Modelling thermal transport in nanostructured materials

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Abstract
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Modelling thermal transport in nanostructured materials

by Ankita Katre

Thermal conductivity is primary property of interest for applications as thermoelectrics and thermal barriers. For other applications, as nanoelectronics, heat assisted magnetic recordings, thermal medical therapies etc, the thermal transport plays a governing role in their efficiency. For further advancements in these technologies, it is important to understand theoretically the thermal transport in the building nano-materials before fabricating these devices. However, \textit{ab initio} calculations at large length scales for such complex materials are unfeasible and the reliable simplified potentials are still needed.

In this thesis, we have developed simple and short ranged models for simulation of thermal conductivity and other thermal properties. Moreover, we have also worked on \textit{ab initio} thermal transport study in nanostructured materials, where effect of nanostructuring is included as a model.

A short ranged force constant model is developed first for correctly calculating the thermal properties of $\text{Si}_x\text{Ge}_{1-x}$ random alloys. This model opens up the possibility of short ranged potentials for correct calculations of long ranged interactions to determine thermal properties of complex nanostructures. Furthermore, a new thermal conductivity code is developed, in collaboration with Prof. Atsushi Togo, based on solving Boltzmann transport equation (BTE) for phonons. The code is tested by studying interesting thermal conductivity cross-over at nanoscale in Zinc-Chalcogenides with \textit{ab initio} calculations. The nanostructuring is included as an empirical model in this study. New results of the cross-over are obtained which are explained in terms of different phonon contributions in Zinc-Chalcogenides.
Moreover, to perform precise calculations at large length scales, without any approximation for nanostructures, we have developed a tight binding (TB) model for Si which carries quantum bonding information in its parameters. The model is simple and short ranged and it predicts thermal expansion and conductivity for Si in good agreement with experiments. Furthermore, we show the transferability of our model to other structures of Si. We expect this newly developed short ranged model to be helpful for accurately studying thermal transport at large length scales for Si nanostructures.
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Dedicated to my Aai and Baba . . .
Chapter 1

Introduction

Thermal transport in nano-materials is known to show interesting features which are different from bulk.[7, 8] However, the theoretical studies for these materials are challenging due to the complexity of the nanostructures and the theoretical method. Molecular dynamics (MD) simulations are conceptually simple and can be used to calculate thermal conductivity for these structures directly. However, due to the time and length scales involved, these MD simulations have to be based on simplified potentials. This leads to both a lack of transferability and a poor agreement with experimental results. On the other hand, density functional theory (DFT) has been used to calculate the thermal conductivity directly from the Boltzmann transport equation (BTE). These calculations show excellent agreement with experiment, but are limited to bulk materials and the role of alloying and nanostructuring has to be included through model scattering rates.

The tight binding (TB) scheme offers a compromise in this respect, Fig. 1.1. It is more precise than the empirical potentials and computationally less demanding than the \textit{ab initio} methods. The main goal of this thesis is to explore short-ranged TB models as a method to calculate thermal conductivity. We do this over the next five chapters. In the next two chapters we give a literature review and develop the theory behind the BTE relaxation time approximation (RTA). This is followed by a three parts documenting the different aspects of developing the model, Fig. 1.1. In Chapter 4, we develop a short ranged model of thermal properties. We show its ability to reliably reproduce anharmonic effects such as thermal expansion. We thereby demonstrate that these are not inherent limits of short ranged models. Chapter 5 presents the \textit{ab initio} thermal conductivity results.
with a newly developed code for calculating the thermal conductivity within the BTE-RTA. We thereby validate our code and demonstrate the detailed insight that can be obtained from this type of study. Finally, in Chapter 6 we develop a short-ranged orthogonal TB model for Si. We show how it can be used to reliably calculate the thermal conductivity and discuss its transferability.

1.1 Brief summary of chapters

In Chapter 2, we review the literature on the thermal transport in nanostructures. We discuss the experimental findings on the thermal conductivity in bulk and different nanostructures. We also discuss earlier theoretical investigations on thermal transport and compare different methodologies for calculating the thermal conductivity of nanostructures.

Chapter 3 presents the theory of phonons. The determination of the phonon frequencies and thermal properties within harmonic and quasi-harmonic approximation are presented. We also discuss the anharmonicity and derive the expression for thermal conductivity within BTE-RTA which gives the phonon-phonon scattering rate. The expression for the phonon scattering due to various isotopes present in the material is also derived. At last we discuss the basics of the computational schemes used in our study.
In Chapter 4, a short ranged model is developed for thermal properties of Si$_x$Ge$_{1-x}$ random alloys. Si$_x$Ge$_{1-x}$ random alloys, experimentally known to be good thermoelectric materials, are difficult to explore from \textit{ab initio} approach due to lack of symmetry. Hence we have developed a second nearest neighbour (2NN) force constant model to calculate the thermal properties of Si$_x$Ge$_{1-x}$ random alloys. The model parameters are derived from DFT which promise good reproduction of the phonon frequencies and thermal properties. The model is developed for pure Si, Ge and Si$_{0.5}$Ge$_{0.5}$ ordered structures and shows transferability to Si$_x$Ge$_{1-x}$ random alloy structures. The 2NN model confirms the applicability of short ranged models for calculating the long ranged interactions. This chapter is a review of the work published in Ref. [4].

In Chapter 5, we study the thermal transport in the nanostructured Zinc chalcogenides using the \textit{ab-initio} method. Zinc-chalcogenides, which also crystallise in the diamond structure as Si and Ge, are technologically interesting due to their low thermal conductivities. They also exhibit interesting thermal conductivity cross-over behaviour at nanoscale. Within BTE-RTA approach, the thermal conductivity cross-over in ZnS, ZnSe and ZnTe is studied and explained in terms of phonon contributions to their thermal conductivities at particular grain size. The thermal conductivity calculations in this study are done using a thermal conductivity code developed in collaboration with Prof. Atsushi Togo. We tested the code in its early stages of developments and contributed to the implementation of isotope scattering in it. This was important to get correct isotope scattering rate and precise thermal conductivity determination for zinc-chalcogenides. The work presented in this chapter is published in Ref. [9].

In Chapter 6, we have developed a short ranged and simple tight binding model for Si focussed mainly to calculate the thermal properties. The tight binding parameters are obtained from DFT as discussed in Chapter 3. The model is tested for the reproduction of the thermal properties of Si bulk which show a good agreement with DFT results and an improvement over earlier TB models. Furthermore, the transferability of the model is tested by applying it to the other structures of Si.
Chapter 2

Background

2.1 Nanoscale thermal transport

The study of thermal transport at the nanoscale has become crucial with the technological advancement as heat transfer plays a key role in many of the emerging applications. In some applications, the thermal conductivity is required to be high which includes mainly the high-power micro and nanoelectronics.[10] The electronic industry has grown very fast, and is continuing to do so, mainly due to constant miniaturization of the device sizes and high operating frequencies of devices. The miniaturization of electronic devices is possible due to improvements in fabrication techniques as well as drastic increase in the density of the transistors on the integrated circuits.[11] All these factors have made the thermal management very critical in nanoelectronic devices as high operating temperatures lead to decreased lifetimes and degraded performances. Moreover, the problem of heat dissipation also limits the further increase in operating frequency as well as instructions per clock in the microprocessors.[11] Good thermal conductivity of the materials is required to avoid the problem of the hot-spots in these devices. Similar to the nanoelectronics, there are other applications in which the thermal conductivity, although not being a primary property of interest, plays a major role in determining their performances. These applications include phase-change memory devices, heat assisted magnetic recordings and thermal medical therapies.[12]

On the other hand, the thermal transport is the primary metric for the technologies such as thermal barriers and thermoelectric generators and coolants. The thermal barrier coatings are used on high operating temperature machineries as
gas turbines and aero-engine parts for the thermal management. Thus low thermal conductivity oxide materials are desirable for the thermal barriers applications.[13] Thermoelectric generators, used for the waste heat recovery, and thermoelectric coolants, which find applications in refrigerants, maintaining laser frequency[14] and heat-sinks for the nanoelectronic devices[15–17], also require low thermal conductivity to reduce parasitic thermal transport. Thermoelectric materials, which provide a direct conversion of heat into electricity, also need a good electrical conductivity to maximise the thermoelectric efficiency.[7] The thermoelectric efficiency is quantified in terms of dimensionless thermoelectric figure of merit (\( zT \)) given as,[18]

\[
zT = \frac{\sigma S^2 T}{\kappa} = \frac{\sigma S^2 T}{\kappa_e + \kappa_l}
\]

(2.1)

where \( \sigma \) denotes electrical conductivity and \( S = \partial V/\partial T \) is the Seebeck coefficient which gives a measure of the induced thermoelectric voltage when a temperature difference is maintained across the material. The thermal conductivity \( \kappa \) has the contributions from the electronic thermal conductivity \( \kappa_e \) and the lattice thermal conductivity \( \kappa_l \). A thermoelectric generator with high \( zT \) can be very useful in reusing the waste heat as around 60% of the world’s energy is lost in the form of heat.

Efforts are being made to find low cost, sustainable and durable thermoelectric materials with high \( zT \). Semiconductors turn out to be good thermoelectric materials compared to insulators which have poor electronic conductivities and metals with relatively low Seebeck coefficients as well as high thermal conductivities due to large \( \kappa_e \) contribution.[14] This is the result of the trade-off between \( \sigma, S \) and \( \kappa \), due to Eq. (2.1), in semiconductors which have low \( \kappa \) than metals and high power factor \( (\sigma S^2) \) with appropriate carrier concentrations. There has been research going on for some years to either discover new thermoelectrics or to enhance \( zT \) of the existing materials. The discovery of new thermoelectric materials is mainly based on the experimental finding of new stable phases of materials with good thermoelectric properties. However, computational high-throughput studies are also emerging as powerful way to find new phases and calculate corresponding transport properties. By carrying out the high throughput calculations, Ag doped SnS under S-rich conditions has been found to exhibit high electrical conductivity and power factor interesting for thermoelectric applications.[19] To improve the \( zT \) of existing materials, one way is to enhance the power factor which is achieved
by proper doping of material or introducing the defects in the systems which alter the electronic band-structure.[19–23]

The other way is to employ techniques to lower the thermal conductivity, Eq. (2.1). $\kappa_e$ is directly related to the electrical conductivity $\sigma$ with the Weidemann-Franz law as, $\kappa_e = L\sigma T$, where $L$ is the Lorentz number. Thus, $\kappa_e$ increases with the increase in the electrical conductivity $\sigma$ which brings out the importance of drastic reduction in lattice thermal conductivity, $\kappa_l$, required to reduce total thermal conductivity, $\kappa$. Materials can have low $\kappa_l$ either due to the introduction of defects, dislocations and nanostructuring[24–26] or due to their atomic structure and interatomic bonding.[26–28] Complex crystal structures such as skutterudites also show a significant reduction in their lattice thermal conductivity $\kappa_l$ with the introduction of heavy atoms in their voids.[26]

Thus various fields of interests as thermoelectrics, thermal barriers, nanoelectronics, which depend differently on the heat transport, require us to have a better understanding of the thermal conductivity at nanoscale. The lattice thermal conductivity $\kappa_l$ in a material is primarily due to the quasi particles called phonons which are quanta of lattice vibrations. Depending on their modes of vibrations, phonons are broadly categorised into acoustic and optic phonons. The $\kappa_l$ of the material is determined by the interactions of these phonons. Hence to tune the $\kappa_l$ of a material according to the application, the knowledge of phonons and the different mechanisms to scatter them is required. These deep insights can be obtained from theory and experiments.

## 2.2 Experimental findings in thermal transport

The experimental techniques as time domain thermoreflectance (TDTR)[29–31] and the $3\omega$ scanning thermal microscopy (SThM)[32] for the thermal conductivity measurements have emerged as powerful methods over last decade. TDTR can be used for bulk materials, thin layers and the interfaces making it applicable to wide range of materials. However, the method is quite sensitive to the roughness of the samples (required $<15$ nm) as well as to the high anisotropy of the materials.[12] The applicability of TDTR at temperatures below 30K is also limited. The improvements for the measurements of in-plane thermal conductivity for thin layers
with TDTR is still being researched.[33, 34] The other method, $3\omega$-SThM, provides a high resolution in the measurements. The fine resolution of $\approx 10$ nm can be achieved with a nanometer scale probe tip which measures the temperature of the sample surface. The temperature precision up to $\approx 50$ mK and measurements of nanoscale heat flow $\approx 10$ pW are too made possible with the recent developments in SThM.[12]

A wide range of materials have been studied for their lattice thermal conductivities which span up to 6 orders of magnitude. At one extreme, the nanostructures of carbon i.e., graphene and carbon nanotubes (CNT) have been studied extensively to understand their thermal transport. Graphene exhibits a very high thermal conductivity of $3080$-$5300$ Wm$^{-1}$K$^{-1}$ around room temperature which gives the prospects of its use for thermal management in nanoelectronic devices.[35, 36] The thermal conductivity of graphene is also higher than the single wall and multi wall CNTs which have been reported to be around $3500$ Wm$^{-1}$K$^{-1}$[37] and $3000$ Wm$^{-1}$K$^{-1}$[38] at room temperature. On the other extreme, the thin films of WSe$_2$ show very low cross-plane thermal conductivity of $0.05$ Wm$^{-1}$K$^{-1}$ at $300$K which has been found to be 30-times smaller than the thermal conductivity in c-axis of WSe$_2$ single crystal.[39] Such low thermal conductivity of WSe$_2$ thin films material, is in same order of magnitude of that of air and other gases.

Bulk materials with complex crystal structures also exhibit interesting thermal transport behaviour. Recently, it has been found that SnSe, in a layered orthorhombic structure, has a thermal conductivity of around $0.4$ Wm$^{-1}$K$^{-1}$ at $300$K in the x-axis (long direction) of the crystal which is half of the thermal conductivity in the y-axis. This was attributed to the softer vibrational modes in x-axis which arise due to the weak interatomic bonding and high anharmonicity.[40] Crystal structures such as skutterudites and clathrates posses big voids which can even accommodate the rare earth elements. Inclusion of the heavy rare earth elements in the voids, known as rattlers in the structure, enhances the phonon scattering and can reduce the thermal conductivity up to an order of magnitude.[41, 42]

Alloying the pure bulk materials too show considerable effects on the thermal transport. (Sb-Bi)$_2$Te$_3$ random alloy showed a thermal conductivity reduction of $\approx 35\%$, as compared to pure Bi$_2$Te$_3$, with no change in its electrical conductivity.[43] Further $\kappa_l$ reduction was found with the substitution of S or Se in place of Te in (Sb-Bi)$_2$Te$_3$. Similarly for the Si-Ge random alloys, the thermal conductivity was found to be an order of magnitude lower than the pure Si and Ge.[44] The main
cause of $\kappa$ reduction due to alloying is the mass disorder introduced in the systems which results into the phonon scattering.

The thermal conductivity of a material can be further tailored by engineering the material at nanoscale to tune the phonon scattering.[45] There are several nanostructures as nanowires, nanoporous materials and nanointrusions. Silicon nanowires were studied too for their use in thermoelectric applications[46, 47] because of reduced thermal conductivity due to high phonon scattering. Nanostructuring the Si$_{0.8}$Ge$_{0.2}$ random alloy also lead to $\approx 40\%$ reduction in the thermal conductivity.[24, 25, 48] This was mainly attributed to the grains of 15-20 nm size, prepared by ball milling and hot pressing, that scattered just the heat carrying phonons without hindering the electronic motion. Thus nanostructuring gave an added advantage to the Si-Ge alloying which itself provides resistance to the heat flow.

Superlattices are also very interesting structures for the study of their thermal conductivities. By engineering the artificial superlattices, the anisotropy in the in-plane and cross-plane thermal conductivity is obtained.[12] The superlattices with the nanoscale periodicities provide efficient resistance to the heat transfer.[26] Taking the examples of Si-Ge systems, a precise control over thermal conductivity of Si-Ge nanodot multilayers was obtained by engineering the phonon scattering nanodot barriers.[45] Even the thermal conductivity for Si-Ge superlattice is also reported to be less than the bulk random alloy and thin film random alloy of Si-Ge.[49] All these studies show the different effects of nanostructuring on the thermal transport of a material. Moreover, the thermal conductivity reduction for a particular nanostructure also varies from material to material. These interesting features can be attributed to the variation in the phonon scattering with the nanostructure and material.

### 2.3 Theoretical determination of thermal conductivity

The contributions to the phonon scattering can be due to other phonons, defects, dislocations or because of the electron-phonon coupling. These different processes of the phonon scattering can be studied theoretically and the contribution of each
scattering mechanisms can be understood separately. This could prove beneficial for designing the materials cost-efficiently in a rational way.

The theoretical studies of the thermal transport in materials can be done with molecular dynamics simulations or *ab initio* lattice dynamics calculations as shown in Fig. 1.1.

### 2.3.1 Molecular dynamics simulations

The thermal conductivity using the molecular dynamics (MD) simulations can be calculated by two ways: 1) Non-equilibrium MD in which temperature gradient $\nabla T$ is set across the sample and $\kappa_l$ is calculated directly from Fourier’s law $J = -\kappa_l \nabla T$ where $J$ is heat current.[50] 2) Equilibrium MD in which $\kappa_l$ is calculated by determining the equilibrium auto-correlation function for heat current $J$.[51, 52] The thermal transport studies with MD require simulations at large length and time scales. Therefore, these MD studies are based on simplified potentials. The dependence of MD simulations on the simple potentials leads mostly to just qualitative agreement with experiments.

This can be seen in the non-equilibrium molecular dynamics study performed by Skye *et al.*[53] to predict the thermal transport in Si-Ge random alloys using the Stillinger-Weber potential.[54] The $\kappa_l$ predicted was found to be around an order of magnitude lower than the experiments and also independent of temperature. Another study of the $\kappa_l$ in Si slab containing nano-voids and monoatomic vacancies was performed recently by Wang *et al.*[55] which discussed the effects of nano-voids and defects on phonon scattering. The study was performed again using Stillinger-Weber potential[54] and predicted the $\kappa_l$ of pure Si to be an order of magnitude smaller than experiments. The other empirical potentials such as Tersoff potential[2, 3] and environmental dependent interatomic potential[56, 57] are also found to either over or underestimate the thermal expansion, $\alpha_T$, and $\kappa_l$ as compared to experiments. [1]. Fig. 2.1 shows the differences in the experiments and the calculated $\alpha_T$ and $\kappa_l$ with two different versions of the Tersoff potential.[2, 3] It is also evident from Fig. 2.1 that for a particular parameter set, the variation from the experiments are in same order of magnitude for both $\alpha_T$ and $\kappa_l$. This underlines that $\alpha_T$ and $\kappa_l$ are codependent[1] and hence a minimal requirement for a simplified potential to accurately determine the thermal conductivity at larger length scales using MD simulations is to correctly reproduce $\alpha_T$. 
The reliable simplified potentials are also necessary for the study of thermal transport in the complex structures with defects, voids, nanostructures etc, which can be considered directly in MD studies without any approximations. [53, 55] This suggests that the precise agreement for the complex structures can be obtained from MD simulations with the use of an accurate potential.

2.3.2 Ab initio approach: Boltzmann transport equation

A different approach to calculate the \( \kappa_l \) of the materials is the based on solving the Boltzmann transport equation(BTE) for phonons. The phonon interactions for calculating \( \kappa_l \) in this approach are determined from the interatomic force constants calculated using \textit{ab initio} method. In the harmonic approximation, the second order interatomic force constants (2\textsuperscript{nd}FCs) are required to calculate the phonon frequencies. Using these phonon frequencies, the thermal properties such as heat capacity of the material, entropy, free energy and phonon group velocities can be determined. This provides a better understanding of the thermal properties at low temperatures which is not captured in their classical description.
The *ab-initio* knowledge of more properties like $\alpha_T$ and Grüneisen parameters, $\gamma$, require the calculations in the quasi-harmonic approximation (QHA). This approximation considers the volume-dependent effects on phonons to include the anharmonicity. The Grüneisen parameters show the variation of phonon frequencies with the changes in crystal volume and thermal expansion is the change in equilibrium volume of the crystal with the temperature. These quantities give a good idea of the anharmonicity without performing the explicit anharmonic calculations. A good agreement of $\alpha_T$ from experiments and from density functional theory (DFT) calculations within QHA can be seen for Si in Fig. 2.1.

Explicit calculations of the higher order force constants are required for determining the phonon-phonon scattering or anharmonic scattering. The anharmonic scattering, which varies with crystal structure and temperature, contributes to a major part of the phonon scattering in materials to bring down their $\kappa_l$ to finite values.[58]. For determining anharmonic scattering, the third order force constants $3^{rd}$ FCs are calculated from DFT. Then BTE is solved either iteratively or in relaxation time approximation (RTA) for calculating the $\kappa_l$. The phonon lifetimes and the $\kappa_l$ using both of these methods are calculated in past for pure structures.[5, 6, 59–63] Esfarjani et al.[6] calculated the $\kappa_l$ within BTE-RTA for Si and found good agreement with the experiments for a large temperature range. $\kappa_l$ determination for Si by iteratively solving BTE, studied by Ward et al.[5], also shows good correspondence with the experiments, Fig. 2.1, proving the applicability of this approach.

The $\kappa_l$ for different complex alloys and nanostructures have also been studied from DFT. However, the effects of different scattering mechanisms as from defects, grain boundaries, vacancies etc are approximated. Garg et al.[28] have studied the *ab initio* thermal transport in Si-Ge random alloys using a perturbative approach called Virtual Crystal Approximation (VCA). VCA considers the mass variations in the random alloys as the perturbation over a symmetric crystal. This approach, although considers mass variation, but ignores the bond length variation throughout the structure. Moreover, the boundary scattering of phonons in CNT,[64] graphene and graphite,[65] and boron nitride[66]; and vacancy scattering in defected zinc antimonides[67] have been studied using simple models of their scattering rates.[68, 69]

A further advantage of the BTE studies is that precise information of the phonon
scattering for each phonon mode and different scattering mechanisms can be obtained. An example is the study for Si-Ge superlattices which showed that their $\kappa_t$ can be tailored by changing the superlattice period thickness.[27] The short-period (2 atomic layers) Si-Ge [001] and [111] superlattices exhibit higher thermal conductivity than the pure Si and Ge. By engineering the mass-mismatch, further improvement in thermal conductivities could be achieved,[27] which is interesting for high thermal conductivity requiring applications. This increase in thermal conductivity is found to be mainly because of the reduction in acoustic-optic phonon scattering which is achieved by reducing the thickness of the superlattice periods. Thick period superlattices have the combined effects of anisotropy as well as high acoustic-optic phonon scattering.

Such detailed insights of different scattering processes obtained from BTE studies can be used for tuning the thermal conductivity of materials according to the applications. Moreover, these insights are also beneficial for efficient and accurate modelling of phonons. The accurate models of thermal properties thus can be used for the thermal transport studies in nanostructures with MD at large length scales.
Chapter 3

Theoretical Basics

3.1 Theory of thermal transport

The lattice thermal transport is due to phonons which are quanta of lattice vibrations. We study the thermal transport in a material by understanding the motion and interactions of these phonons using lattice dynamics. In this chapter, the understanding of the theory of lattice thermal conductivity is developed as discussed in Ref. [70]. First we discuss the calculations of phonons followed by the interactions of the phonons due to anharmonic contributions to the potential. Furthermore phonon-isotope scattering mechanisms which contribute to determine the thermal conductivity are derived. Finally, density functional theory and tight binding modelling are discussed which are used for the force calculations in this thesis.

3.1.1 Potential energy expansion

The harmonic vibrations in a crystal and the interactions of these vibrations leading to the anharmonicity can be obtained by considering the Taylor series expansion of the potential energy in terms of atomic displacements. The potential energy $V$, in terms of atomic displacements $u$ in directions $\alpha_1, \alpha_2, \alpha_3$ for atoms with position vectors $b, b', b''$ in unit cells identified by vectors $l, l', l''$, is expressed
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as,

\[ V = V_0 + \frac{1}{2!} \sum_{lb \neq b' \alpha_1 \alpha_2} \Phi_{\alpha_1 \alpha_2}(lb, l'b')u_{\alpha_1}(lb)u_{\alpha_2}(l'b') + \frac{1}{3!} \sum_{lb \neq b' \neq b'' \alpha_1 \alpha_2 \alpha_3} \Psi_{\alpha_1 \alpha_2 \alpha_3}(lb, l'b', l''b'')u_{\alpha_1}(lb)u_{\alpha_2}(l'b')u_{\alpha_3}(l''b'') + \ldots \]  

Equation (3.1)

The first derivative of the energy, \( V_1 = \sum_{lb \alpha_1} \frac{\partial V}{\partial u_{\alpha_1}(lb)} \bigg|_0 u_{\alpha_1}(lb) \) is zero at the equilibrium, hence is excluded from Eq. (3.1). The second and the third derivatives of the energy result in second and third order force constants represented by matrices \( \Phi \) and \( \Psi \) respectively. The second order force constant matrix comprise of 3\(^2\) and third order force constant matrix consist of 3\(^3\) elements and are given as

\[ \Phi_{\alpha_1 \alpha_2}(lb, l'b') = \frac{\partial^2 V}{\partial u_{\alpha_1}(lb) \partial u_{\alpha_2}(l'b')} \bigg|_0, \]  

Equation (3.2)

\[ \Psi_{\alpha_1 \alpha_2 \alpha_3}(lb, l'b', l''b'') = \frac{\partial^3 V}{\partial u_{\alpha_1}(lb) \partial u_{\alpha_2}(l'b') \partial u_{\alpha_3}(l''b'')} \bigg|_0. \]  

Equation (3.3)

3.1.2 Harmonic vibrations in crystals

Assuming the harmonic approximation i.e., restricting the contributions up to second order term in Eq. (3.1), the harmonic potential is written as,

\[ V^{\text{harm}} = V_0 + \frac{1}{2!} \sum_{lb \neq b' \alpha_1 \alpha_2} \Phi_{\alpha_1 \alpha_2}(lb, l'b')u_{\alpha_1}(lb)u_{\alpha_2}(l'b'). \]  

Equation (3.4)

By imposing the crystal translation symmetry and introducing new variable \( h = l' - l \) which denotes the relative position between unit cells, the force constant matrix can be written as,

\[ \Phi_{\alpha_1 \alpha_2}(lb, l'b') = \Phi_{\alpha_1 \alpha_2}(0b, (l' - l)b') = \Phi_{\alpha_1 \alpha_2}(0b, hb'). \]  

Equation (3.5)

Due to atomic displacements in a crystal, there are forces experienced by the atoms. The component of force in \( \alpha_1 \) direction on atom \( b \) arising when another
atom \( b' \) is displaced with magnitude \( u \) in \( \alpha_2 \) direction is written as,

\[
F_{\alpha_1}(0b) = -\Phi_{\alpha_1\alpha_2}(0b, hb')u_{\alpha_2}(hb').
\] (3.6)

Using Eq. (3.6), the equation of motion can be written as,

\[
m_b\ddot{u}_{\alpha_1}(0b, t) = -\sum_{hb'\alpha_2} \Phi_{\alpha_1\alpha_2}(0b, hb')u_{\alpha_2}(hb', t),
\] (3.7)

where \( m_b \) represents the mass of atom at \( b \) position in a unit cell. The vibrations in an unbound crystal are given as travelling waves extending throughout the entire crystal. Thus the displacement, which is the solution of Eq. (3.7), is written as

\[
u_{\alpha_1}(hb, t) = \frac{1}{\sqrt{m_b}} \sum_q A_{\alpha_1}(b|q)e^{i(qh-\omega_q t)},
\] (3.8)

where \( A_{\alpha_1}(b|q) \) describes the maximum amplitude and direction of motion of the \( hb \) atom (atom at \( h + b \) position), as produced by the travelling wave of \( q \) wave vector and \( \omega_q \) frequency.

Substitution of Eq. (3.8) into Eq. (3.7) leads to the matrix eigen equation

\[
\omega^2(jq)e_{\alpha_1}(b|jq) = \sum_{b'\alpha_2} D_{\alpha_1\alpha_2}(bb'|q)e_{\alpha_1}(b'|jq),
\] (3.9)

where the dynamical matrix \( D_{\alpha_1\alpha_2}(bb'|q) \) is

\[
D_{\alpha_1\alpha_2}(bb'|q) = \frac{1}{\sqrt{m_bm_b'}} \sum_h \Phi_{\alpha_1\alpha_2}(0b, hb')e^{iqh}.
\] (3.10)

The phonon frequencies \( \omega(jq) \) are obtained by diagonalising the dynamical matrix, Eq. (3.10). \( jq \) stands for a particular phonon mode with \( j^{th} \) phonon dispersion branch and \( q \) wave-vector. There are \( 3N \) phonon dispersion branches for a crystal having \( N \) atoms in its unit cell. For each \( q \) vector, there is a mode of vibration with frequency \( \omega(jq) \) and the \( e(b|jq) \) eigenvector which gives the pattern of the atomic displacements for mode \( jq \). The phonon eigenvectors satisfy the orthogonality and closure relations,

\[
\sum_b e^*(b(jq)e(b|jq) = \delta_{jj'},
\] (3.11)

\[
\sum_j e^*_{\alpha_1}(b(jq)e_{\alpha_2}(b'jq) = \delta_{\alpha_1\alpha_2}\delta_{bb'},
\] (3.12)
which means that the eigenstates are decoupled and do not interact with each other. This can also be derived from the harmonic vibrational Hamiltonian. Considering $p(lb)$ to be the momentum operator for $lb$ atom with mass $m_b$ and displacement vector $u(lb)$, Eq. (3.4), harmonic Hamiltonian can be written as,

$$H_{\text{harm}} = \sum_{lb} \frac{p(lb) \cdot p(lb)}{2m_b} + \frac{1}{2!} \sum_{lb, b', \alpha_1 \alpha_2} \Phi_{\alpha_1 \alpha_2}(lb, l'b') u_{\alpha_1}(lb) u_{\alpha_2}(l'b').$$  \hspace{1cm} (3.13)

We proceed with carrying out the Fourier analysis of $u$ and $p$,

$$u(lb) = \frac{1}{\sqrt{N_0 \Omega}} \sum_{q} U(qb) e^{iql}, \hspace{1cm} (3.14)$$

$$p(lb) = \frac{1}{\sqrt{N_0 \Omega}} \sum_{q} P(qb) e^{-iql}, \hspace{1cm} (3.15)$$

where $N_0 \Omega$ denotes the crystal volume having $N_0 = N_1 \times N_2 \times N_3$ unit cells and $N_1, N_2, N_3$ are number of unit cells in three directions whereas $\Omega$ is the unitcell volume. The Fourier representations of $U(qb)$ and $P(qb)$ in Eq. (3.14) and Eq. (3.15) are in such way that they satisfy commutation relation,

$$[U(qb), P(q'b')] = \frac{1}{N_0 \Omega} \sum_{ll'} e^{-i(ql-q'l')}$$

$$[u(lb), p(l'b')].$$  \hspace{1cm} (3.16)

Using $[u(lb), p(l'b')] = \hat{I} i\hbar \delta_{ll'} \delta_{bb'}$ and representing $\delta_{qq'}$ as Fourier transform of $\delta_{ll'}$,

$$[U(qb), P(q'b')] = \frac{1}{N_0 \Omega} \sum_{ll'} e^{-i(ql-q'l')} \hat{I} i\hbar \delta_{ll'} \delta_{bb'}$$

$$= \hat{I} i\hbar \delta_{qq'} \delta_{bb'}. \hspace{1cm} (3.17)$$

Now we use Eq. (3.14) and Eq. (3.15) to rewrite the Hamiltonian in Eq. (3.13) as

$$H_{\text{harm}} = \frac{1}{N_0 \Omega} \sum_{qq'} \frac{P(qb) \cdot P(q'b')}{2m_b} e^{-i(q+q')l}$$

$$+ \frac{1}{2} \frac{1}{N_0 \Omega} \sum_{qq'} \sum_{lb, b', \alpha_1 \alpha_2} \Phi_{\alpha_1 \alpha_2}(lb, l'b') U_{\alpha_1}(qb) U_{\alpha_2}(q'b') e^{iql-q'l'}. \hspace{1cm} (3.18)$$
We perform summation over \( l \) and write the first term of Eq. (3.18) as

\[
\hat{K} = \sum_{qq' b} \frac{P(qb) P(q'b)}{2m_b} \frac{1}{N_0 \Omega} \sum_l e^{-i (q+q') l}.
\]  

(3.19)

Using \( \sum_l e^{-i (q+q') l} = N_0 \Omega \delta_{q+q',0} \),

\[
\hat{K} = \sum_{qb} \frac{P(qb) P(qb)^\dagger}{2m_b}.
\]  

(3.20)

Similarly the second term of Eq. (3.18) can be simplified using \( h = l' - l \), as in Eq. (3.10),

\[
\hat{V}_2 = \frac{1}{2} \sum_{qbb'} \sum_{\alpha_1\alpha_2} \Phi_{\alpha_1\alpha_2} (0b, h b') U_{\alpha_1} (qb) U_{\alpha_2}^\dagger (qb') e^{-i h b},
\]  

(3.21)

where \( U(-qb) = U^\dagger (qb) \) and \( P(-qb) = P^\dagger (qb) \) since \( u(lb) \) and \( p(lb) \) (Eq. (3.14) and Eq. (3.15) are Hermitian. Now we introduce,

\[
\Phi_{\alpha_1\alpha_2} (bb'|q) = \sum_h \Phi_{\alpha_1\alpha_2} (0b, h b') e^{-i h b} = \sqrt{m_b m_{b'}} D_{\alpha_1\alpha_2} (bb'|q),
\]  

(3.22)

where \( D \) is the dynamical matrix. Thus we can rewrite Eq. (3.21) as

\[
\hat{V}_2 = \frac{1}{2} \sum_{qbb'} \sum_{\alpha_1\alpha_2} \Phi_{\alpha_1\alpha_2} (bb'|q) U_{\alpha_1} (qb) U_{\alpha_2}^\dagger (qb').
\]  

(3.23)

Using Eq. (3.20) and Eq. (3.23), the total Hamiltonian in the harmonic approximation can be written as,

\[
H^\text{harm} = \sum_{qb} \frac{P(qb) P(qb)^\dagger}{2m_b} + \frac{1}{2} \sum_{qbb'} \sum_{\alpha_1\alpha_2} \Phi_{\alpha_1\alpha_2} (bb'|q) U_{\alpha_1} (qb) U_{\alpha_2}^\dagger (qb').
\]  

(3.24)

Eq. (3.24) has no phonon interaction term. Thus the eigenstates of this harmonic Hamiltonian are completely independent. These are called normal modes of vibrations.

We further introduce another set of transformation making use of phonon eigenvectors \( e(b|jq) \) which allows us to continue the discussion considering the phonon vibrational branches \( (j) \) instead of the atomic position vectors \( (b) \). Hence we
transform $U(qb)$ and $P(qb)$ to

$$U(jq) = \sum_b \sqrt{m_b} \epsilon^*(b|jq) U(qb),$$  \hspace{1cm} (3.25)$$

$$P(jq) = \sum_b \sqrt{m_b} \epsilon(b|jq) P(qb),$$  \hspace{1cm} (3.26)$$

with $P(jq)$ being canonically conjugate to $U(jq)$. We finally introduce the annihilation and creation operators($a_{jq}$ and $a^\dagger_{jq}$) and write them in terms of $U(jq)$ and $P(jq)$,

$$a_{jq} = \frac{1}{\sqrt{2\hbar \omega(jq)}} P(jq) - i \sqrt{\frac{\omega(jq)}{2\hbar}} U^\dagger(jq),$$  \hspace{1cm} (3.27)$$

$$a^\dagger_{jq} = \frac{1}{\sqrt{2\hbar \omega(jq)}} P^\dagger(jq) + i \sqrt{\frac{\omega(jq)}{2\hbar}} U(jq),$$  \hspace{1cm} (3.28)$$

which follow the commutation relation,

$$[a_{jq}, a^\dagger_{jq}] = \delta_{qq'} \delta_{jj'} \hat{I}. \hspace{1cm} (3.29)$$

Using $\omega(-jq) = \omega(jq)$, $U^\dagger(jq) = U(-jq)$ and $P^\dagger(jq) = P(-jq)$, Eq. (3.27) and Eq. (3.28) allow us to write $U(jq)$ and $P(jq)$ as

$$U(jq) = -i \sqrt{\frac{\hbar}{2\omega(jq)}} (a^\dagger_{jq} - a_{-jq}) \hspace{1cm} (3.30)$$

$$P(jq) = \sqrt{\frac{\hbar \omega(jq)}{2}} (a_{jq} + a^\dagger_{-jq}) \hspace{1cm} (3.31)$$

and finally from Eq. (3.25), Eq. (3.26), Eq. (3.30) and Eq. (3.31) we have

$$U(qb) = \frac{1}{\sqrt{m_b}} \sum_j \epsilon(b|jq) U(jq)$$

$$= -i \sum_j \sqrt{\frac{\hbar}{2m_b \omega(jq)}} \epsilon(b|jq)(a^\dagger_{jq} - a_{-jq}), \hspace{1cm} (3.32)$$

$$P(qb) = \frac{1}{\sqrt{m_b}} \sum_j \epsilon^*(b|jq) P(jq)$$

$$= \sum_j \sqrt{\frac{m_b \hbar \omega(jq)}{2}} \epsilon^*(b|jq)(a_{jq} + a^\dagger_{-jq}). \hspace{1cm} (3.33)$$

Thus $U(qb)$ and $P(qb)$ are written in terms of phonon annihilation and creation
where we have also used the eigenequation

\[ H^{\text{harm}} = \frac{1}{4} \sum_{jqa^b} \hbar \omega (j|q) e(b|j) e^*(b|j) (a_{j} + a^\dagger_{j}) (a^\dagger_{j} + a_{-j}) \]

\[ + \frac{1}{2} \sum_{q^{bb} j^a j^b} \Phi_{\alpha_1 \alpha_2} (bb|q) \frac{\hbar}{2 \omega (j|q)} \frac{1}{\sqrt{m b m b'}} \]

\[ e_{\alpha_1} (b|j) e^*_{\alpha_2} (b'|j) (a^\dagger_{j} - a_{-j}) (a_{j} - a^\dagger_{-j}). \]

Using Eq. (3.22) and knowing that \( D_{\alpha_1 \alpha_2} (bb'|q) = D_{\alpha_1 \alpha_2} (bb|q) \), we get,

\[ H^{\text{harm}} = \frac{1}{4} \sum_{jqa^b} \hbar \omega (j|q) e(b|j) e^*(b|j) (a_{j} + a^\dagger_{j}) (a^\dagger_{j} + a_{-j}) \]

\[ + \frac{1}{2} \sum_{q^{bb} j^a j^b} \frac{\hbar}{2 \omega (j|q)} \sum_{b' \alpha_2} D_{\alpha_1 \alpha_2} (bb'|q) e^*_{\alpha_2} (b'|j) q \]

\[ e_{\alpha_1} (b|j) e^*_{\alpha_2} (b'|j) (a^\dagger_{j} - a_{-j}) (a_{j} - a^\dagger_{-j}) \]

\[ = \frac{1}{4} \sum_{jqa^b} \hbar \omega (j|q) e(b|j) e^*(b|j) (a_{j} + a^\dagger_{j}) (a^\dagger_{j} + a_{-j}) \]

\[ + \frac{1}{4} \sum_{q^{bb} j^a j^b} \hbar \omega (j|q) e^*_{\alpha_1} (b|j) e_{\alpha_1} (b|j) (a^\dagger_{j} - a_{-j}) (a_{j} - a^\dagger_{-j}). \]

(3.35)

where we have also used the eigenequation \( \omega^2 (j|q) e_{\alpha_1} (b|j) = \sum_{b' \alpha_2} D_{\alpha_1 \alpha_2} (bb'|q) e_{\alpha_2} (b'|j) q \) and the equality \( \omega^2 (j|q) = \omega^2 (-j|q) \).

Now using Eq. (3.11) and realizing that summation over \(-q\) is similar to summation over \(q\), \( H^{\text{harm}} \) can be written as,

\[ H^{\text{harm}} = \frac{1}{4} \sum_{jqa^b} \hbar \omega (j|q) [(a_{j} + a^\dagger_{-j}) (a^\dagger_{j} + a_{-j}) + (a^\dagger_{j} - a_{-j}) (a_{j} - a^\dagger_{-j})] \]

\[ = \frac{1}{4} \sum_{jqa^b} \hbar \omega (j|q) (a_{j} a^\dagger_{j} + a^\dagger_{j} a_{j} + a_{-j} a^\dagger_{-j} + a^\dagger_{-j} a_{-j}) \]

\[ = \frac{1}{2} \sum_{jqa^b} \hbar \omega (j|q) (a_{j} a^\dagger_{j} + a^\dagger_{j} a_{j}). \]

(3.36)
Using the commutation relation of phonon creation and annihilation operators, Eq. (3.29), the harmonic Hamiltonian can be further simplified as,

$$H^{\text{harm}} = \sum_{j\mathbf{q}} \hbar \omega(j\mathbf{q}) \left( a^\dagger_{j\mathbf{q}} a_{j\mathbf{q}} + \frac{1}{2} \right).$$  \hspace{1cm} (3.37)

This expression for harmonic Hamiltonian comprise of phonon annihilation and creation and is in the diagonal form. This is also called the second quantisation method as we have used two step transformation to get Eq. (3.37). First step involves changing of particle to wave picture by replacing atomic coordinates \( lb \) with the wave modes and wave vectors \( j\mathbf{q} \). The second quantisation variables, \( a_{j\mathbf{q}} \) and \( a^\dagger_{j\mathbf{q}} \), are introduced in next step which provide quasi particle picture. Applying harmonic Hamiltonian, Eq. (3.37), on a state \( |s_{j\mathbf{q}}\rangle \) having \( s \) number of phonons in mode \( j\mathbf{q} \) gives the energy of phonons in that mode.

### 3.1.3 Thermal conductivity formalism

To understand the thermal transport in a material, we make use of the Boltzmann Transport Equation. BTE describes the statistical behaviour of the thermodynamic system not in equilibrium. BTE is given as

$$\left( \frac{\partial \eta}{\partial t} \right) = \left( \frac{\partial \eta}{\partial t} \right)_{\text{force}} + \left( \frac{\partial \eta}{\partial t} \right)_{\text{diffusion}} + \left( \frac{\partial \eta}{\partial t} \right)_{\text{scatt}},$$  \hspace{1cm} (3.38)

where \( \eta \) represents the phonon distribution which is given by Bose-Einstein distribution function (BE-distribution). The total rate of change of the phonon distribution in Eq. (3.38) has been divided into the separate contributions from force, phonon diffusion and phonon collisions. The \( \left( \frac{\partial \eta}{\partial t} \right)_{\text{force}} = 0 \) as there is no external force applied. In the presence of temperature gradient in the material, only the phonon diffusion \( \left( \frac{\partial \eta}{\partial t} \right)_{\text{diffusion}} \) and scattering \( \left( \frac{\partial \eta}{\partial t} \right)_{\text{scatt}} \) terms have significant contributions which are responsible for the phonon distribution variation across the material. Considering the steady state of heat flow through solid, the total rate of change of \( \eta \) is zero. This makes Eq. (3.38) as

$$\left( \frac{\partial \eta}{\partial t} \right)_{\text{diffusion}} + \left( \frac{\partial \eta}{\partial t} \right)_{\text{scatt}} = 0.$$  \hspace{1cm} (3.39)
The phonon diffusion rate term can be expressed as

\[
\left( \frac{\partial \eta}{\partial t} \right)_{\text{diffusion}} = -\mathbf{v} \cdot \nabla \eta,
\]

(3.40)

where \( \mathbf{v} \) is the phonon group velocity and \( \nabla \eta \) denotes the spatial variation of phonon population \( \eta \). Hence we can write the Eq. (3.39) as

\[
\mathbf{v} \cdot \nabla \eta = \left( \frac{\partial \eta}{\partial t} \right)_{\text{scatt}}.
\]

(3.41)

We will solve further Eq. (3.41) in Sec. 3.1.3.3 and now we will concentrate on the phonon collision term following Ref.[70].

3.1.3.1 Anharmonic potential

The anharmonic Hamiltonian can be written with the help of third order or further higher order terms in the potential energy expansion, Eq. (3.1) as,

\[
H = H^{\text{harm}} + \frac{1}{3!} \sum_{lb'l'b''} \sum_{\alpha_1 \alpha_2 \alpha_3} \Psi_{\alpha_1 \alpha_2 \alpha_3} (lb, l'b', l''b') u_{\alpha_1} (lb) u_{\alpha_2} (l'b') u_{\alpha_3} (l''b'').
\]

(3.42)

In Eq. (3.42), we have considered the contributions up to third order term. The higher order terms are neglected whose contributions are not significant around room temperature for our systems of interest. Furthermore, the calculations of these higher order terms are much more computationally expensive as compared to third order term. The analysis of different contributions to the potential energy for Si is represented in Fig. 3.1. The parameters are obtained by fitting the DFT calculations, using GPAW[71], for Si at a range of interatomic distances, to the Morse potential,

\[
V(R) = D_e [1 - e^{-a_e(R - R_e)}]^2,
\]

(3.43)

where \( R \) is interatomic distance, \( R_e \) is equilibrium bond distance, \( D_e \) denotes the depth of potential and \( a_e \) represents the width of the potential. The fitting parameters obtained are \( R_e = 2.35\text{Å} \), \( D_e = 10.6\text{eV} \) and \( a_e = 1.22 \). We see that the 3rd order contribution is able to reproduce the potential energy in the range of roughly 10% of the interatomic distance whereas the displacements of the atoms are around an order smaller than this. Hence, truncating the potential energy to the third order contributions to study anharmonicity is sufficient around
Figure 3.1: The potential energy for Si using Morse potential fitted to the DFT calculations. The reproduction of potential energy is tested by using Taylor expansion and restricting the contributions up to 2\textsuperscript{nd} order (harmonic), 3\textsuperscript{rd} order and 4\textsuperscript{th} order term.

room temperature. At very high temperatures (nearly melting temperatures), the contributions of fourth order term becomes significant and needs to be considered.

Using Eq. (3.14) and Eq. (3.15) the Hamiltonian becomes as,

\begin{equation}
H = H_{\text{harm}} + \frac{1}{3!} \sum_{lb' b''} \sum_{\alpha_1 \alpha_2 \alpha_3} \psi_{\alpha_1 \alpha_2 \alpha_3} (lb', l'b', l''b') \\
U_{\alpha_1} (qb) U_{\alpha_2} (q'b') U_{\alpha_3} (q''b'') e^{i(ql + q'l' + q''l')} \\
= H_{\text{harm}} + V_3,
\end{equation}

where $H_{\text{harm}}$ is the harmonic Hamiltonian as in Eq. (3.37).
We introduce new variables $h'' = l - l'$ along with $h' = l - l$ and use $\Psi_{a_1a_2a_3}(q b, q' b', q'' b'') = \sum_{h''} \Psi_{a_1a_2a_3}(0 b, h' b', h'' b'')e^{i(q' h' + q'' h'')}$ to get

$$
\tilde{V}_3 = \frac{1}{3!} \frac{1}{N_0 \Omega^{3/2}} \sum_{qq'q''} \sum_{bb'bb''} \sum_{a_1a_2a_3} e^{i(q+q'+q'')} l \times \Psi_{a_1a_2a_3}(0 b, h' b', h'' b'')e^{i(q' h' + q'' h'')}
\times U_{a_1}(q b) U_{a_2}(q' b') U_{a_3}(q'' b')
= \frac{1}{3!} \frac{1}{N_0 \Omega^{3/2}} \sum_{qq'q''} \sum_{bb'bb''} \sum_{a_1a_2a_3} e^{i(q+q'+q'')} l \times \Psi_{a_1a_2a_3}(q b, q' b', q'' b'')U_{a_1}(q b) U_{a_2}(q' b') U_{a_3}(q'' b'),
$$

(3.45)

We sum over $l$ to get

$$
\tilde{V}_3 = \frac{1}{3!} \frac{1}{\sqrt{N_0 \Omega}} \sum_{qq'q''} \delta_{G,q+q'+q''} \sum_{a_1a_2a_3} e^{i(q+q'+q'')} l \times \Psi_{a_1a_2a_3}(q b, q' b', q'' b'')U_{a_1}(q b) U_{a_2}(q' b') U_{a_3}(q'' b'),
$$

(3.46)

where $\sum_{l} e^{i(q+q'+q'')} l = N_0 \Omega \delta_{G,q+q'+q''}$ and $G$ is the reciprocal lattice vector.

Expanding $U(q b)$ in Eq. (3.46), in terms of phonon annihilation $a_{j q}$ and creation $a_{j q}^\dagger$ operator using Eq. (3.32),

$$
\tilde{V}_3 = \frac{1}{3!} \frac{1}{\sqrt{N_0 \Omega}} \sum_{j a j' a' j'' a''} \sum_{a_1a_2a_3} \sqrt{h^3} \frac{8 m_b m_g m_y \omega(j q) \omega(j' q') \omega(j'' q'')} {8 m_b m_g m_y \omega(j q) \omega(j' q') \omega(j'' q'')}
\times \delta_{G,q+q'+q''} \Psi_{a_1a_2a_3}(q b, q' b', q'' b'') e_{a_1}(b | j q) e_{a_2}(b' | j' q') e_{a_3}(b'' | j'' q'')
\times (a_{j q}^\dagger - a_{-j q})(a_{j' q'}^\dagger - a_{-j' q'})(a_{j'' q''}^\dagger - a_{-j'' q''}).
$$

(3.47)

Further introducing

$$
\tilde{\Psi}(j q, j' q', j'' q'') = \frac{1}{\sqrt{N_0 \Omega}} \sqrt{\frac{h^3}{8 \omega(j q) \omega(j' q') \omega(j'' q'')}} \sum_{bb'bb''} \Psi_{a_1a_2a_3}(q b, q' b', q'' b'')
\times \frac{e_{a_1}(b | j q)}{\sqrt{m_b}} \frac{e_{a_2}(b' | j' q')}{\sqrt{m_y}} \frac{e_{a_3}(b'' | j'' q'')}{\sqrt{m_y}}
$$

(3.48)
in Eq. (3.47), we get,

\[
\hat{V}_3 = \frac{1}{3!} \sum_{j_1 q_1 q_1' q_1''} \delta_{q_1+q_1'+q_1''} \tilde{\Psi}(j_1 q_1, j_1' q_1', j_1'' q_1'') \times (a_{j_1 q_1}^\dagger - a_{-j_1 q_1})(a_{j_1' q_1'}^\dagger - a_{-j_1' q_1'})(a_{j_1'' q_1''}^\dagger - a_{-j_1'' q_1''}).
\]  

(3.49)

\[\text{Figure 3.2: Three phonon scattering processes where (a) 'Coalescence' process leads to 2 phonons into 1 and (b) 'decay' process leads to 2 phonons out of 1.}\]

3.1.3.2 Phonon-phonon scattering rates

The cubic term in the potential energy Hamiltonian, \(\hat{V}_3\), considered for the anharmonicity, signify three phonon interactions due to \((a_{j_1 q_1}^\dagger - a_{-j_1 q_1})(a_{j_1' q_1'}^\dagger - a_{-j_1' q_1'})(a_{j_1'' q_1''}^\dagger - a_{-j_1'' q_1''})\) term in Eq. (3.49). Terms as \(a_{-j_1 q_1} a_{-j_1' q_1'} a_{j_1'' q_1''}\) and \(a_{-j_1 q_1} a_{j_1' q_1'} a_{-j_1'' q_1''}\) are obtained from the expansion of \((a_{j_1 q_1}^\dagger - a_{-j_1 q_1})(a_{j_1' q_1'}^\dagger - a_{-j_1' q_1'})(a_{j_1'' q_1''}^\dagger - a_{-j_1'' q_1''})\) which correspond to different categories of the phonon interactions: 'coalescence' and 'decay' processes, Fig. 3.2. Two phonons dissolve into one during the 'coalescence' processes and one phonon splits up into two phonons during 'decay' processes. Both of these processes obey the momentum and energy conservation.

For 'coalescence' processes,

\[
q + q' = q'' + G
\]

\[\omega(jq) + \omega(j'q') = \omega(j''q''),\]

(3.50)

and for 'decay' processes,

\[
q + G = q' + q''
\]

\[\omega(jq) = \omega(j'q') + \omega(j''q'').\]

(3.51)
To calculate the transition probabilities corresponding to the upper explained three phonon processes, we make use of Fermi’s golden rule

\[
P^I_i(3ph) = \frac{2\pi}{\hbar} |\langle f|\hat{V}_3|i \rangle|^2 \delta(E_f - E_i), \quad (3.52)
\]

where \(i\) and \(f\) represent the initial and the final states. \(E_f\) and \(E_i\) are the energies of initial and final states and \(\delta(E_f - E_i)\) confirms the energy conservation between initial and final states as given in Eq. (3.50) and Eq. (3.51). Eq. (3.52) for ‘coalescence’ processes can be written as

\[
P^{j''q''}_{j,q,j'q'} = \frac{2\pi}{\hbar} \left| \langle \eta_{jq} - 1, \eta_{jq'} - 1, \eta_{jq''} + 1 | \hat{V}_3 | \eta_{jq}, \eta_{jq'}, \eta_{jq''} \rangle \right|^2 \\
\times \hbar \delta(\omega(jq) + \omega(j'q') - \omega(j''q'')) ,
\]

where \(\eta_{jq}\) represents the phonon occupation for state \(jq\). We use \(\hat{V}_3\) in Eq. (3.49) to write \(P^{j''q''}_{j,q,j'q'}\) as

\[
P^{j''q''}_{j,q,j'q'} = 2\pi \left| \frac{1}{3!} \sum_{j,q,j',q''} \delta_{G,-q-q'+q''} \tilde{\Psi}(-jq, -jq', jq'') \right|^2 \\
\times \left( \langle \eta_{jq} - 1, \eta_{jq'} - 1, \eta_{jq''} + 1 | (a_{jq}^\dagger - a_{jq'}) (a_{jq''}^\dagger - a_{jq''}) \rangle \right)^2 \\
\times \delta(\omega(jq) + \omega(jq') - \omega(jq'')).
\]

From the expansion of \((a_{jq}^\dagger - a_{jq'}) (a_{jq''}^\dagger - a_{jq''})\) term in Eq. (3.49) and Eq. (3.54), only \(a_{jq}^\dagger a_{jq''}^\dagger\) term remains which relates the initial and final states in \(P^{j''q''}_{j,q,j'q'}\). Also 1/3! gets cancelled because of 3! number of equivalent terms in the summation over \(qq'q''\) which gives us

\[
P^{j''q''}_{j,q,j'q'} = 2\pi |\tilde{\Psi}(-jq, -jq', jq'')|^2 \eta_{jq}\eta_{jq'}(\eta_{jq''} + 1) \\
\times \delta(\omega(jq) + \omega(jq') - \omega(jq'')).
\]

The transition probability for the 'decay' processes is written in the similar way as

\[
P^{j'q',j''q''}_{jq} = 2\pi |\tilde{\Psi}(-jq, jq', jq'')|^2 \eta_{jq}(\eta_{jq'} + 1)(\eta_{jq''} + 1) \\
\times \delta(\omega(jq) - \omega(jq') - \omega(jq'')).
\]
Chapter 3. Theoretical Basics

The net scattering rates for 'coalescence' and 'decay' processes are given as the difference between forward and backward scattering as

\[ P^{j''q''}_{j,q,j'q'} - P^{j'q'}_{j',q''} = 2\pi \delta(\omega(jq) + \omega(j'q') - \omega(j''q''))|\tilde{\Psi}(-jq, -j'q', j''q'')|^2 \]

\[ \left[ \eta_{jq}\eta_{j'q'}(\eta_{j''q''} + 1) - (\eta_{jq} + 1)(\eta_{j'q'} + 1)\eta_{j''q''} \right], \]

\[ P^{j'q'}_{j,q,j''q''} - P^{j''q'}_{j',q,j''q''} = 2\pi \delta(\omega(jq) - \omega(j'q') + \omega(j''q''))|\tilde{\Psi}(-jq, j'q', j''q'')|^2 \]

\[ \left[ \eta_{jq}(\eta_{j'q'} + 1)(\eta_{j''q} + 1) - (\eta_{jq} + 1)\eta_{jq} \eta_{j'q'} \eta_{j''q''} \right]. \]

(3.58)

At equilibrium, the net scattering is zero due to which Eq. (3.57) give us the balanced equation

\[ \tilde{\eta}_{jq}\tilde{\eta}_{j'q'}(\tilde{\eta}_{j''q''} + 1) = (\tilde{\eta}_{jq} + 1)(\tilde{\eta}_{j'q'} + 1)\tilde{\eta}_{j''q''}, \]

(3.59)

which can also be written as

\[ \tilde{\eta}_{j'q'} - \tilde{\eta}_{j''q''} = \frac{\tilde{\eta}_{j'q'}(\tilde{\eta}_{j''q''} + 1)}{\tilde{\eta}_{jq} + 1}, \]

(3.60)

where \( \tilde{\eta} \) represents the equilibrium phonon population given by BE-distribution as \( \eta_{jq} = \frac{1}{e^{\frac{\omega(jq)}{k_BT}} - 1} \). Similarly Eq. (3.58) leads us to the balanced equation at equilibrium

\[ \tilde{\eta}_{jq}(\tilde{\eta}_{j'q'} + 1)(\tilde{\eta}_{j''q''} + 1) = (\tilde{\eta}_{jq} + 1)\tilde{\eta}_{j'q'}\tilde{\eta}_{j''q''}, \]

(3.61)

rewritten as

\[ 1 + \tilde{\eta}_{j'q'} + \tilde{\eta}_{j''q''} = \frac{\tilde{\eta}_{j'q'\tilde{\eta}_{j''q''}}}{\tilde{\eta}_{jq}}. \]

(3.62)

We write the perturbed phonon population \( \eta_{jq} \) as an expansion around equilibrium using first order perturbation \( \psi_{jq} \). This is done in order to linearise the scattering rates.

\[ \eta_{jq} = \frac{1}{e^{\frac{-\omega(jq)}{k_BT}} - 1} \approx \tilde{\eta}_{jq} - \frac{\partial \tilde{\eta}_{jq}}{\partial \omega(jq)} \psi_{jq}, \]

(3.63)

which gives

\[ \eta_{jq} = \tilde{\eta}_{jq} + \tilde{\eta}_{jq}(\tilde{\eta}_{jq} + 1)\psi_{jq}. \]

(3.64)

Substituting Eq. (3.64) in Eq. (3.57) we can write it as

\[ P^{j''q''}_{j,q,j'q'} - P^{j'q'}_{j',q'',j''q''} = \tilde{P}^{j''q''}_{j,q,j'q'}(\psi_{jq} + \tilde{\psi}_{j'q'} - \tilde{\psi}_{j''q''}), \]

(3.65)
where
\[ \tilde{P}_{jq}^{j'q',j''q''} = 2\pi \bar{n}_{jq} \tilde{n}_{jq'} (\bar{n}_{jq''} + 1) |\tilde{\Psi}(-j_q, -j'q', j''q'')|^2 \]
\[ \times \delta(\omega(j_q) + \omega(j'q') - \omega(j''q'')) \]  \hspace{1cm} (3.66)
and substitution of Eq. (3.64) in Eq. (3.58) gives
\[ \tilde{P}_{jq}^{j'q',j''q''} = \tilde{P}_{jq}^{j'q',j''q''} (\psi_{jq} - \psi_{jq'} - \psi_{jq''}), \]  \hspace{1cm} (3.67)
where
\[ \tilde{P}_{jq}^{j'q',j''q''} = 2\pi \bar{n}_{jq} (\bar{n}_{jq'} + 1) (\bar{n}_{jq''} + 1) |\tilde{\Psi}(-j_q, j'q', j''q'')|^2 \]
\[ \times \delta(\omega(j_q) - \omega(j'q') - \omega(j''q'')). \]  \hspace{1cm} (3.68)

The final scattering rate including both 'coalescence' and 'decay' processes is given by their sum
\[ -\frac{\partial n_{jq}}{\partial t}_{\text{scatt}} = \sum_{j'q',j''q''} \left[ (P_{jq,j'q'}^{j'q',j''q''} - P_{jq,j''q''}^{j'q',j''q''}) + \frac{1}{2} (P_{jq,j'q''}^{j'q',j''q''} - P_{jq,j''q''}^{j'q',j''q''}) \right] \]
\[ = \sum_{j'q',j''q''} \tilde{P}_{jq,j'q''}^{j'q',j''q''} (\psi_{jq} + \psi_{jq'} - \psi_{jq''}) + \frac{1}{2} \tilde{P}_{jq,j''q''}^{j'q',j''q''} (\psi_{jq} - \psi_{jq'} - \psi_{jq''}) \]
\[ = \nonumber \]  \hspace{1cm} (3.69)
where the factor 1/2 is to avoid double counting during summation.

### 3.1.3.3 Relaxation time approximation

The relaxation time approximation (RTA) assumes that the scattering rate of a particular phonon mode is independent of the other phonon mode perturbations. This implies that perturbations corresponding to \( j'q' \) and \( j''q'' \) are set to zero \( (\psi_{j'q'}, \psi_{j''q''} = 0) \) for computing scattering rate of \( j_q \) mode within RTA. Hence we write Eq. (3.69) using Eq. (3.60) and Eq. (3.62) as
\[ -\frac{\partial n_{jq}}{\partial t}_{\text{scatt}} = \bar{n}_{jq} (\bar{n}_{jq} + 1) \psi_{jq} \pi \sum_{j'q',j''q''} |\tilde{\Psi}(-j_q, j'q', j''q'')|^2 \]
\[ \times [2(\bar{n}_{jq'} - \bar{n}_{jq''}) \delta(\omega(j_q) + \omega(j'q') - \omega(j''q'')) + (1 + \bar{n}_{jq'} + \bar{n}_{jq''}) \delta(\omega(j_q) - \omega(j'q') - \omega(j''q''))]. \]
\[ \]  \hspace{1cm} (3.70)
This can be written in simplified manner using Eq. (3.64) as

$$\frac{\partial \eta_jq}{\partial t} \bigg|_{\text{scatt}} = \frac{\eta_jq(\bar{\eta}_jq + 1)\psi_{jq}}{\tau_{jq}} = \frac{\eta_jq - \bar{\eta}_jq}{\tau_{jq}},$$

which represents the exponential decay of the perturbed phonon population to the equilibrium. \(\tau_{jq}\) is the relaxation time corresponding to \(jq\) mode given as

$$\frac{1}{\tau_{jq}} = \pi \sum_{j'q'j''q''} |\tilde{\Psi}(-jq, j'q', j''q'')|^2 \times [2(\bar{\eta}_{j'q'} - \bar{\eta}_{j''q''}) \delta(\omega(jq) + \omega(j'q') - \omega(j''q'')) + (1 + \bar{\eta}_{j'q'} + \bar{\eta}_{j''q''}) \delta(\omega(jq) - \omega(j'q') - \omega(j''q''))],$$

calculated from the third order force constants. \(\delta(\omega(jq) + \omega(j'q') - \omega(j''q''))\) and \(\delta(\omega(jq) - \omega(j'q') - \omega(j''q''))\) terms in Eq. (3.72) signify the phonon 'coalescence' and 'decay' processes. These processes are subdivided into \(N\)-processes (Normal) and \(U\)-processes (Umklapp) where \(N\)-processes have the resulting states within the first Brillouin zone after scattering. \(U\)-processes have the resulting states out of the first Brillouin zone which are flipped back into first Brillouin zone using the reciprocal lattice vector \(G\). Hence, the \(U\)-processes provide the thermal resistance, Fig. 3.3. In RTA, both the \(N\) and \(U\) processes contribute in purely resistive manner due to the use of \(G\) vector for confining phonons to first Brillouin zone while calculating transitions rates to obtain Eq. (3.72). Thus RTA tends to underestimate the lattice thermal conductivity \((\kappa_l)\) as compared to full
iterative solution of BTE\cite{1, 72} and the experiment, mainly in the materials with weak $U$-scattering such as diamond, with $\approx 50\% \kappa_l$ underestimation at 300K.\cite{5} and graphene, with an order of magnitude $\kappa_l$ underestimation.\cite{73} However, the differences between RTA and iterative BTE results are very less for the materials with dominant $U$-scattering i.e., materials with low thermal conductivity. This has been studied for Mg$_2$Si and Mg$_2$Sn where the $\kappa_l$ underestimations with RTA are of 1.7\% and 0.5\% respectively at 300K.\cite{74} Even for Si and Ge, which have around an order of magnitude higher $\kappa_l$ than Mg$_2$-IV compounds, less than 10\% of deviations are obtained for RTA results as compared to iterative BTE solutions and experiments at 300K.\cite{5} Another class of low $\kappa_l$ materials studied in Chapter 5, Zn-VI compounds, also show a good agreement of $\kappa_l$ calculated within RTA as compared to experiments.\cite{9} In this thesis, we are interested in low thermal conductivity materials, hence we proceeded with the RTA formulation for calculating the anharmonic scattering rates.

With the precise determination of $\tau_{jq}$ based on third order force constants, Eq. (3.72), thermal conductivity can be calculated from the Boltzmann transport equation within RTA,

$$v_{jq} \nabla \eta_{jq} = \left. \frac{\partial \eta_{jq}}{\partial t} \right|_{scatt} = -\frac{\eta_{jq}}{\tau_{jq}}(\nabla \eta_{jq}).$$

(3.73)

We impose the diffusion approximation and define perturbation as

$$\delta_{jq} = \eta_{jq} - \bar{\eta}_{jq},$$

(3.74)

where $\delta_{jq}$ is considered to be very small compared to $\bar{\eta}_{jq}$. Using the above equation we write Eq. (3.73) as

$$v_{jq} \nabla \bar{\eta}_{jq} = -\frac{\delta_{jq}}{\tau_{jq}},$$

(3.75)

where $v_{jq} \nabla \delta_{jq}$ term, being very small, drops out. This helps us to write Eq. (3.75) as

$$\eta_{jq} = \bar{\eta}_{jq} - \tau_{jq}(v_{jq} \nabla \bar{\eta}_{jq}).$$

(3.76)

Lattice thermal conductivity $\kappa_l$ is given by Fourier’s law. Fourier’s law says that if a temperature gradient is applied in a material then the heat flux $J$ is proportional to the temperature gradient $\nabla T$ with $\kappa_l$ as the proportionality constant,

$$J = -\kappa_l \nabla T.$$  

(3.77)
We will now deduce the Fourier’s law to obtain the $\kappa_l$ formulation. Due to the temperature gradient across the material Eq. (3.76) can be expanded as,

$$\eta_{jq} = \bar{\eta}_{jq} - \tau_{jq} \left( v_{jq} \frac{d\bar{\eta}_{jq}}{dT} \right) \nabla T,$$  \hspace{1cm} (3.78)

The above equation tells that $\bar{\eta}_{jq}$ is isotropic but not $\eta_{jq}$ which has direction because of temperature gradient. This means that although the phonon motions remain random but are now biased by the temperature gradient.

The heat current due to a phonon with mode $jq$ having energy $\hbar \omega_{jq}$ and moving with a velocity $\mathbf{v}_{jq}$ can be written as

$$J_{jq} = \hbar \omega_{jq} \mathbf{v}_{jq}.$$  \hspace{1cm} (3.79)

This can be integrated over all the phonon modes in the crystal Brillouin zone to express the total heat current for a crystalline material as,

$$J = \sum_j \int \hbar \omega_{jq} \mathbf{v}_{jq} \eta_{jq} \frac{dq}{8\pi^3}.$$  \hspace{1cm} (3.80)

While we substitute Eq. (3.78) in Eq. (3.80), we can take advantage of the isotropic behaviour of $\bar{\eta}_{jq}$ which leads to $\sum_j \int \mathbf{v}_{jq} \bar{\eta}_{jq} dq = 0$ and we get,

$$J = \sum_j \int \hbar \omega_{jq} \mathbf{v}_{jq} \mathbf{v}_{jq} \tau_{jq} \left( \frac{d\bar{\eta}_{jq}}{dT} \right) \frac{dq}{8\pi^3}$$

$$= - \left( \sum_j \int \frac{dq}{(2\pi)^3} \mathbf{v}_{jq} \mathbf{v}_{jq} \tau_{jq} C_{V,jq} \right) \nabla T.$$

Eq. (3.81) is the Fourier’s law and the proportionality term between $J$ and $-\nabla T$ represents the lattice thermal conductivity.

$$\kappa_l = \frac{1}{3} \sum_j \int \frac{dq}{(2\pi)^3} \mathbf{v}_{jq}^2 \tau_{jq} C_{V,jq},$$  \hspace{1cm} (3.82)

where $C_V$ is the heat capacity at constant volume. The relaxation time $\tau$ can be calculated using Eq. (3.72).
3.1.3.4 Phonon-isotope scattering

Although the major contribution to the $\tau$ is from the phonon-phonon scattering whose rate is calculated with Eq. (3.72), significant contributions are also from the phonon scattering due to imperfections present in the real material like isotopes, grain boundary, vacancies, dislocations etc. According to Matthiesen’s rule, scattering rates corresponding to each mechanism can be calculated separately and added to get the total scattering time, $\tau$. We have studied the effect of phonon-isotope scattering in this thesis for which the scattering rate formulation is discussed next as derived in Ref.[75, 76].

We consider a crystal for which the kinetic part of the Hamiltonian can be written as,

$$\hat{K} = \frac{1}{2} \sum_{\lambda b \alpha_1} m(\lambda b) \dot{u}_{\alpha_1}^2 (\lambda b),$$  \hspace{1cm} (3.83)

where atom at position $b$ in the unit cell with position vector $l$ is displaced with $u$ magnitude in direction $\alpha_1$. Considering just the presence of isotopes in the material and no other defects, the Hamiltonian in Eq. (3.83) can be separated into unperturbed and perturbed parts as,

$$\hat{K} = \hat{K}_0 + \hat{K}_f.$$ \hspace{1cm} (3.84)

The unperturbed Hamiltonian $H_0$ considers the uniform average mass of all the isotopes of atoms in the crystal. Thus the phonon frequencies and the eigenvectors for the average crystal are obtained straight forwardly in the harmonic approximation by solving Eq. (3.10). The unperturbed Hamiltonian is

$$H_0 = \hat{K}_0 + \hat{V}_2 = \frac{1}{2} \sum_{\lambda b \alpha_1} \tilde{m}(b) \dot{u}_{\alpha_1}^2 (\lambda b) + \hat{V}_2,$$ \hspace{1cm} (3.85)

where $\hat{V}_2$ is the second order term represented in Eq. (3.21). $\tilde{m}(b)$ in Eq. (3.85) represents the concentration weighted average mass of the isotopes of unit cell atom at $b$ position and is given as

$$\tilde{m}(b) = \sum_i f_i(b) m_i(b),$$ \hspace{1cm} (3.86)

where $f_i$ and $m_i$ are the concentration and mass respectively of the isotope $i$ of atom at $b$ position. The atomic displacement $u(\lambda b)$ of atom $\lambda b$ (atom at $l + b$) can
be written in terms of phonon eigenvectors $e(b|jq)$ using Eq. (3.14) and Eq. (3.32) as,

$$u(lb) = -i \sum_{jq} \sqrt{\frac{\hbar}{2\bar{m}(b)N_0\omega(jq)}} e(b|jq) (a_{jq}^\dagger - a_{-jq}) e^{i(ql + \omega(jq)t)},$$

(3.87)

where $a_{jq}^\dagger$ and $a_{jq}$ are the creation and annihilation operator for phonon mode $jq$. The time derivative of above equation gives,

$$\dot{u}(lb) = \sum_{jq} \sqrt{\frac{\hbar\omega(jq)}{2\bar{m}(b)N_0}} e(b|jq) (a_{jq}^\dagger - a_{-jq}) e^{i(ql + \omega(jq)t)}.$$  \hspace{1cm} (3.88)

The interaction Hamiltonian $\hat{K}_I$ governs the scattering of the eigenstates in the average crystal by considering local mass disorder. The interaction Hamiltonian is given as,

$$\hat{K}_I = \frac{1}{2} \sum_{lb_{\alpha l}} [m(lb) - \bar{m}(b)] \dot{u}_{\alpha l}^2 (lb) = \frac{1}{2} \sum_{lb_{\alpha l}} \Delta m(lb) \dot{u}_{\alpha l}^2 (lb),$$

(3.89)

where $\Delta m(lb) = m(lb) - \bar{m}(b)$ represents the perturbation at the atomic site $lb$. We further use Eq. (3.88) leaving the time dependence term $e^{i\omega(jq)t}$ as its contribution is limited to a phase factor which yields unity while calculating the scattering rates. The interaction Hamiltonian $\hat{K}_I$ using Eq. (3.88), without $e^{i\omega(jq)t}$ term, can be written as,

$$\hat{K}_I = \frac{\hbar}{4} \sum_{bqq'} \sum_{jq'q} \sum_l \sqrt{\omega(jq)\omega(jq')} \frac{\Delta m(lb)}{N_0\bar{m}(b)}$$

$$\times e(b|jq)e(b|jq') [a_{-jq}a_{jq'}^\dagger + a_{jq}^\dagger a_{-jq'}] e^{i(ql + q'l)},$$

(3.90)

where only the relevant annihilation and creation phonon processes are considered. We now introduce $\Delta \tilde{M}_b(Q)$ as the Fourier transform of $\Delta m(lb) = \Delta m(lb)/\bar{m}(b)$:

$$\Delta \tilde{M}_b(Q) = \frac{1}{N_0} \sum_l \Delta M(lb) e^{-iql}.$$  \hspace{1cm} (3.91)

This transformation helps us to write

$$\frac{\Delta m(lb)}{N_0\bar{m}(b)} = \sum_Q \Delta \tilde{M}_b(Q) e^{iql},$$

(3.92)
which is then substituted in Eq. (3.90) to write \( \hat{K}_I \) as,

\[
\hat{K}_I = \frac{\hbar}{4} \sum_{bqq'Q} \sum_{jj'} \sqrt{\omega(jq)\omega(j'q')} \Delta \tilde{M}_b(Q) \\
\times e(b|jq)e(b|j'q')[a_{-jq}a_{j'q'}^\dagger + a_{jq}^\dagger a_{-j'q'}] \sum_l e^{i(a+q'+Q)l}.
\]

(3.93)

We sum over \( l \) and obtain,

\[
\hat{K}_I = \frac{\hbar}{4} \sum_{bqq'Q} \sum_{jj'} \sqrt{\omega(jq)\omega(j'q')} \delta(q + q' + Q) \Delta \tilde{M}_b(Q) \\
\times e(b|jq)e(b|j'q')[a_{-jq}a_{j'q'}^\dagger + a_{jq}^\dagger a_{-j'q'}].
\]

(3.94)

The transition scattering rate for the isotope scattering can also be written using Fermi’s golden rule, similar to the three phonon interaction,

\[
P_i^f = \frac{2\pi}{\hbar} |\langle f|\hat{K}_I|i \rangle|^2 \delta(E_f - E_i).
\]

(3.95)

The net scattering rate for a phonon mode is then given as,

\[
- \frac{\partial \eta_{jq}}{\partial t} \bigg|_{\text{scatt}} = \sum_{j'q'} (P_{j'q'}^{jq} - P_{jq}^{j'q'}),
\]

(3.96)

where

\[
P_{j'q'}^{jq} = \frac{\pi}{2} \eta_{jq}(\eta_{j'q'} + 1)\omega(jq)\omega(j'q') \\
\times \left| \sum_{bQ} \Delta \tilde{M}_b(Q)e(b|jq)e^*(b|j'q')\delta(-q + q' + Q) \right|^2 \delta(\omega(jq) - \omega(j'q')).
\]

(3.97)

We have used the property \( e(b|jq) = e^*(b|j'q') \) in the above equation. The energy conservation suggests that \( \omega(jq) = \omega(j'q') \) which makes the \( P_{j'q'}^{jq} \) expression as,

\[
P_{j'q'}^{jq} = \frac{\pi}{2} \eta_{jq}(\eta_{j'q'} + 1)\omega^2(jq) \\
\times \left| \sum_{bQ} \Delta \tilde{M}_b(Q)e(b|jq)e^*(b|j'q')\delta(-q + q' + Q) \right|^2 \delta(\omega - \omega(j'q')).
\]

(3.98)
In the similar way $P_{j'q'}^j$ is written as
\[
P_{j'q'}^j = \frac{\pi}{2} (\eta_{jq} + 1) \eta_{jq'} \omega^2(jq) \times \sum_{bQ} \Delta \tilde{M}_b(Q)e(b|jq)e^*(b|jq')\delta(q - q' + Q) \left| \frac{\delta(\omega - \omega(j'q'))}{\delta(\omega - \omega(j'q'))} \right|^2
\]

Thus using Eq. (3.98) and Eq. (3.99), the net scattering rate can be written as,
\[
- \frac{\partial \eta_{jq}}{\partial t} \bigg|_{scatt} = \frac{\pi}{2} \omega^2(jq) \sum_{j'q'} \sum_{bQ} \Delta \tilde{M}_b(Q)e(b|jq)e^*(b|jq')\delta(q - q' + Q) \left| \frac{\delta(\omega - \omega(j'q'))}{\delta(\omega - \omega(j'q'))} \right|^2
\]
\[
m_{jq} \eta_{jq'}(\eta_{jq'} + 1) - (\eta_{jq} + 1) \eta_{jq'} = \delta \eta_{jq}
\]
\[
(\eta_{jq} - \eta_{jq'}) = \delta \eta_{jq} - \delta \eta_{jq'}
\]

\[
\eta_{jq} = \bar{\eta}_{jq} + \delta \eta_{jq}
\]

This makes
\[
\eta_{jq}(\eta_{jq'} + 1) - (\eta_{jq} + 1) \eta_{jq'} = \eta_{jq} - \eta_{jq'}
\]
\[
= (\eta_{jq} + \delta \eta_{jq}) - (\eta_{jq'} - \delta \eta_{jq'})
\]
\[
= (\eta_{jq} - \eta_{jq'}) + (\delta \eta_{jq} - \delta \eta_{jq'})
\]
\[
= \delta \eta_{jq} - \delta \eta_{jq'}
\]

In the above equation $\eta_{jq} - \eta_{jq'} = 0$ due to the energy conservation leading to $\omega(jq) = \omega(jq')$ and hence $\eta_{jq} = \eta_{jq'}$. We use RTA now which says that the scattering process for each phonon mode is independent of other mode perturbations and thus leads to $\delta \eta_{jq'} = 0$ in Eq. (3.102) making it as,
\[
\eta_{jq}(\eta_{jq'} + 1) - (\eta_{jq} + 1) \eta_{jq'} = \delta \eta_{jq}
\]

and Eq. (3.100) as
\[
- \frac{\partial \eta_{jq}}{\partial t} \bigg|_{scatt} = \frac{\delta \eta_{jq}}{\tau_{jq}} = \frac{\eta_{jq} - \bar{\eta}_{jq}}{\tau_{jq}},
\]
where \( \tau_{tq}^{iso} \) is the phonon relaxation time corresponding to the phonon-isotope scattering given by,

\[
\frac{1}{\tau_{tq}^{iso}} = \frac{\pi}{2} \omega^2(j|q) \sum_{j'|q'} \left| \sum_{b|Q} \Delta \tilde{M}_b(Q)e(b|j|q)e^*(b|j'|q') \delta(q - q' + Q) \right|^2 \delta(\omega - \omega(j'|q')).
\]  

(3.105)

We now introduce the mass variance parameter \( m_i^{(2)}(b) \) given as

\[
m_i^{(2)}(b) = \sum_i f_i(b) \left( \bar{m}(b) - m_{lb} \right)^2,
\]

(3.106)

which is obtained by taking an ensemble average of the random distribution of masses,

\[
\langle \Delta M(lb)\Delta M(l'b') \rangle_{avg} = \langle (\Delta M(lb))^2 \rangle_{avg} \delta_{ll'} \delta_{bb'} = m_i^{(2)}(b) \delta_{bb'}.
\]

(3.107)

We use the above equation to write \( |\Delta \tilde{M}_b(Q)|^2 \) in Eq. (3.105) in terms of \( m_i^{(2)}(b) \) as,

\[
|\Delta \tilde{M}_b(Q)|^2 = \sum_{l'\ell} |\Delta \tilde{M}_b(Q)| \Delta \tilde{M}_{l'b'}(Q')
\]

\[
= \frac{1}{N_0} \sum_{l'\ell} \Delta M(lb)\Delta M(l'b')e^{-i(Ql - Q'l)}
\]

\[
= \frac{1}{N_0} \sum_{ll'} m_i^{(2)}(b) \delta_{bb'} e^{-i(Ql - Q'l)} \delta_{ll'}
\]

(3.108)

Substitution of Eq. (3.108) in Eq. (3.105) gives,

\[
\frac{1}{\tau_{tq}^{iso}} = \frac{\pi}{2N_0} \omega^2(j|q) \sum_{j'|q'} \delta(\omega - \omega(j'|q')) \sum_b m_i^{(2)}(b) |e(b|j|q)e^*(b|j'|q')|^2.
\]

(3.109)

Eq. (3.109) is the phonon-isotope scattering relaxation time which can be calculated for the crystal having mass disorder due to presence of various isotopes of the constituting elements. The \( (\tau_{tq}^{iso})^{-1} \) expression requires only the phonon frequencies \( \omega(j|q) \), vibrational eigenvectors \( e(b|j|q) \) and the mass variance parameter \( m_i^{(2)}(b) \).
To get to a further simple expression for the cubic crystals, we use a symmetry property related to their eigenvectors as,

$$\sum_{j\mathbf{q}} F(j\mathbf{q}) e_{a_1}(b|j\mathbf{q}) e_{a_2}^*(b|j\mathbf{q}) = \frac{\delta_{a_1 a_2}}{3} \sum_{j\mathbf{q}} F(j\mathbf{q}) |e(b|j\mathbf{q})|^2,$$

(3.110)

where $F(j\mathbf{q})$ denotes an arbitrary function which is dependent on mode $j\mathbf{q}$ through $\omega(j\mathbf{q})$. Using this, we can rewrite Eq. (3.109) as

$$\left(\tau_{\text{iso}}^{\text{iso}}\right)^{-1} = \frac{\pi}{6N_0} \omega^2(j\mathbf{q}) \sum_{j'\mathbf{q}'} \delta(\omega - \omega(j'\mathbf{q}')) \sum_b m_{i}^{(2)}(b) |e(b|j\mathbf{q})|^2.$$

(3.111)

We know that $\sum_{j'\mathbf{q}'} \delta(\omega - \omega(j'\mathbf{q}'))/N_0 = \Omega g(\omega)$ where $\Omega$ is the unit cell volume and $g(\omega)$ represents the phonon density of states (phononDOS). $g(\omega)$ can be also written in the terms of partial phononDOS $g_b(\omega)$ as

$$g(\omega) = \sum_b g_b(\omega),$$

(3.112)

which makes Eq. (3.111) as

$$\left(\tau_{\text{iso}}^{\text{iso}}\right)^{-1} = \frac{\pi}{6N_0} \omega^2(j\mathbf{q}) \Omega \sum_b m_{i}^{(2)}(b) g_b(\omega) |e(b|j\mathbf{q})|^2.$$

(3.113)

The total phonon relaxation time, as given by Matthiessen’s rule[78, 79] is

$$\frac{1}{\tau_{j\mathbf{q}}} = \frac{1}{\tau_{\text{anh}}^{\text{anh}}} + \frac{1}{\tau_{\text{iso}}^{\text{iso}}},$$

(3.114)

where $\frac{1}{\tau_{j\mathbf{q}}}$ is calculated from Eq. (3.72).

We applied this method to calculate the thermal conductivity of Si and compare it with earlier results and experiment.[5, 6] Fig. 3.4 shows a good agreement of our results for Si $\kappa_l$ from BTE-RTA method as compared to the full iterative solution of BTE and the experiment.[5, 6] Slight underestimation of $\kappa_l$ is seen for BTE-RTA method which has been discussed in Sec. 3.1.3.3. However, the simplicity of RTA method compared to iterative method along with the fair agreement of RTA results with experiments for low thermal conductivity materials, which we are interested in, make it suitable for our studies in this thesis.
3.1.4 Quasi-harmonic approximation

In Sec. 3.1.3.2, we discussed the interaction of phonons due to anharmonicity. However, anharmonicity has further effect of thermal expansion too which has important roles in determining thermal properties of crystals. The effect of thermal expansion on other thermal properties can be studied within quasi-harmonic approximation (QHA). This approximation considers the influences of volume variations on phonons to calculate the thermal properties of crystal. Different thermodynamic properties like free energy, entropy, Grüneisen parameters, heat capacity and thermal expansion coefficient are calculated in next section.

3.1.4.1 Harmonic thermodynamic properties

At 0K, phonons occupy the lowest energy level and higher levels are occupied with increasing temperature which is described by BE-distribution. This variation
in the phonon populations with the temperature make these thermal properties temperature dependent.

Heat capacity is defined as the vibrational energy derivative with respect to the temperature. The average energy of phonons in mode \( j \mathbf{q} \) is evaluated as,

\[
\bar{E}_{j \mathbf{q}} = \sum_{n_{j \mathbf{q}}} E_{n_{j \mathbf{q}}} e^{-E_{n_{j \mathbf{q}}}/k_B T} Z_{j \mathbf{q}},
\]

where the energy of harmonic oscillator \( E_{n_{j \mathbf{q}}} = \left( n_{j \mathbf{q}} + \frac{1}{2} \right) \hbar \omega(j \mathbf{q}) \) corresponds to the \( n_{j \mathbf{q}} = 0, 1, 2, \ldots \) phonons in mode \( j \mathbf{q} \). \( E_{n_{j \mathbf{q}}} \) can be obtained using Eq. (3.37) as \( a_{j \mathbf{q}}^\dagger a_{j \mathbf{q}} |n_{j \mathbf{q}}\rangle = n_{j \mathbf{q}} |n_{j \mathbf{q}}\rangle \). \( Z_{j \mathbf{q}} \) is the partition function for a phonon mode given as,[80]

\[
Z_{j \mathbf{q}} = \sum_{n_{j \mathbf{q}}} e^{-E_{n_{j \mathbf{q}}}/k_B T}.
\]

Thus, Eq. (3.115) becomes,

\[
\bar{E}_{j \mathbf{q}} = \frac{\sum_{n_{j \mathbf{q}}} E_{n_{j \mathbf{q}}} e^{-E_{n_{j \mathbf{q}}}/k_B T}}{\sum_{n_{j \mathbf{q}}} e^{-E_{n_{j \mathbf{q}}}/k_B T}} = \frac{\sum_{n_{j \mathbf{q}}} \left( n_{j \mathbf{q}} + \frac{1}{2} \right) e^{-\left( n_{j \mathbf{q}} + \frac{1}{2} \right) \hbar \omega(j \mathbf{q})/k_B T} \hbar \omega(j \mathbf{q})}{\sum_{n_{j \mathbf{q}}} e^{-\left( n_{j \mathbf{q}} + \frac{1}{2} \right) \hbar \omega(j \mathbf{q})/k_B T} \hbar \omega(j \mathbf{q})}.
\]

Using a power series expansion, Eq. (3.117) can be simplified as

\[
\bar{E}_{j \mathbf{q}} = \hbar \omega(j \mathbf{q}) \left( \frac{1}{2} + \eta_{j \mathbf{q}} \right).
\]

The total vibrational energy thus can be written as sum over all phonon modes as,

\[
\bar{E} = \sum_{j \mathbf{q}} \hbar \omega(j \mathbf{q}) \left( \frac{1}{2} + \eta_{j \mathbf{q}} \right),
\]

where \( \eta_{j \mathbf{q}} = \frac{1}{e^{\hbar \omega(j \mathbf{q})/k_B T} - 1} \) is the BE-distribution. Derivative of Eq. (3.119) w.r.t. temperature gives the heat capacity at constant volume \( C_V \) as,

\[
C_V = \left( \frac{\partial \bar{E}}{\partial T} \right)_{V} = \sum_{j \mathbf{q}} \hbar \omega(j \mathbf{q}) \frac{\partial \eta_{j \mathbf{q}}}{\partial T}.
\]
The free energy is given as\[70\]
\[ F = E_0 + F_{\text{vib}}, \]  
(3.121)

where \( E_0 \) is the electronic energy contribution and \( F_{\text{vib}} \) the vibrational free energy term. \( F_{\text{vib}} \) is expressed as\[70, 80\],
\[ F_{\text{vib}} = -k_B T \ln(Z). \]  
(3.122)

where \( Z \), the partition function in Eq. (3.122), is expressed as the product of individual mode partition functions given in Eq. (3.116),
\[ Z = \prod_{j\mathbf{q}} Z_{j\mathbf{q}} = \prod_{j\mathbf{q}} \frac{e^{-\hbar \omega(j\mathbf{q})/2k_B T}}{1 - e^{-\hbar \omega(j\mathbf{q})/k_B T}}. \]  
(3.123)

Substituting it in Eq. (3.122) gives,
\[ F_{\text{vib}} = \frac{1}{2} \sum_{j\mathbf{q}} \hbar \omega(j\mathbf{q}) + k_B T \sum_{j\mathbf{q}} \ln(1 - e^{-\hbar \omega(j\mathbf{q})/k_B T}), \]  
(3.124)

which leads to Eq. (3.121) as
\[ F = E_0 + \frac{1}{2} \sum_{j\mathbf{q}} \hbar \omega(j\mathbf{q}) + k_B T \sum_{j\mathbf{q}} \ln(1 - e^{-\hbar \omega(j\mathbf{q})/k_B T}). \]  
(3.125)

The vibrational entropy then becomes
\[ S_{\text{vib}} = -\frac{\partial F_{\text{vib}}}{\partial T} = k_B \sum_{j\mathbf{q}} \left[ \frac{\hbar \omega(j\mathbf{q})/k_B T}{e^{\hbar \omega(j\mathbf{q})/k_B T} - 1} - \ln(1 - e^{-\hbar \omega(j\mathbf{q})/k_B T}) \right]. \]  
(3.126)

Fig. 3.5 shows the \( C_V, F_{\text{vib}} \) and \( S_{\text{vib}} \) variations with temperature for Si calculated using above derived formulae in harmonic approximation. We also calculated the \( F_{\text{vib}} \) and \( C_P \) variation with temperature taking into account the thermal expansion for Si through quasi-harmonic approximation. It can be seen in Fig. 3.5 that the difference in the harmonic and quasi-harmonic approximation results are very small. This is because the thermal expansion coefficient for Si is in the orders of \( 10^{-6}/\text{K} \), discussed in Chapter 3. However, these differences seem to be small on absolute scale but play an important role in estimating the anharmonicity of a material.
3.1.4.2 Quasi-harmonic thermal properties

For determining Grüneisen parameters and thermal expansion coefficient, we write the equation of state for a crystal with free energy $F$, considering its dependence only on volume $V$ as

$$P = -\left.\left(\frac{\partial F}{\partial V}\right)\right|_T. \quad (3.127)$$

Using Eq. (3.121), the equation of state is expanded as

$$P = -\left.\left(\frac{\partial F}{\partial V}\right)\right|_T = -\left.\left(\frac{\partial E_0}{\partial V}\right)\right|_T - \left.\left(\sum_{j\mathbf{q}} \frac{\partial F_{\text{vib}}}{\partial \omega(j\mathbf{q})} \frac{\partial \omega(j\mathbf{q})}{\partial V}\right)\right|_T \
= -\left.\left(\frac{\partial E_0}{\partial V}\right)\right|_T + \frac{1}{V} \sum_{j\mathbf{q}} \gamma(j\mathbf{q})(\frac{1}{2} \hbar \omega(j\mathbf{q}) + \hbar \omega(j\mathbf{q}) \eta(j\mathbf{q})) \right|_T. \quad (3.128)$$

The last part of Eq. (3.128) has a term called Grüneisen parameter $\gamma(j\mathbf{q})$ and is given as,

$$\frac{\partial \omega(j\mathbf{q})}{\partial V} = -\gamma(j\mathbf{q}) \frac{\omega(j\mathbf{q})}{V}$$

$$\gamma(j\mathbf{q}) = -\frac{\partial \ln \omega(j\mathbf{q})}{\partial \ln V}. \quad (3.129)$$
As the mathematical definition suggests, Grüneisen parameters $\gamma(jq)$ show the effect of the crystal volume variations on phonon frequencies.

Thermal expansion is the tendency of matter to change its volume($V$) in response to change in temperature($T$) at constant pressure. The degree of expansion divided by the change in temperature is called the material’s thermal expansion coefficient $\alpha_T$ given as,

$$\alpha_T = \frac{1}{3V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{1}{3B} \left( \frac{\partial P}{\partial T} \right)_V,$$

where bulk modulus $B$ is given as,

$$B = -V \left( \frac{\partial P}{\partial V} \right)_T.$$ (3.131)

The factor 3 in denominator of Eq. (3.130) is used for cubic crystals. Now substituting Eq. (3.128) into Eq. (3.130) gives,[81]

$$\alpha_T = \frac{1}{3BV} \sum_{jq} \gamma(jq) \hbar \omega(jq) \frac{\partial \eta_{jq}}{\partial T}$$

$$\alpha_T = \frac{1}{3BV} \sum_{jq} \gamma(jq) C_V(jq) = \frac{1}{3BV} \gamma C_V.$$ (3.132)

The specific heat at constant pressure ($C_p$) is also affected by the thermal expansion as,

$$C_p = \left( \frac{\partial E}{\partial T} \right)_p = C_V + 3\alpha_T VT \left( \frac{\partial S}{\partial V} \right)_T.$$ (3.133)

Eq. (3.132) also shows that thermal expansion $\alpha_T$ and Grüneisen parameters $\gamma(jq)$ are interrelated. The mode independent Grüneisen parameter $\gamma$ is defined as the specific heat weighted sum of the mode dependent Grüneisen parameters as

$$\gamma = \frac{1}{C_V} \sum_{jq} \gamma(jq) C_V(jq).$$ (3.134)

The calculation of $\gamma(jq)$ and $\alpha_T$ gives a good measure of anharmonicity in the material. The third order force constants $\Psi$, Eq. (3.3), also relate to the Grüneisen
parameters $\gamma(jq)$ as\[1\]

$$
\gamma(jq) = -\frac{1}{6\omega^2(jq)} \sum_{b'b'\alpha_1\alpha_2\alpha_3} \sum_\alpha \Psi_{\alpha_1\alpha_2\alpha_3}(lb, l'b', l'b'') \\
\times \frac{e^{*}_{\alpha_1}(b|jq)e_{\alpha_2}(b'|jq)}{\sqrt{m_bm'_b}} e^{i\omega_l(l + b')(l' + b'')}_{\alpha_3},
$$

(3.135)

where $(l' + b'')_{\alpha_3}$ denotes the $\alpha^{th}_3$ component of the position vector of atom specified by vector $b''$ in the unit cell characterised by vector $l'$. Eq. (3.135) links the phonon relaxation time for thermal conductivity calculation and quasi-harmonic properties. Early theoretical studies for the $\kappa_l$ were also based on its relation to the $\gamma$.\[82–84\] Although it is an efficient way to calculate $\kappa_l$ from $\gamma$ than from computationally expensive $\Psi$, the $\kappa_l$ expression in terms of $\gamma$ requires several approximations\[1, 82\]. However, the relation of $\gamma$ and $\Psi$ in Eq. (3.135) confirms that to check a simplified potential for correct prediction of $\Psi$ and $\kappa_l$, it is necessary to reproduce accurately quasi-harmonic properties i.e., $\gamma$ and $\alpha_T$. This serves as the base for the development of simplified models for correct calculations of thermal properties discussed in Chapter 4 and Chapter 6.

### 3.2 Computational Background

The energy calculations for the structures with atomic displacements to get its second and third order derivatives, $\Phi$ and $\Psi$ respectively, are done with Density Functional Theory (DFT) codes GPAW\[71\] and VASP\[85\]. Furthermore, we have also developed short ranged simple models for calculating $\Phi$ and $\Psi$, at large length scales, for complex nanostructures exhibiting interesting thermal transport. First model is a force constant mode, presented in Chapter 4, and other is tight binding model, developed in Chapter 6. The force constant model is discussed in detail in Chapter 4 whereas we discuss the theory of tight binding model in this section along with DFT.

#### 3.2.1 Density functional Theory

The theoretical studies for a material from the quantum mechanical perspectives is based on solving the time-independent, n-particles($X$ nuclei and $Y$ electrons)
Schrödinger equation written as,

$$\hat{H}\psi_i(x_1, x_2, ..., x_Y, R_1, R_2, ..., R_X) = E_i\psi_i(x_1, x_2, ..., x_Y, R_1, R_2, ..., R_X), \quad (3.136)$$

where $\hat{H}$ is the total energy Hamiltonian for the system. $\psi_i(x_1, x_2, ..., x_Y, R_1, R_2, ..., R_X)$ represents the wavefunction where $x_i$ stands for the combined electronic state of $i^{th}$ electron with $r_i$ position and $s_i$ spin. The $R_I$ denotes the position of $I^{th}$ atom. The Hamiltonian $\hat{H}$ is written as the sum of the contributions from different nuclei and electronic interactions,

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \frac{1}{2}\sum_{l=1}^{M}\frac{1}{m_l}\nabla_l^2 - \sum_{i=1}^{N}\sum_{l=1}^{M}\frac{Z_i}{r_{il}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} + \sum_{l=1}^{M}\sum_{J>l}^{M}\frac{Z_iZ_J}{R_{IJ}}. \quad (3.137)$$

The first two terms are Kinetic energy operators for electrons and nuclei respectively. Other terms represent potential energies corresponding to electron-electron, electron-nucleus and nucleus-nucleus interactions. The famous Born-Oppenheimer approximation suggests that the kinetic energy term for nuclei can be neglected. The large difference in the masses and velocities of the electron and the nucleus is the reason behind it due to which nuclei seem to be the stationary particles having negligible kinetic energy as compared to the kinetic energies of electrons. Similarly, the potential energy term corresponding to nucleus-nucleus interaction can also be considered as a constant. Hence, the Hamiltonian shrinks to,

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{l=1}^{M}\frac{Z_i}{r_{il}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}}$$

$$= \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{\text{ee}}, \quad (3.138)$$

which makes the Schrödinger equation as,

$$\hat{H}_{\text{elec}}\psi_{\text{elec}} = E_{\text{elec}}\psi_{\text{elec}}. \quad (3.139)$$

Then the total energy can be calculated as,

$$E_{\text{tot}} = E_{\text{elec}} + E_{\text{nuc}}, \quad (3.140)$$

where $E_{\text{nuc}} = \sum_{l=1}^{M}\sum_{J>l}^{M}\frac{Z_iZ_J}{R_{IJ}}$. To solve the Eq. (3.139) for a specific atomistic system, the $\hat{H}$ needs to be set accordingly i.e., the information regarding the number of electrons $Y$ and the
potential corresponding to nucleus-electron interactions, also known as external potential, $V_{ext}$ is needed. Then the eigenfunctions $\psi_i$ and corresponding eigenvalues $E_i$ can be calculated by solving Eq. (3.139) which then helps to calculate the other properties of the material. However, this trivial sounding problem is computationally unfeasible, even with the modern age computers, due to large number of atoms and electrons in real material and the complicated representation of many-electron wave function. No exact solution for the problem is found till date although there are different approximations developed for solving Eq. (3.139). The Hartree approximation treats the electrons to be independent and thus the many-electron wavefunction($\psi^H$) is given as,

$$\psi^H = \psi_1(x_1)\psi_2(x_2)\ldots\psi_Y(x_Y).$$ \hspace{1cm} (3.141)

This representation, however, neglects the anti-symmetry of the wavefunction. Furthermore, the independent electrons assumption leads to no interaction i.e., no hybridization hence failing to describe the cohesion in solid. In Hartree-Fock approximation, the anti-symmetry of the wavefunction is taken care of by writing it as Slater determinant,

$$\psi^{HF} = \frac{1}{Y!} \text{det}\{\psi_1(x_1) \psi_2(x_2)\ldots\psi_Y(x_Y)\}.$$ \hspace{1cm} (3.142)

The Hartree-Fock Hamiltonian has the exact exchange term but neglects the correlation of electrons.

In 1964, Hohenberg and Kohn[87] proved that the total energy of a system can be written as a unique functional of electron density $n(x)$ instead of expressing it in terms of the many-electron wavefunction, where $n(x)$ is given as,

$$n(x) = \int |\psi(x_1, x_2, \ldots x_Y)|^2 dx_2 dx_3 \ldots dx_Y.$$ \hspace{1cm} (3.143)

The two theorems by Hohenberg and Kohn[87] state:

**Theorem 1:** The external potential $V_{ext}(x)$ for any system of the interacting particles, is a unique functional of its ground state particle density $n_0(x)$.

**Theorem 2:** The density $n(x)$ of the interacting system can be used to express a universal energy functional $F[n(x)]$ which is valid for any $V_{ext}(x)$. Then the ground state energy $E_0$ for this system, which is global minimum of $F[n(x)]$, can
be obtained variationally where the density that minimises this functional is the exact ground state density \( n_0(x) \).

These theorems are the basis of the Kohn-Sham DFT framework, which gives a practical way to get the density that minimises the energy functional.\[^{[88]}\] The Kohn-Sham (KS) equation reduces the many-body Schrödinger equation of interacting particles to the single particle equation for non-interacting electrons. The KS equation energy functional \( F[n(x)] \) is given as,

\[
F[n(x)] = T_s[n(x)] + E_H[n(x)] + E_{xc}[n(x)],
\]

(3.144)

where \( T_s \) represents the kinetic energy of the non-interacting electrons. \( E_H \) denotes the Hartree energy, which is the Coulomb energy of the charge density and is given as

\[
E_H = \frac{e^2}{2} \int \int \frac{n(x_1)n(x_2)}{|x_1 - x_2|} dx_1 dx_2.
\]

(3.145)

The exchange-correlation energy \( E_{xc} \) in KS equation is basically the remaining part after comparing the true kinetic(\( T \)) and electron-electron interaction energy(\( E_{ee} \)) to KS kinetic energy and Hartree energy,

\[
T + E_{ee} = T_s + E_H + E_{xc}.
\]

(3.146)

The KS equation is then written as,

\[
\left( -\frac{\hbar^2}{2m} \nabla^2 + V_{eff}(x) \right) \psi_i(x) = \epsilon_i \psi_i(x),
\]

(3.147)

where \( \epsilon_i \) represent the eigen energies and the effective potential \( V_{eff} \) is given as sum of Hartree potential \( V_H \), exchange-correlation potential \( V_{xc} \) and external potential \( V_{ext} \) as,

\[
V_{eff} = \frac{\delta E_H[n(x)] + \delta E_{xc}[n(x)]}{\delta n(x)} + V_{ext} = V_H(x) + V_{xc}(x) + V_{ext}(x).
\]

(3.148)

Eq. (3.147) is solved self-consistently where the Kohn-Sham density \( n(x) \) and Kohn-Sham energy \( E[n(x)] \) are obtained as,

\[
n(x) = \sum_i f_i \psi_i^*(x) \psi_i(x),
\]

(3.149)
and
\[ E[n] = \sum_i f_i \epsilon_i - \frac{1}{2} \int n(x) V_H d x - \int n(x) V_{xc} d x + E_{xc}[n], \] (3.150)

where \( f_i \) represents the occupancy. The self-consistency loop starts with the initial guess of charge density \( n(x) \). The \( V_{\text{eff}} \) is then calculated with \( n(x) \) and Eq. (3.147) is solved to obtain the eigenfunctions \( \psi_i(x) \). The density is recalculated using Eq. (3.149). This is repeated till the self consistent solution of density is obtained. This is the ground state density \( n_0 \) and the corresponding ground state energy \( E_0[n] \) is calculated from \( n_0 \) using Eq. (3.150).

### 3.2.2 Basics of tight binding modelling

Density functional theory provides an efficient way to investigate a material’s properties through the quantum mechanical perspective, however these studies are limited by their computational expenses. Thus it is practically impossible to study the properties of materials at larger length scales with defects and dislocations, grain boundaries and nanostructures with DFT.[89]

This brings us to the pre-DFT time when interatomic potentials were used for materials simulations. Easier mathematical representations of total energy with less number of parameters make the simulations quite faster than DFT calculations. However, the parameters for empirical potentials are obtained by fitting the pairwise interactions in the crystal to the experimental data which makes the parameters less transferable. Such a study of transferability of different interatomic potentials for Si was done in Ref.[1] and can be seen in Fig. 2.1. Two different sets of Tersoff potential,[2, 3], Stillinger-Weber potential,[54] and Environmental-dependent (ED) interatomic potentials[56, 57] were tested for the thermal properties of diamond Si. The obtained results were around an order of magnitude deviated from the experiments.

Tight binding (TB) method has turned out to be one of the attractive ways to model the properties of a material as care of orbital interactions is also taken in TB. In general, TB represents the total binding energy as the sum of many-body bonding term and a repulsive pair potential. The TB energy functional is then written as,
\[ E_{\text{TB}} = E_{\text{bond}} + E_{\text{rep}}, \] (3.151)
The first term, $E_{\text{bond}}$, is the bond energy stored in the bonds between different atoms. $E_{\text{bond}}$ is calculated from the quantum mechanical information of the bonding i.e., from the interaction between the valence electrons of neighbouring atoms. The bond energy is given as,

$$E_{\text{bond}} = \sum_{i\mu} \int_{-\infty}^{\epsilon_F} (\epsilon - \epsilon_{i\mu}) g_{i\mu}(\epsilon) d\epsilon,$$

(3.152)

where $\epsilon_{i\mu}$ is the energy level corresponding to atomic orbital $|i\mu\rangle$ and $i$ is the atom index whereas $\mu$ corresponds to the angular character $lm$. $g_{i\mu}(\epsilon) = dN_{i\mu}/d\epsilon$ represents the local density of states and $\epsilon_F$ is the Fermi level. Eq. (3.152) is the onsite representation of the $E_{\text{bond}}$. The intersite representation is given as,

$$E_{\text{bond}} = \sum_{i\mu j\nu} H_{i\mu j\nu} n_{i\mu j\nu},$$

(3.153)

where $H_{i\mu j\nu}$ and $n_{i\mu j\nu}$ represent the two centred Slater-Koster Hamiltonian and density matrix elements for the interactions between the electrons of orbitals $|i\mu\rangle$ and $|j\nu\rangle$. These Hamiltonian elements $H_{i\mu j\nu}$ are parametrised by rotating them into the bond-oriented coordinate system as,[89]

$$\beta_{i\mu j\nu} = \sum_{\mu'\nu'} \bar{R}_{i\mu j\nu}^* H_{i\mu' j\nu'} R_{i\mu' j\nu'},$$

(3.154)

where $R_{i\mu j\nu}$ corresponds to the rotation matrix. $\beta_{i\mu j\nu}$ are the bond integrals which are parametrised as they can be seen as the basic unit of $E_{\text{bond}}$. The Hamiltonian $H$ can be constructed either by fitting to the electronic band-structure whereas we have adopted systematic downfolding procedure to get it from DFT. The two centred TB method is linked to the DFT-LCAO (Linear Combination of Atomic Orbitals) method by downfolding the pseudo-atomic orbital basis to a minimal basis. This downfolding procedure, as derived in Ref.[89], is demonstrated next.

The basis functions for LCAO, whose linear combinations give the molecular orbitals, are given as the product of radial ($R$) and angular function ($Y$) as,

$$\varphi_{iJ\mu} = \varphi_{iJlm} = R_{iJl}(r) Y_{lm}(\hat{r}),$$

(3.155)

where $J$ corresponds to the number of radial functions for an angular character $\mu$. There could be many radial functions for a particular $\mu$ which is termed as
multiple-ζ basis functions. We write the KS orbital wavefunctions in terms of basis functions as,

$$
|\psi_n\rangle = \sum_{iJ\mu} c_{iJ\mu}^{(n)} |\varphi_{iJ\mu}\rangle
$$

(3.156)

and the KS equation in matrix form as,

$$
\sum_{jJ\nu} H_{iJ\mu jJ\nu} c_{jJ\nu}^{(n)} = \epsilon_n \sum_{jJ\nu} S_{iJ\mu jJ\nu} c_{jJ\nu}^{(n)},
$$

(3.157)

where the Hamiltonian matrix is $H_{iJ\mu jJ\nu} = \langle \varphi_{iJ\mu} | H | \varphi_{jJ\nu}\rangle$ and overlap matrix is $S_{iJ\mu jJ\nu} = \langle \varphi_{iJ\mu} | \varphi_{jJ\nu}\rangle$. For maintaining the precision of the systematic-grid or plane-wave basis, the self-consistent DFT calculations for the total energies are done first with precise grid basis. Then the eigenstates $|\psi_n\rangle$ obtained are expanded in terms of 3-ζ basis as in Eq. (3.156). DFT code GPAW[71] is used for this procedure as it has both the grid basis and atomic orbital basis. For obtaining the minimal 1-ζ basis, we first realize that the closure relation for the non-orthogonal minimal basis $\{|\vartheta_{i\mu}\rangle\}$ is given with the help of the contra-variant basis $\langle\vartheta_{i\mu}\rangle$ and the overlap matrix for minimal basis $S_{i\mu j\nu} = \langle \vartheta_{i\mu} | \vartheta_{j\nu}\rangle$ as

$$
\langle \vartheta_{i\mu} | = \sum_{j\nu} S_{i\mu j\nu}^{-1} \langle \vartheta_{j\nu} | \\
\sum_{i\mu} |\vartheta_{i\mu}\rangle \langle \vartheta_{i\mu} | = \mathbf{1}.
$$

(3.158)

This closure relation is considered as projection operator which tells that how well $|\psi_n\rangle$ can be represented with the minimal basis $\{|\vartheta_{i\mu}\rangle\}$. Thus the projection of $|\psi_n\rangle$ expanded in terms of $\{|\varphi_{iJ\mu}\rangle\}$, Eq. (3.156), on $\{|\vartheta_{i\mu}\rangle\}$ is given as,

$$
P_n = \sum i\mu \langle \psi_n | \vartheta_{i\mu} \rangle \langle \vartheta_{i\mu} | \psi_n \rangle \text{ and } P = \frac{1}{N_e} \sum_n f_n P_n,
$$

(3.159)

where $n$ represents the eigenstate, $f_n$ is its occupation and $N_e$ is the number of valence electrons. Basis function $\vartheta_{i\mu}$ is written using $\varphi_{iJ\mu}$ as,

$$
\vartheta_{i\mu} = \sum_J \alpha_{iJ} \varphi_{iJ\mu}(r),
$$

(3.160)

where $\alpha_{iJ}$ is obtained by maximising $P$, Eq. (3.159). $H_{i\mu j\nu}$ and $S_{i\mu j\nu}$ can be constructed using $\vartheta_{i\mu}$ and the bond integrals are obtained from Eq. (3.154).

The repulsive part $E_{rep}$ is obtained by parametrising the $E^{binding}_{DFT} - E_{bond}$ as a
function of interatomic distance $r_{ij}$ as a sum over pairwise repulsive energy $\phi_{ij}$ given as

$$E_{\text{rep}} = \sum_{ij}^{i \neq j} \phi_{ij} r_{ij}. \quad (3.161)$$

The other terms can also be added to Eq. (3.151) such as $E_{\text{prom}}$, $E_{\text{mag}}$ and $E_{\text{chg}}$. $E_{\text{prom}}$ represents the promotion energy which is related to the repopulation of the onsite levels after bond formations. It is given as,

$$E_{\text{prom}} = \sum_{i\mu} \epsilon_{\mu}^{(0)} (N_{e_{i\mu}} - N_{\nu_{e_{i\mu}}}), \quad (3.162)$$

where $N_{e_{i\mu}}$ is the number of electrons in the bonded atom and $N_{\nu_{e_{i\mu}}}$ in the free atoms. $E_{\text{mag}} = -1/4 \sum_i I_i m_i$ (with magnetic moment $m_i$ and Stoner parameter $I_i$) and $E_{\text{chg}} = \sum_{ij}^{i \neq j} 1/2 J_{ij} q_i q_j$ (with Coulomb integral $J_{ij}$) are the magnetic and charge transfer contributions respectively to the tight binding energy and can be parametrised depending on the material and properties of interest.

### 3.2.3 Frozen phonon approach

Using the density functional theory code and tight binding model, we calculate the force constants for the lattice dynamics simulations. These lattice dynamics calculations can be performed either by employing the direct approach or the linear response method.[70] The dynamical matrix can be directly evaluated using the linear response theory through the density functional perturbation theory[91, 92] where the perturbation expansions for the calculation of phonon energies are considered to be the small perturbations on the crystal structures. We use the frozen phonon approach[93], a direct approach, which is simple conceptually in comparison to linear response theory.[94, 95] In the frozen phonon approach, the distorted crystal is treated as the frozen state of the perfect crystal when the lattice wave is passed through it. Thus in this direct approach of calculating the phonon frequencies, the crystal is perturbed by slight displacement of atoms and energy and force calculations are performed for the distorted crystals. This frozen phonon approach, developed by Kunc et al.,[96] enables to calculate the accurate phonon frequencies for the crystal without any approximations[97] except for the approximations made in the computational methods i.e., approximation for exchange-correlation energy in DFT and approximations in tight binding model. The frozen phonon
approach has been found to work well not only for the calculations of the phonon frequencies and the anharmonic phonon interactions\cite{6, 59, 61–63, 74, 98–100} but also for the prediction of crystal structure stability, calculating phase transitions, elastic constants and pressure dependences.\cite{96} For the calculation of phonon frequencies, displacement of an atom is made in the lattice and the forces on the other atoms are calculated to get the corresponding $3 \times 3$ force constant matrices. The calculation for $3 \times 3 \times 3$ anharmonic force constants require displacements of two atoms simultaneously and corresponding force calculations on other atoms. The method requires to consider large supercell to make sure that there are no extra forces on atoms due to periodicity of the crystal structure.

### 3.2.4 Non-analytic term correction

The phonon frequencies calculated with the direct approach are exact for given wavevectors $q$\cite{97} however, more information is required to accurately calculate the phonon frequencies of longitudinal optic (LO) modes for the polar materials. The LO phonons experience the macroscopic electric fields for polar materials near the Γ-point in Brillouin zone ($q \rightarrow 0$) which arise due to the long ranged behaviour of the Coulomb forces. Hence, in the limit of long wavelength, the lattice distortion is accompanied by the macroscopic electric field which has to be treated carefully. In the case of finite $q$ vectors, the treatment is similar to that for non-polar materials. Hence, the total force constant matrix for polar materials is expressed as sum of short ranged analytic and long ranged non-analytic contributions\cite{101–103},

$$\Phi_{\alpha_1 \alpha_2}^{\alpha_1 \alpha_2}(b, b') = \Phi_{\alpha_1 \alpha_2}^{an}(b, b') + \Phi_{\alpha_1 \alpha_2}^{na}(b, b')$$  \hspace{1cm} (3.163)

and the non-analytic part $\Phi_{\alpha_1 \alpha_2}^{na}(b, b')$ is given as\cite{103},

$$\Phi_{\alpha_1 \alpha_2}^{na}(b, b') = \frac{4\pi e^2}{V} \frac{[q, Z^*(b)]_{\alpha_1} [q, Z^*(b')]_{\alpha_2}}{q \cdot \epsilon^{\infty} \cdot q},$$  \hspace{1cm} (3.164)

where $\epsilon^{\infty}$ represents the high frequency static dielectric tensor i.e., the electronic contribution to the dielectric permittivity tensor. $Z^*(b)$ is the Born effective charge tensor for the atom at position $b$ in the unit cell. $e$ is the electronic charge and $V$ represents the volume of unit cell. The transverse optic (TO) branches are not affected by these ionic displacements because of their perpendicular direction of propagation to the displacements. This gives the well known LO-TO splitting.
in the polar materials which is evaluated by including the non-analytical term correction (NAC), Eq. (3.164), to the dynamical matrix.
Chapter 4

2NN lattice dynamical model for Si$_x$Ge$_{1-x}$ alloys

4.1 Introduction

There has been a huge interest in silicon-germanium technology as it is well suited for electronic and optical devices[104–107] and also for the thermoelectric applications.[18, 108, 109] The driving forces such as the enhanced operating speeds, low noise and low power consumption in electronic devices have lead to the increased popularity of silicon-germanium as compared to silicon.[104] It is also becoming the material of choice for the low power radio-frequency (RF) chips required for the communication industries. Si-Ge technology thus provides a bridge between low cost silicon chips having low operating frequency and the expensive, high-frequency chips from III-V semiconductors as GaAs, InP.

The Si-Ge alloys are also known for their thermoelectric properties. They are used in high temperature thermoelectric applications, such as NASA’s radio isotope thermoelectric generators for space applications.[110] This is possible because of competitive figure of merit $zT \sim 1$ for Si-Ge alloys at temperatures around 900°C.[26] An important contribution for such higher $zT$ is the reduction in thermal conductivity as compared to pure Si and Ge. A further decrease in thermal conductivity is achieved by nanostructuring the Si-Ge alloys which has shown a $zT$ improvement up to 1.4 at 900°C for these alloys.[24, 25]
In the past, there have been studies on the stability of the Si-Ge alloys. Si and Ge are miscible at room temperatures for all the compositions leading to Si$_x$Ge$_{1-x}$ random alloys where $x$ denotes the composition. The random character of Si-Ge alloys has been confirmed with both experimental and theoretical studies which have shown that the Si-Ge alloys are thermodynamically stable in the random composition without any long or short ranged chemical ordering.[106, 111] Moreover, as Si and Ge lattice constants differ by only 4.2%, the strained Si-Ge alloys can be grown on either Si or Ge substrates[106] and various other Si-Ge nanostructures can also be developed with less energy cost. Molecular beam epitaxy can be used to grow these highly complex structured lattices at the nano-scale.[45] However, the theoretical studies of thermal conductivity in these complex random alloys and their nanostructuress are not straight forward due to the length scales involved. Within virtual crystal approximation (VCA), the theoretical studies for these complex structures have been performed previously.[28] In VCA, the random alloy is considered to have crystal symmetry with just mass variations at different sites. However, the bond length variations in the structure are neglected in VCA. Furthermore, several studies have reported that the thermal conductivity study of nanostructured alloys depends on the detailed atomic structure.[45, 112–114]

Due to the complexity of these structures, it is important to develop short ranged simplified model of their properties which also exhibits transferability to other structures. One approach to modelling the thermodynamic properties of the random alloys aims at directly parametrising the force constants by introducing the bond stiffness versus bond length model.[94] Wei et al.[115] have developed a model for pure Si and Ge where the interactions are considered up to 8th nearest neighbour(8NN). The interplanar forces are determined using frozen phonon approach and performing supercell calculations. Then the force constant matrices up to 8NN are parametrised and further used to calculate phonon frequencies for Si and Ge.

In this work,[4] we have developed a short range model (2NN) which reliably reproduces the thermal properties of the Si-Ge systems. One of these properties is the thermal expansion coefficient, $\alpha_T$ which is calculated as the change in equilibrium volume with temperature within quasi-harmonic approximation, Eq. (3.130). $\alpha_T$ can also be obtained from Eq. (3.132) which is dependent on Gr"uneisen parameters, $\gamma$, Eq. (3.129), and the specific heat at constant volume $C_V$. Gr"uneisen parameters are related to the third order force constants too, Eq. (3.135), whereas the phonon
relaxation times, required to calculate the thermal conductivity, Eq. (3.82), are also calculated from third order force constants, Eq. (3.72). This confirms the link between the volume dependent quasi-harmonic properties as Grüneisen parameters, thermal expansion and the explicit anharmonic properties as thermal conductivity taking phonon-phonon interactions into account. Hence, a correct reproduction of $\alpha_T$ can have important implications for the development of short range potentials to quantitatively reproduce the lattice thermal conductivity $\kappa_l$.\[^{[4]}\] A good reproduction of $\alpha_T$ can thus be seen as minimal requirement for the correct calculation of thermal conductivity $\kappa_l$ with the simple potential. This is also seen in Fig. 2.1,\[^{[1]}\] where both the thermal expansion and thermal conductivity for Si, calculated with Tersoff interatomic potential, are deviated by same order of magnitude from the experiments.

In this Chapter, we have introduced the possibility of parametrising the force constants using short-ranged interatomic distances for the correct determination of thermal properties in Si$_x$Ge$_{1-x}$ random alloys. We extract the nearest-neighbour stretching and bending terms from DFT which show an exponential variation with bond length. Further the effective parameters are used for 2NN interactions in our model. It is shown that a correct reproduction of the harmonic and quasi-harmonic properties of Si and Ge can be achieved with a short ranged model. Furthermore the transferability of our model to the complex Si-Ge random alloys is also tested. The work has been published in Ref.[4]

### 4.2 Second nearest neighbour force constant model

For the development of the model, the force constants are obtained from the forces calculated using DFT code GPAW[^{[71]}], a Grid based Projector Augmented Wave method. Frozen phonon approach as implemented in program PHONOPY[^{[116]}] is followed to get the force constants. The force calculations for pure Si, pure Ge and ordered Si$_{0.5}$Ge$_{0.5}$ are performed in a $4 \times 4 \times 4$-fcc supercell containing 128 atoms. For the correct ab initio calculations of the force constants, we have carried out an extensive series of convergence tests of the parameters as grid spacing, $\mathbf{k}$-mesh, plane-wave cut-off, supercell size and finite displacements of the atoms. Especially the mode dependent Grüneisen parameters $\gamma(j\mathbf{q})$, which represent the change in phonon frequencies with change in volume, were influenced significantly with the chosen grid spacing and atomic displacements, shown in Fig. 4.1. This
is crucial as \(\alpha_T\) is also related to \(\gamma(j\mathbf{q})\), Eq. (3.132). Based on these tests, the converged parameters discussed in Ref. [4], are used for the calculations of precise force constants to get the correct thermal properties. In Table 4.1 we compare our calculated Grüneisen parameters of diamond Si with earlier studies. A good agreement of our results is found with those of Wei et al. [117], who also used the frozen phonon approach. The agreement is reasonable with the results of Rignanese et al. [118], who used density functional perturbation theory and a smaller energy cut-off of 272 eV for their calculations as compared to our calculations using larger plane-wave basis with 450 eV energy cut-off.

Before starting parametrisation of the model, we carried out the analysis of neighbour shell contributions to the phonon density of states (pDOS) of Si at 0K by truncating the force constant matrices \(\Phi\). This is shown in Fig. 4.2 where the contributions from 1NN up to 6NN are considered for determining the pDOS. We see that with the first nearest neighbour interactions only, we get a good reproduction of the high energy optical phonons peak in the pDOS, however, a deviation for the low energy acoustic peak is seen from its actual trend. This is because the atoms in the 1NN shell experience the highest force due to the atomic displacement and

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.1.png}
\caption{Convergence test of Si Grüneisen parameters at \(X\) point of fcc Brillouin zone with respect to the GPAW grid and atomic displacements. The converged grid spacing of 0.1 Å is used in our calculations.}
\end{figure}
Chapter 4. 2NN lattice dynamical model for Si$_x$Ge$_{1-x}$ alloys

Table 4.1: Comparison of transverse acoustic mode Grüneisen parameters($\gamma_{TA}$) of Si and Ge with earlier studies at X and L $\mathbf{q}$-points of the Brillouin zone.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma_{TA}(X)$</td>
<td>$\gamma_{TA}(L)$</td>
</tr>
<tr>
<td>DFT</td>
<td>-2.28$^a$</td>
<td>-1.88$^a$</td>
</tr>
<tr>
<td></td>
<td>-1.78$^b$</td>
<td>-1.45$^b$</td>
</tr>
<tr>
<td></td>
<td>-2.3$^d$</td>
<td>-1.5$^d$</td>
</tr>
<tr>
<td>Expt.</td>
<td>-1.4±0.3$^e$</td>
<td>-1.3±0.3$^e$</td>
</tr>
</tbody>
</table>

$^a$ Present work
$^b$ Reference [118]
$^c$ Reference [119]
$^d$ Reference [117]
$^e$ Reference [120]
$^f$ Reference [121]

hence vibrate at very high frequencies leading to the correct reproduction of optical phonons. The acoustic peak shows a slow oscillatory convergence with respect to the cut-off, due to the long ranged behaviour of the force constants.[115] Reproduction of acoustic phonon peak is important as these long wavelength phonons play a major role in determining the thermal properties. However, as we focus on short ranged modelling scheme, our model parameters are obtained for the interactions up to second nearest neighbours. For this, we analysed next the force constant matrices for 1NN and 2NN for their parametrisation.

Figure 4.2: Results of truncating the DFT force constant matrices.
Chapter 4. 2NN lattice dynamical model for $Si_xGe_{1-x}$ alloys

The force constant matrices $\Phi(i, j)$, determining the force on atom $i$ due to displacement of atom $j$, are symmetric for a 1NN interaction in the diamond structures of Si and Ge. These $\Phi(i, j)$s can be diagonalised by aligning the first Cartesian axis in the direction of the line joining atoms $i$ and $j$ by making use of Euler’s rotations. The 1NN force constant matrices in bond oriented coordinate system are obtained as

$$\Phi(i, j)_{1NN}^B = \begin{pmatrix} s & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & b \end{pmatrix}$$ (4.1)

where $s$ and $b$ give the force components in the direction of and perpendicular to the bond respectively. Thus, $s$ is said to be the stretching term and $b$ are the bending terms.

We found an exponential trend of the stretching and bending terms with bond lengths for our structures. However in earlier studies, to model the bond bending and stretching terms, generally simple linear fits are used which are sometimes extended to second order polynomial function for fitting the stretching term.[94] In this work, we have modelled the stretching term using a function motivated by a Morse-like potential,

$$s = a_r e^{-b_r(R - R_0)} - a_b e^{-b_b(R - R_0)}$$ (4.2)

where $R_0$ is the equilibrium interatomic distance. The equilibrium interatomic distance $R_0$ and cohesive energy were fixed while fitting $s$. The bond stretching decreases with the increasing bond length and approaches zero. The variation of the bending term with bond length is interestingly different from the stretching, Fig. 4.3. The bond bending increases with the bond length first followed by its decrease at larger bond lengths due to weakened atomic interaction and is expected to tend to zero at infinite distance. We capture this tendency of the bending term in our model by parametrising it as,

$$b = \{b_{\text{slope}}(R - R_0) + b_0\} e^{-b_{\text{exp}}(R - R_0)}$$ (4.3)

The fitted parameters for Si-Si, Ge-Ge and Si-Ge interactions are listed in Table. 4.2.

The second nearest neighbour force constant matrix is not symmetric[115] and can not be well diagonalised as in the case of first nearest neighbour interaction. Its
rotation into the bond oriented system yields

\[
\Phi(i,j)_{2NN}^B = \begin{pmatrix}
    c & 0 & \mp f \\
    0 & a & 0 \\
    \pm f & 0 & d
\end{pmatrix}
\]  

(4.4)
Chapter 4. 2NN lattice dynamical model for Si$_x$Ge$_{1-x}$ alloys

<table>
<thead>
<tr>
<th>Bond</th>
<th>1NN</th>
<th>2NN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-Si</td>
<td>8.617</td>
<td>7.811</td>
</tr>
<tr>
<td>Ge-Ge</td>
<td>3.719</td>
<td>3.605</td>
</tr>
<tr>
<td>Si-Ge</td>
<td>0.855</td>
<td>0.860</td>
</tr>
<tr>
<td>$a_r$ (eV/Å$^2$)</td>
<td>0.369</td>
<td>0.396</td>
</tr>
<tr>
<td>$b_r$ (Å$^{-1}$)</td>
<td>5.375</td>
<td>4.340</td>
</tr>
<tr>
<td>$a_b$ (eV/Å$^2$)</td>
<td>0.979</td>
<td>0.775</td>
</tr>
<tr>
<td>$b_b$ (Å$^{-1}$)</td>
<td>2.420</td>
<td>4.188</td>
</tr>
</tbody>
</table>

Table 4.2: The model parameters for 1NN, Eq. (4.2) and Eq. (4.3); and 2NN, Eq. (4.5).

The first column of the matrix $\Phi(i,j)^B_{2NN}$ is the force when a displacement is made along the line joining atoms $i$ and $j$. The other two columns correspond to the forces for the displacements made in the direction of two orthogonal axes. The off-diagonal terms mean that when a displacement is made in the direction of the $i-j$ line, a component of the force is in this direction while other components are in the plane orthogonal to that. The origin of the 1NN and 2NN bond stiffness terms, when force constant matrices are rotated in bond oriented coordinate system, can be understood with simple representation presented in Ref.[4]. The force constant matrices up to 2NN shell only are included in the model, however, we implicitly include the effects of further neighbours by adjusting the second-nearest neighbour stiffness terms ($a, c, d, f$) to get correct reproduction of the acoustic peak of pDOS. The 2NN bond stiffness terms are fitted as,

$$f = f_{\text{slope}} R + f_0$$  \hspace{1cm} (4.5)$$

and similarly for $a, c$ and $d$. The fitting results can be seen in Fig. 4.3 and the parameters are listed in Table. 4.2.
4.3 Results of the model: Phonon DOS, thermal expansion

We have tested the model for the pDOS and thermal properties of Si, Ge and ordered Si$_{0.5}$Ge$_{0.5}$ by comparing the model results with DFT and experiments.[122–124] The calculated pDOS for Si, Ge and ordered Si$_{0.5}$Ge$_{0.5}$ are shown in Fig. 4.4. It can be seen that the bandwidth is different for all three systems which depends on the individual bond strength and atomic mass. The pDOS bandwidth reduces with the increasing bond length and atomic masses which leads to the largest phonon bandwidth for Si and smallest for Ge and the pDOS for ordered Si$_{0.5}$Ge$_{0.5}$ lies in between them. Ordered Si$_{0.5}$Ge$_{0.5}$ pDOS also shows a wide acoustic-optic phonon gap which is due to the mass difference of Si and Ge orderedly placed in the structure. We can see in Fig. 4.4 that pDOS with our 2NN model is in good agreement with the DFT pDOS for these structures. The phonon bandwidth is reproduced correctly with our model and the trend of the acoustic phonon peak is also captured well. The reproduction of the acoustic peak, shown in Fig. 4.2, with

![Figure 4.4: Phonon DOS for Si, Ge and ordered Si$_{0.5}$Ge$_{0.5}$ calculated using the second nearest neighbour model (dashed lines) compared with DFT results(solid lines).]
short ranged 2NN model shows the effectiveness of our scheme of incorporating the environmental effects in the 2NN bond stiffness parameters.

The further calculated $\alpha_T$ for all three systems are shown in Fig. 4.5. The negative $\gamma(jq)$ for the acoustic bands, Table. 4.1, give rise to the negative $\alpha_T$ at low
temperatures,[125] seen in Fig. 4.5 for Si, Ge and ordered Si$_{0.5}$Ge$_{0.5}$ with DFT and 2NN model. The underlying reason for negative $\gamma(jq)$ is related to the bonding of these structures and could be understood with the help of bond stiffness parameters. In agreement with a tight binding model[126], the bond bending is substantially smaller than the bond stretching, seen in Fig. 4.3, which means that bending contributes to acoustic phonons and hence will dominate the thermodynamics at low temperature. Furthermore its increase with increasing volume leads to higher acoustic phonon frequencies at larger volumes. This thus gives negative Grüneisen parameters and consequently negative thermal expansion. A good agreement of our model calculated $\alpha_T$ with the DFT results and the experiments is found which is illustrated in Fig. 4.5. The negative expansion coefficient is also reproduced well with our 2NN model and shows the reliability of this short ranged model for reproducing the fine details of these volume dependent thermal properties at low temperature range. Till now we have tested the reproduction of the thermal properties of the pure and ordered structured for which the parameters have been fitted. In the next section, we discuss the transferability of our 2NN model by applying it to the random alloys of Si-Ge.

4.4 Model transferability

The random alloy structures are generated by randomly placing Si and Ge atoms on the diamond lattice by fixing the composition. The 64 atoms unit cells of the random Si$_{0.25}$Ge$_{0.75}$, Si$_{0.5}$Ge$_{0.5}$ and Si$_{0.75}$Ge$_{0.25}$ alloys are generated. For checking the randomness of the structure, we carried out the pair correlation function analysis of all three random alloy compositions. The correlation function is $\prod_{k,m}$, where $k=2,3$ represents the pair and triple correlation functions respectively and $m=1,2,3...$, is the neighbour shell index. The correlation function of a perfectly random structure $A_x B_{1-x}$ is given as $\prod_{k,m} = (2x - 1)^k$, which is 0 for $x = 0.5$.[127] We calculated $\prod_{2,1} = 0.19$ and $\prod_{2,2} = 0.23$ for Si$_{0.25}$Ge$_{0.75}$ and 0.19 and 0.21 for Si$_{0.75}$Ge$_{0.25}$ random structures. For the Si$_{0.5}$Ge$_{0.5}$ alloy we obtained zeros for both $\prod_{2,1}$ and $\prod_{2,2}$. This analysis indicates that our structures are good mimic of the perfect random alloys.

The 2NN model based pDOS is calculated for the three compositions of Si$_x$Ge$_{1-x}$ random alloys. The thermal properties as $C_V$ and $\alpha_T$ are also determined for the Si$_{0.5}$Ge$_{0.5}$ random alloy using our model. We see the pDOS for Si$_{0.25}$Ge$_{0.75}$,
Figure 4.6: Phonon DOS for different compositions of Si$_x$Ge$_{1-x}$ random alloys calculated with the model including contributions up to second nearest neighbours and compared to DFT results.

Si$_{0.5}$Ge$_{0.5}$ and Si$_{0.75}$Ge$_{0.25}$ in Fig. 4.6 calculated with DFT and our model. The difference in the random alloy compositions leads to varying prominence of the pDOS peaks for all three random compositions, Fig. 4.6. For the Si$_{0.25}$Ge$_{0.75}$ composition, the pDOS peaks are at lower frequencies because of the dominating Ge contribution in this composition. There are significant contributions from the Si-Ge interactions as well which give the middle pDOS peaks whereas there is
very small peak corresponding to pure Si. As the fraction of Si in the Si\(_x\)Ge\(_{1-x}\) random alloys increases, this higher energy pDOS peaks get more pronounced. The acoustic peak also shifts to higher frequencies and the starting slope of the acoustic peak in pDOS, which determines the phonon group velocities, show slight changes with the changing composition of Si\(_x\)Ge\(_{1-x}\) random alloys. All these trends are captured by the model and compare well with the DFT results. The \(C_V\) and the \(\alpha_T\) for Si\(_{0.5}\)Ge\(_{0.5}\) random alloy are shown in Fig. 4.7. Again good agreements with the DFT results are found, confirming validity of the 2NN model. This simple model thus allows us to calculate the thermal properties for Si\(_x\)Ge\(_{1-x}\) random alloys.

4.5 Summary and outlook

In this chapter, we have developed a model to calculate the thermal properties of Si-Ge alloys efficiently based on modelling of the force constant matrices in terms of interatomic distances. We carried out DFT calculations with converged parameters for pure Si, Ge and ordered Si\(_{0.5}\)Ge\(_{0.5}\). The bond stiffness terms for Si-Si, Si-Ge and Ge-Ge bonds are then obtained by rotating the DFT calculated force constant matrices in bond oriented coordinate system which are parametrised in the model. The model extends up to second-nearest neighbour contributions however the effective parameters are obtained in our model which account for the long ranged interactions. This gives good acoustic phonons reproduction in pure
Si, Ge and ordered Si$_{0.5}$Ge$_{0.5}$ and is also applicable to a range of compositions of disordered Si$_x$Ge$_{1-x}$ alloys. The correct reproduction of the thermal properties of pure Si, Ge and ordered Si$_{0.5}$Ge$_{0.5}$ structures and the transferability of the model to determine thermal properties of the random structures of Si$_x$Ge$_{1-x}$ alloys show the validity of the developed short ranged model.

This work opens up the possibility of more reliable modelling of thermal conductivity using short range potentials. The thermal conductivity in BTE-RTA formalism, Eq. (3.82), requires heat capacity $C_V$ and phonon group velocity $v$ derived from harmonic phonons and the phonon relaxation time $\tau$ based on anharmonic phonon interactions, Eq. (3.72). Using the 2NN model, we have seen the good agreement of the $C_V$ and $\alpha_T$ for Si-Ge random alloys with the DFT results. Also the acoustic peak in the pDOS, Fig. 4.6, ensures correct calculation of $v$. The efficient reproduction of $\alpha_T$ can be seen as the requirement for the model to correctly calculate $\tau$, however, the detailed calculation of $\tau$ depends on exact determination of third order force constant matrix $\Psi$, Eq. (3.72). Although $\Psi$ and $\alpha_T$ are related, $\Psi$ can not be extracted from $\alpha_T$ and hence has to be modelled separately. The practical way of extracting effective $\Psi$ could be with the help of a mathematical algorithm known as Compressive Sensing (CS).[128] This is a recently developed technique mainly for the data reproduction in the field of signal processing. CS has been widely used as it requires few samples to reproduce a sparse signal accurately, fewer than that in famous Nyquist criteria. This is done by finding a solution that reproduces the sparse signal with minimum number of non-zero components. This scheme has been efficiently applied in material science field too[129, 130] and one application of CS can be to determine the higher order interatomic force constants[131] which are generally sparse in nature. Thus the short ranged models based on the CS technique can be further developed which could reliably and efficiently predict thermal transport in nano-materials.
Chapter 5

*Ab initio* thermal transport study for the nanostructured Zinc-Chalcogenides

5.1 Thermoelectric properties of Zinc-Chalcogenides

Search for good thermoelectrics is not just confined to the bulk materials but has also extended to the nanostructured materials as nanowires, superlattices, nano-grained bulk or nanointrusions. Due to the reduction in the system sizes, interesting effects are seen on the electronic as well as the thermal transport properties of these materials. Hence the nanostructured materials show a great potential in thermoelectrics and in other diverse technologies such as nanoelectronics and optoelectronics.

Nanostructured II-VI semiconductors are one such class of materials exhibiting good thermoelectric properties.[132–135] Mingo *et al.*[133, 134] have studied the thermoelectric properties of CdTe, ZnS, ZnSe and ZnTe and found enhanced figure of merit $zT$, Eq. (2.1), due to both reduction in thermal conductivity and increased power factor at nanoscale as compared to bulk. However cadmium is highly toxic in nature whereas zinc is non-toxic and inexpensive which makes zinc-chalcogenides interesting for commercial use.

For bulk zinc-chalcogenides, the power factor, $\sigma S^2$ where $\sigma$ is electrical conductivity and $S$ is Seebeck coefficient, range from 0.0004 Wm$^{-1}$K$^{-2}$ for ZnS to 0.0009
Wm$^{-1}$K$^{-2}$ for ZnTe with appropriate doping level.[133] Also the bulk lattice thermal conductivities $\kappa_i$ at room temperature for these materials were reported to be 18 Wm$^{-1}$K$^{-1}$ for ZnTe and 19 Wm$^{-1}$K$^{-1}$ for ZnSe and highest among them being 27 Wm$^{-1}$K$^{-1}$ for ZnS.[136] Such low power factors and comparably significant thermal conductivities result to $zT$ around 0.005, 0.01 and 0.015 for ZnS, ZnSe and ZnTe respectively at room temperature.[134]

Nanostructuring these materials increases their power factors and lowers down the thermal conductivities which lead to the $zT$ enhancements. However, the significant increase in $zT$ is seen below the small nanostructure size of 5 nm.[133, 134]. This is because $\sigma S^2$ for zinc-chalcogenides show slow variations for bigger nanostructure sizes. Hence $zT$ improvement is mainly found to be due to $\kappa_i$ reduction which has been reported to bring $zT$ for zinc-chalcogenides between 0.1 to 0.4 at 10nm size. Furthermore it is also shown how the thermal conductivity of the zinc-chalcogenides can potentially show a cross-over in their thermal conductivities i.e., ZnSe and ZnTe have similar $\kappa_i$ in bulk whereas ZnS and ZnSe $\kappa_i$ coincide as the sizes are reduced from bulk to nanoscale.[133, 135] However these interesting reported features are based on the thermal conductivity calculations with a simple model for nanostructures.[135] This thermal conductivity model for nanowires was based on parametrising phonon frequencies and phonon relaxation times for the zinc-chalcogenides to calculate the thermal conductivity within BTE-RTA formalism. The harmonic parameters in the model were obtained by fitting the experimental phonon frequencies. These harmonic parameters were further used to calculate the phonon group velocities. The phonon relaxation time was obtained by fitting the experimental bulk $\kappa_i$. The boundary effects were also included in the model.[135] Then the thermal conductivity of the zinc-chalcogenides was calculated as a function of the nanowire diameter $L$ and it was found that $\kappa_i$ of ZnS and ZnSe exhibit a crossover at $L \approx 30$ nm. It was explained that the different mass ratios of the constituting elements lead to the observed cross-over.[135] The similar slopes of the $\kappa_i$ reduction with $L$ were found for ZnS and ZnTe having similar mass ratios($\sim 2$) whereas ZnSe had smaller slope with mass ratio$\sim 1$. However, till date, no experimental verification nor detailed first-principles studies of the predicted behaviour of the nanostructured $\kappa_i$ have been found.

In this chapter, *ab initio* study of $\kappa_i$ for nanostructured zinc-chalcogenides has been performed by solving BTE within RTA, as discussed in Chapter 3. The performance of this approach for determining thermal conductivity has also been
discussed in Sec. 3.1.3.3. The effects of nanostructuring on $\kappa_i$ of zinc-chalcogenides has been studied using both the diffusive boundary scattering and confined mean free path (MFP) limit. With our ab initio calculations, we indeed find the thermal conductivity cross-over in nanostructured zinc-chalcogenides but already at larger nanostructure size of 0.1-0.2 $\mu$m. This has been explained by studying the contributions of different MFP phonons in determining the thermal conductivities of these materials. The work has been published in Ref. [9].

### 5.2 Calculation of thermal properties for Zinc-Chalcogenides

The thermal conductivity of zinc-chalcogenides is calculated within BTE-RTA formalism as given by Eq. (3.82). The phonon group velocity $v$ and heat capacity $C_V$, required to evaluate Eq. (3.82), are determined using the phonon frequencies obtained from the ab initio calculations within harmonic approximation. The relaxation times $\tau_{jq}$ for the phonon modes $jq$, which have the phonon scattering informations, are calculated by considering the phonon-phonon scattering (or anharmonic scattering) and the phonon-isotope scattering, the two important scattering mechanisms in zinc-chalcogenides. The anharmonic phonon-phonon interactions are taken into account by calculating the third order force constants using ab initio and further getting the phonon-phonon scattering times $\tau_{jq}^{an}$, Eq. (3.72). For the calculation of phonon-isotope scattering times $\tau_{jq}^{iso}$, Eq. (3.113) is used which gives the scattering time for the materials in cubic symmetry. The mass variance for the calculation of $\tau_{jq}^{iso}$ is determined using Eq. (3.106). The final relaxation time $\tau_{jq}$ for phonons is given by Matthiessen’s rule[78, 79] as in Eq. (3.114).

Full ab initio calculations for obtaining the forces are performed using projector augmented wave method implemented in the VASP package.[85] $4 \times 4 \times 4$ supercells of the fcc-primitive unit cells are considered for the force calculations for ZnS, ZnSe and ZnTe. The force constants are derived from the forces calculated for each symmetry reduced displacement following the frozen phonon approach as implemented in the program PHONOPY.[116] The amplitude of 0.06 Å for the atomic displacements are taken for the force calculations. We have carried out the calculations with different atomic displacement amplitude too (0.01 Å ) for the convergence test and we found that the phonon energies change maximally by 0.25 meV. The
calculations in the quasi harmonic approximation were done in the volume range of ±9% to further compute the thermal properties as Grüneisen parameters and thermal expansion coefficients. The longitudinal optic (LO) - transverse optic (TO) splitting at the Γ-point for zinc-chalcogenides is also included in our calculations by taking the Born effective charges into account. This gives the non-analytic correction term (NAC) to the dynamical matrix, Eq. (3.164).[101, 102] The calculations of the Born effective charges and static dielectric constants, required for determining NAC term, are calculated using the VASP package and found to be 2.03, 2.1, 2.08 and 5.89, 7.28, 8.96 for ZnS, ZnSe and ZnTe respectively.

The calculation of 3\textsuperscript{rd} order force constants for determining $\tau_{\text{anh}}^q$[60] require two simultaneous atomic displacements in the frozen phonon approach. The displacements of 0.06 Å amplitude are used, similar to the harmonic calculations. These calculations are a lot more computationally expensive as compared to that with single displacements. Hence the 3\textsuperscript{rd} order force constants calculations are performed for $2 \times 2 \times 2$-cubic supercells of ZnS, ZnSe and ZnTe structures having 64 atoms with denser k-mesh as compared to that used in the calculations for $4 \times 4 \times 4$ supercells. The converged results for phonon scattering rates, Eq. (3.72), are obtained with the 32×32×32 k-mesh and the Gaussian smearing with a 0.1 THz smearing width.

5.2.1 Phonon dispersion and thermal expansion

The phonon dispersions and the linear thermal expansion coefficients $\alpha_T$ for ZnS, ZnSe and ZnTe are shown in Fig. 5.1. We have done the DFT calculations with two different approximations for the exchange-correlation energy ($E_{xc}$ in Eq. (3.150)): PW92[137] which is a local density approximation (LDA) and PBE[138] which is generalised gradient approximation (GGA). For the phonon dispersions in zinc-chalcogenides, LDA and PBE results show good agreement with experiments.[139] However, some variations in the phonon frequencies with the choice of exchange-correlation functional is due to the different equilibrium lattice constants obtained with LDA and PBE (see Sec. 5.2.2 for details). We also obtained the LO-TO splitting with the inclusion of NAC term during the determination of dynamical matrices to calculate phonon frequencies. The calculated LO-TO splitting also matches very well with the experiments as seen in Fig. 5.1.
Figure 5.1: Phonon dispersions considering Born effective charges (left) and linear thermal expansion coefficient $\alpha_T$ (right) for (a) ZnS, (b) ZnSe, (c) ZnTe compared to experiments. $\alpha_T$ is calculated from quasi harmonic approximation (bold lines). Eq. (3.132) is also used to calculate $\alpha_T$ from the Grüneisen parameters obtained from (i) the 3rd order force constants (upper thin lines) and (ii) the quasi harmonic approximation (lower thin lines).

The $\alpha_T$, Fig. 5.1, for the zinc-chalcogenides were calculated from the quasi-harmonic approximation, Eq. (3.130), and are compared to the experiments.\cite{140, 141} We obtain the negative thermal expansion at low temperatures for zinc-chalcogenides, in agreement with the experiments. The negative expansion is related to the
variation of bond bending with the the bond length and is explained in Sec.4.3 of Chapter 4. We also calculated $\alpha_T$ from the Grüneisen parameters using Eq. (3.132) where the Grüneisen parameters were calculated from (i) the quasi-harmonic approximation method, Eq. (3.129) and (ii) from the anharmonic force constants, Eq. (3.135). This was done to validate our 3rd order force constants. Fig. 5.1 shows that the $\alpha_T$ calculated from these different Grüneisen parameters are in good agreement with each other and experiments. It is also seen in Fig. 5.1 that that LDA results are in better agreement with experiment as compared to the PBE results.

5.2.2 Bulk thermal conductivity

<table>
<thead>
<tr>
<th></th>
<th>$a$</th>
<th>$\kappa_{\text{anh}}^l$</th>
<th>$\kappa_l$</th>
<th>$P(%)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS</td>
<td>PBE</td>
<td>5.45Å</td>
<td>37</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>Expt$^a$</td>
<td>5.41Å</td>
<td>49</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>LDA</td>
<td>5.30Å</td>
<td>72</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>$\kappa_{\text{Expt}}^l = 27^{b,c}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ZnSe</td>
<td>PBE</td>
<td>5.743Å</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>Expt$^a$</td>
<td>5.667Å</td>
<td>20</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>LDA</td>
<td>5.575Å</td>
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<td>21</td>
</tr>
<tr>
<td></td>
<td>$\kappa_{\text{Expt}}^l = 19^{b,c}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ZnTe</td>
<td>PBE</td>
<td>6.186Å</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>Expt$^a$</td>
<td>6.103Å</td>
<td>24</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>LDA</td>
<td>6.002Å</td>
<td>26</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>$\kappa_{\text{Expt}}^l = 18^c$</td>
<td></td>
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</table>

* Table 5.1: Thermal conductivity (in Wm$^{-1}$K$^{-1}$) of ZnS, ZnSe and ZnTe considering just anharmonic scattering ($\kappa_{\text{anh}}^l$) and along with isotope scattering ($\kappa_l$) at 300K for different lattice constants ($a$). For the experimental volumes PBE is applied. The effect of isotope scattering is quantified with the percent isotope factor ($P$).

After confirming the validity of our anharmonic force constants by checking the reproducibility of the $\alpha_T$, we calculated the thermal conductivity $\kappa_l$ of zinc-chalcogenides. Fig. 5.2 shows the thermal conductivity variation with temperature in the range of 20-1000 K for ZnS, ZnSe and ZnTe. A good agreement with
experiment can be seen in Fig. 5.2 for the LDA and PBE results around room temperature. This is also compared in Table. 5.1 where the exact $\kappa_l$ values calculated at 300K are listed. It is evident from the Table. 5.1 and Fig. 5.2 that the choice of exchange-correlation functional influences the results. This is mainly attributed to the difference in predicted equilibrium lattice constants with LDA and PBE. In general, PBE predicts higher equilibrium cell volume than the experiment and LDA, Table. 5.1, which translates into the softer interatomic bonds in the material. This leads to decreased thermal conductivity as a result of enhanced scattering and reduced group-velocities and specific heat per unit volume. This has been quantified by replacing in turn the LDA values of $C_V$, $v$ and $\tau$ in Eq. (3.82) by the PBE values. The results are shown in Table. 5.2

<table>
<thead>
<tr>
<th></th>
<th>$\kappa_{l\text{anh}}$</th>
<th>$%\text{var}$</th>
<th>$\kappa_{l\text{anh}}$</th>
<th>$%\text{var}$</th>
<th>$\kappa_{l\text{anh}}$</th>
<th>$%\text{var}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS</td>
<td>72</td>
<td></td>
<td>23</td>
<td></td>
<td>26</td>
<td></td>
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<tr>
<td>PBE-\tau</td>
<td>40</td>
<td>44</td>
<td>22</td>
<td>5</td>
<td>21</td>
<td>22</td>
</tr>
<tr>
<td>PBE-$C_V$</td>
<td>67</td>
<td>7</td>
<td>21</td>
<td>9</td>
<td>24</td>
<td>9</td>
</tr>
<tr>
<td>PBE-$v$</td>
<td>60</td>
<td>17</td>
<td>21</td>
<td>9</td>
<td>25</td>
<td>4</td>
</tr>
<tr>
<td>PBE</td>
<td>37</td>
<td></td>
<td>16</td>
<td></td>
<td>17</td>
<td></td>
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</tbody>
</table>

**Table 5.2**: The effects of exchange-correlation functional on the thermal conductivity $\kappa_{l\text{anh}}$ (in Wm$^{-1}$K$^{-1}$) of ZnS, ZnSe and ZnTe. The PBE calculated thermal properties $\tau$, $C_V$ and $v$ substitute the LDA results to get the corresponding $\kappa_{l\text{anh}}$. Furthermore the $\%\text{var}$, i.e., the percentage variations from $\kappa_{l\text{anh}}$(LDA), are calculated.

The striking large reduction of 44% due to the substitution of LDA $\tau$ with the PBE $\tau$ is seen for ZnS in Table. 5.2. This can be explained from the phonon dispersion, Fig. 5.1, which shows a very wide energy gap between acoustic and optical phonon branches. This gap influences the phonon scattering due to the energy conservation rules in the three phonon scattering processes, Eq. (3.50) and Eq. (3.51). Fig. 5.1 shows that the acoustic-optical gap with PBE is smaller than LDA which results in the higher phonon scattering and hence significant reduction in thermal conductivity calculated using PBE functional. Similar is the case of ZnTe too which has larger acoustic-optic gap variation with the choice of exchange-correlation functional as compared to ZnSe. For other contributions, a reduction of 4-17% in thermal conductivities is obtained.

Table. 5.1 also shows our calculations for experimental lattice constants[142] which lie between the two theoretical predictions of thermal conductivities. Along with
that, the thermal conductivity results including isotope scattering are shown too which are in good agreement with experiment.[136]

![Figure 5.2: $\kappa_l$ calculated with LDA (solid line) and PBE (dashed line) for (a) ZnS, (b) ZnSe ($\kappa_l/10$) and (c) ZnTe ($\kappa_l/100$) incorporating isotope scattering and compared to experiments (squares).](image)

The anharmonic and isotope scattering in materials, affecting their thermal conductivities, show interesting variations with the phonon frequencies, Fig. 5.3. This depends on the different scattering strengths experienced by different phonon modes. However, a general trend of $\tau_{\text{anh}}^{-1} \propto \omega^2$ for the variation of anharmonic phonon scattering rate with phonon frequency is seen in materials.[6, 99, 135] The phonon bandwidths and the acoustic-optic phonon gaps in zinc-chalcogenides, Fig. 5.1, lead to the deviation from this trend as seen in Fig. 5.3(a). Fig. 5.3(b) shows the $\omega^4$ dependence of isotope scattering rate, $\tau_{\text{iso}}^{-1} \propto \omega^4$, which results in more prominent isotope scattering at higher frequencies as compared to anharmonic scattering. Fig. 5.3(b) also shows that ZnTe has highest isotope scattering rate, $\tau_{\text{iso}}^{-1}$, at a particular phonon frequency, followed by ZnSe and then ZnS. This is unexpected as the mass variance parameters, Eq. (3.106), show a different trend of $m_{\text{Zn}}^{(2)}(1.7 \times 10^{-4}) < m_{\text{Te}}^{(2)}(2.8 \times 10^{-4}) < m_{\text{Se}}^{(2)}(4.6 \times 10^{-4})$. Moreover, large mass variance parameter, $m_{\text{Zn}}^{(2)} = 6.0 \times 10^{-4}$, of heavier constituting element Zn in ZnS is expected to strengthen the isotope scattering in ZnS.[61] Instead $\tau_{\text{iso}}^{-1}$ seems to follow the trend of the chalcogenide-to-zinc mass ratios: ZnTe(2.0) > ZnSe(1.2) > ZnS(0.5) for a particular frequency. We found that this trend of $\tau_{\text{iso}}^{-1}$ comes
Chapter 5. *Ab initio* thermal transport study for the nanostructured Zn-Chalcogenides

**Figure 5.3:** (a) $\tau_{\text{anh}}$ at 300 K and (b) $\tau_{\text{iso}}$ for ZnS, ZnSe and ZnTe. The $\omega^2$ and $\omega^4$ trend lines were obtained by least square fit to all the data points.

from the pDOS contributions, $g_A(\omega)$, in Eq. (3.113). The slope of acoustic bands decreases and pDOS increases with the average mass, shown in Fig. 5.4a, leading to the same trend for $\tau_{\text{iso}}^{-1}$. Inspite of $\tau_{\text{iso}}^{-1}$ trend of ZnTe > ZnSe > ZnS at a given frequency due to the pDOS, the overall effect of isotope scattering is found to be highest in the case of ZnS as compared to ZnSe and ZnTe. This is seen in Table 5.1 where the percent isotope factor ($P = (\kappa_{l,\text{anh}}/\kappa_l - 1) \times 100$)[61] ranges from 19-33 % for ZnS down to 6-9% for ZnTe. This is explained with the help of the anharmonic and isotope scattering trends with frequency and confirmed from Fig. 5.4 which shows the pDOS and the cumulative $\kappa_l$ with respect to phonon frequencies (Cum.$\kappa_l(\omega) = \int_0^{\omega} \kappa_l(\omega') d\omega'$). It is evident that the $\tau_{\text{iso}}^{-1} \propto \omega^4$ behaviour for isotope scattering dominates $\tau_{\text{anh}}^{-1} \propto \omega^2$ at higher frequencies. It means that, if there are
high frequency acoustic phonons in a material contributing in heat transport, then significant effect of isotope scattering is seen depending on mass variance. This is true for the case of ZnS having the high frequency acoustic phonon modes of energy 7 meV-10 meV as compared to ZnSe and ZnTe, Fig. 5.4(a). ZnS has a prominent contribution to $\kappa_l$ from these modes with energy of 7 meV-10 meV, Fig. 5.4(b), This contribution is lacking in ZnSe and ZnTe which explains the larger overall isotope scattering effect on ZnS $\kappa_l$ than ZnSe and ZnTe, Fig. 5.4.

Fig. 5.4(b) also shows the contribution of interband scattering i.e., the acoustic-optic (a-o) scattering in the thermal conductivity of zinc-chalcogenides. If a-o scattering is not included, we see that $\kappa_l$(ZnS)$ > \kappa_l$(ZnSe)$ > \kappa_l$(ZnTe). Turning on the scattering contributions from optic modes strongly decreases the thermal conductivity of all three materials. However the effect is largest for ZnSe due to the similar masses and resulting lack of the a-o gap, Fig. 5.1. This brings $\kappa_l$(ZnSe) and $\kappa_l$(ZnTe) to similar values, which remains true after the inclusion of isotope scattering too, whereas $\kappa_l$(ZnS) is largest.
5.3 Cross-over results and discussions

For understanding the effect of nanostructuring on the thermal conductivities of ZnS, ZnSe and ZnTe, we have applied two different models: the diffusive boundary scattering and the confined MFP limit. The diffusive boundary scattering rate can be included as:

\[
\frac{1}{\tau_{db,jq}} = \frac{v_{j,q} L}{L}
\]  \hspace{1cm} (5.1)

where \(L\) is the crystallite dimension. The schematic of a diffusive boundary scattering is seen in Fig. 5.5(a) which shows that some of the resulting phonons from the scattering of high MFP phonon diffuses through the boundary and further carry heat. Another approach of studying the effect of nanostructuring is by considering a complete blockage of the heat carried by the phonons with a MFP (\(\Lambda\)) larger than the grain size \(L\).[28, 74]

\[
\frac{1}{\tau_{cl,jq}} = \begin{cases} \infty & \Lambda > L \\ 0 & \Lambda < L \end{cases}
\]  \hspace{1cm} (5.2)

This corresponds to a confined limit where the phonons are scattered back at the boundary as shown in Fig. 5.5(b). These scattering rates, Eqs. (5.1)-(5.2), are added to those due to anharmonic and isotope scattering using Matthiesen’s rule, Eq. (3.114), for the calculation of thermal conductivity.

For the confined limit, a large drop in \(\kappa_l\) of ZnS is seen when \(\Lambda\) is limited to...
Chapter 5. *Ab initio* thermal transport study for the nanostructured Zn-Chalcogenides

Figure 5.6: (a) $\kappa_l$ calculated at 300K with respect to nanostructure size ($L$) for ZnS, ZnSe and ZnTe 1) including diffusive boundary scattering (full lines), Eq. (5.1) and 2) with confined phonon MFP limit (dashed lines), Eq. (5.2). (b) MFP ($\Lambda$) distribution of phonons.

$L = 2 - 3 \, \mu m$, Fig. 5.6(a) (dashed lines). We have also calculated the same curve for isotopically pure structures and found similar drop, which would indicate to the strong contribution of anharmonic scattering to this curve. Such drop is not seen for ZnSe and ZnTe in Fig. 5.6(a) (dashed lines). This points to the phonon
modes having energy around 7-10 meV, which have significant contributions to $\kappa_l$ of ZnS. This is also seen in Fig. 5.4(b). These observations suggest that anharmonic scattering is lower for the states around 7-10 meV in ZnS, Fig. 5.3(a) leading to high MFP for these states. This is further confirmed from Fig. 5.6(b) which shows that the states around 7-10 meV in ZnS indeed have MFPs around $\Lambda = 2 - 3 \mu m$. Removing these high MFP states in ZnS by nanostructuring thus brings down the thermal conductivity with a steep slope as compared to ZnSe and ZnTe and results in $\kappa_l$ cross-over. For the diffusive boundary scattering, no sudden decrease in the ZnS $\kappa_l$ is found, Fig. 5.6(a) (full lines). Instead a difference in the slopes of $\kappa_l$ as a function of $L$ for ZnS and ZnSe is observed. This is because in diffusive boundary scattering, some of the resulting phonons further carry heat, Fig. 5.5(a), and increase the population of heat carrying low MFP phonons as compared to the confined limit case. This shifts the $\kappa_l$ cross-over towards $L = 0.1 - 0.2 \mu m$, Fig. 5.6(a) (full lines).

In the end this shows that both the larger thermal conductivity of ZnS and the cross-over have a similar origin, namely the reduced scattering of the acoustic modes due to the gap in the phonon states induced by the mass difference.

Ref. [135] also used the diffusive boundary scattering model. With our ab initio study, we also get the cross-over in zinc-chalcogenides as predicted by earlier model[135] i.e., ZnS and ZnSe $\kappa_l$ coincide at smaller $L$ whereas bulk ZnSe and ZnTe have similar $\kappa_l$. However, the cross-over for ZnS and ZnSe $\kappa_l$ in our calculations is found to be $\approx 0.1 - 0.2 \mu m$ which has been predicted earlier to be at very low $L$ of $\approx 0.03 \mu m$. We also notice that the thermal conductivity in a nanostructured material is lower by a factor of 2 than predicted by earlier model. This means that a thermal conductivity $\approx 3 \text{ Wm}^{-1}\text{K}^{-1}$ can be reached at grain size around 100 nm which could be interesting for thermoelectric applications.

### 5.4 Summary and Outlook

This chapter focuses on the ab initio calculation of bulk thermal conductivity of zinc-Chalcogenenides and the prediction of the thermal conductivity cross-over at nanoscale in these materials. We determined the lattice thermal conductivity using the Boltzmann transport equation within the relaxation time approximation with the full ab initio calculation of anharmonic scattering. We have also included
the isotope scattering in our calculations of thermal conductivity. We analysed the
effect of acoustic-optic phonon gap, high frequency acoustic phonons, mass vari-
ances which affect the anharmonic and isotope scattering strength in determining
the thermal conductivity of these materials. We found that there are phonon states
of energy 7-10 meV in ZnS with larger phonon MFPs which contribute more to
its thermal conductivity. This helped us to explain the reason for large thermal
conductivity in bulk ZnS than ZnSe and ZnTe as well as to understand the cross-
over origin in these materials when nanostructured. The effect of nanostructuring
is studied using both the diffusive boundary scattering and confined MFP limit.
It has been found that, while the thermal conductivity cross-over has a similar
trend as the model results[135], the thermal conductivity cross-over of ZnSe and
ZnS occurs at larger nanostructure sizes of 0.1-0.2 µm. The reason of cross-over
could be attributed to large acoustic-optic phonon gap in ZnS induced by mass
difference of constituting elements which reduces scattering of acoustic phonon
modes in ZnS.

We further find a low thermal conductivity of ≈ 3 Wm⁻¹K⁻¹ in thermal conduc-
tivity of ZnS nanostructures with grainsize of around 100 nm. This reduction in
thermal conductivity is smaller by a factor of 2 than the earlier model prediction
thereby making it interesting for thermoelectric applications. This behaviour of
ZnS κl could be technologically interesting as ZnS is composed of non-toxic and
low-cost elements and hence could be further studied for determining its electronic
transport properties from ab initio calculations.
Chapter 6

Tight binding model for Si

Use of \textit{ab initio} methods for the thermal conductivity predictions is of great relevance as it provides minute details of the underneath phonon scattering processes. The contributions of acoustic and optical phonon modes can also be quantified separately, as can be seen in Chapter 5. These insights help to understand the trends of thermal conductivities in different material classes and thus give the knowledge about how a material’s thermal conductivity can be tuned according to the application.

However, the computational cost of these \textit{ab initio} calculations limits their use for predicting thermal conductivities of materials at different length scales. The number of force calls for calculations of anharmonic(3\textsuperscript{rd} order) force constants scales as $O(n^2)$ for $n$ atoms compared to the linear scaling for the harmonic(2\textsuperscript{nd} order) force constants. The computational complexity increases further with the inclusion of even higher order terms. Moreover, the thermal conductivity calculations for complex nanostructures (1D, 2D quantum confined structures; structures with defects, grain boundaries & dislocations; and superlattices & random alloy structures) are practically undoable using \textit{ab initio} methods.

The use of simplified potentials show another efficient way of dealing with these computationally demanding thermal conductivity calculations for complex and large structures. However, the crucial step of the development of the simplified potentials has to be addressed carefully. The problem with empirical potentials of under or overestimating the thermal expansion and conductivity by an order of magnitude arises from their fitting procedures (see discussion of Fig. 2.1).[1]
These models are fitted empirically to the bulk energetics as a function of inter-atomic distances. Thus the model parameters overlooks any quantum bonding information and hence show less transferability to unfitted properties.

In this chapter, we discuss a different scheme of developing simplified potentials, namely tight binding (TB) modelling, which takes orbital interactions into account for parametrising the bonding in materials. The general theory of TB modelling has been discussed in Sec. 3.2.2. We have developed a TB model for Si with the main focus of the correct reproduction of the thermal transport properties. There are various orthogonal and non-orthogonal TB models for Si developed in past years which can reproduce the energetics.[145–150] However, there is still need of models which can efficiently and correctly calculate long ranged interactions and the computationally demanding thermal properties.

In the next sections, we discuss the parametrisations and performances of existing orthogonal TB models for Si. We apply these models to calculate the thermal properties of Si and check their transferability. We present next our orthogonal tight binding model for Si and discuss the parametrisation scheme for the bonding and repulsive term in the TB energy functional, Eq. (3.151). This is followed by the determination of thermal properties for different structures of Si using our model. We also show the transferability of our model.

6.1 Review of earlier TB models for Si

6.1.1 Parametrisation details of the models

The four earlier orthogonal tight binding models by Goodwin et al., (GSP)[145] Kwon et al., (KBS)[146] Lenosky et al., (LER)[147] and Wang et al., (WCH)[148] are discussed here for the calculations of thermal properties.

The GSP model[145] introduced a ‘rescaling’ method for obtaining the TB parameters. The ‘rescaling’ method helps to model the bonding and repulsive potentials in terms of the parameters at equilibrium volume, using an appropriate functional form. The functional form used in GSP model for parametrising the bond integrals
\[ \beta_{i\mu j\nu}(R) = \beta_{i\mu j\nu}^0 \left( \frac{R_0}{R} \right)^n \exp \left[ n \left( - \left( \frac{R}{R_c} \right)^{n_c} + \left( \frac{R_0}{R_c} \right)^{n_c} \right) \right]. \] (6.1)

where \( i\mu j\nu \) represents the four types of orbital interactions for Si: \( ss\sigma, sp\sigma, pp\sigma \) and \( pp\pi \) between atoms \( i \) and \( j \) and orbitals denoted by \( \mu \) and \( \nu \). \( \beta^0 \) represents bond integrals at equilibrium interatomic distance \( R_0 \). \( R_c \) is the cut-off distance and \( n \) and \( n_c \) are further fitting parameters. At equilibrium, \( R = R_0 \) which leads to \( \beta_{i\mu j\nu}(R_0) = \beta_{i\mu j\nu}^0 \). As \( R \) deviates from equilibrium \( R_0 \), then \( \left( \frac{R_0}{R} \right)^n \) and the exponential term have values different from 1 which rescale the \( \beta_{i\mu j\nu}^0 \) to give \( \beta_{i\mu j\nu}(R) \) for \( R \neq R_0 \). The exponential part of Eq. (6.1) thus changes the slope.
Chapter 6. Tight binding model for thermal conductivity of Si

with interatomic distance but not the value at equilibrium. The $\beta$s for GSP model are shown in Fig. 6.1a as a function of $R$ which were obtained by fitting the Si electronic bandstructure. GSP model used a step cut-off function originally for bringing the $\beta$s down to zero at $R_c$ which is chosen between first and second nearest neighbour shells. However, while studying the thermal properties of Si with GSP model, we used a cosine cut-off for a smooth decay of $\beta$s to zero at $R_c$, as shown in Fig. 6.1a.

The pairwise repulsive term $\phi_{ij}$ in GSP model was parametrised in the similar function form as $\beta$s, although with different exponent $m$. $\phi_{ij}$ in GSP model is thus given as

$$\phi_{\mu\nu}(R) = \phi_{ij}^0 \left(\frac{R_0}{R}\right)^m \exp \left\{ m \left( -\left(\frac{R}{R_c}\right)^n + \left(\frac{R_0}{R_c}\right)^n \right) \right\}. \quad (6.2)$$

which shows that $\phi_{ij}(R)$ is obtained by rescaling $\phi_{ij}^0$. The parameters for repulsive part were fitted to the energy-volume curves for different structures of Si. Furthermore the transferability of the model was checked by applying it to Si clusters for the energy calculations.

A modification to the GSP model was presented in 1993 by Kwon et al.\cite{146} (KBS). In addition to the energy calculations, the KBS model focussed on describing the elastic constants, defect formation energies for vacancies and interstitials in Si crystal. They also reported the model calculated phonon frequencies and Grüneisen parameters at a few special points of Brillouin zone and compared them to the $ab\ initio$ results. The model used the same short ranged rescaling function for $\beta$s and $\phi$ as proposed in GSP model, Eq. (6.1) and Eq. (6.2). However, unlike the GSP model, the KBS model has separate parameters for all different types of orbital interactions of Si and uses a cubic polynomial cut-off function. The $\beta$s for KBS model are shown in Fig. 6.1b.

Fig. 6.1 also shows the $\beta$s from the other two models namely LER model\cite{147} and WCH model\cite{148}. Both LER and WCH models are long ranged as seen in Fig. 6.1. The atomic interactions up to $4^{th}$-$5^{th}$ nearest neighbour shells in diamond Si are included in these models whereas the interaction range is limited between $1^{st}$-$2^{nd}$ nearest neighbour shells for GSP and KBS models. The $\beta$s for LER model also exhibit an unusual behaviour, due to the applied fitting strategy. The $\beta$s and the repulsive part $\phi$ were fitted together to the $ab\ initio$ total energies and forces calculated for liquid, amorphous, bulk and different clusters of Si. Moreover, the
experimental elastic constants, phonon frequencies and Grüneisen parameters for bulk Si were also fitted. Cubic spline function with seven evenly spaced spline knots were used for fitting $\beta$s and $\phi$ to these above mentioned properties which lead to large number of parameters. The use of long ranged function with large number of parameters makes LER model the most complex model with the heaviest parameter set among all four models.

WCH model parametrises the bond integrals $\beta$s using the Harrison’s universal $R^{-2}$ trend.[148] The $\beta$s were obtained by fitting to the electronic band structure of diamond Si at a range of volumes. The repulsive potential, $\phi$, was then fitted as a difference between the total energy, $E_{\text{tot}}$, and the bond energy, $E_{\text{bond}}$, for diamond Si.[148] Firstly, $E_{\text{tot}}$ for diamond Si was fitted using exponential function and $E_{\text{bond}}$ was calculated from the parametrised $\beta$s as a function of nearest neighbour distance. Then obtained $E_{\text{bond}}$ vs neighbour distance curve was reparametrised using third order polynomial function. WCH model, fitted only to the diamond Si energy-volume curve, has no huge parameter set. However the long ranged behaviour and slow $R^{-2}$ scaling of $\beta$s is a hurdle for performing the molecular dynamics simulations.[146]

### 6.1.2 Electronic density of states for different Si structures

For the simulations of Si nanostructures with different bonding geometries, it is crucial for a simplified model to show transferability to different structures. We have calculated the DOS for Si in different structures using the orthogonal models, discussed above, and compared them to DFT. Fig. 6.2 show the calculated DOS for Si in groundstate diamond, silicene (2D buckled graphene-like structure), simple cubic and $\beta$-tin structures respectively. The results show that the LER model poorly captures the DOS of diamond structure, which is also reported in Ref. [147], and also shows least transferability to other structures among all four models. This is because the electronic band structures for different geometries of Si are not included in the fitting data for LER model. Instead the bond integrals $\beta$s together with the repulsive parameters are fitted directly to the total energies and forces for different structures of Si using cubic splines with seven knots. Such long ranged modelling scheme, although exhibits good results for the fitted properties, lacks transferability.
Figure 6.2: DOS for Si in (a) diamond (b) silicene (c) simple cubic and (d) β-tin structures at respective DFT optimised volumes calculated using earlier tight binding models and compared to DFT results.

The other long ranged model (WCH) shows reasonable agreement of the DOS with DFT but with the overestimated bandwidths for diamond, silicene and β-tin structures, Fig. 6.2. A large disagreement for Si in simple cubic structure can also be seen in Fig. 6.2.

The other two short ranged models, GSP and KBS, reproduce the DOS for different structures of Si with an improvement or similar to the long ranged LER and WCH models. A general conclusion thus can be drawn with these tests that the long ranged potentials, fitted with more parameters to certain structures and properties, are less transferable to other geometries.
6.1.3 Thermal properties for Si bulk

The pDOS with all the four models are shown in Fig. 6.3 and compared to the DFT result. The two main properties to be noticed in the Fig. 6.3, which affect further thermal properties as $\gamma$, $C_V$, $v$, $\alpha_T$ and $\kappa_l$, are correct reproduction of, 1), the acoustic phonon peak and, 2), the phonon bandwidth. The acoustic phonon peak have significant contributions from the long ranged interactions which was analysed in Fig. 4.2. To reproduce such long ranged properties with short ranged potentials is one of the modelling aims. This is achieved quite convincingly with the short ranged GSP model for the reproduction of acoustic phonon peak as compared to other three models (KBS, LER, WCH), Fig. 6.3. However, the overestimation of phonon bandwidth with GSP model is also seen in Fig. 6.3. The phonon bandwidth is reproduced well with LER model among all four models, Fig. 6.3. This is because the LER model is fitted to the phonons.

We further study $\alpha_T$ and $\kappa_l$ with earlier TB models and explain the obtained results with respect to their pDOS reproduction, seen in Fig. 6.3. Fig. 6.4 shows the $\alpha_T$ calculated with GSP, KBS, LER and WCH models and compared to DFT.
Figure 6.4: Thermal expansion for Si using earlier tight binding models compared with DFT (LDA) results.

and experiment. For GSP model, the difference, mainly at high temperatures, is seen between the model calculated $\alpha_T$ and DFT, Fig. 6.4. This is due to the overestimation of phonon bandwidth with GSP model. However the low temperature behaviour of $\alpha_T$ obtained using GSP model is comparable to DFT which could be because of correct prediction of acoustic phonons, Fig. 6.3.

Another short ranged KBS model, is not able to reproduce the prominent feature for Si of negative $\alpha_T$ at lower temperatures, Fig. 6.4. The high temperature $\alpha_T$ also deviates from the DFT results. This can be attributed to large deviation of both the acoustic phonons and the overall phonon bandwidth as compared to DFT, Fig. 6.3.

Next to GSP model, in reproducing well the acoustic phonon peak of pDOS, is the long ranged WCH model, Fig. 6.3. Also, similar to the case of GSP model, WCH model overestimates the phonon bandwidth. However, the bandwidth overestimation is less for WCH model than GSP model. This also reflects in the high temperature $\alpha_T$ reproduction with WCH model, Fig. 6.4. The deviation of low
Figure 6.5: Thermal conductivity variation with temperature for Si using earlier tight binding models compared with DFT (LDA) results.

temperature $\alpha_T$, however, is more for WCH model than GSP model as compared to the DFT results due to the better acoustic peak reproduction with GSP model.

The long ranged LER model, fitted to the diamond Si phonons, reproduces the correct bandwidth of the phonon DOS, Fig. 6.3. However, deviations in the reproduction of acoustic phonons can also be seen in Fig. 6.3. Inspite of these deviations, the low temperature behaviour of $\alpha_T$ with LER model is comparable to DFT, Fig. 6.4. This is due to the fitting of LER model to Grüneisen parameters for diamond Si, which are related to $\alpha_T$ (see Eq. (3.132)). However, the slope of $\alpha_T$ with temperature obtained from LER model is different from the DFT results.

The reproduction of acoustic phonons and the correct phonon bandwidth also affects the $\kappa_l$ determination. The phonon bandwidth plays an important role in determination of the thermal conductivity $\kappa_l$ by influencing the acoustic-optic (a-o) interband phonon scattering. The overestimation of the phonon bandwidth leads to a low a-o phonon scattering and hence results in a high thermal conductivity. The $\kappa_l$ calculated with the earlier models is seen in Fig. 6.5 compared to the DFT results. The deviation of $\kappa_l$ with KBS model as compared to DFT is largest.
among the four earlier models. This is due to the big difference in the phonon bandwidth with KBS model as compared to DFT as well as poor acoustic phonon reproduction, Fig. 6.3.

The other short ranged GSP model, also due to its overestimation of phonon bandwidth, predicts high thermal conductivity than DFT, Fig. 6.5. However, the $\kappa_l$ from GSP model around room temperature is very similar to the $\kappa_l$ obtained from long ranged WCH model, as seen in Fig. 6.5. This could be attributed to the balance between better acoustic peak reproduction in GSP model and phonon bandwidth reproduction in WCH model, Fig. 6.3. However, such a performance of short ranged model, similar to a long ranged potential, confirms that there is possibility of a carefully modelled short ranged potential for the correct reproduction of thermal conductivity and other thermal properties.

The $\kappa_l$ determination with the long ranged LER model shows an extremely good comparison with DFT results, Fig. 6.5. However, this is mainly because of the fitted Grüneisen parameters for diamond Si in LER model. The Grüneisen parameters are also related to the thermal conductivity through the anharmonic force constants, Eq. (3.135). Thus fitting the model to Grüneisen parameters confirms the good reproduction of $\kappa_l$ which is seen in Fig. 6.5 for LER model. However, such a scheme of fitting huge dataset, adopted in LER model, not only requires large number of parameters but also leads to lack of transferability of the model. This can be seen in Fig. 6.2 for the determination of electronic properties with LER model.

### 6.2 Need for new tight binding model

The review of the parametrising schemes and performances of the four orthogonal TB models, the GSP, KBS, LER and WCH models, show that there is still need of the short ranged potential for determining correct thermal properties of Si. Although the earlier TB models perform much better than the empirical Tersoff and Stillinger-Weber potentials to predict the thermal properties of Si bulk (compare Fig. 6.5 and Fig. 2.1), an improvement in the results could be further obtained by carefully modelling a new short ranged TB model with the main focus of Si thermal properties reproduction. In Sec. 6.1.2, we learnt that the short ranged GSP and KBS models show better transferability to different structures of Si as
compared to long ranged LER and WCH models. The fitting of long ranged models with more parameters to certain structures and properties leads to their lack of transferability. On the other hand, the reproduction of thermal properties is seen in better comparison to DFT results for the long ranged LER and WCH models compared to the short ranged GSP and KBS models, Sec. 6.1.3. This could lead to the impression that long ranged behaviour in a model serves to be beneficial for the reproduction of thermal properties. However, Chapter 4 confirms that there could be a short ranged potential which captures long ranged interactions for correct determination of the thermal properties in its parameters. The short ranged force constants model in Chapter 4, worked well for the accurate predictions of thermal properties not only for pure Si and Ge but also for Si$_x$Ge$_{1-x}$ random alloys. This analysis gave us the guidelines for the development of our tight binding model to calculate the thermal properties of Si:

- The model needs to be simple, short ranged, with small parameter set and should correctly predict thermal properties of Si.
- To fit model parameters to less properties, however, to capture correct physics for ensuring the transferability to different structures of Si.
- To use GSP function which gives separate handles to tune equilibrium and curvature of potential energy.
- To capture long ranged interactions in our short ranged model for thermal properties.

### 6.3 Model development

We developed the orthogonal tight binding model by following the scheme discussed in Sec. 3.2.2. The binding energy of Si in our model is given as the sum of the bonding term $E_{\text{bond}}$ and repulsive term $E_{\text{rep}}$. The promotional energy $E_{\text{prom}}$ is also included in the model, Eq. (3.162), which is the energy for promoting $s$ and $p$ orbital electrons in Si for bonding, thus leading to orbital hybridisation. The $E_{TB}$ for our model is then given as,

$$E_{TB} = E_{\text{bond}} + E_{\text{rep}} + E_{\text{prom}}$$  \hspace{1cm} (6.3)
$E_{bond}$ is calculated from Eq. (3.153) by parametrising the tight binding Hamiltonian elements $\beta$ for different orbital interactions, Eq. (3.154), obtained from the DFT. $E_{rep}$ is calculated by modelling the pair repulsive term, Eq. (3.161).

### 6.3.1 Bond integral parametrisation at equilibrium

For deriving the $\beta$s from *ab initio* calculations, we follow the downfolding procedure, discussed in Sec. 3.2.2. We calculated the bandstructures at a range of interatomic distances for different structures of Si. The DFT code GPAW[71] with the grid basis was used first for the self-consistent energy calculations followed by diagonalisation using 3-\(\zeta\) pseudo atomic orbital(PAO) basis in LCAO mode of GPAW. The 3-\(\zeta\) basis is then projected onto 1-\(\zeta\) minimal basis to get 4\(\times\)4 Hamiltonian with the elements corresponding $ss\sigma$, $sp\sigma$, $pp\sigma$ and $pp\pi$ interactions.

![Figure 6.6: Bond integrals $\beta$s for different orbital interactions in range of structures of Si as a function of interatomic distances. The $\beta$s of diamond structures are highlighted by the lines.](image)

The bond integrals $\beta$s for all $s$ and $p$ orbital interactions as a function of interatomic distances are shown in Fig. 6.6 for various structures of Si. We see that the $\beta$s show exponential decay behaviour in general but also have some discontinuities
at shorter interatomic distances. Moreover, less transferability is seen between the $\beta$s of different structures of Si in Fig. 6.6.

\[\text{Figure 6.7: Electronic density of states for diamond Si calculated at DFT optimised volume with our model compared to DFT results.}\]

The bonding parameters, fitted to the pure $\beta$s obtained from DFT downfolding procedure shown in Fig. 6.6, overestimated the electronic density of states (DOS) bandwidth. Hence we rescaled the equilibrium parameters ($\beta^0$s) in Eq. (6.1) along with the onsite energy difference ($E_s-E_p$) by fitting them to the DOS for diamond Si at equilibrium. The fitting parameters at equilibrium are listed in Table 6.1 and the calculated the DOS at equilibrium is shown in Fig. 6.7. The model calculated DOS shows good correspondence to the DFT results and improvement over the earlier TB models DOS for diamond Si, Fig. 6.2.

<table>
<thead>
<tr>
<th>$\beta^0_{ss\sigma}$</th>
<th>$\beta^0_{sp\sigma}$</th>
<th>$\beta^0_{pp\sigma}$</th>
<th>$\beta^0_{pp\pi}$</th>
<th>$E_s-E_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.64 eV</td>
<td>1.84 eV</td>
<td>2.68 eV</td>
<td>-1.16 eV</td>
<td>-5.60 eV</td>
</tr>
</tbody>
</table>

\[\text{Table 6.1: The bonding parameters ($\beta^0$s) at equilibrium (}$R_0=2.36\ \text{Å}$\text{) for the developed Si tight binding model.}\]
6.3.2 Fitting volume dependent repulsive and bonding parameters

The bonding slope parameter \( n \), the repulsive parameters \( \phi_0 \) and \( m \) in Eq. (6.2)) and the damping parameter \( n_c \) in our model are fitted together to the DFT(PBE) calculated energy-volume curve for diamond Si. Moreover, the fitting of bonding slope parameters directly to the energy-volume data gave extra flexibility to our model for capturing the potential energy surface precisely. This is crucial to get correct forces and hence the phonons and thermal properties.

To keep the model short ranged, a small \( R_c \), between the first and the second nearest neighbour interatomic distances, is chosen. To converge the \( \beta \)s and \( \phi \) to zero at \( R_c \), we have used a simple cosine cut-off function in our model, Fig. 6.8, as compared to cubic polynomial cut-offs used in KBS and LER models. Thus we have a simple, short-ranged model which has less number of parameters than the earlier models[146–148]. The model parameters are listed in Table 6.2 and the \( \beta \)s and the \( \phi \) for our model are shown in Fig. 6.8.

![Figure 6.8](image)

**Figure 6.8:** (a) The bonding integrals \( (\beta) \) and (b) the repulsive pair potential \( (\phi) \) as a function of the interatomic distance for the developed model.

<table>
<thead>
<tr>
<th>( \phi_0 )</th>
<th>( m )</th>
<th>( n )</th>
<th>( n_c )</th>
<th>( R_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.76 eV</td>
<td>4.66</td>
<td>2.10</td>
<td>9.48</td>
<td>3.67 Å</td>
</tr>
</tbody>
</table>

**Table 6.2:** The developed Si tight binding model parameters. The bonding slope parameters \( (n \) and \( n_c \)) along with the repulsive parameters \( (\phi_0 \) and \( m \)) are fitted only to DFT energy-volume curve for diamond Si. The model is kept short ranged by choosing \( R_c \) between first and second nearest neighbour distance.
6.4 Model testing for energetics

We test the energetics for diamond Si with our model. Fig. 6.9 shows the formation energy ($E_f$) curve with volume for Si calculated with our tight binding model and compared to the DFT results. A good agreement between model calculated energy-volume curve and DFT is seen, Fig. 6.9. The model predicted equilibrium lattice constant ($a_0$) and binding energy per atom ($E_0$) are also close to DFT results, as seen in Table. 6.3.

![Figure 6.9](image)

**Figure 6.9:** Formation energy-volume curve for Si in diamond structure calculated with our model and compared to DFT (PBE).

Along with the accurate reproduction of $a_0$ and $E_0$, a model is also expected to correctly predict the energy required to create small displacements. This translates to a good reproduction of elastic constants as well as phonon frequencies. Although our model is not fitted to the elastic constants, it is still able to describe the elastic constants ($C_{11}$, $C_{12}$, $C_{44}$) and bulk modulus ($B_0$) for bulk Si in fair agreement to DFT, Table. 6.3. Our model predicts the $B_0$ with 7% deviation and $C_{11}$, $C_{12}$, $C_{44}$ with maximum 24% deviation from DFT results.
Chapter 6. Tight binding model for thermal conductivity of Si

<table>
<thead>
<tr>
<th></th>
<th>$a_0$ (Å)</th>
<th>$E_0$ (eV)</th>
<th>$B_0$ (GPa)</th>
<th>$C_{11}$ (GPa)</th>
<th>$C_{12}$ (GPa)</th>
<th>$C_{44}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT (PBE)</td>
<td>5.468</td>
<td>-5.424</td>
<td>88.65</td>
<td>161.41</td>
<td>63.67</td>
<td>77.15</td>
</tr>
<tr>
<td>Our Model</td>
<td>5.465</td>
<td>-5.421</td>
<td>82.18</td>
<td>125.72</td>
<td>61.53</td>
<td>57.92</td>
</tr>
<tr>
<td>Our Model2</td>
<td>5.467</td>
<td>-5.425</td>
<td>86.25</td>
<td>129.66</td>
<td>65.70</td>
<td>58.62</td>
</tr>
</tbody>
</table>

Table 6.3: The equilibrium lattice constant ($a_0$), energy ($E_0$), bulk modulus ($B_0$) and the elastic constants ($C_{11}$, $C_{12}$, $C_{44}$) for diamond Si calculated with Our Model (Table.6.2) and Our model2 (Table.6.2) compared with DFT. Our Model2 is a variant of the first model, fitted to DFT energy-volume curve and the elastic constants for diamond Si.

6.4.1 Fitting to Si elastic constants

To improve the reproduction of elastic constants, we fitted our model parameters to the diamond Si elastic constants along with its energy-volume curve. We included 21 energies (at 7 volumes for each elastic constants: $C_{11}$, $C_{12}$ and $C_{44}$) for bulk Si in the fitting dataset. Various fitting tests were carried out as, weighting the energies for elastic constants by a factor of 10, starting with random model parameters for optimisation, fitting equilibrium bonding parameters too and trying different optimisers. However, no drastic improvements were seen in the results. Table 6.4 lists the model parameters fitted to the weighted energies for diamond Si elastic constants.

<table>
<thead>
<tr>
<th>$\phi^0$ (eV)</th>
<th>$m$</th>
<th>$n$</th>
<th>$n_c$</th>
<th>$R_c$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.76</td>
<td>4.74</td>
<td>2.12</td>
<td>9.26</td>
<td>3.67</td>
</tr>
</tbody>
</table>

Table 6.4: A variant of the developed Si tight binding model in Table.6.2. The model parameters are fitted to DFT energy-volume curve and the elastic constants for diamond Si. Negligible changes in parameters are seen as compared to Table.6.2.

As compared to Table. 6.2, the model parameters for the new fitted model, Table. 6.4, show very small variations. The maximum change is seen in $n_c$ parameters of 2%. We also checked the equilibrium energies, bulk modulus and elastic constants with this new model, labelled ‘Our Model2’ in Table. 6.3, which vary slightly as compared to our first model results. We therefore continued using our first model (Table. 6.2) to study the thermal properties of Si.
6.5 Si thermal properties with our model

As a test of transferability of our model, we applied our model to calculate the unfitted thermal properties of diamond structured Si. We calculated the properties in harmonic and quasi-harmonic approximation as phonon DOS and thermal expansion. Moreover, we have also applied our model to calculate the anharmonic phonon interactions to get thermal conductivity for diamond Si.

6.5.1 Phonon DOS and thermal expansion

![Figure 6.10: Si phonon DOS using our TB model compared with DFT(PBE) results.](image)

Fig. 6.10 shows the pDOS for Si using our tight binding model which is in good agreement with the DFT results. Our model also performs better than the earlier long and short ranged models to capture the phonons, Fig. 6.3. The correct reproduction of the acoustic phonon peak in Fig. 6.10 is very good with our short ranged model. An overall good reproduction of pDOS from our model is because of the correct modelling of the potential energy curvature for diamond Si, Fig. 6.9, which helps to correctly determine the forces and the force constants required to get the phonon frequencies. Also, such a performance of our model again confirms
the idea of correctly modelling the long ranged interactions with short ranged models, as first presented in Chapter 4.

![Graph of thermal expansion](image)

**Figure 6.11:** Thermal expansion for Si using our TB model compared with DFT(PBE) results.

We further calculated the thermal expansion, $\alpha_T$, which is a very sensitive thermal property. Fig. 6.11 shows temperature variation of $\alpha_T$ for Si bulk. A good comparison is again seen with the DFT results. As the model parameters are fitted to the DFT(PBE) data which overestimates the thermal expansion, the $\alpha_T$ with our model is also higher than experiments, Fig. 6.4. However, a good comparison of $\alpha_T$ from our model to DFT results show that our model is able to capture the trends of the potential it is fitted to. The negative thermal expansion is also reproduced well with our short ranged model. The small deviations at large temperatures could be due to the variations in the optic phonons peak in Fig. 6.10, which have significant contributions at high temperatures.

### 6.5.2 Thermal conductivity

The calculated thermal conductivity with our model is seen in Fig. 6.12, which is compared with the DFT results. Considering the simplicity of our tight binding model, we see a good prediction of lattice thermal conductivity, $\kappa_l$, for Si
Chapter 6. Tight binding model for thermal conductivity of Si

Figure 6.12: Lattice thermal conductivity variation with temperature for Si using our TB model compared with DFT(PBE) results.

bulk with our model. Moreover, our model performs better than the earlier short ranged (GSP[145] and KBS[146]) and long ranged (WCH[148]) models, Fig. 6.5, for prediction of $\kappa_l$ (e.g., at 300K, $\kappa_l^{DFT}=126$ Wm$^{-1}$K$^{-1}$, $\kappa_l^{\text{OurTB}}=186$ Wm$^{-1}$K$^{-1}$ whereas $\kappa_l^{TB}=225, 445$ and 211 Wm$^{-1}$K$^{-1}$ for GSP, KBS and WCH models respectively). The other long ranged model (LER[147]) predicts precise $\kappa_l$ (124 Wm$^{-1}$K$^{-1}$) as compared to DFT because the model is fitted to the anharmonic properties of Si. However, with our simple and short ranged orthogonal TB model, fitted only to energy-volume curve of diamond Si, correct predictions of energetics and thermal properties are obtained in good comparison to DFT results. This confirms the transferability of our model to unfitted properties. Variations to the existing model could be tried further to reduce the difference in the model and DFT calculated $\kappa_l$.

6.6 Transferability to different structures

We checked the transferability of our model by applying them to the different structures of Si for calculating their energetics. Furthermore, we also show the
applicability of our model to calculate phonons in silicene (2D buckled structure).

### 6.6.1 Energetics for other structures

![Figure 6.13: Electronic density of states for Si in (a) simple cubic (b) β-Tin (c) silicene structures calculated at respective DFT optimised volumes with our model compared to DFT results.](image)

We first calculated the DOS for Si in simple cubic structure, β-Tin structure and silicene. All of these structures of Si show the metallic behaviour which is also captured with our model, seen in Fig. 6.13. A good agreement of the model calculated DOS as compared to DFT is obtained, Fig. 6.13. The bandwidths of the DOS and the reproduction of the peaks are comparable to DFT and show improvement over the earlier orthogonal models, Fig. 6.2.[145–148] Although, a slight overestimation of the DOS bandwidth is seen for β-tin, Fig. 6.13, it is less than the earlier model results, Fig. 6.2. A good reproduction of DOS peaks and bandwidths are seen for the cases of simple cubic Si and silicene.

The formation energy-volume curve for Si in β-tin structure is calculated next, which is the high pressure phase for Si. Fig. 6.14 shows the β-tin crystal structure for Si. The first and the second nearest neighbours (dark and lighter blue atoms) to the central atom (black atom) are highlighted in the figure (with turquoise atoms in environment). It can be seen that the β-tin structure has 4 nearest and 2 second nearest neighbours to each atom. However, the ratio of $\sim 1.06$ for second to first neighbour distance leads to the 6-fold coordination behaviour in β-tin structure as opposed to the 4-fold coordination in diamond structure. Such a high coordination of atoms in β-tin structure is the reason for the stability of the β-tin Si at lower volume than the diamond Si.
Figure 6.14: Si in β-tin structure. The first nearest neighbours (dark blue) and second nearest neighbours (lighter blue) to the central atom (black) are also highlighted. The similar first and second neighbour distance makes the structure 6-fold coordinated.

![Figure 6.14: Si in β-tin structure.](image)

Figure 6.15: Formation energy versus relative volume per atom for Si in β-tin and diamond structures calculated with (a) DFT and (b) our model.

![Figure 6.15: Formation energy versus relative volume per atom for Si in β-tin and diamond structures calculated with (a) DFT and (b) our model.](image)

Fig. 6.15 shows the energy-volume curve for β-tin structure plotted relative to the Si diamond equilibrium volume calculated with DFT and our TB model. We see that our model overestimates the equilibrium energy of the β-tin structure for Si. Such high formation energy prediction makes the β-tin Si unstable with our model. However, as our model is not fitted to the energies for β-tin Si, it is...
understandable that our model does not predict correct equilibrium for $\beta$-tin Si. Thus our present TB model could be extended further to include the energies for different structures in the fitting data.

![Graph showing DOS of Si diamond structure at 80% and 72% volume](image)

**Figure 6.16:** Electronic density of states for diamond structured Si at (a) 80% volume and (b) 72% volume of the optimised DFT structure. 72% volume of diamond structure is similar to the optimised volume for $\beta$-tin structure (see Fig. 6.15).

For this, we first analysed the performance of our model to calculate the electronic properties for diamond Si at lower volumes. This is done to check the applicability of the bonding parameters of our model to other structures at lower equilibrium volumes than diamond Si. Fig. 6.16 shows the DOS of Si diamond structure at 80% and 72% volume with our model compared to GSP model and DFT results. 72% of the diamond Si volume correspond to the equilibrium volume of Si in $\beta$-tin structure. It can be seen that at 80% volume, the DOS with our model is in good comparison to the DFT results, Fig. 6.16. However, at further low volume of 72% of equilibrium, our model shows deviations from DFT results. Although, compared to GSP model, our model performs well to capture the DOS at lower volumes, the slight variations at $\beta$-tin equilibrium volume shows that the fitting of bonding parameters in our model still needs consideration to correctly predict the energies for different structures of Si.

We also checked the repulsive energy per atom per coordination ($E_{\text{rep}}$) as a function of interatomic distance for different structures of Si, as seen in Fig. 6.17. $E_{\text{rep}}$ for different structures is calculated as

$$E_{\text{rep}} = \frac{E_{\text{binding}}^{\text{DFT}} - (E_{\text{bond}} + E_{\text{prom}})}{N_{\text{atoms}} \times N_{\text{coord}}}$$  \hspace{1cm} (6.4)
where $E_{\text{bond}}$ and $E_{\text{prom}}$ are bonding and promotion energies, Eq. (6.3), and $N_{\text{atoms}}$ is number of atoms in unit cell whereas $N_{\text{coord}}$ represents coordination number. Fig. 6.17 shows that $E_{\text{rep}}$ for other structures of Si are away from the diamond structure, to which our model is fitted. As seen in Fig. 6.17, our model predictions for $\beta$-tin structure are higher by $\sim 0.1$ eV than the $E_{\text{rep}}^{\beta\text{-tin}}$ obtained from Eq. (6.4) (calculated per coordination). This shifts up the formation energy curve of $\beta$-tin Si by $\sim 0.5$ eV with our model as compared to DFT, Fig. 6.15. For correctly describing the energies of other Si phases, one possibility is to choose a slightly smaller $\phi_0$ in our model, Eq. (6.2), to bring down the repulsive potential ($\phi$) of our model between the $E_{\text{rep}}$ curves of different structures, Fig. 6.17. This will not affect the thermal properties as no changes in the slope of $\phi$ will be made. Another possibility is to fit the bonding parameters of our model exactly to the Si electronic bandstructures, at different volumes, below the Fermi level. This will help to reproduce precise $E_{\text{bond}}$s for different structures and will bring their $E_{\text{rep}}$s on same curve, which can be fitted accurately. The model can be further tested for the Si structures as $\beta$-tin, clathrates and different nanostructures of Si.
6.6.2 Phonon DOS for silicene

We applied our model to the silicene which is 2D structure of Si. Our simple model is able to give a reasonable reproduction of the phonon dispersion for silicene, Fig. 6.18. The parabolic behaviour of the ZA phonon branch (flexural vibrational mode), occurring due to the 2D confinement, is also captured in our model. Moreover, the phonon bandwidth for silicene with our model is also determined correctly.

We also checked the performances of earlier models for calculating the phonon dispersion in silicene. The earlier short ranged GSP and KBS models either predict unstable structure or overestimation of phonon bandwidth. The long ranged and complex LER model is not fitted to silicene structure and leads to negative phonon frequencies, predicting unstable silicene structure. The other long ranged WCH model predicts the phonon dispersion near to DFT but could not capture the phonons around the Brillouin zone centre in agreement to DFT.

6.7 Conclusions and outlook

In this Chapter, we presented a new tight binding model for Si focussed mainly on the correct prediction of thermal properties in Si. The bonding parameters in our model are obtained by fitting the bond integrals obtained from DFT downfolding procedure. Furthermore the bonding parameters at equilibrium are rescaled to...
capture correct DOS bandwidth for diamond Si. Then other parameters in our model are fitted only to the DFT calculated energy-volume curve for diamond Si. The model has less number of parameters and is kept short ranged with a cut-off between first and second nearest neighbour. We tested our model for the reproduction of energetics and applied to calculate the thermal properties for bulk Si. Our simple and short ranged model gives a good agreement of phonons, thermal expansion and thermal conductivity with the DFT results. Our model also outperforms the earlier orthogonal TB models for the calculations of thermal properties.

The transferability tests of our model show that a simple, short ranged model with small parameter set could work for different structures of Si. The electronic density of states with our model for different structures of Si are comparable to DFT results. Moreover, our model correctly reproduces the phonons of silicene. The model could be optimised further to capture the energies and phonons of other structures with our model.
Chapter 7

Conclusions and future directions

7.1 Conclusions

The thermal transport study is important for the technologies such as thermoelectric generators and coolers, thermal barriers and heat management in the nanoelectronic devices. The performances of these nano-devices and the advancements in the technologies depend on the nanoscale thermal transport in their constituting materials. However, the thermal transport in nano-materials differ drastically as compared to the bulk. Moreover, different effects of a particular nanostructuring are seen on different materials. Therefore, a prior understanding of thermal transport in these nano-materials would be convenient to tailor their thermal properties, with particular nanostructuring, according to the application. This is achieved by theoretically investigating the thermal transport in materials.

However, the thermal conductivity simulations for nanostructured materials are unfeasible with \textit{ab initio} because of the required large simulation cells due to lack of symmetry. Use of simplified potentials provides an efficient way of calculating thermal conductivity of a material at larger length scales. However, the existing short ranged empirical models exhibit deviations of up to an order of magnitude for the thermal conductivity of pure materials, as compared to experiments, Fig. 2.1.\cite{1} Furthermore, not much work has been done on extending these potentials to alloys and nanostructures.

In this thesis, we developed simplified potentials for simulation of thermal properties of nanostructures. Furthermore, we also studied the effect of nanostructuring
on thermal conductivity of materials from first principles. For the determination of thermal conductivity, Boltzmann Transport Equation (BTE) for phonons was solved in relaxation time approximation (RTA). In RTA, the scattering rate for a phonon mode is considered to be independent of the perturbations to other phonon modes. Within this framework, precise understanding of scattering of each phonon mode is obtained. The effect of different scattering channels, due to nanostructuring, on the scattering rate of each phonon mode can also be calculated separately. Such a study provides important insights of the thermal transport behaviour of a material with particular nanostructuring, which could be beneficial to engineer material with desired thermal conductivity. The theory of this framework to calculate thermal conductivity is discussed in Chapter 3.

In Chapter 4, we developed a short ranged force constant model for the precise determination of the thermal properties of Si<sub>x</sub>Ge<sub>1−x</sub> random alloys. The parameters for our force constant model were extracted from DFT calculations with the effective contributions of long ranged interactions in our short ranged model parameters. Capturing long ranged interactions in our model helped to reproduce correct acoustic phonons which significantly contribute to the thermal properties. The model was tested for the thermal properties as thermal expansion, Grüneisen parameters and heat capacity for pure Si, Ge, and ordered structure of Si<sub>0.5</sub>Ge<sub>0.5</sub> using PHONOPY package. A good reproduction of anharmonic properties as Grüneisen parameters and thermal expansion was obtained with our model, which indicates that thermal conductivity can also be calculated accurately with a short ranged model, Fig. 4.5. Furthermore, a good transferability of our model was confirmed by applying it to the different compositions of Si<sub>x</sub>Ge<sub>1−x</sub> random alloys, Fig. 4.7. This simple model thus confirms the possibility of having a short ranged potential for calculating the long ranged interactions to correctly reproduce the thermal properties of complex structures.

For the thermal conductivity determination based on the BTE-RTA formalism, we used a new computer program as an extension to PHONOPY, developed in collaboration with Prof. Atsushi Togo. We studied the thermal transport in nanostructured zinc-chalcogenides which crystallise in the similar structure as Si and Ge, presented in Chapter 5. Furthermore, zinc-chalcogenides show interesting thermal conductivity cross-over at nanoscale. We carried out full ab initio study to understand this cross-over behaviour in detail. The isotope and grain boundary, along with anharmonic scattering, were considered in our calculations and the
effect of nanostructuring on thermal conductivity was studied by understanding
the contributions of different mean free path (MFP) phonons at nanoscale in zinc-
chalcogenides. We found that origin of both the thermal conductivity cross-over
for ZnS and ZnSe at nanoscale and higher bulk thermal conductivity of ZnS is the
large contribution of long MFP phonons in ZnS which are scattered strongly with
nanostructuring, Fig. 5.6. The acoustic-optic phonon gap in ZnS, which arises
due to mass difference of constituting elements, gives birth to these long MFP
phonons in ZnS, in contrast to ZnSe and ZnTe. Moreover, our ab initio study
showed the thermal conductivity cross-over at larger grain size of ~100-200 nm as
compared to 30 nm predicted by earlier model, Fig. 5.6.[135] We also found the
thermal conductivity to be half of the earlier model predictions for ZnS at 100nm
grain size which could be technologically important.

The boundary scattering, in Chapter 5, was calculated within an empirical model
due to the computational expenses associated with explicit ab initio calculations
for nanostructures. Considering this challenge and inspired by the performance of
short ranged model for thermal properties of Si$_x$Ge$_{1-x}$ random alloys in Chapter 4,
we have developed a tight binding (TB) model for Si, presented in Chapter 6. TB
models take into account the quantum bonding information of a material by mod-
eling its orbital interactions. We reviewed earlier short and long ranged orthogonal
TB models for Si and analysed their performances for calculating thermal expan-
sion and thermal conductivity. These earlier TB models were fitted for the correct
determination of energetics and showed some deviations for thermal properties.

Hence we modelled a new short ranged and simple orthogonal TB model for ther-
mal properties of Si. The bond integrals were derived from DFT using a downfold-
ing procedure.[89] Furthermore, a simple functional form, as proposed by Goodwin
et al[145], was used for bonding and repulsive terms. The model parameters were
obtained by fitting only to potential energy for diamond Si. The model calculated
Si thermal expansion, Fig. 6.11, and thermal conductivity, Fig. 6.12, gave a good
agreement with DFT results and showed improvement over the earlier orthogonal
TB models for Si. Our model also exhibited transferability to electronic proper-
ties of different structures of Si, Fig. 6.13 . Deviations from DFT for the binding
energy curves of different structures of Si were found with our model which would
indicate the need to further optimise our model. However, the phonons for 2D
structure of Si (silicene) calculated with our model showed a very good agreement
with DFT, Fig. 6.18. Thus our short ranged model fitted to small dataset reproduces the energetics and thermal properties of diamond Si. Moreover, it also exhibits transferability to some other structures of Si.

### 7.2 Future directions

The future directions of this thesis includes the application of our developed models for materials simulations at larger length scales. Furthermore, our models could also be extended for improving their performances. The force constant modelling scheme, presented in Chapter 4, parameterised the second order force constant matrices which are used to obtained the thermal properties in harmonic and quasi-harmonic approximations. However, the calculation of thermal conductivity requires determination of higher order force constants which needs to be modelled. Considering the sparseness of third order force constants matrix, a new mathematical algorithm called Compressive Sensing (CS), could serve beneficial.\[128\] CS is a recently developed algorithm in the field of signal processing and is finding interest in material science field as it requires few number of samples to reproduce a signal correctly. Thus the short ranged models, based on CS technique, can be developed to reproduce anharmonic force constants for the efficient and accurate calculations of the thermal conductivity of different nanostructures.

For the case of our TB model for Si, presented in Chapter 6, our model could be extended to correctly predict the energetics of other structures of Si. This includes the prediction of stable phase of \(\beta\)-tin Si with our model. Thus the next step would be to try out different strategies for fitting our model to the energetics of different structures of Si and testing it for stable Si structures as \(\beta\)-tin and clathrates.

The molecular dynamics (MD) studies at larger length scales can also be performed efficiently for bulk Si as well as silicene with our model. Furthermore, with the improvement in transferability of our model to other structures, one can do MD studies for thermal conductivity of different nanostructures.

One more future perspective would be to develop an orthogonal TB model for Ge following the similar modelling strategy as used for Si TB model, presented in Chapter 6. This will help to study the thermal transport in Si-Ge random alloys as well as in various other Si-Ge nanostructures at larger length scales.
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