\nu'}-\omega_{\boldsymbol{q}_{2}'\nu''}).$$
(2.39)

Finally, by combining Eqns. 2.4, 2.31, and 2.37, the following expression for the linearized BTE can be obtained:

$$v_{\boldsymbol{q}\nu}^{\alpha} \frac{\partial n_{\boldsymbol{q}\nu}^{o}}{\partial T} \frac{\partial T}{\partial \alpha} = \frac{1}{k_{B}T} \frac{\partial T}{\partial \alpha} \bigg[\sum_{\boldsymbol{q}'\nu'} \sum_{\boldsymbol{\nu}''} \bigg\{ \Upsilon_{\boldsymbol{q}\boldsymbol{q}'\boldsymbol{q}_{1}''}^{\boldsymbol{\nu}\nu'\nu''} \left(\Theta_{\boldsymbol{q}\nu} + \Theta_{\boldsymbol{q}'\nu'} - \Theta_{\boldsymbol{q}''\nu''} \right) + \frac{1}{2} \Upsilon_{\boldsymbol{q}\boldsymbol{q}'\boldsymbol{q}_{2}''}^{\boldsymbol{\nu}\nu'\nu''} \left(\Theta_{\boldsymbol{q}\nu} - \Theta_{\boldsymbol{q}'\nu'} - \Theta_{\boldsymbol{q}''\nu''} \right) \bigg\} + \sum_{\boldsymbol{q}'\nu'} \Upsilon_{\boldsymbol{q}\boldsymbol{q}'}^{\boldsymbol{\nu}\nu'} \left(\Theta_{\boldsymbol{q}\nu} - \Theta_{\boldsymbol{q}'\nu'} \right) \bigg],$$

$$(2.40)$$

where $\Upsilon_{qq'}^{\nu\nu'}$ is

$$\Upsilon_{\boldsymbol{q}\boldsymbol{q}'}^{\nu\nu'} = \frac{\pi}{2N} \omega_{\boldsymbol{q}\nu} \omega_{\boldsymbol{q}'\nu'} \sum_{\boldsymbol{b}} g_2(\boldsymbol{b}) n_{\boldsymbol{q}\nu}^o(n_{\boldsymbol{q}'\nu'}^o + 1) \left| \boldsymbol{e}_{\boldsymbol{b},\boldsymbol{q}\nu}^* \cdot \boldsymbol{e}_{\boldsymbol{b},\boldsymbol{q}'\nu'}^* \right|^2 \delta\left(\omega_{\boldsymbol{q}\nu} - \omega_{\boldsymbol{q}'\nu'} \right).$$
(2.41)

On simplifying Eqn. 2.40 to solve for $\Theta_{\boldsymbol{q}\nu}$ by evaluating $\frac{\partial n_{\boldsymbol{q}\nu}^o}{\partial T}$, canceling $\frac{\partial T}{\partial \alpha}$, and by

taking terms involving $\Theta_{\boldsymbol{q}\nu}$ on the left hand side, we get

$$\Theta_{\boldsymbol{q}\nu} \left[\sum_{\boldsymbol{q}'\nu'} \sum_{\boldsymbol{\nu}''} \left(\Upsilon_{\boldsymbol{q}\boldsymbol{q}'\boldsymbol{q}_{1}''}^{\nu\nu'\nu''} + \frac{1}{2} \Upsilon_{\boldsymbol{q}\boldsymbol{q}'\boldsymbol{q}_{2}''}^{\nu\nu'\nu''} \right) + \sum_{\boldsymbol{q}'\nu'} \Upsilon_{\boldsymbol{q}\boldsymbol{q}'}^{\nu\nu'} \right] = \frac{v_{\boldsymbol{q}\nu}^{\alpha} n_{\boldsymbol{q}\nu}^{o} (n_{\boldsymbol{q}\nu}^{o} + 1)\hbar\omega_{\boldsymbol{q}\nu}}{T} + \sum_{\boldsymbol{q}'\nu'} \sum_{\boldsymbol{\nu}''} \left(\Upsilon_{\boldsymbol{q}\boldsymbol{q}'\boldsymbol{q}_{1}''}^{\nu\nu'\nu''} (\Theta_{\boldsymbol{q}''\nu''} - \Theta_{\boldsymbol{q}'\nu'}) + \frac{1}{2} \Upsilon_{\boldsymbol{q}\boldsymbol{q}'\boldsymbol{q}_{2}''}^{\nu\nu'\nu''} (\Theta_{\boldsymbol{q}''\nu''} + \Theta_{\boldsymbol{q}'\nu'}) \right) + \sum_{\boldsymbol{q}'\nu'} \Upsilon_{\boldsymbol{q}\boldsymbol{q}'}^{\nu\nu'} \Theta_{\boldsymbol{q}'\nu'}.$$

$$(2.42)$$

After rearranging and defining $\Pi_{\boldsymbol{q}\nu}$ as

$$\Pi_{\boldsymbol{q}\nu} = \sum_{\nu''} \left(\Upsilon_{\boldsymbol{q}\boldsymbol{q}'\boldsymbol{q}_{1}''}^{\nu\nu'\nu''} + \frac{1}{2} \Upsilon_{\boldsymbol{q}\boldsymbol{q}'\boldsymbol{q}_{2}''}^{\nu\nu'\nu''} \right) + \sum_{\boldsymbol{q}'\nu'} \Upsilon_{\boldsymbol{q}\boldsymbol{q}'}^{\nu\nu'}, \qquad (2.43)$$

the expression to solve for $\Theta_{q\nu}$ from Eqn. 2.40 can be obtained as

$$\Theta_{\boldsymbol{q}\nu} = \frac{v_{\boldsymbol{q}\nu}^{\alpha} n_{\boldsymbol{q}\nu}^{o}(n_{\boldsymbol{q}\nu}^{o}+1)\hbar\omega_{\boldsymbol{q}\nu}}{T\Pi_{\boldsymbol{q}\nu}} + \frac{1}{\Pi_{\boldsymbol{q}\nu}} \bigg[\sum_{\boldsymbol{q}'\nu'} \sum_{\boldsymbol{\nu}''} \left(\Upsilon_{\boldsymbol{q}\boldsymbol{q}'\boldsymbol{q}'}^{\nu\nu'\nu''}(\Theta_{\boldsymbol{q}''\nu''} - \Theta_{\boldsymbol{q}'\nu'}) + \frac{1}{2} \Upsilon_{\boldsymbol{q}\boldsymbol{q}'\boldsymbol{q}'}^{\nu\nu'\nu''}(\Theta_{\boldsymbol{q}''\nu''} + \Theta_{\boldsymbol{q}'\nu'}) + \sum_{\boldsymbol{q}'\nu'} \Upsilon_{\boldsymbol{q}\boldsymbol{q}'}^{\nu\nu'}\Theta_{\boldsymbol{q}'\nu'}\bigg].$$

$$(2.44)$$

2.1.4 Relaxation Time Approximation, Iterative Solution of the BTE, and Lattice Thermal Conductivity

Under the application of a temperature gradient, $\partial T/\partial \alpha$, across a material in the α direction, the lattice thermal conductivity is related to the phonon distribution function through Eqn. 2.3 (derived in Sec. 2.1) as (one component of Eqn. 2.3)

$$-k_{\alpha}\frac{\partial T}{\partial\alpha} = \sum_{\boldsymbol{q}\nu} \frac{1}{V}\hbar\omega_{\boldsymbol{q}\nu}v_{\boldsymbol{q}\nu}^{\alpha}n_{\boldsymbol{q}\nu}.$$
(2.45)

On substituting $n_{q\nu}$ from Eqn. 2.35 into Eqn. 2.45, we get

$$-k_{\alpha}\frac{\partial T}{\partial\alpha} = -\sum_{\boldsymbol{q}\nu} \frac{1}{V}\hbar\omega_{\boldsymbol{q}\nu}v_{\boldsymbol{q}\nu}^{\alpha} \left[n_{\boldsymbol{q}\nu}^{o} + \frac{n_{\boldsymbol{q}\nu}^{o}(n_{\boldsymbol{q}\nu}^{o}+1)}{k_{B}T}\frac{\partial T}{\partial\alpha}\Theta_{\boldsymbol{q}\nu}\right].$$
(2.46)

The first term in the summation on the right side of Eqn. 2.46 represents the equilibrium heat flux (i.e., without any temperature gradient) and is, therefore, zero. Cancellation of $-\partial T/\partial \alpha$ from both sides of Eqn. 2.46 results in

$$k_{\alpha} = \sum_{\boldsymbol{q}\nu} \frac{\hbar\omega_{\boldsymbol{q}\nu}}{V} \frac{n^{o}_{\boldsymbol{q}\nu}(n^{o}_{\boldsymbol{q}\nu}+1)}{k_{B}T} v^{\alpha}_{\boldsymbol{q}\nu} \Theta_{\boldsymbol{q}\nu}.$$
(2.47)

Equation 2.47 can be further rearranged to get:

$$k_{\alpha} = \sum_{\boldsymbol{q}\nu} \frac{\hbar\omega_{\boldsymbol{q}\nu}}{V} \frac{\hbar\omega_{\boldsymbol{q}\nu} n^{o}_{\boldsymbol{q}\nu} (n^{o}_{\boldsymbol{q}\nu} + 1)}{k_{B}T^{2}} (v^{\alpha}_{\boldsymbol{q}\nu})^{2} \frac{T\Theta_{\boldsymbol{q}\nu}}{v^{\alpha}_{\boldsymbol{q}\nu}\hbar\omega_{\boldsymbol{q}\nu}}, \qquad (2.48)$$

$$= \sum_{\boldsymbol{q}\nu} \frac{\hbar\omega_{\boldsymbol{q}\nu}}{V} \frac{\partial n^{o}_{\boldsymbol{q}\nu}}{\partial T} (v^{\alpha}_{\boldsymbol{q}\nu})^{2} \frac{T\Theta_{\boldsymbol{q}\nu}}{v^{\alpha}_{\boldsymbol{q}\nu}\hbar\omega_{\boldsymbol{q}\nu}}, \qquad (2.49)$$

$$= \sum_{\boldsymbol{q}\nu} c_{\boldsymbol{q}\nu} (v_{\boldsymbol{q}\nu}^{\alpha})^2 \tau_{\boldsymbol{q}\nu}, \qquad (2.50)$$

where $c_{\boldsymbol{q}\nu} = \frac{\hbar\omega_{\boldsymbol{q}\nu}}{V} \frac{\partial n_{\boldsymbol{q}\nu}^o}{\partial T}$ (Eqn. 2.6) is the phonon specific heat and $\tau_{\boldsymbol{q}\nu} = \frac{T\Theta_{\boldsymbol{q}\nu}}{v_{\boldsymbol{q}\nu}^a\hbar\omega_{\boldsymbol{q}\nu}}$ is the phonon scattering time. The phonon scattering time depends on $\Theta_{\boldsymbol{q}\nu}$, which is obtained from Eqn. 2.44 by solving it iteratively with $\Theta_{\boldsymbol{q}\nu} = \frac{v_{\boldsymbol{q}\nu}^a n_{\boldsymbol{q}\nu}^o (n_{\boldsymbol{q}\nu}^o+1)\hbar\omega_{\boldsymbol{q}\nu}}{T\Pi_{\boldsymbol{q}\nu}}$ as an initial guess. The initial guess of $\Theta_{\boldsymbol{q}\nu}$ results in $\tau_{\boldsymbol{q}\nu} = \frac{n_{\boldsymbol{q}\nu}^o (n_{\boldsymbol{q}\nu}^o+1)}{\Pi_{\boldsymbol{q}\nu}}$ and is referred to as single mode relaxation time (SMRT) approximation or the RTA solution of the BTE.

2.1.5 Solving the Linearized BTE

The prediction of phonon thermal conductivity using Eqn. 2.50 requires the evaluation of $\Theta_{q\nu}$ from Eqn. 2.44. Eqn. 2.44 represents coupled system of linear equations in $\Theta_{q\nu}$ and can

be solved using different numerical approaches. Here we discuss some of these approaches for the numerical solution of Eqn. 2.44.

For convenience, rewriting Eqn. 2.44 as

$$\Theta_{\boldsymbol{q}\nu}^{i+1} = \Theta_{\boldsymbol{q}\nu}^o + \Delta\Theta_{\boldsymbol{q}\nu}^i, \qquad (2.51)$$

where $\Theta^{o}_{\boldsymbol{q}\nu}$ and $\Delta\Theta^{i}_{\boldsymbol{q}\nu}$ are

$$\Theta_{\boldsymbol{q}\nu}^{o} = \frac{v_{\boldsymbol{q}\nu}^{\alpha} n_{\boldsymbol{q}\nu}^{o} (n_{\boldsymbol{q}\nu}^{o} + 1) \hbar \omega_{\boldsymbol{q}\nu}}{T \Pi_{\boldsymbol{q}\nu}}, \\
\Delta\Theta_{\boldsymbol{q}\nu}^{i} = \frac{1}{\Pi_{\boldsymbol{q}\nu}} \bigg[\sum_{\boldsymbol{q}'\nu'} \sum_{\boldsymbol{\nu}''} \left(\Upsilon_{\boldsymbol{q}\boldsymbol{q}'\boldsymbol{q}''}^{\boldsymbol{\nu}\nu''} (\Theta_{\boldsymbol{q}''\nu''}^{i} - \Theta_{\boldsymbol{q}'\nu'}^{i}) + \frac{1}{2} \Upsilon_{\boldsymbol{q}\boldsymbol{q}'\boldsymbol{q}''}^{\boldsymbol{\nu}\nu''} (\Theta_{\boldsymbol{q}''\nu''}^{i} + \Theta_{\boldsymbol{q}'\nu'}^{i}) \right) + \sum_{\boldsymbol{q}'\nu'} \Upsilon_{\boldsymbol{q}\boldsymbol{q}'}^{\boldsymbol{\nu}\nu'} \Theta_{\boldsymbol{q}'\nu'}^{i} \bigg],$$
(2.52)

the simplest possible approach to solve Eqn. 2.44 is to solve it iteratively. Eqn. 2.51 can be solved by using $\Theta_{q\nu}^{o}$ as the initial guess and by adding $\Delta \Theta_{q\nu}^{i}$ to $\Theta_{q\nu}^{o}$ after every iteration *i*, where $\Delta \Theta_{q\nu}^{i}$ is calculated using a current iteration value of $\Theta_{q\nu}$ (i.e., $\Theta_{q\nu}^{i}$) [54]. The process is repeated until the change in values of $\Theta_{q\nu}$ (or thermal conductivity from Eqn. 2.50 which depends on $\Theta_{q\nu}$) after two consecutive steps ($|\Theta_{q\nu}^{i+1} - \Theta_{q\nu}^{i}|$) is less than some pre-defined small number. This approach is simple to implement but for some systems (we found for graphene) result in non-convergence of $\Theta_{q\nu}$ (or thermal conductivity).

A slightly modified approach to solve Eqn. 2.44 is discussed by Chernatynskiy and Phillpot [58], where the authors rigorously proved that the matrix representing Eqn. 2.44 is positive definite and symmetric and as such should always result in a converged solution. The authors introduced a simple mixing rule,

$$\Theta_{\boldsymbol{q}\nu}^{i+1} = \frac{1}{2}\Theta_{\boldsymbol{q}\nu}^{i} + \frac{1}{2}\left\{\Theta_{\boldsymbol{q}\nu}^{o} + \Delta\Theta_{\boldsymbol{q}\nu}^{i}\right\},\tag{2.53}$$

and found that iterating on this new scheme always results in a convergence (we also found iterative solution to convergence for graphene with this new scheme).

By using the same fact that matrix representing Eqn. 2.44 is symmetric and positive definite, Fugallo et al. [59] developed a variational approach with pre-conditioning and conjugate gradient algorithm to solve for $\Theta_{q\nu}$ from Eqn. 2.44. This approach, like Chernatynskiy and Phillpot approach [58], always converges. It also results in a faster convergence as compared to previous two approaches but is computationally more involved.

We used the Chernatynskiy and Phillpot approach [58] in this work as it is easy to implement and always leads to convergence.

2.1.6 Extracting Harmonic and Cubic Force Constants from DFT Calculations

The calculation of the phonon dynamical matrix and phonon scattering rates from Eqns. 2.12 and 2.44 requires harmonic and cubic force constants as an input. Here we discuss approaches for extracting these force constants from empirical inter-atomic potentials or from DFT calculations.

2.1.6.1 Taylor Series Fitting

The force constants were introduced in Eqn. 2.7 in the expression for the potential energy of the system. Equation 2.7 can be differentiated to obtain an expression for the forces on the atoms in terms of force constants as

$$F_i^{\alpha} = -\frac{\partial U}{\partial u_i^{\alpha}},\tag{2.54}$$

$$\approx -\sum_{j} \Phi_{ij}^{\alpha\beta} u_{j}^{\beta} - \frac{1}{2} \sum_{jk} \Psi_{ijk}^{\alpha\beta\gamma} u_{j}^{\beta} u_{k}^{\gamma}.$$
(2.55)

The force constants can be obtained using Eqn. 2.55 by creating different displaced structures/supercells and calculating forces on different atoms. The displaced supercells have one or more atoms displaced from their equilibrium position and forces can be calculated on these displaced supercells using empirical inter-atomic potentials or from DFT. The calculated forces on different atoms in displaced supercells can then be simultaneously fitted to extract both harmonic and cubic force constants at the same time by rewriting Eqn. 2.55 in matrix from as,

$$\boldsymbol{u}\boldsymbol{\Phi} = \boldsymbol{F},\tag{2.56}$$

where \boldsymbol{u} is the displacement matrix (displacement of atoms from their equilibrium positions), $\boldsymbol{\Phi}$ is the unknown force constants vector and includes both harmonic and cubic force constants, and \boldsymbol{F} is the force vector (forces acting on different atoms in displaced supercells). The number of rows in the displacement matrix equals the number of forcedisplacement equations for force constant fitting. For a three-dimensional system in which force-displacement equation can be written for N_a atoms in the supercell (this number can be less than number of atoms in a supercell, see App. A) and with N_s displaced supercells, the number of force-displacement equations are $3N_aN_s$. The number of columns in the displacement matrix equals the number of unknown harmonic and cubic force constants. If the number of unknown force constants are less than number of equations, then considered system of linear equations is over-specified and can be solved using least-square fitting to obtain the best fit solution for the unknown force constants (using Singular Value Decomposition).

2.1.6.2 Finite Difference

The harmonic and cubic force constants are the second and third derivatives of the potential energy (first and second derivatives of force)

$$\Phi_{ij}^{\alpha\beta} = \frac{\partial^2 U}{\partial u_i^{\alpha} \partial u_j^{\beta}} = -\frac{\partial F_i^{\alpha}}{\partial u_j^{\beta}}, \qquad (2.57a)$$

(2.58a)

$$\Psi_{ijk}^{\alpha\beta\gamma} = \frac{\partial^3 U}{\partial u_i^{\alpha} \partial u_j^{\beta} \partial u_k^{\gamma}} = -\frac{\partial^2 F_i^{\alpha}}{\partial u_j^{\beta} \partial u_k^{\gamma}}.$$
 (2.57b)

They can be approximated using four point central difference formulas as

$$\begin{split} \Phi_{ij}^{\alpha\beta} &= -\frac{\partial F_i^{\alpha}}{\partial u_j^{\beta}} \\ &\approx \frac{F_i^{\alpha}(u_j^{\beta}=2h) - 8F_i^{\alpha}(u_j^{\beta}=h) + 8F_i^{\alpha}(u_j^{\beta}=-h) - F_i^{\alpha}(u_j^{\beta}=2h)}{12h}, \end{split}$$

$$\begin{split} \Psi_{ijk}^{\alpha\beta\gamma} &= -\frac{\partial^2 F_i^{\alpha}}{\partial u_j^{\beta} \partial u_k^{\gamma}} \\ \approx &-\frac{1}{2h} \left[\frac{\partial F_i^{\alpha}}{\partial u_j^{\beta}} \left(u_k^{\gamma} = h \right) - \frac{\partial F_i^{\alpha}}{\partial u_j^{\beta}} \left(u_k^{\gamma} = -h \right) \right], \\ \approx &\frac{1}{4h^2} \left[F_i^{\alpha} \begin{pmatrix} u_j^{\beta} = h \\ u_k^{\gamma} = -h \end{pmatrix} - F_i^{\alpha} \begin{pmatrix} u_j^{\beta} = h \\ u_k^{\gamma} = h \end{pmatrix} + F_i^{\alpha} \begin{pmatrix} u_j^{\beta} = -h \\ u_k^{\gamma} = h \end{pmatrix} - F_i^{\alpha} \begin{pmatrix} u_j^{\beta} = -h \\ u_k^{\gamma} = -h \end{pmatrix} \right], \end{split}$$

$$(2.58b)$$

where $F_i^{\alpha} \begin{pmatrix} u_j^{\beta} = h \\ u_k^{\gamma} = h \end{pmatrix}$ is the force on atom *i* in the α direction when atoms *j*, *k* are displaced in the β , γ directions by a small amount *h*.

Similar to the procedure described in previous section (Sec. 2.1.6.1), different supercells can be created by displacing one or two atoms by $\pm h$ or $\pm 2h$ from their equilibrium positions. The force constants can then be obtained by calculating forces on different atoms and performing finite difference on forces according to Eqns 2.58. Note that multiple force constants can be obtained from forces on a given displaced supercell. For instance $\Phi_{i'j}^{\alpha'\beta}$, where i' and α' vary over all atoms in the supercell and all directions, can all be obtained from the same displaced supercell with atom j being displaced in the β direction.

We found that thermal conductivity prediction is very sensitive to the quality of the harmonic force constants. Therefore, large interaction cutoffs should be used in the calculation of harmonic force constants. In real-space DFT calculations, using large interaction cutoffs results in larger supercell size. In this work, therefore, harmonic force constants are initially calculated in reciprocal space on a phonon wavevector grid using the DFPT calculations and are later Fourier transformed to real space. The cubic force constants are obtained using the finite-difference of DFT forces.

2.1.6.3 Crystal Symmetries

As discussed in App. A, the extraction of force constants from DFT (using a planewave basis) requires the supercell/computational cell size to be at least twice as large as the force constant range. Moreover, the forces calculated from DFT should be sufficiently accurate in order to extract good quality force constants. The typical computational cell size for DFT force calculation is ~ 100 atoms. The number of such calculations required depends on the number of unknown force constants. Therefore, in order to keep computations tractable, it is imperative to use all the system symmetries to reduce the number of unknown force constants.

Following Esfarjani and Stokes [60], the harmonic and anharmonic force constants satisfy system symmetry constraints, which are categorized as follows. **Permutation Symmetry** The harmonic and cubic force constants are the second and third derivatives of potential energy. Changing the order of differentiation leaves the result unaffected, i.e.,

$$\Phi_{ij}^{\alpha\beta} = \Phi_{ji}^{\beta\alpha}, \qquad (2.59a)$$

$$\Psi_{ijk}^{\alpha\beta\gamma} = \Psi_{jki}^{\beta\gamma\alpha} = \Psi_{kji}^{\gamma\beta\alpha} = \Psi_{ikj}^{\alpha\gamma\beta} = \cdots .$$
(2.59b)

Space Group Symmetry A general space group operation (ST) of a system with rotational and translational operator $S^{\alpha\alpha'}$ and T^{α} , transforms the position vector r_i^{α} into vector $r_{ST(i)}^{\alpha}$ such that $\sum_{\alpha'} S^{\alpha\alpha'} r_i^{\alpha'} + T^{\alpha} = r_{ST(i)}^{\alpha}$. These symmetry operations relate the force constants as,

$$\Phi_{ST(i),ST(j)}^{\alpha\beta} = \sum_{\alpha\prime\beta\prime} \Phi_{ij}^{\alpha\prime\beta\prime} S^{\alpha\alpha\prime} S^{\beta\beta\prime}, \qquad (2.60a)$$

$$\Psi_{ST(i),ST(j),ST(k)}^{\alpha\beta\gamma} = \sum_{\alpha\prime\beta\prime\gamma\prime} \Psi_{ijk}^{\alpha\prime\beta\prime\gamma\prime} S^{\alpha\alpha\prime} S^{\beta\beta\prime} S^{\gamma\gamma\prime}.$$
(2.60b)

Application of permutation and space group symmetry operations in extracting force constants drastically reduces the computational load. For instance, in silicon, considering fifth- and third-neighbor cutoff for harmonic and cubic force constants, system symmetries reduces the unknown number of force constants from 3384 and 90936 to 17 and 95.

2.1.6.4 Translational Invariance

Apart from the above mentioned crystal symmetries, the harmonic and the cubic force constants also need to satisfy the translational invariance (TI) constraint which dictates that displacing the crystal as a whole leaves the force constants unchanged. This requirement results in the following constraint on the force constants [60]:

$$\sum_{i} \Phi_{ij}^{\alpha\beta} = 0 \qquad \forall (\alpha\beta, i), \qquad (2.61a)$$

$$\sum_{k} \Psi_{ijk}^{\alpha\beta\gamma} = 0 \qquad \forall (\alpha\beta\gamma, ij).$$
(2.61b)

While extracting force constants numerically from DFT calculations, the TI constraint is not satisfied due to finite numerical precision errors (in extracting harmonic force constants from DFPT calculations, TI constraint can be satisfied in the DFPT calculations itself). Not satisfying TI results in non-physical results such as non-zero acoustic phonon vibration frequencies at the center of the Brillioun zone. Therefore, TI should be satisfied explicitly in the extraction of force constants from DFT calculations. The TI constraint can be satisfied by either (i) using it along with the symmetry constraints to reduce the number of unknown force constants or (ii) as a post-extraction step in which small correction is added to all extracted force constants so that they will satisfy the TI. The later approach of satisfying TI is discussed in App. B

2.1.7 Implementation Details

2.1.7.1 Delta Functions

The calculation of phonon scattering rates from Eqn. 2.28 requires the evaluation of momentum and energy conservation delta functions. Using the uniformly spaced phonon wavevector grid, the momentum conservation delta function can be satisfied exactly. Due to the finite resolution of the phonon wavevector grid in the numerical calculations, however, the energy conservation delta function can never be satisfied exactly. Here, we discuss numerical ways of handling this challenge in the calculations.

The most common method of handling the delta functions is to approximate them using

a Gaussian or Lorentzian function of constant finite width. In the case of phonon scattering processes, when the width is small, very few processes can satisfy the energy conservation but the contribution from each of such processes is high. As the width is increased, more and more processes can satisfy the energy conservation but the contribution from each process decreases. There is, therefore, an optimal value of width is needed to have a meaningful value of the phonon scattering rate. This optimal value, however, depends on the phonon wavevector grid and convergence is required for all of the phonon wavevector grids separately. This method is, therefore, computationally expensive.

Another method of satisfying the delta function is to interpolate [54]. In this approach, two different grids are used to satisfy the momentum and energy conservation delta functions. The momentum conservation delta functions are still satisfied using a uniformly spaced grid, but another non-uniform grid is used to satisfy the energy conservation delta function exactly. The second non-uniform grid is obtained through the interpolation of energies from the uniform grid so that phonon energies can satisfy the energy conservation delta function. This approach is computationally cheaper than previous approach but is more challenging to implement.

The third approach is to use adaptive broadening and approximate the delta function by [23, 61]

$$\delta(\omega) \approx \frac{1}{\pi} \frac{\epsilon}{\omega^2 + \epsilon^2},\tag{2.62}$$

where ϵ is a small broadening parameter calculated as

$$\epsilon = \frac{1}{2} \left(\frac{\partial n_{\boldsymbol{q}\nu}^{pp}}{\partial t} + \frac{\partial n_{\boldsymbol{q}'\nu'}^{pp}}{\partial t} + \frac{\partial n_{\boldsymbol{q}''\nu''}^{pp}}{\partial t} \right).$$
(2.63)

The delta function is satisfied by providing an initial guess for the broadening parameter and iterating until self-consistency is achieved. This method is straightforward to implement and does not require any convergence with respect to broadening parameter.

In this work, we used adaptive broadening for satisfying energy conservation delta functions in three-phonon scattering processes (Eqn. 2.28) and a Lorentzian of finite-width for the delta functions in phonon-isotope scattering processes (Eqn. 2.31).

2.1.7.2 Computation Flow

A flow chart showing the steps involved in the calculation of thermal conductivity from the BTE using DFT forces is shown in Fig. 2.2. For a given new material, we start with the relaxation of the structure using DFT calculations. An initial choice of electron wavevector grid and planewave energy cutoff is made for this step. With the relaxed structure and choice of harmonic and cubic force constant cutoffs, a full list of harmonic and cubic force constants (containing all possible force constants within specified cutoffs) is generated. Next, crystal symmetry operations are identified for the material under consideration and the full list of force constants is converted into a list of symmetry-reduced force constants. Depending on the number of force constants in the symmetry-reduced list, different displaced supercells (see App. A) are created in which one or two atoms are displaced from their equilibrium position by a small amount. The DFT calculations are then performed on these displaced supercells to calculate forces on different atoms. These forces are next used to calculate force constants in symmetry-reduced list which, after satisfying translational invariance constraints, is mapped back to a full list of force constants. Finally, harmonic and anharmonic lattice dynamics calculations are performed to calculate phonon vibration frequencies, group velocities, and scattering rates using full/ iterative solution of the BTE for all phonons on a uniformly spaced wavevector grid.



Figure 2.2: Computation flow chart for phonon thermal conductivity calculation using DFT forces and full/ iterative solution of the BTE. The red boxes on the left represent computational parameters and thermal conductivity is required to be converged with respect to each of these computational parameters.

2.1.7.3 Thermal Conductivity Convergence Parameters

The calculation of thermal conductivity using the approach discussed in previous sections requires specification of certain computational parameters (some of those are shown in red boxes in Fig. 2.2). Here, we list these parameters:

- 1. Electronic wavevector grid in DFT calculations.
- 2. Electron planewave energy cutoff in DFT calculations.
- 3. DFT supercell size for force constant extraction.
- 4. Small displacement amount for generating displaced supercells for force constant extraction.
- 5. Harmonic and cubic force constants cutoff in lattice dynamics calculations (affects number of DFT calculations).
- 6. Phonon wavevector grid in lattice dynamics calculations.
- 7. Fermi-Dirac function smearing in DFT calculations (in case of metals).
- 8. Amount of vacuum (to remove inter-layer interactions in 2D materials) in DFT calculations.

The choice of these computational parameters varies with the material. For instance, in the case of silicon, we found no change in our thermal conductivity predictions in going from a 64 atom DFT supercell with a Gamma point electronic wavevector grid to a 216 atom DFT supercell with a Gamma point electronic wavevector grid. In gold, however, a 256 atom supercell with a Gamma point electronic wavevector grid results in very different predictions as compared to those from a 256 atom supercell with a $3 \times 3 \times 3$ electronic wavevector grid. Since the required values of these parameters vary with different materials, the convergence of phonon thermal conductivity is needed with respect to all of these parameters for any new material.

2.1.8 Validation

The thermal conductivities predicted from first-principles for pure (i.e., with no isotopes) and naturally occurring silicon and germanium as a function of temperature are plotted in Figs. 2.3(a) and 2.3(b). The continuous lines represent the computational predictions and the discrete data points are experimentally measured values from Ref. [62] (orange), Ref. [63] (purple), Ref. [64] (red), Ref. [65] (brown), and Ref. [66] (green). As can be seen, without using any fitting parameters, the predicted thermal conductivities are in good agreement with the experimental measurements (within 6%) for both pure and naturally occurring silicon and germanium for temperature varying between 100 and 500 K, thereby validating our calculations.

2.1.8.1 Computation Cost Scaling

The thermal transport properties prediction approach presented in this work has two main computational components (i) supercell forces calculation from density functional theory or density functional perturbation theory and (ii) phonon transport properties prediction from lattice dynamics calculations. While the computational cost of each supercell force calculation from density functional theory scales as $\mathcal{O}(n_s^3)$, the computational cost of lattice dynamics calculations scales as $\mathcal{O}(n^4)$ and $\mathcal{O}(N^2)$, where n_s and n are the number of atoms in the density functional theory supercell and lattice dynamics unit-cell and N is the number of unit-cells (number of phonon wavevectors) in the lattice dynamics calculations.



Figure 2.3: Thermal conductivity variation of (a) pure i.e., with no isotopes and (b) naturally occurring silicon and germanium as a function of temperature. The continuous lines represents computational predictions and discrete data points are experimentally measured values from Ref. [62] (orange), Ref. [63] (purple), Ref. [64] (red), Ref. [65] (brown), and Ref. [66] (green).

2.2 Thermal and Electrical Transport in Metals

2.2.1 Electron Transport

The transport properties of electrons can be obtained by solving the BTE and using the Onsager relations as [56]:

$$\sigma_{\alpha\beta} = -\frac{e^2 n_s}{V} \sum_{\kappa m} \frac{\partial f_{\kappa m}}{\partial \epsilon} v_{\kappa m,\alpha} v_{\kappa m,\beta} \tau_{\kappa m},$$

$$[\sigma S]_{\alpha\beta} = -\frac{e n_s}{VT} \sum_{\kappa m} (\epsilon_{\kappa m} - \mu) \frac{\partial f_{\kappa m}}{\partial \epsilon} v_{\kappa m,\alpha} v_{\kappa m,\beta} \tau_{\kappa m},$$

$$K_{\alpha\beta} = -\frac{n_s}{VT} \sum_{\kappa m} (\epsilon_{\kappa m} - \mu)^2 \frac{\partial f_{\kappa m}}{\partial \epsilon} v_{\kappa m,\alpha} v_{\kappa m,\beta} \tau_{\kappa m},$$
 (2.64)

where $\underline{\sigma}, \underline{S}$, and \underline{K} are 3×3 tensors which represent electrical conductivity, Seeback coefficient, and \underline{K} relates to the electronic thermal conductivity, \underline{k}^{e} , as $\underline{k}^{e} = \underline{K} - \underline{S\sigma}\underline{S}T$. The summation in Eqn. 2.64 is over all the electrons enumerated using electronic wavevector κ and band index m. e is the elementary charge, n_s is the number of electrons per state, $f_{\kappa m}$ is the Fermi-Dirac distribution, $\epsilon_{\kappa m}$ is the electron energy, μ is the chemical potential, $v_{\kappa m,\alpha}$ is the α component of electron velocity, $v_{\kappa m} = \frac{1}{\hbar} \frac{\partial e_{\kappa m}}{\partial \kappa}$, and $\tau_{\kappa m}$ is the electron transport relaxation time. Similar to the phonon-phonon scattering, the Fermi's golden rule can also be used to calculate the electron transport relaxation time, limited by electron-phonon scattering as,

$$\frac{1}{\tau_{\kappa m}} = \frac{2\pi}{\hbar} \sum_{\kappa' n} \sum_{q\nu} \left| g_{mn}^{\nu}(\kappa, \kappa', q) \right|^{2} \left\{ \left(n_{q\nu} + f_{\kappa' n} \right) \delta\left(\epsilon_{\kappa m} + \hbar \omega_{q\nu} - \epsilon_{\kappa' n} \right) \Delta\left(\kappa + q - \kappa' \right) + \left(n_{q\nu} + 1 - f_{\kappa' n} \right) \delta\left(\epsilon_{\kappa m} - \hbar \omega_{q\nu} - \epsilon_{\kappa' n} \right) \Delta\left(\kappa - q - \kappa' \right) \right\} \left(1 - \frac{\boldsymbol{v}_{\kappa m} \cdot \boldsymbol{v}_{\kappa' n}}{|\boldsymbol{v}_{\kappa m}||\boldsymbol{v}_{\kappa' n}|} \right),$$
(2.65)

where $g_{mn}^{\nu}(\boldsymbol{\kappa}, \boldsymbol{\kappa}', \boldsymbol{q})$ is the electron-phonon matrix element between states $|\boldsymbol{\kappa}m\rangle$ and $|\boldsymbol{\kappa}'n\rangle$,

$$g_{mn}^{\nu}(\boldsymbol{\kappa},\boldsymbol{\kappa}',\boldsymbol{q}) = \sqrt{\frac{\hbar}{2\omega_{\boldsymbol{q}\nu}}} \left\langle \boldsymbol{\kappa}'n \right| \partial_{\boldsymbol{q}\nu} V \left| \boldsymbol{\kappa}m \right\rangle, \qquad (2.66)$$

and describes the electron-phonon coupling strength when an electron with state $|\boldsymbol{\kappa}m\rangle$ gets scattered into a state $|\boldsymbol{\kappa}'n\rangle$ by phonon $|\boldsymbol{q}\nu\rangle$ of energy $\hbar\omega_{\boldsymbol{q}\nu}$ and occupation $n_{\boldsymbol{q}\nu}$. The delta functions in Eqn. 2.65 ensures energy and crystal momentum conservation in the scattering events.

We note that the additional $\left(1 - \frac{v_{\kappa m} \cdot v_{\kappa' n}}{|v_{\kappa m}||v_{\kappa' n}|}\right)$ factor in Eqn. 2.65 differentiates electron transport relaxation time from electron scattering relaxation time. This additional factor ensures that even after getting scattered by a phonon, a scattered electron can still contribute towards the transport [56].

2.2.2 Phonon Transport

Apart from scattering with other phonons, phonons in metals also scatter with free electrons. The scattering rate of phonons limited by electron-phonon interaction can be calculated using the Fermi's golden rule as

$$\frac{1}{\tau_{\boldsymbol{q}\nu}^{ep}} = \frac{2\pi}{\hbar} \sum_{\boldsymbol{\kappa}mn} w_{\boldsymbol{\kappa}} \left| g_{mn}^{\nu}(\boldsymbol{\kappa}, \boldsymbol{\kappa}', \boldsymbol{q}) \right|^{2} (f_{\boldsymbol{\kappa}m} - f_{\boldsymbol{\kappa}+\boldsymbol{q}n}) \\
\times \Delta \left(\boldsymbol{\kappa} + \boldsymbol{q} - \boldsymbol{\kappa}' \right) \delta \left(\epsilon_{\boldsymbol{k}m} + \hbar \omega_{\boldsymbol{q}\nu} - \epsilon_{\boldsymbol{\kappa}'n} \right),$$
(2.67)

where w_{κ} is the weight of the κ -point normalized to two for non-magnetic calculations. The phonon-phonon and phonon-electron relaxation times can be combined using the Matthiessen rule to obtain an expression for the effective relaxation time, $\tau_{q\nu}^{eff}$, of phonons
(to be used in Eqn. 2.50 for predicting thermal conductivity due to phonons in metals) as

$$\frac{1}{\tau_{q\nu}^{eff}} = \frac{1}{\tau_{q\nu}^{pp}} + \frac{1}{\tau_{q\nu}^{ep}}.$$
(2.68)

2.2.3 Calculation of Electron-Phonon Coupling Coefficients

The calculation of electron-phonon scattering rates require information about electronphonon coupling matrix elements. While one can obtain these coupling coefficients directly from DFT and DFPT theory, the computational cost of calculating these on fine enough electron and phonon wavevector grids is large. In this work, therefore, we use maximally localized Wannier functions (MLWFs) to interpolate the DFT and DFPT calculated electron-phonon coupling coefficients from coarse grids to fine grids. The details related to the interpolation procedure can be found in Ref. [55]

Phonon Transport in Periodic Silicon Nanoporous Films with Feature Sizes Greater than 100 nm

As the dimensions of electronic, optoelectronic, and energy conversion devices are reduced, the thermal conductivities of the device components (e.g., thin films and nanowires) are also reduced [7, 46, 67, 68, 69, 70, 71, 72, 73, 74, 75]. The large electrical power densities in such devices cause Joule heating and the reduced thermal conductivities can lead to high operating temperatures, sub-optimal performance, and poor reliability. Predicting the thermal conductivity reduction in nanostructures is thus a critical part of developing next-generation thermal management strategies.

We focus here on semiconducting and insulating nanostructures, where phonons (quantized lattice vibrations) dominate thermal transport [76]. As a nanostructure gets smaller, its thermal conductivity is reduced due to more frequent scattering between phonons and the system boundaries [7, 46, 67, 68, 69, 70, 71, 72, 73, 74, 75]. For very small systems (e.g., silicon films thinner than 20 nm), changes in the phonon density of states also affect thermal transport [7, 68, 73]. Our interest here is nanostructures large enough that the phonon density of states is bulk-like.

The thermal conductivities of solid silicon thin films and silicon thin films with periodic pore arrays are predicted using a Monte Carlo technique to include phonon-boundary scattering and the Boltzmann transport equation. The bulk phonon properties required as input are obtained from harmonic and anharmonic lattice dynamics calculations. The



Figure 3.1: Thin film with a square array of through cylindrical pores.

force constants required for the lattice dynamics calculations are obtained from forces calculated using density functional theory. For both solid and porous films, the in-plane thermal conductivity predictions capture the magnitudes and trends of previous experimental measurements. Because the prediction methodology treats the phonons as particles with bulk properties, the results indicate that coherent phonon modes associated with the secondary periodicity of the pores do not contribute to thermal transport in porous films with feature sizes greater than 100 nm.

3.1 Introduction

Experimental studies on silicon thin films with a periodic arrangement of unfilled cylindrical pores (i.e., nanoporous films, see Fig. 3.1) measured thermal conductivities two orders of magnitude smaller than bulk silicon [46, 73, 77]. Hopkins et al. studied four 500 nm thick films with a square array of pores with diameters and pitches (pore center-to-center distance) between 300 and 800 nm, finding cross-plane (i.e., parallel to the pore axis) thermal conductivities between 5 and 7 W/m-K at a temperature of 300 K [46]. Yu et al.

studied a 22 nm thick film with a square array of pores with diameter of 11 nm and pitch of 34 nm, finding an in-plane (i.e., normal to the pore axis) thermal conductivity of 2 W/m-K that did not vary significantly between temperatures of 150 and 280 K [73]. Tang et al. studied a 100 nm thick film with a triangular array of pores with diameter of 32 nm and pitch of 55 nm, finding an in-plane thermal conductivity of 2 W/m-K at a temperature of 300 K [77]. Such low thermal conductivities, combined with predictions of bulk-like electrical transport properties [78], suggest the potential application of nanoporous films in thermoelectric energy conversion.

The low thermal conductivities of these silicon nanoporous films, in which phonons dominate thermal transport, cannot be predicted by considering thermal conductivity reduction due to material removal and the presence of phonon-boundary scattering [46, 79]. Based on the modeling work of Hao et al. [80], Tang et al. suggest a "necking effect," whereby phonons with mean free paths longer than the distance between two pores (i.e., the neck, equal to the pitch minus the diameter) become "trapped" behind pores. Yu et al. and Hopkins et al. suggest that the low thermal conductivities are a result of "coherent phonon effects," whereby the phonon band structure and scattering are modified by the secondary periodicity introduced by the pores.

More recently, El-Kady et al. [45] reported in-plane thermal conductivity measurements for nanoporous films similar to those studied by Hopkins et al. They found thermal conductivities between 33 and 80 W/m-K, an order of magnitude larger than the cross-plane results reported by Hopkins et al. For a 500 nm thick solid silicon film, modeling work suggests that the in-plane thermal conductivity will only be 15% larger than the cross plane value [75]. Furthermore, the size of the structural features and the magnitudes of the thermal conductivities measured by El-Kady et al. are similar to previous experimental work on solid films and nanowires [67, 69, 81]. Phonon particle-based models that use bulk properties are able to capture the experimental thermal conductivity trends for these films and nanowires by including phonon-boundary scattering [67, 69, 75, 82].

In this work, we will predict the thermal conductivity of solid silicon films and silicon nanoporous films with feature sizes greater than 100 nm using the phonon free path sampling technique [83]. This technique treats the phonons as particles with bulk properties that are modified by phonon-boundary scattering. As such, any effects of the secondary periodicity on the phonon transport, other than the geometry for the boundary scattering, are excluded. Thus, we can determine if coherent effects play a role in phonon transport in the nanoporous films studied by Hopkins et al. and El-Kady et al. Furthermore, this technique includes Bose-Einstein phonon statistics (i.e., quantum effects), considers the full phonon spectrum, is computationally fast, and can be applied to three-dimensional structures with arbitrary geometry. To ensure an accurate comparison with the experimental measurements, phonon properties obtained from forces calculated using density functional theory (DFT) [33, 60] are used as input, removing the need for empirical force fields or fitting to experimental data.

3.2 Previous Modeling Work

Yang et al. [84], Prasher [85], and Romano et al. [86] solved the Boltzmann transport equation (BTE) under the gray approximation (i.e., frequency-independent phonon properties) for periodic nanoporous films with a square array of cylindrical pores. They all considered the scattering of phonons with other phonons and pore boundaries and found that the inplane thermal conductivity depends not only on porosity, but also on pore size and pitch. Hao et al. used Monte Carlo simulations to study in-plane phonon transport in periodic silicon nanoporous films with a square array of square pores, including frequency-dependent phonon properties [80]. Including this frequency dependence is critical, since recent modeling work has demonstrated the importance of including mode-dependent phonon properties in calculating the thermal conductivity of bulk and nanostructured materials (e.g., the phonon mean free paths in bulk silicon cover five orders of magnitude) [26, 33, 87]. In these numerical and analytical models, the phonon modes that emerge due to the pore periodicity were not included. Moreover, these studies considered two-dimensional geometries and therefore cannot account for phonon scattering from the top and bottom film boundaries or allow for examination of cross-plane thermal transport.

He et al. [88] used molecular dynamics (MD) simulations and lattice dynamics calculations to predict the in-plane thermal conductivity of periodic silicon nanoporous films with diameters and pitches less than 10 nm. By separating the vibrational modes into phonons and diffusons (i.e., non-propagating, diffusive entities) and including pore surface roughness, they found thermal conductivities as much as 70 times smaller than bulk. For the same geometry but with smaller diameters and pitches, Lee et al. used MD simulations to predict thermal conductivities more than 100 times smaller than bulk [89]. Molecular dynamic simulations have the advantage of naturally capturing the wave nature of phonons, but are limited to system sizes less than 100 nm due to computational cost. They therefore cannot be used to model the films of Yu et al., Tang et al., Hopkins et al., or El-Kady et al. Furthermore, MD simulations cannot incorporate Bose-Einstein statistics in the phonon populations.

Dechaumphai and Chen define "coherent" phonons to be those with mean free paths larger than the neck [79]. These phonons are modeled using the in-plane dispersion relation for the periodic pores. They scatter with other phonons, but not from the pores. Phonons with mean free paths shorter than the neck are termed "incoherent," treated as bulk-like, and scatter with other phonons and the pores. Dechaumphai and Chen predict that their coherent phonons will contribute $\sim 1 \text{ W/m-K}$ (i.e., $\sim 50\%$) to the in-plane thermal conductivity of the nanoporous films of Yu et al. and Tang et al., but only 0.01 W/m-K (i.e., less than 0.1 %) to the structures of Hopkins et al. and El-Kady et al. Using a similar approach for the phonon dispersion, Reinke et al. [90] modeled the nanoporous films of El-Kady et al., but do not differentiate in how "coherent" and "incoherent" phonons scatter. They find similar trends compared to the experimental data in thermal conductivity versus neck size and pore pitch, but their predicted magnitudes are ~ 15 W/m-K too high. Hopkins et al. [46] find reasonable agreement with their cross-plane experimental measurements using a similar approach as Reinke et al., with the in-plane phonon dispersion applied to the cross-plane transport.

3.3 Methodology

The phonon free path sampling approach [83] is used to study the phonon thermal transport here. Turney et al. suggest that using bulk phonon properties to model suspended silicon films is valid for limiting dimensions (i.e., film thicknesses) greater than 20 nm [7]. In a nanoporous film, the limiting dimension is the lesser of the film thickness and the neck. As such, the free path sampling technique can be applied to the nanoporous films studied by Hopkins et al. and El-Kady et al., which have limiting dimensions of at least 200 nm. The free sampling technique cannot be applied to the nanoporous films of Yu et al. (limiting dimension 22 nm) or Tang et al. (limiting dimension 23 nm).

Diffuse boundaries are assumed for the phonon-boundary scattering. Modeling work by Duda et al. suggests that all phonon-boundary scattering will be diffuse at a temperature of 300 K [91]. The scattering of phonons by point defects is ignored. Previous experimental measurements on bulk silicon indicate that the effect of phonon-isotope scattering is small compared to phonon-phonon scattering at a temperature of 300 K [92]. The doping concentration of the experimental samples that we compare against is 10^{17} cm⁻³ or lower. Previous experimental measurements indicate that dopant atoms at these concentrations do not significantly affect the thermal conductivity of silicon at a temperature of 300 K [93, 94].

Based on the two-atom (i.e., primitive) unit cell description, harmonic and anharmonic lattice dynamics calculations [23, 33, 95, 96, 97] are performed to calculate the bulk silicon phonon frequencies and mean free paths for an $18 \times 18 \times 18$ grid of uniformly spaced wave vectors centered at the origin of the Brillouin zone. 34, 992 total phonon modes are considered, which includes acoustic and optical branches. The second- and third-order force constants are those obtained by Esfarjani et al. from forces calculated using DFT and a numerical approach that enforces the required symmetries [33, 60]. Bose-Einstein statistics at a temperature of 300 K are used to incorporate quantum effects.

3.4 Thermal Conductivity Predictions

3.4.1 Bulk Silicon

Using Eqn. 2.50, the bulk thermal conductivity of silicon is predicted to be 132 W/m-K, while the experimental value for naturally occurring silicon is 144 W/m-K [92]. Due to the finite resolution of the Brillouin zone, the contributions of phonons in the volume at the Gamma-point are not included in the calculation. Following the approach described by Esfarjani et al. [33], we estimate the contribution of these phonons to be 10 W/m-K. Based on the work of Broido et al. [32], a further 10% increase in the thermal conductivity of silicon is expected if one solves the BTE iteratively without making the relaxation time approximation, making the predicted bulk thermal conductivity 156 W/m-K. This value is higher than the experimental measurement because of the complete absence of point defects, which will be present in any real samples, and uncertainty associated with the

DFT calculations. We note that for this study (silicon nanoporous films), we obtained bulk phonon properties from Esfarjani et al. [33]

3.4.2 Solid Thin Films

To validate the free path sampling technique and the use of bulk phonon properties for modeling nanostructures, we first consider solid silicon thin films that have finite thickness in one direction and are infinite in the other two directions. The predicted thermal conductivity variation with film thickness, L, for heat flow in the in-plane direction obtained using the free path sampling technique and the Matthiessen rule are shown in Fig. 3.2 with available experimental data [6, 45, 67, 73, 77, 81, 98, 99]. The experimental data include the solid films of Yu et al., Tang et al., and El-Kady et al. The thermal conductivity predictions from the Matthiessen rule are obtained using

$$\overline{\Lambda_{pb,i}} = \frac{L}{2\cos\theta_i},\tag{3.1}$$

where θ_i is the angle between the cross-plane direction and the group velocity vector [75].

Also plotted in Fig. 3.2 are the predictions from a closed-form analytical model [101]. This model is based on the Debye approximation for the phonon dispersion and ignores the contribution of optical phonons to thermal conductivity. The lattice constant, a sound speed, and the bulk thermal conductivity are the required inputs.

The thermal conductivity increases with increasing film thickness due to a reduction in phonon-boundary scattering. The free path sampling technique, the Matthiessen rule approach, and the analytical model capture the experimental magnitudes and trend well for thicknesses greater than 50 nm. This transition point is higher than the 20 nm suggested by Turney et al. [7], which was based on the density of states and in-plane thermal conductivity of suspended silicon thin films modeled using the Stillinger-Weber potential. The finite



Figure 3.2: In-plane thermal conductivity of solid silicon thin films vs. film thickness at a temperature of 300 K from the free path sampling technique, the Matthiessen rule, an analytical model, and experiments [6, 45, 67, 73, 77, 81, 98, 99]. For the analytical model, we take the sound speed to be 6733 m/s and the lattice constant to be 5.43 A [100]. The bulk thermal conductivity in the analytical model is set to 132 W/m-K to be consistent with the value found in Section 3.4.1.

simulation size and relaxation time approximation errors are smaller in thin films compared to bulk due to the scattering of long mean free path phonons from film boundaries, which reduces their contribution to the thermal conductivity.

3.4.3 Periodic Nanoporous Films: In-Plane Direction

The periodic nanoporous films of interest have three characteristic length scales: pore diameter, d, pore separation, a, and film thickness, t, as shown in Fig. 3.1. It is not obvious what length scale is appropriate in the Matthiessen rule for these structures. We therefore use the free path sampling technique to predict their thermal conductivities. To allow for comparison with the experimental data, the predicted thermal conductivities must be scaled by a volume correction factor to account for the porosity, ϕ . For the in-plane direction, the correction factor is calculated using the COMSOL Multiphysics[®] simulation package to solve the heat conduction equation with the finite element method (FEM). Our FEM calculations agree with the correction factor, $(1 - \phi)/(1 + 2\phi/3)$ [103], overpredicts the FEM calculations with a deviation that increases with increasing porosity. For a porosity of 0.4, the maximum considered here, the deviation is 10%. The volume correction factor is $1 - \phi$ for the cross-plane direction.

The thermal conductivity variation with porosity for in-plane heat flow in 500 nm thick nanoporous films predicted using the free path sampling technique is shown in Fig. 3.3(a). The pore separations (400 to 900 nm) and diameters (200 to 500 nm) are chosen to match the nanoporous films studied by El-Kady et al. The experimental thermal conductivity measurements of El Kady et al. are also plotted in Fig. 3.3(a). Both the experimental measurements and modeling predictions show a general decrease in thermal conductivity with increasing porosity because of more phonon-pore scattering and a reduced solid fraction.



Figure 3.3: Thermal conductivity variation of periodic nanoporous silicon films vs. porosity from experimental measurements and modeling predictions for (a) in-plane heat flow, and (b) cross-plane heat flow.

The maximum error between the experimental and the predicted thermal conductivities is 6% (corresponding to the solid film, where $\phi = 0$).

At a porosity of around 0.15 in Fig. 3.3(a), measurement and modeling results show an increase in thermal conductivity with increasing porosity. To understand this result, we plot thermal conductivity as a function of pore diameter for a fixed porosity of 0.15 in the inset to Fig. 3.3(a). For this porosity, a thermal conductivity variation of up to 9% can be obtained by varying the pore diameter across the range of diameters considered. This finding is similar to what Yang et al. observed [84].

The predicted thermal conductivities are based on the bulk phonon dispersion and do not take into account changes to the phonon band structure due to the pore periodicity. Based on the good agreement between the measured and predicted thermal conductivities, we do not believe that coherent phonon effects affect thermal transport in the nanoporous films of El Kady et al.

We also predicted the in-plane thermal conductivity of the nanoporous film studied by Song and Chen [98], which had thickness 4.67 μ m, pore diameter 1.9 μ m, and pore pitch 4 μ m, to be 63 W/m-K. This value is higher than the experimental measurement of 44 W/m-K, but the difference is within the discrepancies between the experimental data and modeling predictions for the solid films shown in Fig. 3.2.

In addition to the structure described earlier, Tang et al. also measured the thermal conductivities of 100 nm thick nanoporous films with porosity of 0.35 and average pitch/-neck of 350/152 nm and 140/59 nm. Inspection of Figs. 2(a) and 2(b) in their paper shows large variability in the pore size, shape, and spacing. Furthermore, the second of these films has a limiting dimension of 59 nm, which is close to where the solid film experimental data deviates from the modeling predictions (see our Fig. 3.2). As such, we do not believe that the free path sampling technique, which assumes a perfect periodicity of the pores, is

appropriate for predicting the thermal conductivity of these two structures.

3.4.4 Periodic Nanoporous Films: Cross-Plane Direction

Measured [46] and predicted cross-plane thermal conductivities are plotted in Fig. 3.3(b). As with the in-plane heat flow, the modeling results show a decrease in thermal conductivity with increasing porosity. The experimental results, however, are an order of magnitude smaller than the modeling predictions and show no significant porosity dependence. From calculations on a large number of films, we find that the predicted ratio of the in-plane to cross plane thermal conductivities varies linearly with porosity from 1.2 ($\phi = 0.07$) to 0.82 ($\phi = 0.38$). Moreover, the predicted solid film thermal conductivity (plotted at $\phi = 0$) is almost twice as high as that measured in the experiments.

3.5 Thermal Conductivity Accumulation

Recent experimental measurements suggest the possibility of resolving the contribution of phonons with different mean free paths to thermal conductivity [16, 17, 104, 105, 106]. This information could be used to formulate strategies for reducing thermal conductivity by selectively scattering specific phonon modes using defects, grain boundaries, and surfaces. The thermal conductivity accumulation functions [107, 108] for bulk silicon and solid silicon films with thicknesses of 50, 100, 500, and 1000 nm (in-plane direction) are plotted in Figs. 3.4(a) and 3.4(b). The vertical coordinate of any point on the accumulation function represents the thermal conductivity that comes from phonons with mean free path less than the horizontal coordinate of that point. In Fig. 3.4(a), the bulk mean free path is used to plot the accumulation functions, while the mean free paths in the structure of interest are used in Fig. 3.4(b).

By plotting against the bulk mean free path in Fig. 3.4(a), we see where phonons



Figure 3.4: Thermal conductivity accumulation functions for (a), (b) bulk silicon and solid silicon films, and (c) bulk silicon, a 500 nm thick solid film, and two 500 nm thick periodic nanoporous films with pore pitch of 500 nm and porosities of 0.1 and 0.5. The bulk mean free paths are used to generate the curves in (a) while the mean free paths in the structure of interest are used to generate the curves in (b) and (c). All film accumulation functions are for the in-plane direction.

start to be affected by boundary scattering. For all films, deviations in the accumulation functions from bulk occur at bulk mean free paths smaller than the film thicknesses (e.g., around 100 nm for the 500 nm thick film). This result makes sense because phonons can originate anywhere in the film. It is also important to note that most phonons do not travel purely in the cross-plane direction. As such, depending on how its group velocity vector is oriented compared to the film, each phonon mode will start to be affected at a different film thickness.

When plotted vs. the film mean free path in Fig. 3.4(b), the accumulation functions shift to the left as there are more phonon modes with smaller mean free paths. For the 50 and 100 nm films, the accumulation functions rise more quickly than the bulk curve starting at a mean free path of 20 nm. The film accumulation functions must then cross the bulk curve (at 70 and 95 nm) as their total thermal conductivities are smaller. For the 500 nm film, the mean free path reductions cause the film accumulation function to follow the bulk curve up to a mean free path of 400 nm. It then rises above the bulk curve, crossing back over at 500 nm. For the 1000 nm film, the film accumulation function rises above the bulk curve at 600 nm, then crosses it at 1275 nm. It is interesting to note that the cross-overs occur close to the film thicknesses.

As discussed in Section 3.4.2, the length scale used in the Matthiessen rule for a solid film is related to its thickness [Eqn. 3.1]. The results shown in Fig. 3.4(b) suggest that this length scale can be estimated from the accumulation function from the cross-over mean free path. Extending this idea, we can extract equivalent film thicknesses, L_{eq} , for nanoporous films from their accumulation functions. The accumulation functions for two 500 nm thick nanoporous silicon films with a pore pitch of 500 nm and porosities of 0.1 and 0.5 are plotted in Fig. 3.4(c), along with the bulk curve and that for a solid film of the same thickness. The accumulation functions for the nanoporous films follow the bulk and

ϕ	L_{eq}	k (Matthiessen Rule w/L _{eq})	k(Free Path Sampling)
	(nm)	(W/m-K)	(W/m-K)
0.1	405	91	84
0.2	365	89	78
0.3	275	85	72
0.4	270	85	67
0.5	225	82	62

Table 3.1: Equivalent film thickness extracted from thermal conductivity accumulation function [see Fig. 3.4(c)] and in-plane thermal conductivity predicted using the Matthiessen rule and Eqn. 3.1 for nanoporous films. The pore pitch and film thickness are 500 nm for all structures.

solid film curves closely up to a certain point, after which they level off.

The equivalent film thickness for the two nanoporous films included in Fig. 3.4(c) and three more with different porosities are provided in Table 3.1. The thermal conductivities predicted using these length scales in Eqn. 3.1 with the Matthiessen rule are also provided in Table 3.1 along with those predicted from the free path sampling technique. We note that using the minimum feature size (i.e., the smaller of the pore neck and the film thickness) as the length scale in the Matthiessen rule [90] leads to an isotropic thermal conductivity and so we do not pursue that direction. The relative error between the thermal conductivities predicted from free path sampling and the Matthiessen rule using the equivalent film thickness increases as the porosity increases, reaching a maximum value of 32%. This result reinforces the need to use the free path sampling technique for structures with multiple feature sizes.

3.6 Discussion

The term "coherent phonon mode" has been used to describe vibrational modes that emerge when a secondary periodicity is added to a system (e.g., the layers in a superlattice or the pores in a periodic nanoporous film) [46, 73, 79, 90, 109, 110, 111, 112]. It has been argued that these phonons affect thermal transport in periodic nanoporous films by modifying the dispersion curves and/or by changing the nature of the phonon scattering [46, 73, 79, 90].

Coherence implies the interference of waves, either constructively or destructively. In a periodic nanoporous film, coherent phonon modes will emerge if (i) the phonons scatter specularly off the pores, maintaining information about their phase, and (ii) these phonons do not scatter with other phonons between the pore collisions, allowing for interference to develop. Specular scattering requires that the scale of the surface roughness be much smaller than the phonon wavelengths that contribute to thermal transport. An absence of scattering is a good approximation for light (photons) and a reasonable approximation for phonons at acoustic frequencies (i.e., kHz to MHz). For thermal phonons, which have THz frequencies, very low phonon-phonon scattering rates require a lack of scattering channels. Such a condition may be found at low temperatures, in materials with a large phonon band gap or reduced dimensionality, or in nanostructures with feature sizes much smaller than the bulk mean free paths.

As discussed in Section 3.3, we expect that phonon-pore scattering at a temperature of 300 K will be primarily diffuse. Furthermore, as shown in Fig. 3.4(a), the majority of the bulk mean free paths in silicon at a temperature of 300 K are comparable to or smaller than the feature sizes of the nanoporous films studied by El Kady et al. and Hopkins et al. Based on these two arguments, it is unlikely that coherent phonon effects are important in those structures. This statement is supported by the agreement of the predictions of the

free path sampling technique (which considers only bulk-like phonons and their interactions with each other and system boundaries) with the in-plane experimental measurements, as shown in Fig. 3.3(a).

That being said, it is worthwhile to discuss the conditions under which coherent phonon effects may emerge and play a role in thermal transport. Generally speaking, for a secondary periodicity to affect thermal transport, it should be on a length scale comparable to wavelengths of the phonons that contribute to thermal transport. In bulk silicon at room temperature, the phonons that dominate thermal transport have wavelengths of 1-5 nm [33], two orders of magnitude smaller than the feature sizes of the films studied by Hopkins et al. and El-Kady et al. Luckyanova et al. recently reported thermal conductivity measurements on multi-layer GaAs/AlAs structures with layer thickness 12 nm that indicate the increasing importance of phonons related to the secondary periodicity as temperature decreases from 150 K to 30 K [112].

In addition to a feature size that aligns with the dominant phonon wavelengths, there is a second important criterion for the emergence of coherent phonon effects: the quality of the periodicity. Consider the Si/Ge superlattices studied by Landry and McGaughey using MD simulations, which have period lengths between 3 and 12 nm [27]. They predicted the period-length dependence of the thermal conductivity of superlattices with perfect interfaces and with interfaces where 12% of the atoms were switched in the layers next to the interfaces. The superlattices with perfect interfaces show an initially decreasing thermal conductivity with increasing period length that levels off, a trend consistent with the secondary periodicity affecting thermal transport [113, 114, 115]. The results are completely different for the superlattices with interfacial species mixing. At the smallest period length, the thermal conductivity is almost an order of magnitude smaller than that for the perfect interfaces and increases with increasing period length. This trend is related to phonon-interface scattering. As the period length increases, the interface density decreases, and thermal conductivity increases. The key observation here is that a small amount of disorder destroyed the coherent effects. When mixing is present, the phonon modes are defined within each layer, but not across the interfaces. In the majority of experimental superlattice samples (except systems such as GaAs/AlAs superlattices [112], where epitaxial layers can be grown) such disorder will always be present. It thus seems unlikely that coherent effects can explain experimental superlattice thermal conductivity measurements, particularly at room temperature.

A similar argument can be made when considering the nanoporous films of Yu et al. and Tang et al. which have pore pitches of 34 and 55 nm. Their structures show a strong variability in pore size, shape, and spacing. It therefore seems unlikely that coherent phonon effects will emerge. Only at very low temperatures, where the dominant phonon wavelengths become comparable to the pore pitch might such effects be relevant.

How then to interpret the very low thermal conductivity measurements of Yu et al. and Tang et al.? As suggested by the modeling work of He et al. [88], the thermal conductivity reduction may be a result of the emergence of non-propagating vibrational modes in confined geometries. Such a mechanism could be present in rough silicon nanowires, which also have very low thermal conductivities [70, 116].

3.7 Summary

We used bulk silicon phonon properties obtained from forces calculated from DFT and the free path sampling technique to predict the thermal conductivities of solid and periodic nanoporous films. Application of the Matthiessen rule to the nanoporous films is not possible due to their multiple feature sizes. The free path sampling technique treats the phonons as particles with bulk properties that scatter with the pore boundaries. No effects of the secondary periodicity are included other than the geometry. Our in-plane thermal conductivity predictions are in good agreement with the experimental measurements of El-Kady et al. for periodic nanoporous films with feature sizes greater than 100 nm. This result indicates that coherent phonon effects in these films do not affect thermal transport. At this time, we are not able to explain the cross-plane thermal conductivities measured by Hopkins et al. on films similar to those studied by El-Kady et al.

Thermal conductivity of compound semiconductors: Interplay of mass density and acoustic-optical phonon frequency gap

The thermal conductivities of model compound semiconductors where the two species differ only in mass are predicted using lattice dynamics calculations and the Boltzmann transport equation. The thermal conductivity varies non-monotonically with mass ratio, with a maximum value that is four times higher than that of a monatomic semiconductor of the same density. The very high thermal conductivities are attributed to a reduction in the scattering of optical phonons when the acoustic-optical frequency gap in the phonon dispersion approaches the maximum acoustic phonon frequency. The model system predictions compare well to predictions for real compound semiconductors under appropriate scaling, suggesting a universal behavior and a strategy for efficient screening of materials for high thermal conductivity.

4.1 Introduction

The parameters that affect phonon transport include the lattice structure, the atomic masses, anharmonicity, and defects (e.g., isotopes, dopants, dislocations, and interfaces) [57, 94, 117, 118, 119, 120, 121]. For application in thermoelectric energy conversion,

many previous studies have focused on how to reduce thermal conductivity [122, 123, 124]. Phonon scattering increases with increasing anharmonicity and defect concentration, resulting in lower thermal conductivity. In single species (i.e., monatomic) materials, larger atomic mass reduces the phonon group velocities and thus thermal conductivity.

To identify the features of high thermal conductivity semiconductors, Slack studied diamond, boron nitride, boron phosphide, silicon carbide, and aluminum nitride [47]. He concluded that high thermal conductivity is correlated to strong atomic interactions, low anharmonicity, simple crystal structure, and low average atomic mass. Based on these criteria, he predicted a monotonic variation of thermal conductivity with mass density and estimated the room temperature thermal conductivity of boron arsenide (BAs) to be 210 W/m-K. Recently, Lindsay et al. [125] and Broido et al. [126] studied phonon transport in cubic boron compound semiconductors using first principles calculations and found a non-monotonic thermal conductivity variation with mass density. At a temperature of 300 K, their highest predicted thermal conductivity of 3170 W/m-K was for isotopically-pure BAs, which compares to that of isotopically-pure diamond [127, 128]. They attributed the ultrahigh thermal conductivity of BAs to a large acoustic-optical (a-o) frequency gap in the phonon dispersion, acoustic bunching, strong covalent bonding, and low anharmonicity. The relative importance of each of these effects in determining the thermal conductivity, however, is unknown. A non-monotonic variation of thermal conductivity with mass ratio was also observed by Steigmeier and Kudman for a subset of group III-V semiconductors based on experimental measurements [129].

Our objective in this work is to study the competing effects of the mass density and the phonon dispersion (i.e., a-o gap, acoustic bunching, and acoustic and optical widths) on the thermal conductivity of compound semiconductors. The rest of the chapter is organized as follows. In Section 4.2, the model system is presented and the lattice dynamics- and

Boltzmann transport equation (BTE)-based methodology for predicting phonon properties and thermal conductivity is described. The thermal conductivity predictions are presented and interpreted in Section 4.3, where we argue that an a-o gap that is comparable to or larger than the maximum acoustic phonon frequency is required to obtain high thermal conductivities in compound semiconductors. The model system predictions are compared to available data for a range of compound semiconductors in Section 4.4.

4.2 Methodology

We use a defect-free zinc-blende lattice where the mass of one atom in the primitive unit cell (m_1) is fixed at that of silicon while the second atom's mass (m_2) is varied from $0.1m_1$ to $10m_1$. The mass ratio is defined as m_2/m_1 and values of $0.1, 0.2, 0.25, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 are considered. To isolate the effects of the phonon dispersion and mass density on thermal conductivity, we use classical (i.e., Boltzmann) statistics at a temperature of 500 K. Doing so compared to quantum statistics removes the frequency dependence of the specific heat from the thermal conductivity prediction. The lattice positions in the zinc-blende structure are equivalent. For classical statistics, the thermal conductivity for a system with mass ratio of <math>m_2/m_1$ is proportional to that of a system with ratio m_1/m_2 through the scaling factor of $[(m_1 + m_2)/(m_1 + 1/m_2)]^{-1/2}$ [130]. The Stillinger-Weber potential as parameterized for silicon [131] is used to model all atomic interactions so that we can focus on the effects of the mass density and the dispersion.

The calculation of phonon scattering rates by considering phonon-phonon scattering processes must satisfy the delta functions (i.e., the selection rules) in Eqn. 2.28 (energy conservation and lattice translational invariance). In compound semiconductors, for acoustic (a) phonons, a-a-a, a-a-o, and a-o-o processes are generally possible, where 'o' denotes an

optical phonon. For optical phonons, because of their high frequencies and narrow width, o-o-o processes typically cannot satisfy energy conservation. Optical phonons, therefore, generally only scatter through a-o-o and a-a-o processes (i.e., they require an acoustic phonon) [125]. We note that all phonon modes are active in the classical systems we are studying. As such, all phonon-phonon scattering processes that satisfy the selection rules can occur.

4.2.1 Phonon wave vector grid density dependence of thermal conductivity

We predict thermal conductivity using a phonon wave-vector grid with an equal number of uniformly-spaced grid points, N_o , in each direction (i.e., $N = N_o^3$). Of the systems considered here, we find the maximum thermal conductivity at a mass ratio of 0.25 [132]. The thermal conductivity for this system is plotted in Fig. 4.1(a) vs N_o . The green squares, purple crosses, and orange circles represent the acoustic phonon contribution, the optical phonon contribution, and the total thermal conductivity. The acoustic phonon contribution converges after $N_o = 32$. Because of the low scattering rate of optical phonons at this mass ratio (to be discussed in Section 4.3), their contribution continues to decrease even at $N_o = 64$. To resolve this issue, we obtain the bulk thermal conductivity by plotting 1/k(the inverse of the total thermal conductivity) vs. $1/N_o$ in Fig. 4.1(b) and extrapolating a linear fit to the $N_o \rightarrow \infty$ limit. Systems with $N_o = (24, 28, 32, 36, 40, 44)$ [open circles in Fig. 4.1(b)] are used for fitting and extrapolation. The solid circles $[N_o = (48, 52, 56, 56, 56)]$ (60, 64) are used to assess the quality of the fit. The extrapolation technique works well and all non-fitted points lie on the fitted line. We note that 1/k increases with decreasing $1/N_o$. This behavior is opposite to that observed in other studies, where 1/k decreases with decreasing $1/N_o$ [23, 33]. In those cases, the 1/k vs $1/N_o$ fitting and extrapolation



Figure 4.1: For the system with a mass ratio of 0.25: (a) Variation of total, acoustic, and optical thermal conductivities with phonon wave-vector grid density. The acoustic contribution converges after $N_o = 32$. (b) 1/k versus $1/N_o$ and linear fit for extrapolation to the bulk thermal conductivity. The line is only fitted to the six rightmost points (open circles).

is used to include the contribution of acoustic phonon modes close to the center of the Brillioun zone. We observe this effect in our systems typically for $N_o < 22$ and those data are not used for fitting.

We employ $N_o = 44$ to specify the acoustic phonon thermal conductivity for all mass ratios. For cases where the total thermal conductivity is not converged at $N_o = 44$ (mass ratios of 0.1 to 0.3 and 4 to 10), $N_o = (24, 28, 32, 36, 40, 44)$ systems are used to perform the 1/k vs $1/N_o$ fitting and extrapolation. The optical contribution is then obtained by subtracting the acoustic phonon contribution at $N_o = 44$ from the extrapolated total thermal conductivity.

4.3 Results

4.3.1 Dispersion

We first consider the phonon dispersion to study the effect of mass ratio on the a-o gap, bunching, and acoustic and optical widths. For the analysis to follow, we define: (i) the a-o gap as the difference between the maximum acoustic frequency and the minimum optical frequency, (ii) the acoustic (optical) width as the difference between the maximum and minimum acoustic (optical) frequencies, and (iii) the acoustic bunching as the maximum difference between the maximum frequencies of the three acoustic phonon polarizations [125]. The maximum and minimum frequencies in these definitions are based on the entire first Brillioun zone.

In Fig. 5.2(a), the dispersion in the [100] direction is plotted for mass ratios less than 1. The optical phonon frequencies increase with a reduction in the mass ratio, while the acoustic phonons are largely unaffected. As a result, the a-o gap increases while the acoustic width and bunching remain unchanged as mass ratio is reduced. The effect of



Figure 4.2: Effect of mass ratio on the [100] phonon dispersion for (a) $m_2/m_1 < 1$, and (b) $m_2/m_1 \ge 1$. The a-o gap, the acoustic bunching, the acoustic width, and the optical width are identified for select cases. In the analysis, these quantities are calculated based on the entire first Brillioun zone.

increasing the mass ratio beyond 1 is shown in Fig. 5.2(b) for the [100] direction. The a-o gap increases and the acoustic width and bunching decrease with an increase in the mass ratio. For the monatomic system (mass ratio = 1), the acoustic and optical branches intersect at the zone boundary (i.e., the a-o gap is zero). The optical width is a maximum for the monatomic system and decreases with increasing and decreasing mass ratio.

4.3.2 Thermal conductivity

The total and acoustic thermal conductivities are plotted in Fig. 4.3(a) versus the mass ratio. Also plotted is the total thermal conductivity of a monatomic system with the same mass density as the corresponding compound semiconductor. For the monatomic system, the thermal conductivity scales as $[(m_1 + m_2)]^{-1/2}$ and is always lower than that of the corresponding compound semiconductor.

For the compound semiconductors, the minimum total thermal conductivity occurs at a mass ratio of 1, where it equals that of the monatomic system. Moving away from the mass ratio of 1, the total thermal conductivity initially increases with increasing mass ratio, reaches a peak at a mass ratio of 4, then decreases with further increase in the mass ratio. As expected, due to the mass ratio scaling, the trend is similar for mass ratios smaller than 1, where the peak in total thermal conductivity occurs at a mass ratio of 0.25. This behavior of total thermal conductivity in compound semiconductors is in contrast to that in monatomic semiconductors, where thermal conductivity monotonically decreases with increasing mass ratio.

The acoustic thermal conductivity is 93% of the total thermal conductivity at a mass ratio of 1. On increasing the mass ratio, the acoustic thermal conductivity follows the total thermal conductivity until the mass ratio reaches 3. The contribution of optical phonons to the total thermal conductivity increases from 4% for a mass ratio of 3 to 34% for mass ratio



Figure 4.3: (a) Total and acoustic thermal conductivity variation with mass ratio, and (b) a-o gap, acoustic width, and optical width variation with mass ratio. In (a), the purple line corresponds to the thermal conductivity of a monatomic semiconductor that has the same mass density as the corresponding compound semiconductor. The dashed vertical lines represent where the a-o gap and the acoustic width are equal.

of 4. The acoustic thermal conductivity thus deviates from the total thermal conductivity beyond a mass ratio of 4, decreasing with further increase in the mass ratio. Between mass ratios of 4 and 10, the acoustic thermal conductivity decreases from 487 to 333 W/m-K (i.e., by 32%) which is comparable to the decrease in the thermal conductivity of the monatomic semiconductor in this regime (33%). This decrease in thermal conductivity is mainly due to the reduction in phonon group velocities with an increase in the mass density. For mass ratios less than 1, the acoustic thermal conductivity increases with decreasing mass ratio, but deviates from the total thermal conductivity for mass ratios below 0.4, where the optical phonon contribution strongly increases.

4.3.3 Role of a-o gap

To understand the origin of the peaks in the total thermal conductivity and the large contribution of optical phonons for certain mass ratios, we plot the variation of the a-o gap, the acoustic width, and the optical width with mass ratio in Fig. 4.3(b). The locations of the crossings of the a-o gap and the acoustic-width curves are shown in Fig. 4.3 using vertical dashed lines.

In the neighborhood of a mass ratio of 1, the contribution of optical phonons to the total thermal conductivity of the compound semiconductor is 7%. With increasing mass ratio, the a-o gap widens, resulting in fewer a-a-o processes [36]. The acoustic and optical thermal conductivities therefore both increase with increasing mass ratio in this region. At a mass ratio of 4, the a-o gap is 86% of the acoustic-width, thereby reducing a-a-o processes significantly. The optical phonon contribution to thermal conductivity increases to 34%. Beyond this point, a-a-o processes are eliminated and optical phonons can only scatter through a-o-o processes, while acoustic phonons can still scatter through a-a-a and a-o-o processes. For mass ratios greater than 4, the mass density effect (reduction in phonon

group velocities with an increase in the mass density) dominates the thermal conductivity trend and the acoustic and optical contributions decrease with increasing mass ratio.

With a reduction in the mass ratio below 1, both the mass density and a-o gap effects favor an increase in the thermal conductivity. The acoustic thermal conductivity, therefore, increases with decreasing mass ratio. For optical phonons, the thermal conductivity increases with decreasing mass ratio up to a mass ratio of 0.25 and then decreases with further decrease in the mass ratio. In Section 4.3.4, we will argue that this decrease is a result of a reduction in the already small group velocities of optical phonons.

4.3.4 Roles of acoustic bunching, acoustic width, and optical width

To this point, we have not considered the effects of acoustic bunching, acoustic width, and optical width. Bunching affects the phonon-phonon scattering rates [125, 126] and the widths affect the group velocities. The effect of these changes on thermal conductivity is now analyzed.

In Figs. 4.4(a) and 4.4(b), the mass-ratio-dependent thermal conductivities, a-o gaps, acoustic widths, and optical widths from Figs. 4.3(a) and 4.3(b) are replotted after scaling with $[(m_1 + m_2)]^{1/2}$. This scaling factor eliminates any dependence of thermal conductivity on the mass density of the system. Also plotted in Fig. 4.3(b) is the acoustic bunching. The data are plotted versus the maximum of m_2/m_1 and m_1/m_2 and, as expected, collapse onto one curve (i.e., the scaled value for a mass ratio of m_2/m_1 is the same as that for m_1/m_2). Also, as expected, the scaled thermal conductivity of the monatomic system is constant with mass ratio. The location of the crossing of the a-o gap and the acoustic-width curves is shown in Fig. 4.4 using a vertical dashed line. The region to the left of the line has a-o gaps less than the acoustic width (Region 1) and region to the right has a-o gaps



Figure 4.4: (a) Scaled total and acoustic thermal conductivity variation with mass ratio, and (b) scaled a-o gap, acoustic bunching, acoustic width, and optical width variation with mass ratio. The scaling factor of $[(m_1 + m_2)]^{1/2}$ is used in order to eliminate the effect of mass density.

greater than the acoustic width (Region 2). In Region 2, a-a-o processes cannot satisfy the energy conservation selection rule. The a-o gap therefore has minimal effect on either acoustic or optical thermal conductivities in this region. The acoustic and optical thermal conductivities in Region 2 are, therefore, mainly affected by acoustic bunching, acoustic width, and optical width. We note that the peak total thermal conductivity occurs just before the a-o gap exceeds the acoustic width.

The scaled acoustic bunching and scaled acoustic width in Region 2 decreases by 8% and 4% between mass ratios of 5 to 10, while the scaled acoustic thermal conductivity is almost constant (decreases by 1%). This result suggests that there is a minimal effect of acoustic bunching and acoustic width on the acoustic thermal conductivity for this model system. The scaled optical thermal conductivity in Region 2 decreases by 61% for a 9% decrease in the optical width. This result suggests that the reduction in the optical phonon group velocities dominates over an increase in their lifetimes due to the reduced scattering.

4.4 Comparison with Real Compound Semiconductors

Our results suggest that thermal conductivity can increase or decrease with a change in mass density depending on the relative sizes of the a-o gap and the acoustic width. For materials that have an a-o gap less than the acoustic-width, the total, acoustic, and optical thermal conductivity trends are predominantly decided by the a-o gap, with thermal conductivity increasing with increasing a-o gap. For materials that have an a-o gap greater than the acoustic-width, the acoustic and the optical thermal conductivities decrease with increasing mass density. Recently, Mukhopadhyay and Stewart also observed an a-o gap dependent thermal conductivity for cubic BN through the application of mechanical stress



Figure 4.5: Thermal conductivity variation of real compound semiconductor (squares) and our model system (circles) versus the a-o gap to acoustic-width ratio. The thermal conductivities are scaled by $1/(\overline{m}a\theta_{\rm D}^3/T)$. Dashed lines are added to the BX and BeX series to guide the eye.
[133].

In our model system, we kept the same atomic interactions for all mass ratios. To check the applicability of our findings to real materials, we now compare our model system predictions to available data for a range of monatomic and compound semiconductors. The materials considered have a zinc-blende structure and are from group III-V (BN, BP, BAs, BSb, AlP, AlAs, AlSb, GaP, GaAs, GaSb, InP, InAs, and InSb), group II-VI (BeS, BeSe, and BeTe), and group IV (Si, Ge, SiC, GeC, and diamond). The thermal conductivities used are from first-principles calculations of defect-free isotopically-pure structures at a temperature of 300 K, as reported by Lindsay et al. [37, 125, 134] We use first-principles based thermal conductivities predictions because experimental measurements are not available for isotopically-pure compounds.

To compare the data, all thermal conductivities are scaled by the Slack parameter

$$1/(\overline{m}a\theta_{\rm D}^3/T),\tag{4.1}$$

where \overline{m} is the average atomic mass in the unit cell, a is the lattice constant, θ_D is the Debye temperature [135], and T is the temperature [47, 136]. The Slack parameter attempts to normalize the effects of mass density, crystal structure, atomic interactions, and temperature on the thermal conductivity. Before scaling the thermal conductivities of the model system, the values are first normalized so that the $m_2/m_1 = 1$ system has the same thermal conductivity as first-principles silicon at a temperature of 500 K. Based on the findings in Section 4.3, the thermal conductivities are plotted in Fig. 4.5 versus the ratio of the a-o gap to the acoustic width. The phonon dispersions needed to specify the a-o gap and the acoustic width for the real materials are calculated using density functional perturbation theory as implemented in the plane-wave based density functional theory package Quantum Espresso [40, 137]. The scaled thermal conductivity of the model system increases with increasing a-o gap/acoustic width ratio, reaches a peak when the ratio is 0.86, and then decreases with further increase in the ratio. The trend is similar for the compound semiconductors, where the peak in scaled thermal conductivity is for BAs, which has an a-o gap to acoustic-width ratio of 0.87. As observed by Lindsay et al. [125], the thermal conductivity varies non-monotonically for BX compounds (purple points). The same is true for BeX compounds (green), where the scaled thermal conductivity is a maximum for BeSe, which has an a-o gap to acoustic-width ratio of 1.03. All other compounds [AIX (brown), GaX (blue), InX (black)] have an a-o gap less than the acoustic width. As a result, thermal conductivity increases with increasing ratio and there is no peak in the scaled thermal conductivity decreases in going from BN to BP. We believe that the deviations between the real materials and our model system predictions are due to the lack of anharmonicity in the scaling factor and the RTA solution of the BTE. The overall agreement in the trend, however, suggests that we have identified a universal behavior.

4.5 Summary

We used lattice dynamics calculations and the BTE to study the competing effects of mass density, a-o gap, acoustic width, optical width, and acoustic bunching on the thermal conductivity of a family of model compound semiconductors where the species differ only in mass. As shown in Figs. 4.3 and 4.4, we found that thermal conductivity depends strongly on the mass difference of the two species and how it affects the a-o gap and the acoustic-width. The thermal conductivity increases with increasing a-o gap to acoustic-width ratio, attains a maximum close to ratio of 1, and decreases with further increase in the ratio. The observed peak in the thermal conductivity is due to the competing effects of mass density

(phonon group velocities, affected by widths) and phonon-phonon scattering rates (mainly affected by a-o gap to acoustic-width ratio).

Our findings hold true for real compound semiconductors, where the atomic interactions also vary with the atomic species. As shown in Fig. 4.5, the scaling factor proposed by Slack along with the a-o gap to acoustic-width ratio can be used to estimate the thermal conductivity of a wide variety of compound semiconductors. The material properties involved in the Slack scaling factor and the a-o gap to acoustic-width ratio are all based on the material structure and phonon dispersion and provide a simple measure for future screening of high thermal conductivity materials.

We arrived at the results in this study by considering only three-phonon scattering processes, classical statistics for phonons at one temperature, and the RTA solution of the BTE [132]. The effects of four-phonon processes, quantum statistics, and different temperatures on the mass ratio dependence of thermal conductivity are intriguing directions for future efforts.

Strongly anisotropic in-plane thermal transport in single-layer black phosphorene

Using first principles calculations, we predict the thermal conductivity of the two-dimensional materials black phosphorene and blue phosphorene. Black phosphorene has an unprecedented thermal conductivity anisotropy ratio of three, with predicted values of 110 W/m-K and 36 W/m-K along its armchair and zigzag directions at a temperature of 300 K. For blue phosphorene, which is isotropic with a zigzag structure, the predicted value is 78 W/m-K. The two allotropes show strikingly different thermal conductivity accumulation, with phonons of mean free paths between 10 nm and 1 μm dominating in black phosphorene, while a much narrower band of mean free paths (50-200 nm) dominate in blue phosphorene. Black phosphorene shows intriguing potential for strain-tuning of its thermal conductivity tensor.

5.1 Introduction

Two-dimensional (2D) materials (e.g., graphene, MoS_2 , silicene) are a focus of intense research because of their rich physics and potential for integration into next-generation electronic and energy conversion devices [9, 10, 11, 12]. As opposed to their bulk counterparts, the optical, electronic, mechanical, and thermal properties of 2D materials can be easily tailored through the application of external strain, by introducing defects, or by



Figure 5.1: Crystal structure of (a) black phosphorene and (b) blue phosphorene. Atoms in different planes are denoted by different colors and the unit cell and the in-plane lattice vectors are shown in the top views. Black phosphorene has a four-atom unit cell with an armchair structure along \mathbf{a}_1 and a zigzag structure along \mathbf{a}_2 . Blue phosphorene has a two-atom unit cell with the zigzag structure along \mathbf{a}_1 and \mathbf{a}_2 . The side views show the armchair and zigzag structures. The lattice constants are $|\mathbf{a}_1| = 4.43$ Å and $|\mathbf{a}_2| = 3.28$ Å for black phosphorene, and $|\mathbf{a}_1| = |\mathbf{a}_2| = 3.15$ Å for blue phosphorene.

stacking multiple layers of the same or different 2D materials. For example, the thermal conductivity of freely-suspended single-layer graphene is reduced from 3000-5000 W/m-K to 600 W/m-K by depositing it on amorphous SiO₂ [138].

Recently, a new and promising 2D semiconductor, black phosphorene, was fabricated by exfoliating a few layers from bulk black phosphorus [14, 15]. Similar to graphene, black phosphorene has a honeycomb-like structure, but it is non-planar [Fig. 5.1(a)]. Single-layer black phosphorene is a direct-gap semiconductor with a predicted band gap of 2 eV [139]. The band gap decreases with an increasing number of layers and is 0.3 eV for the bulk phase. Performance characteristics similar to or better than other 2D materials have been achieved for a black phosphorene-based transistor.[15] What distinguishes black phosphorene from other 2D materials is its anisotropic structure, which leads to direction-dependent optical and electronic properties that vary by as much as 50% [139, 140].

Our objective is to study the lattice thermal conductivity of single-layer black phosphorene, for which there is no existing experimental data available. Ong et al. investigated the effect of strain on the ballistic thermal conductance of black phosphorene using nonequilibrium Green's functions based on harmonic lattice dynamics calculations [141]. Our aim is to predict the thermal conductivity of black phosphorene by including anharmonic phonon-phonon scattering. Thermal transport characterization is important for application in most devices, where large electrical currents can lead to Joule heating, non-radiative recombination, and potentially high operating temperatures. We find that the in-plane thermal transport in black phosphorene is strongly anisotropic, with thermal conductivity varying by a factor of three over the two orthogonal directions. While strong anisotropy in thermal conductivity is observed for van der Waals layered materials when comparing the in-plane and cross-plane directions (e.g., two orders of magnitude in graphite [142]), no other covalently-bonded 2D or 3D materials show the in-plane anisotropy we predict for black phosphorene.

We also investigate the thermal transport in blue phosphorene, another single-layered allotrope of phosphorus [Fig. 5.1(b)], which was recently predicted to be nearly as stable as black phosphorene [143]. First principles calculations predict a band gap in blue phosphorene in excess of 2 eV [143], but unlike black phosphorene, blue phosphorene is isotropic.

5.2 Methodology

Thermal transport in semiconductors like black phosphorene and blue phosphorene is dominated by atomic vibrations whose energy is quantized as phonons (Section 2.1). At a temperature of 300 K, the electronic contribution to the thermal conductivity of black phosphorene is predicted to be less than 3 W/m-K for a typical carrier concentration of 10^{12} cm⁻² [144].

In our thermal conductivity calculations, the only required inputs are harmonic and anharmonic force constants, which are obtained from density functional theory (DFT) and density functional perturbation theory (DFPT) calculations. We use a scalar relativistic pseudopotential generated using the projector augmented-wave method as implemented in the plane wave-based quantum-chemistry package Quantum Espresso [40]. The plane wave energy cutoff is 50 Ry. To remove inter-layer interactions due to the periodicity of the computational cell, we use a vacuum of 30 Å for black phosphorene and 17 Å for blue phosphorene. For black phosphorene, the harmonic force constants are calculated on phonon and electronic wave-vector grids of $14 \times 12 \times 1$. The cubic force constants are obtained by finite differencing of Hellmann-Feynman forces on a 144-atom supercell with a Gamma-point electronic wave-vector grid. For blue phosphorene, the electronic and phonon wave-vector grids for the harmonic force constants are $10 \times 10 \times 1$ and the Hellmann-Feynman forces are obtained using a 128-atom supercell with a Gamma-point electronic wave-vector grid. For the thermal conductivity calculation, the phonon wave vector grid is $50 \times 50 \times 1$ for both allotropes. Translational invariance (i.e., the acoustic sum rule) for the cubic force constants is enforced using the Lagrangian approach presented by Li et al. [145] We note that the thermal conductivities are converged within 20% (10%) for black (blue) phosphorene for the above choice of parameters. Further details regarding these choices are provided in App. C.

5.3 Results

5.3.1 Phonon Dispersion

The phonon dispersion in the high-symmetry directions of the first Brillouin zone for black phosphorene and blue phosphorene are plotted in Figs. 5.2(a) and 5.2(b) and closely match those reported by Zhu et al [143]. Black(blue) phosphorene has a four(two)-atom unit cell, resulting in twelve(six) dispersion branches. The maximum phonon frequency is similar in both allotropes (14.0 THz in black and 16.3 THz in blue), but the phonon band gap in blue phosphorene (4.9 THz) is almost double that in black phosphorene (2.5 THz). The longitudinal acoustic phonon group velocity close to the Γ point (i.e., the sound speed), is 7,733 m/s in the $\Gamma-Y$ (armchair) direction and 4,168 m/s in the $\Gamma-X$ (zigzag) direction for black phosphorene, an indication of anisotropic phonon transport. For blue phosphorene, the sound velocity is 8,287 m/s in both the $\Gamma - M$ and $\Gamma - K$ directions.

5.3.2 Thermal Conductivity

The thermal conductivities of black phosphorene and blue phosphorene for temperatures between 200 and 500 K are plotted in Fig. 5.3(a). For black phosphorene, thermal transport is anisotropic and we plot the thermal conductivity in both the armchair and zigzag directions [see Fig. 5.1(a)]. Predicting the thermal conductivity of a 2D material requires specification of the layer thickness. We choose the bulk layer separation, which is 5.25 Å for black phosphorus [146] and 5.63 Å for blue phosphorus [143]. As the thermal conductivity scales linearly with the layer thickness, the values reported here can be easily modified for other choices.

Thermal conductivity decreases with increasing temperature, as expected for a phonondominated crystalline material. At a temperature of 300 K, the predicted thermal con-



Figure 5.2: Phonon dispersion in the high symmetry directions for (a) black phosphorene and (b) blue phosphorene. The slope of the longitudinal acoustic phonon branches at the Gamma point (shown as dashed straight lines), which represents the sound velocity, is anisotropic for black phosphorene and isotropic for blue phosphorene.



Figure 5.3: (a) Temperature-dependent thermal conductivity of black phosphorene and blue phosphorene. The thermal conductivities are obtained using an iterative solution of the linearized BTE. The predictions (symbols) are connected using lines to guide the eye. (b) Thermal conductivity accumulation functions for black phosphorene and blue phosphorene at a temperature of 300 K.

ductivities are 110 W/m-K (zigzag) and 36 W/m-K (armchair) for black phosphorene and 78 W/m-K for blue phosphorene. For black phosphorene, the thermal conductivity in the zigzag direction is three times higher than that in the armchair direction. This anisotropy could be useful in the design of heat channeling in micro- and nano-devices. We attribute this anisotropy in thermal conductivity to the anisotropic phonon dispersion, which leads to direction-dependent group velocities [Fig. 5.2(a)]. Based simply on the zone-center longitudinal acoustic group velocities, Eqn. 2.50 predicts a thermal conductivity anisotropy of 3.5, which is comparable to that from the full calculation. For blue phosphorene, the thermal conductivity is isotropic and is up to 1.8 times lower than the zigzag direction thermal conductivity of black phosphorene.

Our thermal conductivities are obtained using an iterative solution of the linearized BTE. For single-layer graphene, Lindsay et al. showed that the commonly used relaxation time approximation (RTA) of the BTE under-predicts the thermal conductivity by more than a factor of five at a temperature of 300 K [13]. We find that the RTA under-predicts the thermal conductivity by up to a factor of 1.3 for black phosphorene and 2.0 for blue phosphorene at a temperature of 300 K (see App. C).

The thermal conductivity of black phosphorene has recently also been predicted by other researchers. Zhu et al. used the RTA to predict values of 84 W/m-K (24 W/m-K) in the zigzag (armchair) direction [143]. These values closely match our RTA predictions of 81 W/m-K (30 W/m-K) (see App. C). Qin et al. predict black phosphorene thermal conductivities a factor of three lower than our values [147]. This difference may be due to (i) their use of the RTA, (ii) their choice of the cubic force constant cutoff, and/ or (iii) the implementation of a translational invariance constraint on the third-order force constants. Our predictions of the effects of these factors on thermal conductivity are presented in the App. C.

In Fig. 5.3(b), we plot the thermal conductivity accumulation functions for black phosphorene and blue phosphorene at a temperature of 300 K. The thermal conductivity accumulation function describes the contribution of different mean free path phonons towards the total thermal conductivity of a material [107]. Phonons with mean free paths spanning over two orders of magnitude (10 nm to 1 μ m) contribute towards the thermal conductivity in black phosphorene. For blue phosphorene, however, the accumulation function closely resembles a step function, with the major contribution coming from phonons with mean free paths between 50 and 200 nm. This steep thermal conductivity accumulation in blue phosphorene is similar to that in silicene (which also has buckled hexagonal structure), where phonons with mean free path between 5 and 20 nm contribute more than 80% to the thermal conductivity [148]. The thermal conductivity accumulation functions indicate that, unlike in graphene where thermal conductivity is predicted to increase with sample sizes even greater than 10 μ m, changing the sample size beyond 10 μ m will have a minimal effect on the thermal conductivity of either phosphorene allotrope at a temperature 300 K.

As mentioned above, the structure of blue phosphorene is similar to that of silicene. Blue phosphorene, however, has a thermal conductivity of 78 W/m-K at a temperature of 300 K, which is more than eight times higher than that predicted for silicene (9.4 W/m-K) [148]. This higher thermal conductivity of blue phosphorene is the result of a larger sound velocity and the larger frequency gap in its phonon dispersion [Fig. 5.2(b)], which reduces the number of three-phonon scattering processes that can satisfy the energy conservation selection rule [36, 125, 126, 149]. The zigzag direction thermal conductivities of black and blue phosphorene are comparable in magnitude to that predicted for a 10 μ m MoS₂ sample prediction at a temperature of 300 K (108 W/m-K) [150].

At a temperature of 300 K, Lindsay et al. [38] predicted the thermal conductivity of graphene to be 3,600 W/m-K, which is more than 30 times higher than the thermal conduc-

Material	Total thermal	LA	ТА	ZA	Optical
	conductivity (W/m-K)	(%)			
Black phosphorene (zigzag)	110	32	22	31	15
Black phosphorene (armchair)	36	28	33	12	27
Blue phosphorene	78	26	27	44	3
MoS_2 [150]	108	28	24	39	9
Graphene [38]	3600	8	15	76	1

Table 5.1: Contribution of different phonon modes branches [longitudinal acoustic (LA), transverse acoustic (TA), out-of-plane acoustic (ZA), and all optical] towards the total thermal conductivity in black phosphorene, blue phosphorene, MoS_2 (10 µm sample [150]), and graphene (10 µm sample [38]) at a temperature of 300 K.

tivity of either black phosphorene or blue phosphorene. We believe that the lower thermal conductivity of the phosphorene allotropes is due to their: (i) smaller sound velocities (4,000-8,000 m/s compared to 21,300 m/s in graphene [151]), (ii) lower Debye temperatures [500 K (see App. C) compared to 2,300 K for graphene [152]], resulting in higher phonon-phonon scattering rates as more phonon modes are active at a given temperature, and (iii) non-planar structure, which breaks the out-of-plane symmetry. This out-of-plane symmetry exists in graphene and restricts the participation of odd numbers of ZA phonons in phonon-phonon scattering events [13]. As a result, the predicted contribution of ZA phonons to thermal conductivity in the phosphorene allotropes varies from 12%-44% as compared to 76% in graphene at a temperature of 300 K [38], as presented in Table 5.1. We note that the thermal conductivity contributions of the different acoustic phonon branches in black phosphorene and blue phosphorene are similar to those predicted for MoS_2 [150], which also has a non-planar structure. More information is provided in the App. C.

The thermal conductivity of freely-suspended single-layer graphene at a temperature of 300 K is reduced from 3000-5000 W/m-K to 600 W/m-K when it is deposited on amorphous SiO_2 [138], This more than a factor of five reduction in the thermal conductivity is due to the increased scattering of ZA phonons in supported graphene. The results presented in this work are for suspended phosphorene. As can be seen in Table 5.1, the contribution of ZA phonons is 31% (12%) in the zigzag (armchair) direction in black phosphorene and 44% in blue phosphorene. We expect a comparable decrease in the thermal conductivity of supported phosphorene samples.

5.3.3 Strain Tuning of Thermal Conductivity

We now consider the possibility of strain-tuning the thermal conductivity of black phosphorene and blue phosphorene. In Fig. 5.4(a), we plot the stresses in both allotropes when they are subjected to a bi-axial tensile strain. For black phosphorene, the stress is anisotropic and is three times lower in the armchair direction compared to the zigzag direction. For blue phosphorene, which has a zigzag structure, the stress is isotropic and is 1.5 times larger than the stress in the zigzag direction of black phosphorene.

As can be seen from Eqn. 2.50, thermal conductivity scales as the square of the phonon group velocities. We plot the strain-dependence of the sound velocities in Fig. 5.4(b) for black phosphorene and blue phosphorene under the bi-axial strain conditions. The sound velocities are maximum at zero strain for both materials and decrease with increasing strain. Using this reduction as a guide, we estimate that the thermal conductivities of both allotropes may decrease by a factor of 1.7 at a strain of 8%. Similar calculations for uni-axial strains suggest the possibility for strain-tailoring the thermal conductivity anisotropy in black phosphorene. For example, the estimated anisotropy in the thermal conductivity of black phosphorene is a factor of 4.6 (2.2) for uni-axial strain of 6% along



Figure 5.4: (a) Stress and (b) sound velocity in black phosphorene and blue phosphorene under bi-axial strain. The predicted values (symbols) are connected using lines to guide the eye

Material	$k_{ m max}$	k_{\min}	r
	(W/m-K)		
Graphite $(\exp[153])$	(1000 - 2000)	6	~ 300
h-BN $(\exp[153])$	(200 - 300)	2	~ 100
Black	110	36	31
Phosphorene	110	50	0.1
SnSe $(\exp[154])$	0.70	0.46	1.52
GaN $(pred[37])$	401	385	1.04
AlN $(pred[37])$	322	303	1.06
$NdFeO_3 (pred[155])$	3.01	2.68	1.12
$NdAlO_3 (pred[155])$	6.61	5.72	1.16

Table 5.2: Anisotropy in thermal conductivity for selected materials with layered, wurtzite, and orthorhombic crystal structure at a temperature of 300 K. 'exp ' and 'pred' in the first column denote experimental measurements and simulation predictions.

the armchair (zigzag) direction (see App. C).

5.3.4 Anisotropy

To the best of our knowledge, no other 2D material displays anisotropic in-plane thermal transport. Furthermore, the thermal conductivity anisotropy in black phosphorene is striking when compared to that found in layered, wurtzite, and orthorhombic three-dimensional crystal structures, as compiled in Table 5.2. We quantify anisotropy, r, by the ratio of the maximum and minimum direction-dependent thermal conductivities. The maximum r is in the layered structures graphite and hexagonal boron nitride. These layers are weakly

bonded through van der Waals interactions compared to the strong covalent bonds within the layers, which results in poor inter-layer heat transport. Of the remaining materials in Table 5.2, which are all covalently bonded, the maximum anisotropy is for our prediction for black phosphorene, which is twice as large as the next highest value.

5.4 Summary

We predicted the thermal conductivity of black phosphorene and blue phosphorene using first-principles-driven lattice dynamics calculations and a full (iterative) solution of the BTE. We found a factor of three anisotropy in the thermal conductivity of black phosphorene, which could potentially be tuned up to 4.6 using strain. At a temperature of 300 K, the predicted thermal conductivities of both phosphorene allotropes are larger than that of silicene, similar to that of MoS_2 , and are up to two order of magnitude smaller than that of graphene.

Effect of exchange-correlation on first-principles-driven lattice thermal conductivity predictions of crystalline silicon.

The effects of exchange-correlation (XC) and pseudopotential types on the density functional theory-driven prediction of the thermal conductivity of isotopically pure silicon are studied. The thermal conductivity is predicted by considering three-phonon scattering processes and a full solution of the Boltzmann transport equation. The LDA, PBE, PBEsol, and PW91 XCs predict thermal conductivities between 127 and 148 W/m-K at a temperature of 300 K, which is an under-prediction of the experimental value of 153 W/m-K by 3-17%. The BLYP XC predicts a thermal conductivity of 172 W/m-K, an over-prediction of 12%.

6.1 Introduction

The prediction of lattice thermal conductivity from first-principles-driven density functional theory (DFT) calculations is becoming routine [32, 33, 34, 39]. As opposed to using empirical potentials to describe the atomic interactions, which require fitting parameters and lack true predictive power, DFT-driven calculations are fitting-parameter free. DFTdriven calculations have been successfully used to predict the experimentally-measured thermal conductivities of materials ranging from simple semiconductors such as silicon [33] and diamond [156] to compound semiconductors [39], graphene [38], and SiGe alloys [34]. DFT-driven calculations have also been used to study the effects of strain and isotopes on the thermal conductivity of semiconductors [25, 36, 157] and to predict the thermal conductivity of novel two-dimensional materials [38, 158, 159].

Within the framework of DFT, the many-body problem of interacting electrons is reduced to a tractable problem of non-interacting electrons with an effective potential. This effective potential includes the effects of the Coulombic interactions (i.e., the Hartree term) and many-body interactions [i.e., the exchange-correlation (XC) term]. The major challenge in DFT lies in describing the XC. The simplest form of the XC is the local density approximation (LDA), in which the potential is only a function of the spatially-dependent electron density [160]. A more involved approach, the generalized gradient approximation (GGA), uses the electron density and its gradient. GGA XCs almost always over-predict the experimental lattice constants of crystalline solids while LDA XCs almost always result in an under-prediction [161]. The effect of this under-/over-binding by different XCs on lattice thermal conductivity is unknown.

Thermal transport in semiconducting and electrically insulating crystalline solids is dominated by lattice vibrations (i.e., phonons). The thermal conductivity of these materials is therefore highly-dependent on inter-atomic separation and bonding. Our objective here is to study the effect of different XCs on the thermal conductivity of isotopically-pure silicon. We employ LDA and GGA (PBE [48], PBEsol [49], BYLP [50, 51], and PW91 [52]) XC-based ultrasoft (US), norm-conserving (NC), and projected augmented wave (PAW) pseudopotentials. We find that all XCs, with the exception of BYLP, predict a thermal conductivity between 127 and 148 W/m-K at a temperature of 300 K, which is an underprediction of the experimental value of 153 W/m-K by 3-17% [63]. BLYP, on the other hand, over-predicts the experimental value by 12%. In what follows, we discuss the convergence tests for the DFT calculations in Sec. 6.2. The predictions of the XC-dependence of thermal conductivity are presented in Sec. 6.3 and a comparison to results from the literature is made in Sec. 6.4.

6.2 DFT Parameters Convergence

Phonon frequency and lifetime predictions require harmonic and cubic force constants as inputs. We obtained harmonic force constants from density functional perturbation theory (DFPT) and cubic force constants from finite differencing of DFT forces. We employed the planewave-based electronic-structure calculation package Quantum Espresso for our DFPT and DFT calculations [40, 162]. The harmonic force constants are initially obtained on an $8 \times 8 \times 8$ phonon wave-vector grid and are later interpolated to a $24 \times 24 \times 24$ grid. For the cubic force constants, we calculated forces on different arrangements of a 216 atom supercell with one or more atoms displaced by 0.01 Å from their equilibrium positions. The translation invariance constraint in the calculation of the cubic force constants was enforced using the Lagrangian approach presented by Li et al. [145]. The convergence of the thermal conductivity of silicon with respect to supercell size and displacement amount is discussed in Ref. [39]. We found that the change in thermal conductivity at a temperature of 300 K is less than 1.5% when increasing the phonon wave-vector grid from $24 \times 24 \times 24$ to $26 \times 26 \times 26$. Since we want our results to be converged within 2% (the experimental uncertainty in the thermal conductivity of silicon [63]), we used the $24 \times 24 \times 24$ phonon wave-vector grid for all of our calculations. The phonon scattering rates in the present study are obtained using an iterative solution of the BTE. The iterative solution, as opposed to the commonlyused relaxation time approximation (RTA), does not treat normal three-phonon scattering processes as resistive [32, 163].



Figure 6.1: Variation of (a) total energy and relaxed lattice constant and (b) predicted thermal conductivity of silicon at a temperature of 300 K with electronic wave-vector grid using the LDA XC-based NC pseudopotential. The total energy in (a) is energy per atom relative to energy per atom of the $14 \times 14 \times 14$ electronic wave-vector grid.

To specify the converged electronic wave vector grid (to be used in the self-consistent field calculation), we plot the variation of the total energy, the relaxed lattice constant, and the thermal conductivity at a temperature of 300 K with electronic wave-vector grid density in Figs. 6.1(a) and 6.1(b) for the LDA XC-based NC pseudopotential with a 60 Ry planewave energy cutoff. As can be seen in Fig. 6.1(b), the thermal conductivity decreases by 7% on increasing the electronic wave-vector grid from $6 \times 6 \times 6$ to $8 \times 8 \times 8$ and is converged to within 1.5% with further increase. The 7% decrease in the thermal conductivity in going from the $6 \times 6 \times 6$ wavevector grid to the $8 \times 8 \times 8$ wavevector grid is mainly a result of differences in the vibrational frequencies. For example, the transverse(longitudinal) acoustic phonon group velocities close to the Gamma point in the [100] direction decrease from 4806 m/s (7871 m/s) to 4653 m/s (7558 m/s). The changes in the total energy per atom and the relaxed lattice constant [Fig. 6.1(a)] are less than 0.2 mRy and 0.001Å with an increase in an electronic wave-vector grid beyond $8 \times 8 \times 8$. These results suggest that the total energy per atom and the lattice constant should be converged to within 0.2 mRy and 0.001Å in order to achieve a converged thermal conductivity for silicon (within 2%). We note that the 7% variation in the thermal conductivity with electronic wavevector grid is not simply because of the change in the lattice constant. We performed thermal conductivity calculations using lattice constants between 5.40 and 5.46 Å while keeping the electronic wavevector grid and planewave energy cutoff fixed and found the variation to be less than 4%.

We repeated the above convergence calculations for all the XCs with the criterion of thermal conductivity changes of less than 2%. The converged electronic wave-vector grid obtained for all XCs and pseudopotential types is $8 \times 8 \times 8$. For the planewave energy cutoff, we find convergence at 50 Ry for US and PAW pseudopotentials and 60 Ry for NC pseudopotentials for all of the XCs considered. To see the effect of electronic wavevector grid on the supercell DFT forces (used for both the phonon lifetimes and the Grüneisen parameters), we calculated thermal conductivity using the Gamma point supercell and a supercell with a $2 \times 2 \times 2$ wave vector grid for the LDA XC-based NC pseudopotential. The difference in the two thermal conductivities is 2%, which is within our convergence threshold.

6.3 Results

6.3.1 Lattice Constant

We report the relaxed lattice constants in Table. 6.1. The experimental value is 5.430 Å [164]. All GGA XCs under-bind the lattice and over-predict the lattice constant while the opposite is true for the LDA XC, which underpredicts by 0.6%. The PBEsol XC-predicted lattice constant (5.430 Å) shows the best agreement with the experimental value while the BLYP XC over-predicts the experimental value by the highest amount (1.4%). The PBE and PW91 lattice constants are within 0.7% of the experimental value for the three types of pseudopotential considered.

6.3.2 Phonon Dispersion

We plot the phonon dispersion calculated using the PBEsol (US) and BLYP (NC) XCs in Fig. 6.2(a). As mentioned in Sec. 6.3.1, the PBEsol and BLYP predicted lattice constants show the best and worst agreement with the experimental value. The transverse acoustic phonon vibrational frequencies predicted using PBEsol (green lines) are lower than the experimental values (blue circles [165]), whereas those predicted using BLYP (red lines) are higher. For longitudinal acoustic phonons, both PBEsol and BLYP predict similar vibrational frequencies. In the case of optical phonons, the PBEsol predicted frequencies



Figure 6.2: (a) Phonon dispersion and (b) mode-dependent Grüneisen parameters of silicon calculated using the BLYP XC NC pseudopotential (red) and the PBEsol XC US pseudopotential (green). Experimentally measured frequencies from Ref. [165] and Grüneisen parameters from Ref. [166] are shown using blue circles. LA, TA, LO, and TO in (b) represents longitudinal acoustic, transverse acoustic, longitudinal optical, and transverse optical.

agree well with the experiments whereas BLYP results in an under-prediction. The sound velocities (estimated as the longitudinal acoustic phonon velocity close to the Γ -point in the [100] direction) from the PBEsol (8330 m/s) and BLYP (8510 m/s) XCs both compare well with the experimental value of 8430 m/s [167].

The sound velocities obtained using the different XCs and pseudopotential types are provided in Table 6.1. PW91 underpredicts the sound velocity compared to the experimental value by the maximum amount (5970 m/s, a difference of 29%). The sound velocities predicted from the other XCs and pseudopotential types are within 11% of the experimental value. The sound velocity of a one-dimensional harmonic mass-spring chain in solids is $a\sqrt{\frac{K}{m}}$, where a, K, and m are the lattice constant, the harmonic spring constant, and the atomic mass. In examining Table 6.1, we note that there is not a direct correlation between the sound velocities and the lattice constants. For example, for the LDA XCs, the predicted sound velocities are 8320, 7560, and 8340 m/s from the US, NC, and PAW pseudopotentials even though all predicted lattice constants are within 0.002 Å of each other. This finding points to the important effect of the XC on the harmonic force constants.

6.3.3 Three-Phonon Phase Space

Differences in the phonon dispersions from the different XC and pseudopotential types result in different values of the three-phonon phase space, which is a measure of the scattering space available for three-phonon processes. It is calculated using the phonon dispersion by counting the number of three-phonon scattering processes that satisfy the energy and momentum conservation selection rules [168]. The three-phonon phase spaces obtained from the different XC and pseudopotential types are provided in Table 6.1. The minimum phase spaces are obtained from BLYP and PW91, with values of 0.0085 and 0.0089. All other XC and pseudopotential types predict values between 0.0091 and 0.0093. These results Table 6.1: Predicted relaxed lattice constant, sound velocity, three-phonon phase space, mode-averaged Grüneisen parameter, and phonon thermal conductivity (isotopically pure at T = 300 K) of silicon with different XCs and pseudopotential types. The thermal conductivities are converged to within 2% with respect to all simulation parameters.

Pseudopotential type [162]	Ex- change Correla- tion [162]	Lattice Con- stant (Å)	Sound Velocity (m/s)	Three- Phonon Phase Space (arbi- trary units)	Average Grüneiser Param- eter	Ther- n mal Con- ductiv- ity (W/m- K)
Experiment		$5.430 \\ [164]$	$8430 \\ [167]$			153 [<mark>63</mark>]
	LDA	5.399	8320	0.0091	1.11	142
Ultrasoft	PBE	5.468	8120	0.0092	1.04	148
	PBEsol	5.430	8330	0.0092	1.10	140
	PW91	5.466	5970	0.0089	1.00	127
	LDA	5.402	7560	0.0092	1.04	144
Norm-Conserving	PBE	5.461	8150	0.0093	1.02	148
	BLYP	5.505	8510	0.0085	0.89	172
	LDA	5.400	8340	0.0091	1.11	142
PAW	PBE	5.466	7830	0.0092	1.03	145
	PBEsol	5.430	8320	0.0092	1.11	137

indicate a smaller number of three-phonon scattering processes from the BLYP and PW91 XCs as compared to the other XCs. We note that the strength of these three-phonon scattering processes depends on the cubic force constant and is discussed in Section 6.3.4.

6.3.4 Grüneisen parameters

To examine the effect of XC and pseudopotential types on the cubic force constants, we next plot mode-dependent Grüneisen parameters, γ_i , calculated using the PBEsol (NC) and BLYP (US) XCs in Fig. 6.2(b). The Grüneisen parameters describe the effect of changing the crystal volume on the phonon frequencies and are a measure of crystal anharmonicity. We calculated the Grüneisen parameters with the cubic force constants by using Eqn. 2 of Ref. [169]. For transverse acoustic phonons, PBEsol results in an over-prediction (in magnitude) of the experimentally measured Güneisen parameter |166| at all of the high-symmetry points considered. BLYP, on the other hand, matches the experimental values at Γ and W, while under-predicting (in magnitude) at X and L by a factor of two. The Grüneisen parameters for the transverse acoustic phonons from BLYP are smaller in magnitude (less than half in some cases) than the corresponding values from PBEsol over the entire Brillouin zone. This result suggests weaker anharmonic scattering of transverse acoustic phonons from BLYP compared to PBEsol. For longitudinal acoustic and optical phonons, except for the Γ – L direction, the BLYP- and PBEsol-predicted Grüneisen parameters match with each other in all high-symmetry directions. Both the BLYP- and PBEsol- predicted Grüneisen parameters match with the experiments at all of the highsymmetry points for longitudinal acoustic and optical phonons.

We characterize the anharmonicity of the different XCs by calculating an average Grüneisen parameter, γ , as a heat-capacity weighted average of the absolute values of the mode-dependent Grüneisen parameters as:

$$\gamma \equiv \frac{\sum_{i} c_{ph,i} |\gamma_i|}{\sum_{i} c_{ph,i}}.$$
(6.1)

The average Grüneisen parameters are provided in Table 6.1. The minimum value of 0.89 (i.e., the least anharmonic) is obtained from the BLYP XC. All other XCs and pseudopotential types result in average Grüneisen parameter values between 1.00 and 1.11.

6.3.5 Thermal Conductivity

Thermal conductivities at a temperature of 300 K calculated using the different XC and pseudopotential types are provided in Table 6.1. The maximum and minimum predicted thermal conductivities are 127 W/m-K (from PW91) and 172 W/m-K (from BLYP). All other XCs predict values between 137 and 148 W/m-K, which is an under-prediction of the experimentally-measured thermal conductivity of isotopically pure silicon of 153 W/m-K [63] by 3-11%. As can be seen from Eqn. 2.50, thermal conductivity is proportional to the phonon group velocities squared and the lifetimes. The strong under-prediction of the sound velocity by PW91 (Sec. 6.3.2) is consistent with its low thermal conductivity. For BLYP XC, the three-phonon phase space and average Grüneisen parameter are lower than the other XCs. These lower values of the three-phonon phase space and average Grüneisen parameter are an indication of weaker phonon-phonon scattering, larger phonon lifetimes, and hence higher thermal conductivity. Apart from the XC and pseudopotential types, the predicted thermal conductivities also depend on the pseudopotential generation method, as found by Ward for diamond [54]. We find the predicted thermal conductivities from the LDA XC based NC pseudopotentials generated using the Goedecker-Hartwigsen-Hutter-Teter [170, 171], Martins-Troullier [172], and Von Barth-Car [173] methods to be 130, 134, and 141 W/m-K.



Figure 6.3: Thermal conductivity accumulation function of silicon at a temperature of 300 K from different XC and pseudopotential types. With the exception of BLYP, all XCs result in a similar accumulation.



Figure 6.4: Thermal conductivity variation of silicon with temperature from different XC and pseudopotential types. The experimentally measured thermal conductivities from Refs. [63] and [62] are shown as green and pink filled squares.

The thermal conductivity accumulation function with phonon mean free path (defined as $\tau_i |\mathbf{v}_{g,i}|$) at a temperature of 300 K from the different XC and pseudopotential types is plotted in Fig. 6.3. The accumulation function describes the contribution of different mean free path phonons towards the thermal conductivity [107]. As can be seen from Fig. 6.3, phonons with mean free paths varying over three orders of magnitude (10 nm - 10 μ m) contribute to thermal transport. As compared to the other XCs, which show similar accumulations, BLYP over-predicts the contribution of the mid-range mean free path (~100 nm) phonons.

The temperature variation of the thermal conductivity of silicon between 100 and 500 K from different XC and pseudopotential types is plotted in Fig. 6.4. Also plotted are the experimentally-measured thermal conductivities from Inyushkin et al. [63] (green) and

Glassbrenner and Slack [62] (red). BLYP over-predicts the experimental thermal conductivity at all of the temperatures considered. At a temperature of 100 K, BLYP predicts a value of 1326 W/m-K, while all other XC and pseudopotential types predict values between 993 and 1239 W/m-K. The experimental values at a temperature of 100 K are 1194 and 950 W/m-K from Refs. [63] and [62].

6.4 Comparison with Literature

We now compare our predictions with reported values in the literature. The results are summarized in Table 6.2. As a comparison point, our converged value of thermal conductivity using the LDA XC based NC pseudopotential is 144 W/m-K using the iterative solution of the BTE and 140 W/m-K when the BTE is solved under the RTA.

Lindsay et al. [39] predicted a value of 155 W/m-K using an iterative solution of the BTE. They used the LDA XC based NC pseudopotential with a $6 \times 6 \times 6$ electronic wavevector grid and an 80 Ry planewave energy cutoff. Using the same parameters, our predicted thermal conductivity is 153 W/m-K [175]. As can be seen from Fig. 6.1(b), an electronic wavevector grid of $6 \times 6 \times 6$ is not converged and leads to a 6% over-prediction in the thermal conductivity compared to an $8 \times 8 \times 8$ wavevector grid.

Esfarjani et al. [33] predicted a value of 132 W/m-K using the LDA XC and the RTA of the BTE. They used a 40 Ry planewave energy cutoff and 10 electronic wavevectors in the irreducible Brillouin zone ($4 \times 4 \times 4$ wave-vector grid) of a 64 atom supercell. They used a $18 \times 18 \times 18$ phonon wavevector grid for the thermal conductivity calculation [176]. These choices lead to an under-prediction of thermal conductivity (compared to finer phonon wavevector grids) due to insufficient sampling of phonon modes near the Brillouin zone center [33, 121]. Using the LDA XC based NC pseudopotential, and their parameters we predict a thermal conductivity of 136 W/m-K.

	Relevant/ Unconverged Simulation Parameters	Thermal Conduc- tivity (W/m-K)	Our ther- mal con- ductivity prediction with same parameters (W/m-K)
Present Study	Iterative (RTA) solution of the BTE with LDA NC pseudopotential, $8 \times 8 \times 8$ electronic wave-vector grid, 60 Ry planewave energy cutoff, and $24 \times 24 \times 24$ phonon wave-vector grid	144((140)
Lindsay et al. $[39]$	Iterative solution of the BTE with $6 \times 6 \times 6$ electronic wave-vector grid	155	153
Esfarjani et al. [33]	RTA solution of the BTE and $18 \times 18 \times$ 18 phonon wave-vector grid	132	136
Garg et al. [174]	Iterative (RTA) solution of the BTE and 20 Ry planewave energy cutoff	136 (132)	140 (136)
Li et al. [15]	Iterative solution of the BTE with $5 \times 5 \times 5$ supercell based Γ -point DFT calculations for harmonic force constants using PBE based PAW pseudopotential	172	140
Parrish et al. [25]	Iterative solution of the BTE with 6 \times 6 × 6 electronic wave-vector grid	151	153
Broido et al. [32]	Iterative solution of the BTE with LDA based US pseudopotential	155	
Ward et al. $[54]$	Iterative solution of the BTE with BHS-based NC pseudopotential	145	

Table 6.2: Comparison of isotopically-pure silicon thermal conductivity predictions at a temperature of 300 K between the present study and previous results.

The thermal conductivity predicted by Garg et al. [174] is 136 (132) W/m-K using the full (RTA) solution of the BTE. They used the LDA XC-based NC pseudopotential with an $8 \times 8 \times 8$ electronic wavevector grid and a 20 Ry planewave energy cutoff. With the same parameters, we predict thermal conductivities of 140 (136) W/m-K. These value are an under-prediction of our converged values by 4 W/m-K (for both cases) due to an insufficient planewave energy cutoff.

Li et al. [15] predicted the thermal conductivity of silicon to be 172 W/m-K using an iterative solution of the BTE and the PBE XC based PAW pseudopotential. They used a 23 Ry planewave energy cutoff and calculated harmonic (cubic) force constants on a $5 \times 5 \times 5$ ($3 \times 3 \times 3$) supercell using Γ -point DFT calculations. The harmonic force constants calculated on a $5 \times 5 \times 5$ supercell using Γ -point DFT calculations are equivalent to those from DFPT calculations with $5 \times 5 \times 5$ phonon and electronic wavevector grids. Using the PAW XC based PBE pseudopotential, $5 \times 5 \times 5$ phonon and electronic wavevector grids in the DFPT calculations, and a $3 \times 3 \times 3$ supercell for DFT force calculations, we obtain a thermal conductivity of 140 W/m-K, which differs from the prediction of Li et al. by 32 W/m-K. We hypothesize that Li et al.'s use of DFT forces to extract the harmonic force constants (as opposed to the more accurate DFPT calculations in the present study) is responsible for this difference between the two results.

Parrish et al. [25] predicted a thermal conductivity of 151 W/m-K using an iterative solution of the BTE, the LDA XC based NC pseudopotential, and an 80 Ry planewave energy cutoff with a $6 \times 6 \times 6$ electronic wavevector grid. This value is an over-estimate of our converged value by 5% due to an insufficient electronic wavevector grid.

The thermal conductivity of silicon has also been predicted by Broido et al. [32] and Ward et al. [54]. Their values are 155 and 145 W/m-K using LDA-based US and Bachelet-Hamann-Schlüter (BHS)-based NC pseudopotentials. Because the DFPT phonon wavevector grid for the harmonic force constant calculation is not provided in Ref. [32] and the BHS based NC pseudopotential in not available in Quantum Espresso [40], we are unable to compare our prediction methodology with theirs.

6.5 Summary

We studied the effect of DFT parameters and XC and pseudopotential types on the thermal conductivity of isotopically pure silicon. We found that the total energy per atom and relaxed lattice constant should be converged to within 0.2 mRy and 0.001 Å with respect to all DFT parameters in order to have a 2% convergence in the thermal conductivity. Furthermore, we identified that with the exception of BLYP (which over-predicts by 12%), all other XCs under-predict the experimental thermal conductivity by 3-17% at a temperature of 300 K.

Our conclusions are for isotopically pure silicon. We recommend a careful selection of XC and pseudopotential types for other materials by initially checking the sound velocity and Grüneisen parameters, which can both be obtained with harmonic-level calculations. While some XCs such as LDA and PBE are developed for condensed matter, other XCs are developed for chemical energy calculations of molecules (e.g., BLYP). We also recommend a careful convergence of thermal conductivity with all DFT parameters, especially electronic wave-vector grid and planewave energy cutoff.
Thermal transport by phonons and electrons in metals from first-principles

The phonon thermal transport and electron thermal and electrical transport properties are presented in three different metals (Al, Ag, and Au) by considering phonon-phonon and electron-phonon interactions with input from DFT and DFPT calculations. The temperature dependent phonon and electron contributions toward the total thermal conductivity and contribution of different mean free path carriers (phonons and electrons) towards the thermal conductivity are discussed. The phonon thermal conductivity in Al is compared with that in Si and the factors causing lower phonon thermal conductivity in Al are discussed.

7.1 Introduction

While there are numerous studies in the literature on the first-principles based phonon thermal transport properties prediction in semiconductors [32, 33, 34, 39], the phonon thermal transport in metals is mostly untouched, mainly because of the small contribution of phonons towards the thermal transport in metals [57, 164] and the added computational complexity [due to electron-phonon (e-p) interactions]. Metals, unlike semiconductors, have free electrons that carry both heat and charge. Compared to semiconductors, where heat is primarily carried by phonons, heat is primarily carried by electrons in metals [57, 164]. Phonons create resistance to electron flow in metals through scattering events [57]. Even though the contribution of phonon towards the thermal transport is small in metals, it is important, for instance, in analyzing the pump-probe based experimental thermal conductivity measurement results using the two-temperature model [16, 17, 18, 177, 178] and in the study of interfaces [3, 179].

Our objective in this work is to study the mode-dependent phonon thermal transport in metals by considering both phonon-phonon (p-p) and e-p interactions. We will also calculate the electron transport properties in metals by considering e-p interactions. We investigate transport in three different non-magnetic metals namely Al, Ag, and Au by using the first-principles-based DFT and DFPT calculations [40].

We find that the phonon contribution towards the thermal transport can be as high as 5.5% in bulk Al at a temperature of 100 K. As in experiments [180], we find that the Lorentz number, instead of being constant as suggested by the Wiedemann-Franz law, is a function of both temperature and metal. Further, we also find that as opposed to semiconductors, where phonon mean free paths (mfps) are larger than electron mfps, phonon mfps in metals are up to an order of magnitude smaller than electron mfps. On comparing thermal transport in aluminum with silicon, the most-widely studied semiconductor, we find that, even though aluminum and silicon have similar atomic masses, the phonon contribution towards the thermal conductivity by considering only p-p interactions is an order of magnitude less in aluminum than that in silicon. Our findings, apart from elucidating phonon thermal transport physics in metals, will also help in improving existing metal-semiconductor device designs.

7.2 Methods and Calculation Details

The phonon (electron) transport properties can be obtained by solving the Boltzmann transport equation and using the Fourier law (Onsager relations) with input from DFT and DFPT (see Sec. 2.2 and App. D) [40, 42, 42]. We calculate e-p coupling coefficients using DFPT as implemented in the package Quantum Espresso [40]. The coupling coefficients are initially obtained on coarse $18 \times 18 \times 18$ and $6 \times 6 \times 6$ electron and phonon wavevector grids and are later interpolated to finer $80 \times 80 \times 80$ and $32 \times 32 \times 32$ electron and phonon wavevector grids using the maximally localized Wannier functions basis as implemented in the electron-phonon Wannier (EPW) package [42, 42]. The harmonic and cubic force constants, required for three-phonon scattering rate calculations, are obtained using finite differencing of DFT forces. We calculated forces using 216 atom supercells with a $3 \times 3 \times 3$ electronic wavevector grid and recommended planewave energy cutoffs (listed in Table D.1 of App. D) from the DFT package VASP. The LDA exchange-correlation is employed for all of the calculations. Further details about the calculations and the DFT parameters convergence are provided in Secs. D.1 and D.2 of the App. D.

7.3 Temperature Dependent Thermal and Electrical conductivities

We first plot the temperature variation of the thermal conductivities of Al, Ag, and Au, obtained by considering both p-p and e-p interactions (k_p) and by considering only p-p interactions (k_p^{p-p}) , in Fig. 7.1(a) and in the inset of Fig. 7.1(a). Among the three metals considered for this plot, Al is the lightest followed by Ag and then Au. The lighter mass of Al results in higher phonon group velocities, which is reflected in its highest phonon thermal conductivity (both k_p and k_p^{p-p}) amongst the three metals at all temperatures.



Figure 7.1: Variation of (a) phonon thermal conductivity, k_p , (b) electron thermal conductivity, k_e , inset of (a) phonon thermal conductivity obtained by considering only p-p scattering, k_p^{p-p} , inset (i) of (b) electrical conductivity, σ , and inset (ii) of (b) the Lorentz number, $L = k_e/\sigma T$, with temperature for Al, Ag, and Au. The dashed line in inset (ii) of (b) is the constant L value of 2.44×10^{-8} W- Ω/K^2 from the Wiedemann-Franz law.

With an increase in temperature, T, the number of active phonons in a system increases as $\sim k_{\rm B}T$ where $k_{\rm B}$ is the Boltzmann constant. As a result, due to an increase in e-p and p-p scattering at higher temperatures, both k_p and k_p^{p-p} decreases with rising temperature. The effect of e-p interactions on the phonon thermal conductivity is maximum for Al amongst the three metals. Upon removal of the e-p interactions, the phonon thermal conductivity of Al increases by up to factor of two at a temperature of 100 K while the change is less than 17% for Ag and Au. This result is consistent with the literature where the highest e-p coupling parameters are reported for Al among the three metals [181]. For all three metals, the maximum effect of e-p interactions is observed at a temperature of 100 K (97%, 17%, and 6% increase in thermal conductivity on removing e-p interactions in Al, Ag, and Au) and it decreases with an increase in temperature to 16%, 3%, and 2% at a temperature of 500 K for Al, Ag, and Au.

The temperature variation of electron thermal conductivity (k_e) and electrical conductivity (σ) of Al, Ag, and Au are plotted in Fig. 7.1(b) and inset (i) of Fig. 7.1(b). Amongst the three metals, k_e is highest for Ag followed by Au and Al at all temperatures. While k_e initially decreases and then plateaus with an increase in temperature for Ag, the k_e initially increases and then plateaus with an increase in temperature for Al and Au. The origin of this peak (not seen in Ag for considered temperature range) followed by plateau are the competing affects of increasing electron specific heat (shown in Fig. D.6 in App. D) and decreasing electron lifetime (due to increased e-p scattering at higher temperatures) with increasing temperature. The electrical conductivities follow the electron lifetime trend and decrease linearly with an increase in the temperature for all three metals.

The variation of the Lorentz number, L, calculated as $L = k_e/\sigma_e T$, with temperature is plotted in inset (ii) of Fig. 7.1(b). Based on the free electron gas model [164], the Wiedemann-Franz law predicts L to be constant for all metals and at all temperatures. As can be seen from inset (ii) of Fig. 7.1(b), however, L is dependent on both material and temperature. The maximum variation of L amongst the three metals is seen at a temperature of 200 K with values of 2.74×10^{-8} and 2.09×10^{-8} W- Ω/K^2 for Au and Ag.

From Figs. 7.1(a) and 7.1(b), while it is clear that electrons are the major contributor towards the thermal transport in all three metals at all temperatures considered, the contribution of phonons is as high as 5.5% in Al at a temperature of 100 K. In all three metals considered, the contribution of phonon towards the thermal transport is maximum at a temperature of 100 K (5.5%, 2.5%, and 2.0% for Al, Ag, and Au) and it decreases with an increase in temperature to 1.5%, 0.5%, and 0.5% for Al, Ag, and Au at a temperature of 500 K.

At a temperature of 300 K, our predicted values of total thermal conductivities are 252, 374, and 278 W/m-K for Al, Ag, and Au which agree within 13% with the experimentally measured values of 237, 429, and 317 W/m-K for Al, Ag, and Au [164]. For electrical conductivities, our predicted values are 3.46×10^7 , 5.89×10^7 , and 3.42×10^7 S/m at a temperature of 300 K for Al, Ag, and Au. These predictions agree with experiments within 6% for Al and Ag and within 25% for Au (experimentally measured electrical conductivities are 3.65×10^7 , 6.21×10^7 , and 4.55×10^7 S/m at a temperature of 295 K for Al, Ag, and Au) [164]. This 25% under-prediction of electrical conductivity of Au from DFT calculations is consistent with literature where other researchers also found over-estimation of electrical resistivity of Au from DFT calculations [182].

7.4 Thermal and Electrical Conductivities Accumulation Functions

The electron and phonon thermal conductivities (Eqn. 2.64 and Eqn. 2.50) can be rewritten using the electron and phonon mean free paths, $\Lambda_{\kappa m}$ and $\Lambda_{q\nu}$, as

$$K_{\alpha\beta} = -\frac{n_s}{VT} \sum_{\kappa m} (\epsilon_{\kappa m} - \mu)^2 \frac{\partial f_{\kappa m}}{\partial \epsilon} \frac{v_{\kappa m,\alpha} v_{\kappa m,\beta}}{|v_{\kappa m}|} \Lambda_{\kappa m}, \qquad (7.1)$$

$$k_{p,\alpha\beta} = \sum_{\boldsymbol{q}\nu} c_{\boldsymbol{q}\nu} \frac{v_{\boldsymbol{q}\nu,\alpha} v_{\boldsymbol{q}\nu,\beta}}{|\boldsymbol{v}_{\boldsymbol{q}\nu}|} \Lambda_{\boldsymbol{q}\nu}, \qquad (7.2)$$

where the electron and phonon mean free paths are defined as $\Lambda_{\kappa m} = |\boldsymbol{v}_{\kappa m}| \tau_{\kappa m}$ and $\Lambda_{q\nu} = |\boldsymbol{v}_{q\nu}| \tau_{q\nu}$. The mean free path of a carrier is a measure of the distance the carrier travels before getting scattered. The electron and phonon thermal conductivity accumulations can then be obtained using these new definitions of electron and phonon thermal conductivities as

$$K_{\alpha\beta}(\Lambda) = -\frac{n_s}{VT} \sum_{\kappa m}^{\Lambda_{\kappa m} < \Lambda} (\epsilon_{\kappa m} - \mu)^2 \frac{\partial f_{\kappa m}}{\partial \epsilon} \frac{v_{\kappa m,\alpha} v_{\kappa m,\beta}}{|v_{\kappa m}|} \Lambda_{\kappa m}, \qquad (7.3)$$

$$k_{p,\alpha\beta}(\Lambda) = \sum_{\boldsymbol{q}\nu}^{\Lambda_{\boldsymbol{q}\nu}<\Lambda} c_{\boldsymbol{q}\nu} \frac{v_{\boldsymbol{q}\nu,\alpha}v_{\boldsymbol{q}\nu,\beta}}{|\boldsymbol{v}_{\boldsymbol{q}\nu}|} \Lambda_{\boldsymbol{q}\nu}.$$
(7.4)

We plot the k_p and k_e accumulation functions of Al, Ag, and Au at a temperature of 300 K in Figs. 7.2(a) and 7.2(b). Phonons with mfp spanning around two orders of magnitude contribute towards the k_p in Ag and Au at a temperature of 300 K (2-62 and 1-64 nm in Ag and Au). In Al, the k_p accumulation is quite steep, with major contributions from phonons with mfps spanning over only one order of magnitude (2-22 nm). As can be seen from Fig. 7.2(b), the range of electron mfp is much smaller than that of phonons in the considered metals. At a temperature of 300 K, 90% contribution towards k_e comes from



Figure 7.2: (a) Phonon and (b) electron thermal conductivity $(k_p \text{ and } k_e)$ accumulation functions with respect to phonon/electron mfp for Al, Ag, and Au at a temperature of 300 K. The variation of gray phonon and electron mfp $(\overline{\Lambda_p} \text{ and } \overline{\Lambda_e})$ as a function of temperature for Al, Ag, and Au are shown in insets to (a) and (b).

electrons with mfp between 9-19, 30-53, and 21-38 nm for Al, Ag, and Au. As opposed to semiconductors, where the gray approximation results in incorrect phonon transport physics [107], this narrow range of electron mfp suggests the applicability of the gray approximation for electron transport in metals.

We define gray electron and phonon mean free paths, $\overline{\Lambda_e}$ and $\overline{\Lambda_p}$ as

$$\overline{\Lambda_e} = \frac{\sum_{\kappa m} (\epsilon_{\kappa m} - \mu)^2 \frac{\partial f_{\kappa m}}{\partial \epsilon} \frac{v_{\kappa m,\alpha}^2}{|v_{\kappa m}|} \Lambda_{\kappa m}}{\sum_{\kappa m} (\epsilon_{\kappa m} - \mu)^2 \frac{\partial f_{\kappa m}}{\partial \epsilon} \frac{v_{\kappa m,\alpha}^2}{|v_{\kappa m}|}},$$
(7.5)

$$\overline{\Lambda_p} = \frac{\sum_{\boldsymbol{q}\nu} c_{\boldsymbol{q}\nu} \frac{v_{\boldsymbol{q}\nu,\alpha}^2}{|\boldsymbol{v}_{\boldsymbol{q}\nu}|} \Lambda_{\boldsymbol{q}\nu}}{\sum_{\boldsymbol{q}\nu} c_{\boldsymbol{q}\nu} \frac{v_{\boldsymbol{q}\nu,\alpha}^2}{|\boldsymbol{v}_{\boldsymbol{q}\nu}|}}.$$
(7.6)

The gray phonon and electron mfp $(\overline{\Lambda_p} \text{ and } \overline{\Lambda_e})$ variation with temperature are plotted in the insets of Figs. 7.2(a) and 7.2(b) for Al, Ag, and Au. Both $\overline{\Lambda_p}$ and $\overline{\Lambda_e}$, decrease with an increase in temperature due to increased p-p and e-p scatterings at higher temperatures. Amongst the three metals considered, $\overline{\Lambda_p}$ and $\overline{\Lambda_e}$ are largest for Ag. $\overline{\Lambda_p}$ ($\overline{\Lambda_e}$) decreases from values of 11, 13, and 7 nm (42, 127, and 86 nm) at a temperature of 100 K to 2, 2, and 1 nm (10, 26, and 18 nm) at a temperature of 500 K for Al, Ag, and Au. The phonon mfp in semiconductors are, typically, one to three orders of magnitude larger than the electron mfp. As can be seen from the insets of Figs. 7.2(a) and 7.2(b) for metals, however, $\overline{\Lambda_p}$ is a factor of 4 to a factor of 15 smaller than $\overline{\Lambda_e}$ at all temperatures.

7.5 Phonon Thermal Transport in Aluminum and Silicon

To see the origin of small phonon mfp in metals, we next compare phonon thermal transport in Al with the well studied semiconductor Si by considering only p-p interactions (see



Figure 7.3: Aluminum and silicon phonon dispersion in high symmetry directions of the first Brillioun zone.



Figure 7.4: Frequency dependent three-phonon phase space for p-p scattering in Al and Si. The variation of phonon relaxation times (obtained by considering only p-p scattering) with frequency at a temperature of 300 K is shown in the inset.

Sec. D.4 of App. D for details on Si calculations). Al and Si have similar atomic masses (27 and 28 amu) and sit next to each other on the periodic table. Phonon dispersions of Al and Si along the high symmetry directions of the first Brillioun zone are plotted in Fig. 7.3. Both Al and Si have a face-centered cubic lattice structure with one and two atoms in the primitive unit-cell. The phonon group velocities in Al are smaller than that in Si [for instance, transverse acoustic phonon group velocity close to the Γ point in the Brillioun zone is 2800 m/s in Al as oppose to 4700 m/s in Si (see Fig. 7.3)]. This less than a factor of two difference in group velocities cannot fully explain the order of magnitude difference in Al and Si mfp [$\overline{\Lambda_p}$ is 97 nm in Si at a temperature of 300 K as compared to 4 nm in Al (see Sec. D.5 of App. D)]. To isolate the origin of this difference in Al and Si mfp, we plot the three-phonon phase space for Al and Si in Fig. 7.4.

The three-phonon phase space is a measure of the scattering space available for pp processes and is calculated by counting the number of p-p processes that satisfy the phonon energy and momentum conservation selection rules [168]. As can be seen from Fig. 7.4, for phonons with frequencies less than 4 THz, the available three-phonon phase space in Al is up to five times higher than that in Si. At a temperature of 300 K, this larger three-phonon phase space in Al, along with the larger Grüneisen parameters (see Sec. D.5 of App. D), results in higher p-p scattering and up to two orders of magnitude lower phonon lifetimes in Al than in Si (inset of Fig. 7.4). For phonon modes in Al with frequencies larger than 4 THz, even though three-phonon phase space is smaller in Al than in Si, have phonon lifetimes around an order of magnitude smaller than those in Si due to higher anharmonicity of phonon modes in Al [the heat capacity weighted mode-average value of the Grüneisen parameter in Al is 2.21 as oppose to 1.02 in Si at a temperature of 300 K (see Sec. D.5 of App. D)].

7.6 Summary

We discussed thermal and electrical transport properties of Al, Ag, and Au from firstprinciples based DFT and DFPT calculations. We found that the contribution of phonons towards the thermal transport can be as high as 5.5% in Al at a temperature of 100 K. Further, we also found that the electron mfp in all three metals have a narrower range but larger magnitudes as compared to phonon mfp at a temperature of 300 K. On comparing phonon thermal transport in Al with Si, we found that the near three orders of magnitude smaller phonon mfp in Al, are a result of (i) smaller phonon group velocities in Al, (ii) larger anharmonicity of Al as compared to Si, and (iii) an increased available three-phonon phase space in Al for low frequency phonons. Our calculations elucidate mode-dependent phonon and electron transport properties in metals which could be helpful in improving the design and performance of metal-semiconductor devices.

Summary and Outlook

8.1 Overview

The work presented in this thesis focused on the thermal transport in crystalline semiconductors and metals. The mode-dependent properties of fundamental thermal transport carriers (phonons in semiconductors and phonons and electrons in metals) were predicted from first-principles based density functional theory and density functional perturbation theory calculations. As opposed to the use of empirical force-fields, density functional theory force-fields are fitting-parameter free and result in a good agreement with experimental measurements of thermal conductivity. The mode-dependent transport properties of phonons were obtained from harmonic and anharmonic lattice dynamics calculations by considering phonon-phonon scattering (and electron-phonon scattering in metals). The mode-dependent electron transport properties were initially obtained using density functional theory and density functional perturbation theory on coarse grids and then interpolated using the maximally localized Wannier functions on finer grids.

In Chapter 2, for bulk simple semiconductors such as silicon and germanium, good agreement was obtained between temperature-dependent predicted and measured thermal conductivities for both isotopically enriched and naturally occurring materials. Use of the phonon free path sampling approach to model the additional phonon-boundary scattering in Chapter 3, resulted in an excellent agreement with experimental data for the in-plane thermal transport in silicon nanoporous thin films. The work concluded that coherent phonon affects are not present in silicon nanostructures at a temperature of 300 K with feature size larger than 100 nm. In Chapter 4, in compound semiconductors, apart from a

material's Debye temperature, lattice constant, Grüneisen parameters, and atomic masses, the thermal conductivity was found to also depend on the acoustic-optical phonon frequency gap. The maximum thermal conductivity is obtained when the acoustic-optical phonon frequency gap nearly equals the acoustic phonon frequency width.

For the novel materials black and blue phosphorene (two-dimensional arrangement of phosphorus atoms), for which there is no experimental thermal characterization, temperaturedependent thermal conductivities were predicted and compared with other two-dimensional materials in Chapter 5. The thermal transport in black phosphorene was found to be highly anisotropic and the anisotropy is predicted to be tunable with tensile uni-axial strain. Further, in contrast to graphene where out-of-plane acoustic phonons contribute 75% to the thermal conductivity at room temperature, the contribution of out-of-plane acoustic phonons is found to be less than 45% in both black and blue phosphorene at room temperature.

For isotopically enriched silicon at a temperature of 300 K, the effect of exchangecorrelation function (used in pseudopotential generation for density functional theory calculations) on the predicted thermal conductivity was studied in Chapter 6. All exchangecorrelation functions, with the exception of BLYP, were found to predict similar thermal conductivities that were an under-prediction of the experimental value by 3-17%. The BLYP exchange-correlation, on the other hand, was found to over-predict the experimental thermal conductivity by 13%. Previous first-principles based predictions of silicon thermal conductivity were found to possibly have better agreement with experimental results due to the use of unconverged simulation parameters.

In Chapter 7, the phonon and electron contribution towards the thermal conductivity were predicted in aluminum, silver, and gold by considering phonon-phonon and electronphonon scattering. At a temperature of 100 K, the phonon contribution was found to be as high as 5.5% in aluminum. While the range of phonon mean free paths were found to be larger than the range of electron mean free paths, the gray electron mean free paths were found to be larger than gray phonon mean paths in all three metals at all temperatures. On comparing phonon thermal transport in aluminum with silicon, the origins of smaller phonon mean free paths in aluminum were found to be (i) smaller phonon group velocities, (ii) larger anharmonicity, and (iii) an increased three-phonon scattering phase space.

8.2 Future Work

The work presented in this thesis elucidated thermal transport physics and provides modedependent thermal transport carrier properties in small unit-cell non-polar crystalline semiconductors and metals. Possible future directions include the study of crystals and polar materials.

8.2.1 Large Unit-cell Crystals

Large unit-cell size crystals such as zeolites, hydrates, perovskites, and fullerene derivatives have multiple technological applications, e.g., carbon dioxide capture, catalysts, and solar cells [183, 184, 185, 186, 187]. These large unit-cell size crystals have more than 4 atoms in the unit-cell and are computationally more expensive to study as compared to small unitcell size crystals. The scaling of computational cost with number of atoms is discussed in Sec. 2.1.8.1.

8.2.1.1 Intermediate Unit-cells (4-12 atoms)

For intermediate unit-cell size crystals, depending on the available computational resources, the thermal transport prediction approach presented in this work could be readily applied. The relatively large number of atoms in the unit-cell of intermediate unit-cell size crystals would result in larger number of density functional theory supercell forces calculations as compared to small unit-cell size crystals [the number of DFT calculations depend on types of atoms and symmetry of the unit-cell (see App. A for details)]. The cost of each computation, however, would be similar to small unit-cell size crystals.

8.2.1.2 Large Unit-cells (more than 12 atoms)

While the increase in lattice dynamics calculations cost due to an increase in number of atoms would be partially compensated by reduced number of phonon wavevectors (number of unitcells) needed (Sec. 2.1.8.1), the number of density functional theory supercell calculations and the size of the density functional theory supercell would increase significantly for large unit-cell size crystals. As a result, thermal conductivity predictions for large unit-cell size crystals would require better scaling methods such as linearly-scaling density functional theory [188, 189]. Alternatively, instead of using lattice dynamics for phonon lifetimes calculations, which require a large number of density functional theory supercell calculations, one could also use empirical models with input from density functional theory to study the thermal transport in large unit-cell size crystals [190]).

8.2.2 Polar Materials

Another category of crystals that were not studied in this work are polar materials such as rock-salt ionic crystals, perovskites, and titania. These materials have potential applications in thermoelectric energy conversion, solar cells, and memory devices [191, 192, 193]. The computational challenge in studying these materials is how to handle the long range Coulombic interactions. One of the ways of handling these long-range interactions in the harmonic calculations is to add their contribution as an analytical correction in the phonon dynamical matrices [194, 195]. This analytical correction results in the splitting of longitudinal optical and transverse optical phonon modes close to the Gamma point. The effect of these long-range interactions is, however, still not well studied for cubic force constants (i.e., their effect on phonon-phonon scattering). Due to the long-range interactions, the calculation of cubic force constants for these crystals using the density functional theory results in large computational cell sizes. For instance, Feng et al. [196] studied the thermal transport in SrTiO₃ using 320 atoms supercell for density functional theory based force calculations. A possible alternative to handling these long-range interactions using large supercell sizes is to use the density functional perturbation theory approach for cubic force constants extraction as discussed by Mukhopadhyay and Stewart for cubic-BN under pressure [133].

Force Constants Cutoff and Supercell Size

The thermal conductivity calculated using DFT calculations (and empirical force-fields with electrostatic interactions) depends on the force constants cutoff and the supercell size used in the force constants extraction. While the thermal conductivity converges with using larger force constant cutoff and larger supercell size, using large force constant cutoffs results in a large number of DFT supercell force calculations and a large supercell size results in each supercell force calculation being more computationally expensive. Starting with a small cutoff and increasing to a larger cutoff is troublesome in that not all larger cutoff force constants can be calculated from a given supercell size. Hence, if a thermal conductivity is not converged for the largest possible cutoff in a given supercell, then one needs to repeat all the DFT force calculations on a larger supercell size. Further, even if thermal conductivity is converged with respect to force constant cutoffs in a given supercell, a convergence with respect to supercell size must be performed to make sure that there is no effect of periodic images of atoms on the thermal conductivity. Here we discuss a practical approach that could be helpful in reducing computational load by simultaneous convergence of thermal conductivity with force constants cutoff and supercell size.

A.1 Maximum allowed force constant cutoff in a given supercell

Before discussing an approach to decide on supercell size and get an idea about the force constant cutoff, we first briefly discuss the maximum allowed force constant cutoff in a given supercell due to periodic boundary conditions. As can be seen from Fig. A.1, due to periodic boundary conditions, the displacement given to an atom in the computational cell is reflected in the displacement of atoms in the periodic images of the computational cell. If the supercell is not big enough, then the forces experienced by different atoms in the computational cell will include contribution from the displaced atom in the periodic images as well. To avoid this issue, the computational cell size in the DFT calculations (performed using the periodic planewaves based basis set) should be at least twice as large as the force constant cutoff.

A.2 Force constant cutoff needed

To gauge an idea about the force constant cutoff and the supercell size needed in the thermal conductivity calculations, we displace one atom from its equilibrium position and look at the forces on different atoms in the computational cell. For instance, in Fig. A.2, we displaced one of the corner atoms in a 216 atom silicon computational cell and plot the magnitude of forces acting on different atoms as a function of their distance from the displaced atom. We can make three observations from this force displacement plot:

 The forces acting on different atoms go to less than 1% of the total/maximum force after a distance of around 5 Å, which is less than half of the computational cell size (computational cell size is 3 × 5.4 = 16.2 Å). This result suggests that the maximum force constant cutoff for this system is less than 5 Å and forces calculated using a 216



Figure A.1: Computational/supercell with central atom (red color) displaced from its equilibrium position. The dark atoms represent the central supercell and the light atoms represent neighboring images due to periodic boundary condition. The red atom gets displaced in the neighboring images of the computational cell as well. The force experienced by atom blue is, therefore, the sum of forces due to displacement of the red atom in the computational cell and displacement of red atoms in all periodic images of the computational cell which are within the cutoff radius r_c . To make sure that atom blue experiences force only due to displaced atom in the computational cell, the computational cell size should be at least twice the interaction cutoff (please note that the computational cell shown in this figure does not satisfy this nearest-image convention).



Figure A.2: Forces acting on different atoms in the computational cell when one of the corner atom is displaced by a small amount in a 216 atoms silicon computational cell. The distance is calculated with respect to the displaced atom. The horizontal dashed line is to guide the eye and represents 1% of the maximum force.

atom computational cell will not have any affect due to periodic boundary conditions.

- 2. The 5 Å cutoff represents the total force cutoff and has contributions from both harmonic and cubic force constants (and from higher-order force constants). Typically, cubic force constants are shorter range as compared to the harmonic force constants [60]. As such, one can always calculate harmonic force constants from a larger supercell and subtract out the contribution of these from the forces to gauge an idea about the cubic force constants cutoff (the contribution of harmonic force constants towards the forces can be obtained by using up to harmonic terms in the force Taylor series, i.e., by performing the summation of harmonic force constants times displacement for each atom).
- 3. In this case, if we perform summation of forces then we will see that the summation goes to zero and remains zero after a distance of 5 Å (which is equivalent to satisfying Newton's second law). In some cases, however, we will see that the summation does not go to zero after half of the computational cell size (or even at the cell boundary!). From our experience, we found that this happens due to either very small computational cell size or because of incorrect forces from DFT calculations due to insufficient electron grid sampling or very small planewave energy cutoff.

We note that the 1% threshold that we used here is just for the discussion in this section. Depending on the system, one could need a tighter threshold than 1%. Also, after getting an idea about computational size and force constant cutoff, one still needs to do thermal conductivity convergence with respect to both of these parameters.

The computational cost for this one simple force calculation is much cheaper as compared to the total computational cost of calculating the thermal conductivity. Therefore, one can simply do these simple calculations to get an idea about the initial guesses for force constants cutoffs and computational cell size for a new system.

Implementation of Translational Invariance

The harmonic and cubic force constants obtained using DFT calculations do not satisfy crystal TI constraints due to finite numerical precision errors. A failure to satisfy TI constraints leads to non-physical results such as non-zero acoustic phonon vibration frequencies at the center of the Brillioun zone. The TI constraints can be satisfied by either (i) using TI constraints as extra equations in the force constant extraction, (ii) adding small correction terms in the extracted diagonal/self-force constants elements, or (iii) by using the Lagrange multipliers approach where small correction terms are added to all extracted force constants [instead of adding to only diagonal term in approach (ii)]. In this work, we used the Lagrangian approach. We present the derivation of the correction terms for the cubic force constants here, which can be easily modified for harmonic force constants (if harmonic force constants are extracted from DFPT calculations then TI constraints can be satisfied in DFPT calculations itself). The derivation of correction terms presented here is adopted from Ref. [145].

We present the derivation of the correction terms to be added to the cubic force constants in two different forms. While the derivation is similar for both forms, the first form is for satisfying TI on a full list of force constants and the second form is for a crystal symmetry-reduced list of independent force constants.

B.1 Translational invariance on full list of force constants

The TI constraints for cubic force constants are:

$$\sum_{k} \Psi_{ijk}^{\alpha\beta\gamma,a} = 0 \qquad \forall (\alpha\beta\gamma, ij), \tag{B.1}$$

where $\Psi_{ijk}^{\alpha\beta\gamma,a}$ represents the actual (analytical) cubic force constant element between atoms i, j, and k in the $\alpha, \beta, and \gamma$ directions. In our calculations, atom index i vary over all atoms in the unit-cell, while indices j and k vary over all atoms within the interaction cutoff. Let's say that the extracted numerical force constants are $\Psi_{ijk}^{\alpha\beta\gamma,n}$ and the small correction to be added is $\Psi_{ijk}^{\alpha\beta\gamma,c}$ such that $\Psi_{ijk}^{\alpha\beta\gamma,a} = \Psi_{ijk}^{\alpha\beta\gamma,n} + \Psi_{ijk}^{\alpha\beta\gamma,c}$. Using Eqn. B.1

$$B_{ij}^{\alpha\beta\gamma} \equiv \sum_{k} \left(\Psi_{ijk}^{\alpha\beta\gamma,n} + \Psi_{ijk}^{\alpha\beta\gamma,c} \right) = 0 \qquad \forall (\alpha\beta\gamma,ij).$$
(B.2)

Our objective is to minimize the magnitude of the correction needed for each force constant, i.e., to minimize the cost function C defined as

$$C = \frac{1}{2} \sum_{\substack{ijk\\\alpha\beta\gamma}} \left(\Psi_{ijk}^{\alpha\beta\gamma,c} \right)^2, \tag{B.3}$$

while satisfying Eqn. B.2. This is a standard optimization problem with constraints and can be solved using the Lagrangian multiplier approach. Accordingly, after introducing the Lagrangian multipliers, $\Lambda_{ij}^{\alpha\beta\gamma},$ we have

$$\frac{\partial \left(C + \sum_{\substack{i'j' \\ \alpha'\beta'\gamma'}} \Lambda_{i'j'}^{\alpha'\beta'\gamma'} B_{i'j'}^{\alpha'\beta'\gamma'}\right)}{\partial \Psi_{ijk}^{\alpha\beta\gamma,c}} = 0,$$

$$\frac{\partial \left(\frac{1}{2} \sum_{\substack{i'j'k' \\ \alpha'\beta'\gamma'}} \left(\Psi_{i'j'k'}^{\alpha'\beta'\gamma',c}\right)^2 + \sum_{\substack{i'j' \\ \alpha'\beta'\gamma'}} \left[\Lambda_{i'j'}^{\alpha'\beta'\gamma'} \sum_{k'} \left(\Psi_{i'j'k'}^{\alpha'\beta'\gamma',c} + \Psi_{i'j'k'}^{\alpha'\beta'\gamma',c}\right)\right]\right)}{\partial \Psi_{ijk}^{\alpha\beta\gamma,c}} = 0,$$
(B.4)

which can be solved for the correction term as,

$$\Psi_{ijk}^{\alpha\beta\gamma,c} = -\Lambda_{i'j'}^{\alpha'\beta'\gamma'}.$$
(B.5)

Equation B.5 can be substituted into Eqn. B.2 to solve for $\Lambda_{ij}^{\alpha\beta\gamma}$ as

$$\Lambda_{ij}^{\alpha\beta\gamma} = \frac{\sum_{k} \Psi_{ijk}^{\alpha\beta\gamma,n}}{\sum_{k} 1},\tag{B.6}$$

which by back-substituting into Eqn. B.5 gives,

$$\Psi_{ijk}^{\alpha\beta\gamma,c} = -\frac{\sum_{k'} \Psi_{ijk'}^{\alpha\beta\gamma,n}}{\sum_{k'} 1}.$$
(B.7)

Eqn. B.7 implies that the correction term is same for all force constants involved in a given TI constraint and is the average of the amount by which the TI constraint is not satisfied.

B.2 Translational invariance on symmetry-reduced list of independent force constants

As discussed in Sec. 2.1.6.3, all force constants are not independent. Some of these are related to each other through crystal symmetries. If M_{pq} is the matrix which maps the full list of force constants, Ψ^{f} , to symmetry-reduced list of force constants, Ψ^{r} , then

$$\sum_{q} M_{pq} \Psi_q^r = \Psi_p^f. \tag{B.8}$$

[Please note that, as opposed to Sec. B.1, the cubic force constants here are enumerated with single index p and q which vary over all possible cubic force constant elements in full and symmetry-reduced lists.]

Further, TI constraints on cubic force constants, i.e., Eqn. B.1 can be re-written in the matrix form as

$$\sum_{s} T_{ts} \Psi_s^f = 0 \qquad \forall (t), \tag{B.9}$$

where index t vary over different TI constraints (equals $27 \times n_u \times n_c$, where n_u and n_c are number of atoms in the unit-cell and number of atoms within the interaction cutoff). From Eqn. B.8 and Eqn. B.9, TI constraints can be written in terms of symmetry-reduced force constants as

$$\sum_{pq} T_{tp} M_{pq} \Psi_q^r = 0 \qquad \forall (t) \qquad \text{or},$$
$$\sum_q A_{tq} \Psi_q^r = 0 \qquad \forall (t), \qquad (B.10)$$

where $\boldsymbol{A} = \boldsymbol{T}\boldsymbol{M}$.

Assuming that a small correction factor, Ψ_q^c is needed to be added to the numerically

extracted reduced force constants, Ψ_q^n , such that $\Psi_q^r = \Psi_q^n + \Psi_q^c$, Eqn. B.10 can be rewritten as

$$\sum_{q} A_{tq} \left(\Psi_q^n + \Psi_q^c \right) = 0 \qquad \forall (t).$$
(B.11)

The objective is again to minimize the cost function, which similar to Sec. B.1 is defined as $C = \frac{1}{2} \sum_{q} \Psi_{q}^{c^{2}}$. By using the Lagrangian multiplier, Λ_{t} , the Ψ_{q}^{c} can be obtained from the solution of

$$\frac{\partial \left\{ \frac{1}{2} \sum_{q} \Psi_{q}^{c^{2}} + \sum_{t} \Lambda_{t} \left(\sum_{q} A_{tq} \left(\Psi_{q}^{n} + \Psi_{q}^{c} \right) \right) \right\}}{\partial \Psi_{s}^{c}} = 0,$$
(B.12)

which on solving results in

$$\Psi_s^c = -\sum_t \Lambda_t A_{ts}.$$
(B.13)

Substituting Eqn. B.13 into Eqn. B.11 gives

$$\sum_{q} A_{tq} \left(\Psi_{q}^{n} - \sum_{t'} \Lambda_{t'} A_{t'q} \right) = 0, \quad \text{or}$$
$$\sum_{t'} \Lambda_{t}' \sum_{q} A_{tq} A_{t'q} = \sum_{q} A_{tq} \Psi_{q}^{n} \quad \forall(t). \quad (B.14)$$

Equation B.14 represents a set of linear equations that can be solved for $\Lambda_{t'}$. Once $\Lambda_{t'}$ are known, Eqn. B.13 can then be used to obtain the correction term Ψ_q^c in the numerically extracted symmetry-reduced force constants.

In this work, we enforced TI constraints using the Lagrangian approach on symmetryreduced list of force constants as enforcing TI constraints on the full list result in more numerical noise and lots of redundant/dependent constraints.

Additional Information for "Strongly anisotropic in-plane thermal transport in single-layer black phosphorene"

C.1 Thermal Conductivity Convergence

Predicting thermal conductivity from lattice dynamics calculations and the Boltzmann transport equation (BTE) requires harmonic and anharmonic force constants as input. We obtain these harmonic and anharmonic force constants from first-principles-driven density functional perturbation theory (DFPT) and density functional theory (DFT) calculations. The calculation of thermal conductivity from the DFPT and DFT force constants requires specification of the supercell size, the force interaction cutoffs, and, for 2D materials like black phosphorene and blue phosphorene. the amount of vacuum needed to remove interlayer interactions. In this section, we discuss the convergence of the thermal conductivity of black phosphorene and blue phosphorene with these calculation parameters.

C.1.1 Cubic Force Constant Cutoff

In Figs. C.1(a) and C.1(b), we plot the thermal conductivity of black phosphorene and blue phosphorene as a function of the cubic force-constant interaction cutoff at a temperature of 300 K. The cubic force constants are obtained using 144 (128) atom supercells with 30



Figure C.1: Thermal conductivity variation of (a) black phosphorene and (b) blue phosphorene with the cubic force constant interaction cutoff at a temperature of 300 K.

Å (17 Å) of vacuum for black (blue) phosphorene. Translational invariance (TI) is satisfied using the Lagrangian approach presented by Li et al. [145] The thermal conductivities in these figures are predicted using the relaxation time approximation (RTA) solution of the BTE.

As can be seen from Figs. C.1(a) and C.1(b), the thermal conductivity for both black phosphorene and blue phosphorene converges beyond an interaction cutoff of 5.5 Å. In all reported calculations, we use a interaction cutoff of 6.2 Å for black phosphorene and 6.5 Å for blue phosphorene. The predicted thermal conductivities changes by 12% (10%) when the interaction cutoff is increased from 6.2 Å to 7.6 Å (6.5 Å to 8.6 Å) for black (blue) phosphorene.

C.1.2 DFT Supercell Size and Vacuum Width

To determine the effect of supercell size and vacuum width on the predicted thermal conductivities of black phosphorene and blue phosphorene, we compared cubic force constants calculated using two different supercell sizes and vacuum widths. For black phosphorene,



Figure C.2: The effect of translational invariance on the thermal conductivity of (a) black phosphorene and (b) blue phosphorene.

we compared cubic force constants calculated on a 144 atom supercell with 30 Å of vacuum to those from a 100 atom supercell with 20 Å of vacuum. The two sets of force constants were found to be very close, with differences of less than 2% for the largest (i.e., the self) force constant. For blue phosphorene, we compared force constants calculated on 128 and 98 atom supercells with 17 Å of vacuum and found a difference of less than 1% for the largest force constant.

C.1.3 Translational Invariance of Cubic Force Constants

The cubic force constants obtained using finite differences of the Hellman-Feynman forces do not satisfy crystal symmetries and translational invariance (TI) (i.e., the acoustic sum rule) because of numerical errors. These small numerical errors can result in large changes in thermal conductivity predictions, as shown by Lindsay et al. [39]. It is therefore necessary to satisfy the crystal TI constraint by modifying the cubic force constants. In this study, we satisfied this TI constraint using the Lagrangian approach presented by Li et al. [145]

The effect of TI on the thermal conductivity (calculated using the RTA) of black phos-



Figure C.3: Thermal conductivity prediction of (a) black phosphorene and (b) blue phosphorene using the RTA and iterative (full) solution of the BTE.

phorene and blue phosphorene is shown in Figs. C.2(a) and C.2(b). At a temperature of 300 K, not satisfying the cubic TI constraint results in an under-prediction of thermal conductivity by 40% (47%) in the zigzag (armchair) direction of black phosphorene and by 33% in blue photosphere. We note that the effect of not satisfying TI is more severe in phosphorene, as compared to that reported by Lindsay et al. [39] for Ge (29% at 300 K), because of fewer crystal symmetries in phosphorene.

C.1.4 RTA Versus Full Solution of the BTE

The thermal conductivity variation of black phosphorene and blue phosphorene using the RTA and an iterative solution of the BTE are plotted as a function of temperature in Figs. C.3(a) and C.3(b). The cubic force constants are obtained using the 144 atom supercell with 30 Å of vacuum for black phosphorene and the 128 atom supercell with 17 Å of vacuum for blue phosphorene. The TI for cubic force constants is satisfied as discussed in the previous section.



Figure C.4: Volumetric heat capacity variation of black phosphorene and blue phosphorene with temperature. The dashed vertical line corresponds to the temperature at which the heat capacity is 95% of its maximum value (i.e., the Debye temperature).

As can be seen from Figs. C.3(a) and C.3(b), the RTA solution of the BTE underpredicts the thermal conductivity for both black phosphorene and blue phosphorene. At a temperature of 300 K, the under-predictions are by a factor of 1.4 and 1.2 in the zigzag and armchair directions for black phosphorene and a factor of 2.0 for blue phosphorene. As explained by Lindsay et al. [13] for graphene, these under-predictions in thermal conductivity are due to Normal phonon processes being treated as resistive in the RTA solution of the BTE.

C.2 Debye Temperature

In Fig. C.4, we plot the volumetric heat capacity variation of black phosphorene and blue phosphorene with temperature. In our calculations, we considered only the phonon (lattice)

contribution towards the heat capacity. At a temperature of 300 K, the heat capacity of blue phosphorene is 0.75 times the heat capacity of black phosphorene. We estimate the Debye temperature as the temperature at which the heat capacity is 95% of its maximum value. For both phosphorene allotropes, the Debye temperature is 500 K.

C.3 Contribution of Acoustic Phonon Branches to Thermal Conductivity

We plot the contribution of the different acoustic phonon beaches towards the total thermal conductivity as a function of temperature in Figs. C.5(a) [black phosphorene (zigzag)], C.5(b) [black phosphorene (armchair)], and C.5(c) (blue phosphorene). For black phosphorene, the maximum contribution is from longitudinal acoustic (LA) phonon modes in the zigzag direction and transverse acoustic (TA) phonon modes in the armchair direction. The contribution of out-of-plane (ZA) phonon modes in black phosphorene remains constant with temperature at around 31% (12%) for the zigzag (armchair) direction of heat flow. For blue phosphorene, the maximum contribution comes from the ZA phonon modes and is more than 42% for the range of temperatures considered.

C.4 Sound Velocity Variation with Uni-axial Strain

In Figs. C.6(a) and C.6(b), we plot the stress generated and sound velocity in the zigzag and armchair direction of black phosphorene when it is subjected to a uni-axial strain along the zigzag direction. The sound velocity decreases by 4.5% along the zigzag direction and increases by 20% in the armchair direction when strain is changed from 0 to 6% along the zigzag direction. These changes in the sound velocity suggest (according to Eqn. 1 in the main text) a reduction in the thermal transport anisotropy to 2.2 for 6% strain along the


Figure C.5: Contribution of acoustic phonon branches [longitudinal acoustic (LA), transverse acoustic (TA), and out-of-plane acoustic (ZA)] towards the total thermal conductivity of (a) black phosphorene in the zigzag direction, (b) black phosphorene in the armchair direction, and (c) blue phosphorene.



Figure C.6: Variation of stress and sound velocity in black phosphorene with uni-axial strain along the zigzag [(a) and (b)] and the armchair [(c) and (d)] directions.

zigzag direction.

For uni-axial strain along the armchair direction [Figs. C.6(c) and C.6(d)] in black phosphorene, the sound velocity decreases by only 2% in the zigzag direction and 15% in the armchair direction when strain is changed from 0 to 6%. The thermal conductivity anisotropy, therefore, is estimated to increase to 4.6 under 6% uni-axial strain in black phosphorene along the armchair direction.

Additional Information for "Thermal transport by phonon and electrons in metals from first-principles"

D.1 Simulation Parameters

For electronic transport properties calculations, we calculate the electron Hamiltonian, the phonon dynamical matrix, and the electron-phonon coupling coefficients on coarse $18 \times 18 \times$ 18 electron and $6 \times 6 \times 6$ phonon wavevector grids using the density functional theory (DFT) and density functional perturbation theory (DFPT) calculations as implemented in the package Quantum Espresso (QE) [40]. The electron wavevector grid and planewave energy cutoffs used in the integration of the Brillioun zone for constructing charge density and dynamical matrices are reported in the Table D.1. We carefully checked for convergence of total energy with respect to electronic wavevector grid and planewave energy cutoff. We used Gaussian smearing of 0.1 Ry to improve convergence with number of electronic k-points. After obtaining required properties on coarse grids, we used electron-phonon Wannier (EPW) package to first calculate maximally localized Wannier functions (MLWF) and then to perform the interpolation of required properties to $80 \times 80 \times 80$ electron and $32 \times 32 \times 32$ phonon wavevector grids using Wannier functions [40, 42, 42]. The number of Wannier functions employed for different metals are reported in Table D.1. We used a smearing of 30 meV for satisfying the energy conservation delta functions in electronphonon scattering rate calculations (Eqns. 2.65 and 2.67).

Au	Ag	Al	Metal
11	11	ಲು	Number of Valence Electrons Considered
4.082	4.074	3.984	Relaxed Lattice Constant using QE (Å)
100	90	70	Planewave Energy Cutoff for electron- phonon calculations using QE (Ry)
$12 \times 12 \times 12$	$12 \times 12 \times 12$	$14 \times 14 \times 14$	Electronic Wavevector Grid for integration of charge density over the Brillioun zone
230	250	240	Planewave Energy Cutoff for Force Calculations using VASP (eV)
6	6	4	Number of MLWFs for interpolation using Wannier functions

Table D.1:
DFT
simulation
parameters
used
for
different
metals.

For phonon-phonon scattering rate calculations, the inter-atomic force constants are obtained using a finite differencing of the Hellmann-Feynman forces obtained on a 216 atom supercells with one or two atoms displaced from their equilibrium position by 0.01 Å using a DFT package VASP. We used a $3 \times 3 \times 3$ electronic wavevector gird and first order Methfessel-Paxton smearing of 0.1 eV [197]. The planewave energy cutoffs used are reported in Table D.1. The convergence of phonon properties with respect to supercell size and electron k-point sampling is tested thoroughly by Grabowski et al.[198] We used third nearest neighbors interaction cutoff for cubic force constants and we satisfied translational invariance using the Lagrangian approach [145]. The energy conservation delta functions involved in phonon-phonon scattering rate calculations (Eqn. 2.28) are satisfied using the adaptive broadening approach discussed by Turney et al. [23]

We performed non-spin calculations using the local density approximation (LDA) exchangecorrelation based norm-conserving and projected augmented wave pseudopotentials in QE and VASP. The relaxed lattice structure obtained using QE (lattice constants reported in Table D.1) is used for calculation of force constants in VASP as well. We note that since we are using QE relaxed structure in force calculation from VASP, the extracted force constants do not correspond to zero-pressure. The difference in relaxed lattice constant using QE and VASP is found to be less than 1%. From our previous study on strain affects on thermal conductivity of both a soft and hard material, we expect the effect of 1% strain on the phonon thermal conductivity to be within the numerical uncertainties (10%) [25]. Please note that the choice to use VASP for supercell force calculations is a pragmatic one as we are unable to get forces from QE (on 216 atom supercells with $3 \times 3 \times 3$ electronic wavevector grid) with our computational resources.



Figure D.1: Phonon thermal conductivity variation of Ag with temperature for different cubic force constant interaction cutoffs. The phonon thermal conductivity is obtained by considering only the phonon-phonon scattering in this plot. NN and p-p denotes nearest neighbors and phonon-phonon.

D.2 Convergence Tests

D.2.1 Cubic force constant cutoff

We first plot the phonon thermal conductivity of Ag as a function of temperature by considering different cubic force constant cutoffs in Fig. D.1. The cubic force constant interaction cutoff affects only the phonon-phonon scattering rate and as such we plot the thermal conductivities obtained by considering only phonon-phonon interactions. As can be seen from Fig. D.1, the phonon thermal conductivity of Ag remains unaffected (changes less than 1%) in increasing the cubic force constant cutoff from second to third nearest neighbors. For the other metals, we find that the thermal conductivity difference for including up to second and third nearest neighbors is within the numerical uncertainties also.



Figure D.2: Phonon thermal conductivity variation with phonon wavevector grid for Al at a temperature of 300 K. The phonon thermal conductivity is obtained by considering only the phonon-phonon scattering in this plot. Dashed black-lines are for guiding the eye and represent a 1% variation from $36 \times 36 \times 36$ phonon thermal conductivity. p-p denotes phonon-phonon.

Therefore, we include up to third nearest neighbor interactions in our thermal conductivity calculations for all metals.

D.2.2 Phonon wavevector grid

The phonon thermal conductivity variation of Al as a function of phonon wavevector grid at a temperature of 300 K is plotted in Fig. D.2. The phonon thermal conductivities for this plot are obtained by considering only the phonon-phonon interactions. The dashed lines in the figure are for guiding the eye and denotes 1% variation from the thermal conductivity corresponding to the maximum phonon wavevector grid considered. As can be seen from Fig. D.2, the phonon thermal conductivity is converged within 1% for an increase in the grid size beyond $24 \times 24 \times 24$. For other metals also, we found $24 \times 24 \times 24$ phonon

Coarse Electronic Grid	Fermi Energy (eV)			
Coarse Electronic Grid	Al	Ag	Au	
6	8.1644	13.4523	15.9755	
8	8.0881	13.4310	15.9427	
10	8.1197	13.4372	15.9389	
12	8.1112	13.4402	15.9386	
14	8.1121	13.4409	15.9385	
16	8.1123	13.4410	15.9385	
18	8.1122	13.4410	15.9385	
20	8.1122	13.4410	15.9385	
22	8.1122	13.4410	15.9385	
24	8.1122	13.4410	15.9385	

Table D.2: Fermi energy variation with coarse electronic wavevector grid for different metals. 0.0001 eV convergence is obtained for Al, Ag, and Au for $18 \times 18 \times 18$ electronic wavevector grid.

wavevector grid to be converged within 1% for phonon thermal conductivity. As will be shown in Sec. D.2.5, however, for electron transport properties calculations by considering electron-phonon interactions, we need finer (i.e., $32 \times 32 \times 32$ in present study) phonon wavevector grids than $24 \times 24 \times 24$. We used, therefore, $32 \times 32 \times 32$ phonon wavevector grid for phonon thermal conductivity calculations as well.

D.2.3 Coarse electronic wavevector grid

To determine the converged coarse electronic grid for different metals, we first calculate the Fermi energy using different resolutions of coarse electronic wavevector grid. The Fermi energies obtained for different metals are reported in Table D.2. We note that the values of Fermi energies reported in Table D.2 are obtained directly from the density functional theory calculations without any need of Wannier functions. As can be seen from Table D.2, the Fermi energy converges to within 0.0001 eV for electronic wavevector grids larger than $18 \times 18 \times 18$ for all metals and, therefore, $18 \times 18 \times 18$ coarse electronic wavevector grid is used in this study.

D.2.4 Coarse phonon wavevector grid

To further check the convergence of coarse electronic wavevector grid and to get a converged coarse phonon wavevector grid, we plot the spatial decay of the Hamiltonian, the phonon dynamical matrix, and the electron-phonon coupling matrix elements in the Wannier functions representation for silver in Fig. D.3. All of these quantities should decay to zero to have localized Wannier functions which are necessary for good quality interpolation of these quantities. As can be seen from Fig. D.3, all of these quantities decay very quickly with distance between the unit-cells and thus suggests the sufficiency of coarse electronic and phonon wavevector grids for interpolation.

D.2.5 Fine phonon wavevector grid and energy delta functions for electron-phonon interactions

The variation of electrical conductivity and electron thermal conductivity of Au at a temperature of 300 K with fine phonon wavevector grid and smearing amount for satisfying energy conservation delta functions are shown in Figs. D.4 (a) and (b). The fine electronic



Figure D.3: Spatial decay of the largest component of the (a) Hamiltonian, $H(0, \mathbf{R_e})$, (b) Dynamical matrix, $D(0, \mathbf{R_p})$, (c) electron-phonon coupling matrix element, $g(\mathbf{R_e}, 0)$, and (d) $g(0, \mathbf{R_p})$ for silver. The data are normalized with their largest values and are plotted as a function of position of electron unit-cell, $\mathbf{R_e}$, and phonon unit-cell, $\mathbf{R_p}$, used for describing electrons and phonons in the real space.



Figure D.4: Variation of electrical conductivity and electron thermal conductivity of Au at a temperature of 300 K with (a) phonon wavevector grid and (b) smearing/broadening used in satisfying the energy delta functions. e-p represents electron-phonon.

wavevector grid of $80 \times 80 \times 80$ k-points is used for all of the results reported in Fig. D.4. For Fig. D.4 (a), a smearing of 30 meV is used to satisfy the delta functions and for Fig. D.4 (b) a fine phonon wavevector grid of $32 \times 32 \times 32$ q-points is used. As can be seen from Figs. D.4 (a) and (b), the variation in both electrical conductivity and electron thermal conductivity is less than 5% with varying the fine phonon wavevector grid from $24 \times 24 \times 24$ to $40 \times 40 \times 40$ and varying the semaring amount from 3 meV to 50 meV.

D.2.6 Fine electron wavevector grid

The variation of electrical conductivity and electron thermal conductivity of Au at a temperature of 300 K with fine electron wavevector grid is plotted in Fig. D.5. All data points are calculated using a fine phonon wavevector grid of $36 \times 36 \times 36$ and smearing of 30 meV. As can be seen from Fig. D.5, in varying the fine electronic wavevector grid around $80 \times 80 \times 80$ to $60 \times 60 \times 60$ and $100 \times 100 \times 100$, changes in both electrical conductivity and electron thermal conductivity are less than 11%. We note that among all the simulation



Figure D.5: Variation of electrical conductivity and electron thermal conductivity of Au at a temperature of 300 K with fine electron wavevector grid. e-p represents electron-phonon.

parameters, we found electron transport properties to be most sensitive to the fine electron wavevector grid. For all the metals considered, the minimum variation is seen in Al with variation less than 2%. For Ag, the variation is within 10% with an increase in grid from $70 \times 70 \times 70$ to $80 \times 80 \times 80$.

D.3 Heat Capacity

The contribution of electrons and phonons towards the volumetric heat capacity of Al, Ag, and Au are plotted in Fig. D.6(a) and (b). As can be seen from Fig. D.6(a), the electron contribution towards the heat capacity increases linearly with an increase in the temperature. The phonon contribution, on the other hand, initially increases with temperature at lower temperatures and then plateaus to the Dulong-Petit limit at higher temperatures. For the entire temperature range, the electron contribution towards the heat capacity is less than 1% for both Al, Ag, and Au.



Figure D.6: (a) Electron and (b) phonon volumetric heat capacity variation of Al, Ag, and Au with temperature.



Figure D.7: Phonon thermal conductivity accumulation functions for Al and Si by considering only p-p scattering at a temperature of 300 K.

D.4 Silicon Simulation parameters

We considered isotopically pure silicon. The harmonic force constants are obtained using the DFPT calculations in QE [40]. The cubic force constants for phonon-phonon scattering rate calculations are obtained using a finite differencing of the Hellmann-Feynman forces obtained on a 216 atom supercells with one or two atoms displaced from their equilibrium position by 0.02 Å using a DFT package QE. We used $8 \times 8 \times 8$ electronic wavevector grid, 60 Ry planewave energy cutoff, and LDA exchange-correlation based norm-conserving pseudopotential generated using the Von Barth-Car [173] method. The harmonic force constants are initially obtained on a $8 \times 8 \times 8$ phonon wavevector grid and are later interpolated to a $32 \times 32 \times 32$ grid for phonon scattering rate calculations.

D.5 Aluminum and Silicon

The phonon thermal conductivity accumulation functions for Al and Si at a temperature of 300 K by considering only p-p scattering are plotted in Fig. D.7. While the thermal



Figure D.8: Mode-dependent Grüneisen parameters along the high-symmetry direction of the first Brillioun zone in Al and Si.

transport in Al is due to phonons with mfp spanning over only one order of magnitude, the phonon mfp in Si spans over four orders of magnitude. The gray phonon mfp $(\overline{\Lambda_p})$ for Al and Si at a temperature of 300 K are 97 and 4 nm.

Mode-dependent Grüneisen parameters along the high-symmetry direction of the first Brillioun zone in Al and Si are plotted in Fig. D.8. Grüneisen parameters are a measure of anharmonicity of a system. As can be seen from Fig. D.8, the Grüneisen parameters for Al are significantly higher than that in Si suggesting higher anharmonicity of Al. We characterize the anharmonicity of Al and Si by calculating an average Grüneisen parameter, γ , as a heat-capacity weighted average of the absolute values of the mode-dependent Grüneisen parameters as:

$$\gamma \equiv \frac{\sum_{i} c_{ph,i} |\gamma_i|}{\sum_{i} c_{ph,i}}.$$
 (D.1)

While the γ is 1.02 for Si, it is 2.21 for Al at a temperature of 300 K; thus indicating higher anharmonicity and hence lower lifetime of phonon modes in Al.

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