Nanostructures and Alloys: Multiple Scattering and Nonlinearities in Phonon Transport

by

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Understanding how thermal transport is affected by disorder is crucial to the prediction and engineering of novel materials suitable for thermoelectric and device applications. Ab initio methods have demonstrated accurate calculations of the lattice contribution to thermal conductivity in semiconductors and dielectrics. Effective field theories and scattering theory have been combined to model alloys and systems with embedded nanostructures. The simplest of such effective field theories, the Virtual Crystal approximation, fails to capture short-length scale information due to the inherent coarse graining of the approximation. Additionally, these methods do not take multiple scattering effects into account. In order to address these issues, Green’s function methods are developed to handle multiple scattering phenomena in systems with large numbers of impurities. Explicit calculations from the Green’s functions method are able to capture the deviation from the dilute alloy limit in disordered systems. Multiple scattering theory developed in this thesis allows for a more precise description of the interaction between phonons and nanostructures. The phonon Green’s function is computed from the dispersion relation obtained from Density Functional Theory. Multiple scattering theory predicts resonance scattering that is not accounted for in first order theory. Understanding how these resonances behave in large disordered systems yields insight into thermal transport in alloys. When impurities become closely spaced, the resonances couple and broaden over a range of frequencies that depends upon the strength of the coupling and the number of impurities. These resonant states become significantly coupled in silicon germanium alloys of concentrations over ten percent. Scattering rates, angle dependent scattering amplitudes, and local density of states calculations are subsequently performed for nanostructured germanium slabs embedded in a silicon host. The strong coupling between the densely packed system of impurities causes significant broadening over a wide range of phonon frequencies. The strong coupling highlights the importance of using Green’s functions to capture high frequency effects. Furthermore, scattering rate calculations as a function of frequency highlight the transition from the Rayleigh
regime to the geometric limit. Although approximations exist that describe the low and high frequency behavior, the transition between the two regimes requires multiple scattering theory. The lowest frequency peak in the nanostructure density of states corresponds to the transition frequency between the long and short wavelength asymptotic limits. Angle dependent scattering also provides insight into the transition between the Rayleigh and high frequency limits. The scattering phase functions exhibit isotropic scattering at long wavelengths, which are characteristic of the Rayleigh regime. As phonon frequencies increase, the scattering profile takes on a much more anisotropic profile reminiscent of interfacial scattering at frequencies away from the band edge. High frequency phonon scattering is reminiscent of particle scattering off of hard boundaries.

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Chapter 1

Introduction

The semiconductor revolution of the twentieth century has spurred the development of new devices and an understanding of physics at small length scales. A complete picture of thermal transport in the nanoscale regime is pertinent to technological progress. In dielectric and semiconductor materials, the heat is primarily transported by phonons, the fundamental quanta of lattice vibrations. The phonon picture manifests from a translationally symmetric crystal that can be modeled as a system of masses and springs. The phonons, which carry the heat, interact with other phonons, electrons, defects, impurities, and boundaries. A fundamental description of the aforementioned interactions is extremely nontrivial. Despite such difficulties, we know that thermal conductivity is governed by the dispersion, density of states, group velocity, and scattering rate contributions. Since the dispersion relation is the foundation of more involved thermal transport calculations, idealized dispersions, such as the Debye model, were initially used. While insight may be gained from such toy models, they do not do well to predict thermal properties in real solid-state materials with dispersion and complex crystal symmetries. The first step towards a complete description of thermal transport in real crystal structures therefore requires an accurate method to obtain phonon dispersion relations.
Initially, atomic vibrations were modeled by empirically fitted masses and springs in a crystal lattice. This model allows for simple harmonic oscillation; consequently, a dispersion relation can be obtained and compared against inelastic neutron scattering experiments. Equipped with a rudimentary description of harmonic phonon transport, it became possible to then include the effects of interactions. Without interaction, phonons would travel unperturbed, resulting in an infinite thermal conductivity. In isotopically pure crystals, deviations from the harmonic interatomic potential can be described in terms of phonon-phonon interactions. This anharmonicity is the primary source of thermal conductivity reduction in semiconductor and dielectric materials without significant impurities. Other important factors that affect thermal conductivity are the interactions with electrons, impurities, and defects. To make the description more complete, we could include the effects of these additional contributions in our model. These scattering mechanisms are all ultimately encoded in the relaxation time, \( \tau \), associated with each type of interaction. The unperturbed phonon dispersion is used in combination with the relaxation time to solve the phonon Boltzmann transport equation, which describes the distribution of phonons in a crystal lattice. The thermal conductivity of a crystal lattice can then be calculated as

\[
\kappa = \frac{1}{k_b T^2} \frac{V_{uc}}{8\pi^3} \sum_{\alpha} \int_{BZ} d\vec{q} \hbar^2 \omega_{\omega (q)}^2 v_{\alpha (q)}^2 \tau_{\omega (q)} n_0 (n_0 + 1)
\]

where \( \alpha \) denotes the polarization, \( n_0 \) represents the Bose-Einstein distribution, \( \vec{q} \) corresponds to the wave vector, and \( V_{uc} \) stands for the volume of the unit-cell. Unperturbed phonon dynamics are encoded in \( v_{\alpha (q)} \) and \( \omega_{\omega (q)} \), which stand for phonon group velocity and frequency, respectively.

Historically, the fitting parameters for the various relaxation times were empirically determined and compared to experimental measurements of thermal conductivity. The first successful attempt to reproduce Silicon lattice thermal conductivity
utilized empirical interatomic potentials as inputs into the dynamical equation governing phonon transport [2]. The phonon dispersion relation and the phonon-phonon scattering rates due to the anharmonic potential were obtained, providing accurate thermal conductivity calculations within the framework of the Boltzmann Transport Equation using the relaxation time approximation (RTA) [3] [4] [5] [6].

This empiricism, however, is not sufficient. An adequate model should be able to predict thermal properties described by the underlying interactions of the crystal lattice. We should be able to construct the interatomic potential, which governs phonon propagation, from theories that model fundamental interactions between electrons and nuclei. Although precise results were obtained, a first principles method for constructing the potentials was desired. Density Functional Perturbation Theory (DFPT) provided the means to construct such interatomic potentials free of fitting parameters; consequently, interatomic force constants were obtained, resulting in accurate thermal conductivity calculations for silicon and germanium [4]. This method was made more computationally efficient and allowed for a reproduction of the interatomic force fields were compared to molecular dynamics results [1].

The foundation of ab initio thermal transport methods opens up the avenue to search for materials with very specific thermal properties. As devices become smaller, heat generation becomes a significant problem. Materials with large thermal conductivity can be used to transport heat away from sources of thermal generation. Although diamond is the best three-dimensional conductor of heat, it is not economically viable. Ab initio methods have recently predicted high thermal conductivity in Boron Arsenide, which can hopefully provide a cheap alternative for device applications [7].

On the other end of the spectrum, the search for low thermal conductivity materials is motivated by the optimization of thermoelectric materials. Thermoelectric materials allow for the conversion of heat into electricity [8] [9] [10] [11] [12]. The efficiency of converting thermal energy to electrical energy is characterized by the
thermoelectric figure of merit \( ZT = \sigma S^2 T/k \) where \( \sigma, S, T, \) and \( k \) are the electrical conductivity, Seebeck coefficient, temperature, and thermal conductivity, respectively. The thermal conductivity can be decomposed into contributions from electrical and lattice vibrations. Since the thermal conductivity of semiconductor materials, the most promising candidates for thermoelectric application, is dominated by phonon transport, ab initio phonon methods that can predict materials with low lattice thermal conductivity are of utmost importance. Ultimately, DFT continues to exemplify its usefulness in the search for materials with improved performance.

Ab initio methods now allow us to begin modeling systems with nontrivial nanostructure. Since such methods have provided an accurate description of harmonic and anharmonic phonon transport, we are in a very good position to introduce increasing levels of complexity to our crystal structure. Such investigations into nanostructure is motivated by the additional thermal conductivity reduction that has been achieved through nanostructuring, surface roughening, and alloying [13] [14] [15]. Furthermore, low dimensional structures can enhance thermal conductivity reduction through boundary scattering and altered density of states, the most prominent examples being rough silicon nanowires with a large reported ZT improvement [16]. With the exception of boundary scattering, all of these essential examples of thermal conductivity reduction stem from enhanced phonon scattering due to mass disorder. By introducing mass disorder on various length scales, phonons are scattered over a wide range of frequencies [17]. Because of the strength of phonon scattering in alloys, the first traditional thermoelectric materials were alloys. Realizations of thermoelectric materials that can scatter phonons over a wide range of mean free paths have manifested in measured ZT values of up to 2.2 in PbTe [18]. Furthermore, mass disorder has been identified as the key proponent in thermal conductivity reduction in half-Heusler materials [19].

Now that accurate tools are at our disposal, we can begin to calculate the thermal
effects of mass disorder by replacing a host atom with an impurity. More explicitly stated, how are the phonons of an underlying crystal lattice scattered by heavier or lighter atoms? Previous treatments for modeling the effects of mass disorder were dependent upon phonon frequency regime. The interaction between long wavelength phonons and nanoparticles were treated using first order scattering theory [28]. High frequency phonon scattering is much simpler since it is frequency independent and only involves the size of the nanostructure. A scattering theory that provides a complete description across the entire phonon frequency spectrum should provide insight into the onset of high frequency effects.

Until recently, mass disorder was treated using first-order scattering theory, which corresponds to a phonon scattering off of a single impurity. This approximation ignores the interactions between different impurities. Multiple scattering theory, on the other hand, describes the effects of a phonon interacting with one impurity, propagating, and interacting with other impurities. Such multiple scattering processes can manifest in a phonon resonantly interacting between a localized system of impurities. Although the consequences of resonance states upon thermal transport have been discussed in literature, the fundamental description behind their manifestation was not provided. Instead, an empirically fitted Lorentzian function was used to describe these resonances [20].

Furthermore, multiple scattering theory provides a means to understand mass disorder that extends over an infinite crystal. In an infinite disordered system, phonon propagation is no longer ballistic. The path dependent nature of phonon propagation in a random lattice requires the framework of multiple scattering theory. Phonon interaction with the disordered lattice can manifest in localized phonon states as disorder strength is increased. The key characteristic of a strongly localized state is an exponentially decaying wavefunction as a function of distance [21]. Although Anderson’s analysis focused on electron transport in a random potential, the argument can
be extended to phonon propagation in a lattice with random mass disorder. Strong localization manifests in coherent forward scattering due to a disordered crystal lattice [22].

Modeling mass disorder in bulk materials requires a method to handle the infinite extent of the disorder. Scattering theory is, unfortunately, only good at tackling finite sized systems of impurities. Fortunately, the ab initio thermal conductivity calculation of silicon germanium alloys demonstrated the monumental success of modeling of bulk-disordered systems [23]. The calculation involved two key approximations, the Virtual Crystal Approximation (VCA) [24] [25] and first-order impurity scattering theory [26]. The VCA replaces the disordered crystal with an ordered crystal of one constituent atom; consequently, the VCA modifies the phonon frequencies and group velocities. The scattering due to mass disorder is accounted for in the relaxation time corresponding to scattering from the mass mismatch of a single atom.

 Concurrently, the inclusion of full-order scattering theory was investigated and applied to cluster effects in graphene [27]. The combination of the VCA and full-order scattering allowed for a more accurate description of nanostructures embedded in alloys [28] [29]. Unfortunately, the VCA neglects high frequency information due to the inherent nature of a mean-field description. By washing away the short length scale information, high frequency phonons will ultimately behave markedly different in the presence of an averaged interatomic potential. The VCA ultimately failed to reproduce the thermal conductivity of PbSeTe alloys for a wide range of concentrations [30]. This failure creates questions regarding the validity of the assumptions underlying the VCA and its incusion of mass disorder. Were the high frequency discrepancies the culprit? How much do local configurations contribute to transport? Are the impurities truly independent scattering centers?

To tackle some of these inherent problems with the VCA, intuition can be gained from explicit solutions of finite disordered systems. Qualitatively, full-order scatter-
ing theory encodes all possible interactions of unperturbed bulk phonons with some local (mass) or nonlocal (strain) disorder. The tool underlying these methods is the Green's function describing the ordered and disordered system. By calculating the Green's function of the disordered system within the scattering theory framework, phonon spectral information can be obtained. Since this information is valid at high frequencies, the discrepancies with the VCA can be more explicitly defined. Additionally, by looking at finite disordered systems, intuition can be gained by computing the phonon propagation within specific scattering channels through the system. Finding such impurity configurations that are beneficial or detrimental to thermal transport can aid in the understanding of alloyed semiconductors and dielectrics.

The ultimate goal of this thesis is to compute scattering rates in the framework of multiple scattering theory. The mathematical formalism allows for calculations of the interactions between phonons of an underlying crystal lattice and an arbitrary set of scattering centers due to mass mismatch. The second chapter introduces the mathematical formalism of Green's functions as solutions to Hermitian linear differential operators. Using full-order scattering theory, the perturbation and the unperturbed Green's function can be used to calculate scattering rates and density of states. The third chapter defines the eigenvalue problem derived from the Taylor expansion of the interatomic potential describing lattice vibrations. As a result, the phonon Green's function can be explicitly calculated. Local perturbations to the crystal lattice in the form of mass disorder are then provided a representation in the tight-binding Hamiltonian formalism. Combining these two pieces of information allow for the computation of phonon scattering rates from an arbitrary set of impurities. The fourth chapter briefly touches upon the goal of Density Functional Theory and the method in which interatomic force constants are extracted from the theory. The computational details to obtain phonon Green's functions are then provided.

With the theory and the computational methods defined, scattering rates and
density of states calculations for single, double, and triple impurity systems are calculated in the fifth chapter. Deviations from first order calculations demonstrate the significance of high frequency effects. The final chapter extends this computation to a much larger system of impurities. Density of states calculations are performed for a finite random domain of germanium impurities embedded in a Silicon host. Deviations at higher frequencies demonstrate some of the failings of the Virtual Crystal Approximation. Scattering computations are then computed for germanium nanostructures. Scattering rates and phase functions as a function of frequency illustrate the transition from long wavelength scattering to the short wavelength limit.
Chapter 2

Green’s Functions

2.1 Formalism

The mathematical foundations of quantum mechanics are grounded in an operator formalism described by a Hilbert Space. A Hilbert space is very similar to a traditional vector space in the sense that a notion of length can be defined, additionally, the basis of the space is complete. Unlike a standard Euclidean space, a Hilbert space can be infinite-dimensional; consequently, an integral representation is used to define the norm of the Hilbert space when it is infinite dimensional. When the Hilbert space is finite dimensional, the operators can be represented as matrices. The most important problems in quantum mechanics attempt to solve the eigenvalues of the Hamiltonian, a Hermitian operator. The previous statement can be canonically stated as,

\[ \hat{H} |\psi\rangle = E |\psi\rangle \]  

(2.1)

where \( \hat{H} \) is a Hamiltonian operator, \( E \) is a real scalar, and \( |\psi\rangle \) is an eigenvector in Hilbert space. The set of eigenvalues of the Hamiltonian is known as the spectrum of the operator. The spectrum of the Hamiltonian can also be described by the solution
where $z$ number in the complex plane. Physically, the Green's function can be interpreted as the impulse response to a point source disturbance at $r'$. Since we are dealing with linear differential equations, a general solution can be constructed from a superposition of impulse responses. Hermitian differential operators have real eigenvalues. Since phonons are solutions to such Hermitian operators, their frequencies will consequently be real valued. As a result, phonon propagation is described by a Green's function with real valued $z$. In the operator formalism, this equation can be solved as,

$$G(z) = \frac{1}{z - H}$$

(2.3)

The representation of the Green's function in the basis of the eigenvectors of the Hamiltonian is then,

$$G(z) = \sum_n \frac{|\phi_n\rangle\langle\phi_n|}{z - \lambda_n} + \int dc \frac{|\phi_c\rangle\langle\phi_c|}{z - \lambda_c}$$

(2.4)

where $|\phi_n\rangle$ is the eigenvector, $\langle\phi|$ is its conjugate transpose, and $\lambda$ is the corresponding real-valued eigenvalue. The decomposition into sum and integral terms corresponds to the fact that a Hermitian differential operator can have discrete and continuous spectrum of eigenvalues. The summation is over the discrete eigenvectors and eigenvalues whereas the integral corresponds to the continuous spectrum of eigenvectors and eigenvalues. The spatial representation can then be defined as,

$$\langle r | G(z) | r' \rangle \equiv G(r, r'; z) = \sum_n \frac{\phi_n(r)\phi_n^*(r')}{z - \lambda_n} + \int dc \frac{\phi_c(r)\phi_c^*(r')}{z - \lambda_c}$$

(2.5)

Thus, these Green's functions are described by a sum of simple poles. The Green's functions are non-analytic on the real axis due to the zero in the denominator. In
order to define the Green's functions on the real axis, a limiting procedure must be defined in order to make the problem analytic. From this point forward, \( z \) is now represented by the real number \( \lambda \) because of the aforementioned real frequency solutions. Defining,

\[
G^\pm(r, r'; \lambda) \equiv \lim_{\epsilon \to 0^\pm} G^\pm(r, r'; \lambda \pm i\epsilon)
\]

and,

\[
\lim_{\epsilon \to 0^\pm} \frac{1}{x \pm i\epsilon} = P \frac{1}{x} \mp i\pi\delta(x)
\]

where \( P \) corresponds to the Cauchy Principle Value

\[
\lim_{\epsilon \to 0^+} \left[ \int_a^{b-\epsilon} f(x) \, dx + \int_{b+\epsilon}^c f(x) \, dx \right]
\]

the new definitions can be written in the spatial representation as,

\[
G^\pm(r, r'; \lambda) = P \sum_n \frac{\phi_n(r)\phi_n^*(r')}{\lambda - \lambda_n} \mp i\pi \sum_n \delta(\lambda - \lambda_n)\phi_n(r)\phi_n^*(r')
\]

In a physical context, the summation,

\[
\sum_n \delta(\lambda - \lambda_n)
\]

counts the number of states with an eigenvalue of \( \lambda \). Thus the imaginary part of the diagonal elements, \( G^\pm(r, r; \lambda) \), corresponds to the density of states of the Hamiltonian operator at a given energy or frequency. Additionally, when solving the differential equation

\[
[z - H(r)]u(r) = f(r)
\]

the Green's function serves as the kernel of the solution,

\[
u(r) = \int G^\pm(r, r'; \lambda) \, f(r') \, dr' + \phi(r)
\]
where \( \phi(r) \) is the homogenous solution. From this form, one can get a physical interpretation of the Green's function. The Green's function acts as a propagator that couples the degrees of freedom in the spatial representation. In the context of quantum mechanics, \( G^+(r, r'; \lambda) \) describes the probability of some state with energy \( \lambda \) to transition from \( r' \) to \( r \).

### 2.2 Perturbation Theory

When the solutions to a Hamiltonian are known, small deviations in the system can be analyzed using perturbation theory. The Hamiltonian can be separated as,

\[
H = H_0 + V
\]

(2.13)

where \( H_0 \) and \( V \) are the unperturbed and perturbed part of the Hamiltonian, respectively. Under the assumption that the eigenvalues and eigenvectors of \( H_0 \) are known, the Green's function can be described in terms of the unperturbed Green's function and the perturbation. Defining,

\[
G_0(z) = (z - H_0)^{-1}
\]

(2.14)

and,

\[
G(z) = (z - H)^{-1}
\]

(2.15)

\( G(z) \) can be written as,

\[
G(z) = [1 - G_0(z)V]^{-1}G_0(z) = G_0 + G_0VG_0 + G_0VG_0VG_0 + ... 
\]

(2.16)
A new operator called the t-matrix is now introduced as

\[ T(E) = V G(E)(E - H_0) \]  \hspace{1cm} (2.17)

Using the previous expression for the perturbed Green's function, the t-matrix can be written as

\[ T = V + V G_0 V + V G_0 V G_0 V + ... = (1 - V G_0)^{-1} V \]  \hspace{1cm} (2.18)

Conversely, the perturbed Green's function can be expressed as

\[ G = G_0 + G_0 T G_0 \]  \hspace{1cm} (2.19)

To see how the t-matrix and Green's function can be used as powerful tools, consider the time-independent Schroedinger equation,

\[ (E - H_0) \psi = V \psi \]  \hspace{1cm} (2.20)

and the solution,

\[ \psi^\pm = \phi + G_0^\pm (E) V \psi^\pm \]  \hspace{1cm} (2.21)

where \( \phi \) is the unperturbed solution. Iterating the above solution allows for an expression purely in terms of the unperturbed eigenket,

\[ \psi^\pm = \phi + G_0^\pm V \phi + G_0^\pm V G_0^\pm V \phi + ... = \phi + G_0^\pm T^\pm \phi \]  \hspace{1cm} (2.22)

Additionally, the relationship between perturbed and unperturbed eigenkets are related through the t-matrix,

\[ T^\pm \phi = V \psi^\pm \]  \hspace{1cm} (2.23)
2.3 Scattering Theory

Scattering theory uses the perturbative treatment described in the previous section and applies it to time-dependent solutions to partial differential equations. Consider the time-dependent Schrödinger equation,

\[(i\hbar \frac{\partial}{\partial t} - H_0) |\psi(t)\rangle = V(t) |\psi(t)\rangle \] (2.24)

with the solution,

\[|\psi(t)^\pm\rangle = |\phi(t)\rangle + \int_{-\infty}^{\infty} dt' g_0^\pm (t - t') V(t') |\psi^\pm (t')\rangle \] (2.25)

Expanding this result in terms of the original unperturbed time-dependent wavefunction, \(\phi(t)\) is known as the Dyson Series. In compact notation, a general operator known as the S-matrix is defined,

\[|\psi^+(t)\rangle = S(t, t_0) |\phi_n\rangle \] (2.26)

In a more physical context, the S-matrix describes the behavior of an excitation coming from far away, interacting with a perturbation, and then propagating away from the disturbance. The probability amplitude of a transition between state \(n\) to state \(m\) as a result of a time-independent perturbation reduces to,

\[\langle \phi_m | S | \phi_n \rangle = \delta_{mn} - 2\pi i \delta(E_n - E_m)[\langle \phi_m | V | \phi_n \rangle + \langle \phi_m | V G_0^+ (E_n) V | \phi_n \rangle + ...] \] (2.27)

Which can be expressed even more compactly as

\[\langle \phi_m | S | \phi_n \rangle = \delta_{mn} - 2\pi i \delta(E_n - E_m)[\langle \phi_m | T^+ (E_n) | \phi_n \rangle] \] (2.28)
This result is used to calculate the scattering rate from an initial state to a final state [31],

\[ W_{mn} = \frac{2\pi}{\hbar} |\langle \phi_m | T^+ (E_n) | \phi_n \rangle|^2 \delta(E_m - E_n) \]  \hspace{1cm} (2.29)

Which, when taken to first order in the t-matrix, is the widely used Fermi’s Golden Rule. By integrating over all of the possible final states, the cross-section of the interaction can be calculated using the Optical Theorem in the momentum representation [32],

\[ \sigma = \frac{2\Omega}{v_g} \text{Im} \{ \langle k | T^+ | k \rangle \} \]  \hspace{1cm} (2.30)

where \( v_g \) is the phonon group velocity, and \( \Omega \) is the volume of the normalization of the phonon wavevector in the momentum state \( |k\rangle \).

The optical theorem states that the imaginary part of the forward scattering amplitude can be used to determine the cross-section of the interaction. This greatly simplifies calculations since the summation over final momentum states can be very costly and possibly divergent if the momentums are unrestricted. Now that the formalism is described, it is important to emphasize the significance of computing the unperturbed Green’s function. Once the Green’s function is known and the perturbation in the system is well defined, the t-matrix can be calculated in order to determine differential cross sections and scattering rates. This allows for an analysis of energy and angle dependent scattering. In the next chapter, the representation of the phonon wavefunction, the perturbation to the system, and the methods to compute the unperturbed Green’s function will be defined and discussed.
Chapter 3

Phonon Dynamics

3.1 Atomic Motion

The description of phonon dynamics begins with an analysis of the potential energy stored in a crystal lattice due to atomic displacements. The Taylor expansion of the potential energy $V$ in terms of the atomic displacement yields the expression [33],

$$V = V_0 + \sum_{\mathbf{lb}, \alpha} \frac{\partial V}{\partial u_\alpha(\mathbf{l}b)} u_\alpha(\mathbf{l}b) + \frac{1}{2} \sum_{\mathbf{lb}, \mathbf{l}b', \alpha, \beta} \frac{\partial^2 V}{\partial u_\alpha(\mathbf{l}b) \partial u_\beta(\mathbf{l}'b')} u_\alpha(\mathbf{l}b) u_\beta(\mathbf{l}'b') \quad (3.1)$$

$$+ \frac{1}{3!} \sum_{\mathbf{lb}, \mathbf{l}b', \mathbf{l}b'', \alpha, \beta, \gamma} \frac{\partial^3 V}{\partial u_\alpha(\mathbf{l}b) \partial u_\beta(\mathbf{l}'b') \partial u_\gamma(\mathbf{l}''b'')} u_\alpha(\mathbf{l}b) u_\beta(\mathbf{l}'b') u_\gamma(\mathbf{l}''b'') + \ldots$$

The vector $\mathbf{l}$ labels the unit cell of the atomic displacement while the vector $\mathbf{b}$ designates the basis atom within the unit cell. The spatial degree of freedom is denoted by the subscript $u_\alpha$. When the crystal structure is in equilibrium, the first derivative of the potential energy is zero. The $n^{th}$ derivative corresponds to force constants that couple $n$ degrees of freedom. When one considers simple harmonic oscillation, the third-order and higher terms are zero and the form of the equation can be interpreted as Hooke’s law. The potential energy function can then be expressed as a system of
coupled oscillators. The second derivative is rewritten as the force constant

$$\Phi_{\alpha\beta}(l_b, l_1b') = \frac{\partial^2 V}{\partial u_\alpha(l_b) \partial u_\beta(l_1b')} \quad (3.2)$$

To second order, the potential energy can be expressed more compactly as

$$V = V_0 + \frac{1}{2} \sum_{l_b, l_1b'} \sum_{\alpha\beta} \Phi_{\alpha\beta}(l_b, l_1b') u_\alpha(l_b) u_\beta(l_1b') \quad (3.3)$$

The equations of motion of the degrees of freedom of the system can be written in the standard form

$$m_\beta \ddot{u}_\alpha(l_b) = -\sum_{l_1b'\beta} \Phi_{\alpha\beta}(l_b, l_1b') u_\beta(l_1b') \quad (3.4)$$

Since a crystal lattice exhibits translational symmetry, the equations of motion only depend on the relative position of the two coupled degrees of freedom. This allows for a generalized Fourier decomposition of the atomic displacements,

$$u_\alpha(l_b) = \frac{1}{\sqrt{m_b}} \sum_q U_\alpha(q, b) exp[i(q \cdot l_b - \omega t)] \quad (3.5)$$

Defining the dynamical matrix as the Fourier transform of the force constants,

$$D_{\alpha\beta}(b, b' | q) = \frac{1}{\sqrt{m_b m_{b'}}} \sum_{l_1b'} \Phi_{\alpha\beta}(0b, l_1b') exp[iq \cdot l_1b'] \quad (3.6)$$

The equation of motion reduces to the standard eigenvalue equation [34],

$$\omega^2 U_\alpha(q, b) = \sum_{b'\beta} D_{\alpha\beta}(b, b' | q) U_\beta(q, b') \quad (3.7)$$

Because the equations of motion are diagonalizable, the coupled degrees of freedom can be decomposed into a set of uncoupled vibrational modes with a dispersion relation for each branch.
The dynamical matrix is a Hermitian operator, therefore a Green's function can be defined using the eigenmodes and dispersion relations. The time-independent Green's function in operator form can be expressed as,

$$G(z) = \sum_k \frac{|k\rangle\langle k|}{z - \omega^2(k)}$$

(3.8)

where $|q\rangle$ is the phonon wavevector with momentum $q$. For the purposes of calculations, the position representation of the Green's function, in integral form, is written as,

$$G(l, m; z) = \frac{\Omega}{N(2\pi)^d} \int_{BZ} dq \frac{\exp[iq \cdot (1 - m)]}{z - \omega^2(q)}$$

(3.9)

where $N$ is the number of states normalized by the volume $\Omega$ in dimension $d$. Once the unperturbed Green's function has been calculated using the aforementioned methods, the t-matrix formalism allows for frequency and angular dependent scattering rate calculations. The last object to be defined is the perturbation $H_1$. In order to provide the details of the construction of this perturbation, the tight-binding Hamiltonian will be used because of its convenient position representation.

### 3.2 Tight Binding Hamiltonian

The Hamiltonian describing the energy of a crystal lattice can be represented by the tight-binding model. This model indexes each atomic site by a state $|m\rangle$. The tight-binding Hamiltonian can be written as,

$$H = \sum_l |l\rangle \epsilon_l (l) + \sum_{lm} |l\rangle V_{lm} |m\rangle$$

(3.10)

The first term corresponds to an on site energy while the second term determines a coupling between lattice sites. Due to translational symmetry, the on site energy is identical at all sites with the same basis atom. Additionally, the coupling matrix
element only depends on the relative position of lattice sites.

To draw the relationship between the tight-binding Hamiltonian and the dynamical matrix, the general on-site energies and coupling elements will be defined in terms of the second-order force constants. Additionally, since the tight-binding Hamiltonian indexes by lattice sites, it is convenient to decompose the lattice representation in terms of the components of the lattice vectors for calculation purposes. Adding a subscript \( \epsilon_{ibn} \) denotes the on-site energy projected onto the lattice vector components. The on-site energy can then be written as,

\[
\epsilon_{ibn} = \sum_{l'} \Phi_{aa} (ib, l'b) \quad (3.11)
\]

while the coupling matrix elements are defined as,

\[
V_{ib,mb'} = \Phi_{\alpha\beta} (ib, mb') \quad (3.12)
\]

The new indices allow for spatial decomposition and the inclusion of a crystal with a basis. From this description, Fourier decomposition and translational symmetry allows for diagonalization identical to the method shown above. With the analogy drawn between the dynamical matrix and the tight-binding Hamiltonian, localized perturbations can be defined and used to calculate the perturbed Green’s function.

### 3.3 Mass Difference Perturbation

Impurities introduced to a bulk crystal scatter phonons elastically and contribute to thermal conductivity reductions. The impurity can be modeled as a perturbation to the bulk tight-binding Hamiltonian,

\[
H = H_0 + V \quad (3.13)
\]
where the unperturbed term is expressed in terms of the aforementioned objects,

\[ H_0 = \sum_l |l\rangle \varepsilon_l \langle l | + \sum_{lm} |l\rangle V_{lm} \langle m | \]  

(3.14)

Since perturbations to force constants have a small (< 10%) effect on thermal conductivity in silicon germanium alloys due to the large mass difference between silicon and germanium atoms [25], only mass difference perturbations will be considered in this work. The perturbation lies in the diagonal elements of the tight-binding Hamiltonian,

\[ V = \sum_l |l\rangle \Delta m \omega^2 \langle l | \]  

(3.15)

The perturbation arises because the eigenvalue of the dynamical matrix is \( m \omega^2 \), therefore a local mass mismatch will alter the eigenvalue by \( \Delta m \omega^2 \). The summation runs over the sites in which the host atom is replaced by an impurity. The spatial representation of the t-matrix can be computed as,

\[ \langle l | T(\omega^2) | m \rangle = \langle l | V | m \rangle + \sum_{ij} \langle l | V | i \rangle \langle i | G(\omega^2) | j \rangle \langle j | V | m \rangle + \sum_{ikmn} \langle l | V | i \rangle \langle i | G(\omega^2) | j \rangle \langle j | V | k \rangle \langle k | G(\omega^2) | n \rangle \langle n | V | m \rangle + ... \]  

(3.16)

Because the perturbation \( V \) is local and diagonal, the t-matrix calculation only involves the degrees of freedom which are perturbed. Therefore, for an \( N \) impurity system, the t-matrix to be calculated can be represented by a \( N \times N \) matrix. This formalism also allows for force constant perturbations due to an impurity subsystem. Such perturbations would contribute to the off-diagonal elements of \( V \) which corresponds to a coupling between impurities and host atoms or possibly other impurities depending on the distribution; consequently, the size of the t-matrix to be computed would depend on the nearest neighbor cutoff.

At this point, the formalism is definite enough to physically interpret the terms in
the t-matrix expansion. Consider a plane wave with crystal momentum $k$ propagating towards a domain which contains the impurity. The momentum representation of the first-order term

$$\langle k' | V | k \rangle$$

(3.17)

corresponds to the probability amplitude of a transition from state $k$ to $k'$ due to a single scattering effect. For a diagonal (local) perturbation, the connection to the Fourier transform can be understood through the spatial resolution of the identity,

$$\langle k' | V | k \rangle = \frac{1}{\Omega} \int \int dx \, dx' \langle k'|x \rangle \langle x|V|x' \rangle \langle x' | k \rangle = \int dx \, e^{i(k-k') \cdot x} V(x) = \tilde{V}(k-k')$$

(3.18)

Therefore, to first order, the momentum transition depends on the spatial Fourier transform of the perturbation. Since the t-matrix is diagonal, the solution can be interpreted as a superposition of spherical waves being scattered at every point of the perturbation. The interference due to the superposition of spherical solutions accounts for the diffraction patterns that arise in angular dependent scattering calculations.

Higher-order calculations include intermediate processes which complicate the interpretation. Consider a system with two impurities located close to each other. What are all the ways that these two impurities interact with each other? For two-scattering events, each atom will scatter the incoming wave. The scattered wave can then interact with the impurity again and scatter, or it can interact with the other impurity then scatter. The second-order term

$$\langle l | V | l \rangle \langle l | G(\omega^2) | m \rangle \langle m | V | m \rangle$$

(3.19)

describes a wave being scattered at site $m$, propagating to site $l$ and being scattered
again. By summing over all of the intermediate states, the term

$$\sum_{ij} \langle i V | i \rangle \langle j G(\omega^2) | j \rangle \langle j V | m \rangle$$

(3.20)

encodes all possible two scattering events. Furthermore, the \(n^{th}\) order term describes all possible \(n\) scattering events. The full t-matrix encompasses every possible combination of scattering events for a given set of impurities. For a multiple impurity system, the Green's function has off-diagonal elements that contribute to the off-diagonal elements of the t-matrix. These off-diagonal elements couple the degrees of freedom of the impurity subsystem. The extent to which the impurities are coupled dictates whether one can approximate a set of impurities as independent scattering elements. If the impurities are independent scattering elements, then the cross-section of the total impurity system can be decomposed as,

$$\sigma(\Delta m_1, \Delta m_2, \ldots) = \sigma(\Delta m_1) + \sigma(\Delta m_2) + \ldots$$

(3.21)

Because the perturbation breaks the translational symmetry, calculations of bulk material properties can be handled using different methods. Mean field theory uses an alternate approach by constructing a dynamical matrix from the weighted average of masses and force constants of the bulk/impurity system. The change in bulk material properties stems from a modified dispersion relation. At lower impurity concentrations, the relaxation time due to a single impurity is simply weighted by its concentration in the bulk crystal. This assumes that the impurities are, on average, spaced enough away that multiple scattering effects are not taken into consideration. In other words, terms beyond the first order approximation of the t-matrix are not taken into consideration. Even in single impurity calculations, terms beyond leading order contribute to corrections to the scattering rate.
Chapter 4

Computational Methods

Now that the mathematical formalism and objects of interest are well defined, they must be computed. The dispersion relation for a crystal structure must be determined to calculate the unperturbed Green’s function; consequently, the force constants of the dynamical matrix need to be found. Before the advent of high-performance computing, phonon dynamics were constructed using empirical force constants that would be checked against experimental dispersion relations measured by inelastic neutron scattering. Current methods use perturbation theory within the approximation known as Density Functional Theory (DFT) [35]. Since the many-body Schrödinger equation has a solution that may include strong correlation due to coulomb interactions, methods for exactly solving this system are intractable for \(10^{23}\) degrees of freedom. DFT alleviates the algorithmic burden by approximating the many-body wavefunction as a particle density function \(n(\vec{r})\). The energy functional to be minimized solves the ground state particle density [36],

\[
E[n] = T[n] + U[n] + \int V(\vec{r})n(\vec{r})d^3r
\]  \hspace{1cm} (4.1)

where \(T[n]\) is the kinetic energy, \(U[n]\) is the potential energy due to the lattice, and \(V(\vec{r})\) is the interaction energy. Since the particle density represents single particle
excitations, the subscript $s$ will be used. The single-particle potential can be written as,

$$V_s(\vec{r}) = V(\vec{r}) + \int \frac{e^2 n_s(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r' + V_{XC}[n_s(\vec{r})] \quad (4.2)$$

The second term represents the familiar coulomb interaction while the third expression is quantum mechanical in nature and reflects the correlation and exchange of identical fermions. DFT approximates the third term to various levels in complexity. The local density approximation (LDA) only considers $V_{XC}[n_s(\vec{r})]$ to be a functional of the density at a particular coordinate [36]. Higher-order approximations include the gradient of the density at a particular coordinate in a method known as the generalized gradient approximation (GGA) [37]. The second-order interatomic force constants are determined by calculating the energy shift of the ground state energy due to the displacement of two degrees of freedom. Decomposing the displacements, and hence the force constants, into Cartesian components allows for the construction of the dynamical matrix in the formalism previously described. Higher-order force constants can also be calculated through the perturbation of three or more atomic degrees of freedom [4]. It is easy to see how poorly this scales combinatorially as a function of the number of nearest neighbors.

With the dynamical matrix constructed from first principles, the dispersion relation is calculated and can be visualized in Figure 4.1. The density of states counts the number of states at a particular energy (frequency) normalized by the volume of the phonon momentum quantization. Since the dispersion relations that we consider are three-dimensional, the relationship is expressed as,

$$g(\omega) = \int_{BZ} \delta(\omega - \omega_k) d^3k \quad (4.3)$$

This equation can be interpreted as an integration constrained to the constant fre-
Figure 4-1: Left: Silicon density of states (green) and integrated number of states (purple). Right: Calculated Silicon phonon dispersion (lines) compared to experimental values (marks) [1].

Frequency surface determined by the dispersion relation of the crystal. Functions of the form

\[ F(\omega) = \int_{1BZ} f(k) \delta(\omega - \omega_k) d^3k \]  

(4.4)

define important spectral properties of solids. Equation (2.8) allows one to immediately see the relationship

\[ -\frac{1}{\pi} Im[G^+(1, m; \omega)] = \int_{1BZ} e^{i\mathbf{k}(1-m)} \delta(\omega - \omega_k) d^3k \]  

(4.5)

The diagonal elements of the Green’s function ultimately correspond to the density of states since \( f(k) = 1 \).

### 4.1 Tetrahedron Method

The constant frequency surface integration of (4.4) can be performed in various ways. Because the \( k \)-mesh that discretizes the Brillouin zone is between \( 20 \times 20 \times 20 \) and \( 40 \times \ldots \)
The constant energy surface will not intersect the mesh without considerable floating point round off. One popular method is to replace the delta function with a Gaussian of a user-selected width in order to guarantee convergence since the sum over each k-point is smeared out to more accurately represent a Brillouin integration.

In an interacting theory, an eigensolution at a given k-point has a relaxation time stemming from electron-phonon interactions, phonon-phonon interactions, impurity scattering, and defect scattering. These effects contribute to a diffusive broadening of the phonon spectrum. The broadening is usually modeled as a Lorentzian with a width corresponding to the lifetime of the mode. Many researchers justify Gaussian or Lorentzian broadening in Brillouin zone calculations to physically reflect the lifetimes of an interacting eigenmode.

The other popular method allows for interpolation between k-points in order to calculate the imaginary part of the Green's function. By decomposing a uniform \( N \times N \times N \) mesh of k-space into identical tetrahedrons, the constant frequency surface is represented as a plane in each tetrahedron [38]. This method has since been applied to calculating spectral properties of solids [39]. Since the eigenfrequency of each corner of the tetrahedron is calculated, the frequency along the edges of the tetrahedron are linearly interpolated. The constant energy surface is then constructed from the interpolated points along the edges of the tetrahedron. The integration over this surface is analytical and can be represented as a sum of weights at each k-point in the mesh,

\[
\int_{1BZ} f(k) \delta(\omega - \omega_k) d^3k = \sum_{\tilde{k}} w(\omega) f(\tilde{k})
\]  

(4.6)

The weights are only dependent upon the four eigenvalues corresponding to the corners of the tetrahedron. Additionally, this integration, which is computed using the RHS, can be represented as a sum over tetrahedrons rather than a sum over k points.

The phonon density of states can be calculated by setting \( f(k) \) equal to one. The Gaussian smearing method and the tetrahedron method are compared in Figure 4.2.
for the phonon density of states of silicon.

![Si Phonon Density of States](image)

Figure 4-2: Silicon phonon density of states using the Gaussian broadening (red) and the tetrahedron method (blue).

The tetrahedron method, for a given energy and k-point mesh, captures more crucial aspects of the Brillouin zone calculation. Since the width of the Gaussian smearing is a parameter that must be fine-tuned, it is hard to distinguish key features from the artifacts of the numerical method without greatly increasing the number of k-points. The tetrahedron method, however, is able to calculate the frequencies at which there exists a discontinuity in the density of states (van Hove singularity). The convergence of the density of states as a function of the k-mesh size is shown in Figure 4.3.

In order to justify future calculations, it is important to highlight the flaws of the tetrahedron method. At long wavelengths, the constant frequency surface is a sphere because the phonon dispersion is linear and proportional to the magnitude of the wave vector. Since the approximated constant-frequency surface is constructed from planes intersecting each tetrahedron, errors stem from the curvature of the actual surface. A correction factor to the weights due to this discrepancy is accounted for to leading order in electronic calculations near the Fermi energy [40]. This error is most severe when integrating around local minimums and maximums in eigenfrequency...
Figure 4-3: Silicon density of states using a 30x30x30 mesh (blue) and a 40x40x40 mesh (red).

because the number of planes that construct the constant frequency surface is small compared to its curvature.

As the surface integral being calculated moves away from the minimum, the error is considerably mitigated. The sample calculation

$$\int_{1BZ} f(\mathbf{k}) \delta(\omega - \omega_k) d^3\mathbf{k} = \int_{1BZ} \frac{1}{|\mathbf{k}|^2} \delta(\omega - \omega_k) d^3\mathbf{k}$$

(4.7)

is depicted in Figure 4.4 and highlights the flaws of the Gaussian and tetrahedron methods near the origin. Although this integral is definite at the origin since the measure $d^3\mathbf{k}$ converges faster than the inverse square term diverges, the Gaussian tails at the origin contribute to artificial divergences at non-zero frequencies. On the other hand, the curvature associated error around the origin causes an overestimation in the tetrahedron method. When the constant-frequency surface is outside of the first set of non-zero eigenfrequencies ($\sim 30 cm^{-1}$), the number of tetrahedron planes greatly increases and results in agreement with the Gaussian method at larger frequencies.
4.2 Green's Function Matrix Elements

By computing the density of states, the imaginary part of the Green's function is determined by multiplying by the constant of proportionality $\frac{1}{\pi}$. The analytical structure of the imaginary part of the Green's function is crucial to computing the real part. Since the eigenvalues of the Hermitian operator corresponds to poles on the real axis of the Green's function, the Green's function is analytic in the upper half plane. Let the function $\chi$ of the complex variable $\omega$

\[ \chi(\omega) = \chi_1(\omega) + i\chi_2(\omega) \]  

(4.8)
be analytic in the upper half plane. If $\chi_1(\omega)$ and $\chi_2(\omega)$ are real and $\chi(\omega)$ converges for large values of $\omega$, then the Kramers-Kronig relations relate

$$
\chi_1(\omega) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi_2(\omega')}{\omega' - \omega} d\omega'
$$

and

$$
\chi_2(\omega) = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi_1(\omega')}{\omega' - \omega} d\omega'
$$

The symbol $\mathcal{P}$ denotes the Cauchy principal value. The Kramers-Kronig relations thus allow for the real part of the Green’s function to be computed from its imaginary part [41]. Since the integration to get the real part is performed on a discretized frequency mesh, the Cauchy principal value can be approximated by adding a small imaginary term to broaden the contribution from the simple pole.

$$
\mathcal{P} \int_{-\infty}^{\infty} \frac{\chi_1(\omega')}{\omega' - \omega} d\omega' \approx \int_{-\infty}^{\infty} \frac{\chi_1(\omega')}{\omega' - \omega + i\epsilon} d\omega'
$$

The size of the imaginary part is about half of the size of the frequency mesh. The real part of the Green’s function for the TA1 phonon branch is computed using the Kramers-Kronig relations and the Hilbert transform, the numerical analog of the K-K relations included in various math packages. The comparison of both methods is shown in Figure 4.5.

Unlike the numerical Hilbert transform, the Kramers-Kronig relations accurately capture the asymptotic $\frac{1}{\omega^2}$ behavior of the real part of the Green’s function away from the band edges. The Hilbert transformed real part, on the other hand, causes an unphysical change of sign outside the band because of the finite bandwidth in the density of states.
Figure 4-5: Calculated real (red) and imaginary (blue) part of the Green’s function compared to the imaginary part calculated by a numerical Hilbert transform (green).
Chapter 5

Dilute Impurity Cross Sections

The simplest realization of impurity scattering is described by a single impurity system. The unperturbed Green’s function is obtained from the dispersion relation determined from DFT. The Green’s function and mass mismatch perturbation are then used to calculate scattering amplitudes, cross-sections, and relaxation times using the tight-binding Hamiltonian formalism. Since only one host atom is being replaced in the system, the scattering rates are governed by a scalar equation. In the tight-binding representation, the single impurity t-matrix can be written as

$$T = |1\rangle \frac{\Delta m \omega^2}{1 - \frac{\Delta m}{m} \omega^2 G_0(1, 1; \omega^2)} \langle 1|$$ (5.1)

The analytical structure of this equation highlights the importance of including higher-order terms in a t-matrix calculation. The geometric series allows for the denominator term to diverge when

$$\frac{\Delta m}{m} \omega^2 G_0(1, 1; \omega^2) = 1$$ (5.2)

Since the perturbed Green’s function can be written as

$$G = G_0 + G_0 |1\rangle \frac{\Delta m \omega^2}{1 - \frac{\Delta m}{m} \omega^2 G_0(1, 1; \omega^2)} \langle 1| G_0$$ (5.3)
it can be concluded that poles in the t-matrix correspond to poles in the perturbed Green's function. In order for a pole to exist, the diagonal element of the unperturbed Green's function must be real since any finite imaginary part will broaden the resonance. The t-matrix can therefore only have a pole outside of the band where the density of states is zero since this corresponds to a purely real unperturbed Green's function. Since phonon eigenfrequencies are positive valued, only lighter impurities can push the resonance outside the band to higher frequencies.

The impurity also causes a shift in the local density of states described by the relationship with the unperturbed density of states \( \rho_0 \),

\[
\rho(1, \omega^2) = \frac{\rho_0(1, \omega^2)}{|1 - \frac{\Delta m}{m} \omega^2 G_0(1, 1; \omega^2)|^2} \tag{5.4}
\]

Since the cross-section is

\[
\sigma \sim |\langle \phi_m | T^+(E_n) | \phi_n \rangle|^2 \sim \frac{(\Delta m \omega^2)^2}{|1 - \frac{\Delta m}{m} \omega^2 G_0(1, 1; \omega^2)|^2} \tag{5.5}
\]

it is easy to see that a resonance in the local density of states corresponds to resonant scattering at the same frequency. The relationship between the scattering rate and the cross-section is

\[
\tau^{-1} = v_g \sigma \rho \tag{5.6}
\]

where \( v_g \) is the group velocity and \( \rho \) is the impurity density. Using the optical theorem, the cross-section of a single impurity is calculated for various mass differences in Figure 5.1.

As the mass difference becomes heavier, the resonance in the density of states gets pushed to lower frequencies. It is easy to convince oneself of this by realizing that an infinitely massive atom should have a zero-frequency solution. The calculation in Figure 5.1 also highlights the discrepancy between the signs of the mass difference.
For a negative mass difference of 50 percent, i.e., a lighter mass, the local density of states gets pushed outward. The scattering cross-section begins to diverge near the band edge because the imaginary part of Green's function goes to zero outside the band.

In Tamura theory, the harmonic scattering rate due to mass disorder is

\[
\frac{1}{\tau} = \frac{\pi}{2} f(\Delta m)^2 \omega^2 D(\omega)
\]

(5.7)

where \(f\) is the concentration of impurities and \(D(\omega)\) is the phonon density of states [26]. The deviations from first-order (Tamura) scattering theory are depicted in Figure 5.2. In the long wavelength limit, the scattering rate obeys \(\omega^4\) scaling behavior. When multiple scattering effects become significant at higher frequencies, resonances from the denominator term in the t-matrix cannot be ignored. Such discrepancies are largest at frequencies around 4 THz. First-order theory also predicts a scattering
rate that is independent of the sign of the mass difference. This approximation is valid at long wavelengths but begins to diverge at frequencies around 1 THz when higher order terms contribute significant corrections [42].

A point impurity that only introduces mass disorder is the easiest perturbation to work with because the perturbation does not affect other degrees of freedom. Since the perturbation is diagonal, to first-order, the effects of each impurity will be additive. If one were to include a more physical perturbation that would also consider how the force constants change between the impurity and the host atoms, the frequency dependent cross-section would not show as pronounced of a resonance. The cross-section calculation would change from a scalar to a matrix equation. Due to the denominator term,

$$\frac{1}{1 - VG}$$

(5.8)

it becomes much more difficult to determine whether or not a resonance occurs.
However, the short-wavelength limit should exhibit a larger high frequency cross-section compared to the mass difference impurity because the perturbation couples to neighboring host atoms.

The scattering rate of (2.28) from one momentum state to another can be represented by an angular dependent phase function. Given some initial phonon momentum state, one can calculate the scattering rate as a function of azimuthal and polar angle. Because the current single impurity model is a scalar equation, there is no anisotropy in the angle dependent scattering rate because the phase terms associated with the initial and final phonon states reduce to unity. The isotropic scattering rate as a function of polar angle is shown in Figure 5.3. The introduction of a coupling term with finite size effects will induce small deviations from spherically symmetric scattering solutions. An intuitive way to deduce that there is no angular dependence upon mass difference scattering stems from the fact that the Fourier transform of the dirac delta function, which represents the perturbation at a single lattice site, is a constant value.

![Figure 5-3: Polar angle dependent scattering rate of a LA phonon (ω = 5.4THz) due to a single germanium atom.](image)
5.1 Multiple Independent Scatterers

As mentioned in the previous section, introducing multiple impurities becomes a much harder problem to gain intuition from due to the presence of multiple scattering effects. With multiple perturbations, the equations for the Green’s function and the \( t \)-matrix become matrix equations instead of simpler scalar equations. As a result, the approximation of reducing a system of impurities to independent scattering elements depends on the matrix elements of the \( t \)-matrix.

We will begin with the simplest example, the two-impurity system. Phonon scattering information is encoded in two 2x2 matrices, the perturbing Hamiltonian and the unperturbed Green’s function. The impurity atoms will have the same mass difference for reasons of symmetry. What then should dictate whether or not the system can be decomposed into two independent perturbations? From an algebraic standpoint, a reducible system can be rearranged into diagonal form. A diagonal form merely states that the different degrees of freedom are not (significantly) coupled. The equation can then be separated into independent scalar equations.

Since the perturbation matrix is diagonal, the only way to introduce coupling between the impurity degrees of freedom is through the off-diagonal elements of the Green’s function as depicted in (3.17). Since off-diagonal elements are only introduced in second-order and higher terms, this information is lost when Born’s approximation is used. Looking at the spatial representation of the phonon Green’s function in (3.9), the parameter that dictates the value of the off-diagonal elements of the Green’s function is the relative position between the two impurities.

In the long-wavelength limit, where the dispersion is isotropic, the relative position vector can be reduced to the magnitude of the distance between the impurities,

\[
G(r ; z) = \frac{\Omega}{N(2\pi)^d} \int_{1BZ} dq (4\pi q^2) \frac{exp[iq \cdot r]}{z - \omega^2(q)}
\]  

(5.9)
Although this integral is still not trivial, the oscillatory part of the function provides insight into the asymptotic values of the Green’s function for large $r$. As $r$ becomes large, the integral becomes increasingly oscillatory when one varies $q$; consequently, different infinitesimal portions of the integrand destructively interfere and cancel out. For large $r$, the Green’s function should approach zero. The physical argument makes sense if you recall that the Green’s function serves as the propagator of a solution to a partial differential equation. The probability amplitude for a wave function to transition to a state with great spatial separation should generally approach zero as the distance approaches infinity.

The long wavelength limit allows for intuition of the various terms of the $t$-matrix expansion. The second order term, $VGV$, corresponds to scattering at an impurity, followed by the propagation of the scattered wave, and finally a second scattering event. At large impurity separation distances, a scattered wave will be unlikely to propagate to the other impurity. This corresponds to a small leading order off-diagonal term. Since the second order term of the $t$-matrix is a function of inter-impurity spacing in the long wavelength limit, it can be thought of as the first moment of the distribution of impurities. The higher-order scattering terms capture the asymmetry of a set of impurities, in the same way that distributions can be described by mean, variance, skewness etc. The first-order term is merely the strength of the sum of the scattering elements, the second-order term includes a weighting dependent upon the spacing, while higher-order terms depend on how the various pairwise terms combine.

Now that we are equipped with a physical interpretation of the various terms in the $t$-matrix, we can begin to describe how phonons propagate in a disordered medium. The perturbed Green’s function can be written in terms of the $t$-matrix as,

$$G = G_0 + G_0 T G_0$$  \hspace{1cm} (5.10)
Recall that, in the spatial representation, the matrix elements $\langle x| G(\omega) |y \rangle$ describe the propagation of a phonon from site $x$ to site $y$. Rewriting the perturbed Green's function in the spatial representation,

$$\langle x| G |y \rangle = \langle x| G_0 |y \rangle + \sum_{mn} \langle x| G_0 |m \rangle \langle m| T |n \rangle \langle n| G_0 |y \rangle$$

we can see how higher order contributions due to scattering affect the propagation of a phonon. Not only must we consider how a phonon travels unperturbed from site $x$ to site $y$, we must also consider the propagation from $x$ to the impurity, which then scatters and propagates to $y$. Since the density of states has been previously related to the imaginary part of the Green's function, the diagonal elements of the perturbed Green's function

$$\langle x| G |x \rangle = \langle x| G_0 |x \rangle + \sum_{mn} \langle x| G_0 |m \rangle \langle m| T |n \rangle \langle n| G_0 |x \rangle$$

allow for calculations of the density of states in regions near a localized impurity. Following our analysis of the Green's function, the local density of states is a sum of the bulk density of states plus a correction due to scattering from the impurity region. For the single impurity limit, the local density of states (LDOS) at the impurity is proportional to the scattering rate. Since the mass difference of germanium is large enough to show significant resonance, there should be a corresponding resonance in the local density of states. Calculations of the local density of states for a germanium impurity and the nearest neighbor silicon atom is represented in Figure 5.4. Since the second term in (5.10) is so much larger than the first, the resonance dominates the local density of states. The resonant frequency is roughly 2.2 THz and coincides with the resonance in the scattering rate. The LDOS for the nearest neighbor silicon provides insight into the coupling between an impurity and its host crystal. The LDOS exists as a hybridization of the resonant state and the original silicon DOS.
As one moves further away from the impurity, the strength of the resonance becomes weaker and the LDOS starts to look more and more like the original band structure. By calculating the strength of the resonant state as a function of distance from the impurity, a length scale can be determined. This length scale describes the extent to which the germanium resonance diffuses into the crystal.

Although the coupling of the impurity subspace degrees of freedom are described by the off-diagonal t-matrix elements, what kind of calculable scalars can be used to see this degree of dependence? The scattering rate, which is related to the forward scattering amplitude through the optical theorem, serves as a reasonable quantity to compare multi-impurity systems with independent scatterers in the dilute limit. In Figure 5.5, the scattering rate of the sum of two-independent scattering elements is compared to a system of two impurities separated by a distance of about 10nm. The general overlap of the relaxation times across all frequencies of the two systems demonstrates the validity of decomposing the two-impurity system into a set of two
Figure 5-5: Scattering rate of two independent impurities (blue) compared to two impurities separated by 10nm (red).

Mathematically, this statement is expressed as,

$$\tau_{12}^{-1}(\omega) = \tau_{1}^{-1}(\omega) + \tau_{2}^{-1}(\omega) \forall \omega$$  \hspace{1cm} (5.13)

It should then be helpful to see when this decomposition is not valid. By spacing the impurities closer together, the off-diagonal Green’s function elements should become important. The scattering rate is again calculated for an adjusted inter-impurity spacing of 0.5nm and is compared to the independent limit in Figure 5.6. The discrepancy around the single impurity resonant frequency highlights the effect of strong coupling in the impurity subspace. Since the local density of states is proportional to the scattering rate, the resonance can be interpreted as an isolated impurity mode. As a result of the strong coupling, the resonance gets split into two peaks that are pushed above and below the resonant mode frequency. An analogy can be drawn from quantum mechanical two-level systems. If two originally degenerate eigenstates
become coupled, the degeneracy is lifted and the energy levels split. This notion is generalized in solid-state theory; quasicontinuous band formation stems from the coupling of many \((10^{26})\) degenerate eigenstates [43].

Although the coupling affects the frequencies near resonance most significantly, the long and short wavelength regimes can still be decomposed. With the extreme ends of the coupling regimes described, it is now appropriate to quantify the independence of each scattering element as a function of frequency and spacing. For the purposes of keeping the number of indices to a minimum, the cross-section, \(\sigma\), will be used in lieu of inverse relaxation time since they merely differ by a constant of proportionality. Defining a normalized correlation,

\[
C(\omega) = \frac{\sigma_{tot}(\omega) - \sum_{set} \sigma_{set}(\omega)}{\sum_{set} \sigma_{set}(\omega)}
\]  

(5.14)

allows for a representation of the regimes when a system is strongly or weakly cou-
pled (correlated). If the total cross-section is equal to the cross-section of the sum of individual impurities, the correlation will be zero. The sum over arbitrary subsets of impurities allows for a generalization of single impurity decomposability. For example, a distribution of impurities might not be able to reduce to single impurity systems, but there may exist clusters or impurities that are independent of one another. Independent clusters of impurities represent the rearrangement of the t-matrix into block diagonal form. Although we cannot ignore the coupling between the degrees of freedom within a particular cluster, one can ignore the coupling between different sets of clusters.

Moving back to the two-impurity system, the correlation as a function of frequency and spacing is calculated in Figure 5.7. Since the range of cross-sections lies between zero and infinite for a given frequency, the correlation is bounded below at negative one and unbounded above. The regime where the correlation is large and positive corresponds to the peak splitting behavior in the strong coupling regime.

Figure 5-7: Correlation of a two-impurity system. The y-axis is the phonon wavenumber. The x-axis is the spacing between the two impurities. The unit spacing is the lattice parameter (5.43Å) divided by four.
Since the mode splits to a lower frequency, the cross-section of the system will be much larger than the single impurity system. Since the higher frequency mode splitting is not pushed to high enough frequencies, the correlation still remains negative. The transition between large positive and large negative correlation values (dark red to dark blue) at small spacing corresponds to approximately the frequency of the single impurity resonance.

Because the correlation is both a function of frequency and spacing, a single length scale corresponding to the correlation length cannot be determined. The general functional behavior of the correlation for a fixed frequency is the combination of a monotonically decaying and oscillatory function. The monotonic decay stems from the interference in the integrand for asymptotically large spacing. The oscillatory behavior manifests from fact that the frequency is not large enough for complete destructive interference.

Although there are different correlation lengths for different phonon frequencies, this bulk calculation allows for the determination of a general spacing length where it is safe to say there exists negligible coupling between impurities for all frequencies. For the two impurity system, a spacing of 3nm or greater allows for the decomposition into independent scattering elements.

The large negative correlation for very small frequencies stems from the error around the Gamma point using the tetrahedron method. When there is a local minimum in the eigenvalue for a given k-point, the accuracy of an integral over a surface of constant frequency around such a minimum suffers. If the isofrequency surface lies between the minimum and the next lowest eigenvalue, the number of planes that construct the isofrequency surface will be at a minimum. The error stems from attempting to construct an ellipsoidal surface with only sixteen planes. As the isofrequency surface extends beyond the next highest eigenvalue, more planes are used to construct the surface, resulting in a smaller error. This can be seen in Figure 5.7 at
a frequency of about 30 cm$^{-1}$ where the function becomes well behaved. The lowest set of nonzero eigenvalues are about 26 cm$^{-1}$ which coincide with the previously described error reduction.

The negative correlation for frequencies above 185 cm$^{-1}$ causes an even larger discrepancy. Since we are dealing with acoustic phonons, the band edge corresponds to k-points on the edge of the first Brillouin zone. Constructing an isofrequency surface just below these local maximums corresponds to a partial ellipsoid that centers around a single point on the exterior of the discrete k-mesh. For frequencies close enough to the local maximum, the surface to be integrated will consist of at most half of the number of planes (16) that are used to construct the surface near the Gamma point. If the local maximum lies on a point of high symmetry, the number of planes used in the approximation will be even lower.

Looking within the range where the tetrahedron method is consistent, the oscillatory behavior of the correlation is dependent upon the frequency. In order to understand the oscillatory behavior for a given frequency, it is best to refer to (2.9). The terms that contribute most significantly to the integral are the k-points that are closest to the frequency of the Green's function. For acoustic phonons, the dispersion relation is monotonically increasing away from the Gamma point. Let us consider $G(1, \mathbf{m}; \omega^2)$ for a large value for $\omega$. The most significant terms in the integrand come from large wavevectors. Thus the resulting calculation is thus very sensitive to variation of the spacing parameter $(\mathbf{k} \cdot (1 - \mathbf{m}))$.

The general form of (5.12) allows for arbitrary decomposition of a distribution of impurities. The next example will introduce the evenly spaced, three impurity system. The scattering rate of three impurities with a spacing of 0.5nm is shown in Figure 5.8. The nonlinearity around the resonance is again the highlight of the strong coupling regime. As you can see, the scattering rate has three distinct peaks, one below the resonant frequency and two above. The peak formation is the three-
Figure 5-8: Scattering rate of three independent impurities (blue) compared to three impurities separated by 0.5nm (red).

impurity analog of the band splitting described earlier. The subsequent chapter will focus on how this resonant splitting is crucial to understanding systems with a large number of impurities.

With an additional impurity added, the system has two potential decompositions. For large spacing, it is safe to assume that all three impurities are independent of one another. The correlation for a decomposition into three independent impurities is computed in Figure 5.9. The functional behavior of this correlation is very similar to the two-impurity correlation. The main difference between both results is the magnitude of the correlation at small spacing and frequencies near the single impurity resonance. The largest correlation for the three-impurity system is four times larger than the maximum correlation in the two-impurity system. Although the third impurity affects the magnitude of the correlation, the oscillatory behavior remains unchanged.
The other potential decomposition assumes that the three impurities can be considered to be the sum of a pair of impurities and a single independent impurity. Because the distance between the impurities on opposite ends is twice as far as the nearest neighbors, this pair will not be considered in future calculations. Furthermore, since the phonon wavevector is perpendicular to the line of impurities, the decomposition is independent of which pair is chosen due to symmetry. The correlation for the 2+1 decomposition is shown in Figure 5.10. Although this decomposition still behaves poorly for small spacing and frequencies around the single impurity resonance, the correlation approaches zero quickly as the spacing is increased. This improved behavior of the correlation function stems from the fact that the coupling between the impurities on opposite ends is much weaker since they are twice as far apart.

The final correlation calculation will highlight the generalizability of this idea to larger structures. A square of nanoparticles in the x-y axis is constructed by placing the impurities at the corners of the square. The square has edge lengths of 0.5nm to ensure the impurities are strongly coupled to one another. Another identical square
of nanoparticles has the same coordinates in the x-y plane as the original structure while the z-coordinate is allowed to vary and governs the spacing between the two structures. Since the constituents of the individual squares are strongly coupled, the most reasonable decomposition of the two square system is into a sum of the individual squares. The correlation for square decomposition is calculated in Figure 5.11. The persistent correlation at higher frequencies highlights coherent scattering phenomena between the two structures. Frequencies above $160 \text{ cm}^{-1}$ show strong oscillatory behavior as a function of spacing. Analogous to the solutions of the wave equation in a box, the oscillatory correlations can be interpreted as standing waves resulting from the coupling of the two square nanostructures. The oscillations as a function of spacing represent the interference of scattered waves between the two squares.

When correlations are strong, one cannot say a system of impurities can be independently decomposed. The larger impurity structure is necessary in describing the propagation of phonons. If a system can be decomposed into simpler substruc-
tures, mathematically, this corresponds to the block-diagonalization of the t-matrix. For a system of $N$ impurities, scattering computations scale as $N^2$. Therefore, decomposition allows for tremendous reduction in computational effort. Correlation calculations can be used to construct an algorithm that can break a distribution of impurities into simpler clusters. If applied to an alloyed system where impurities are randomly distributed within a domain, determining whether or not such a distribution is decomposable corresponds to the coupling percolation.

The single impurity resonant state is crucial to understanding the two and three impurity systems. When impurities are close enough together, the resonance couples and the frequency splits into multiple modes which depends on the number of strongly coupled impurities. This coupling sheds insight into systems with a large number of impurities. What relevant systems have large number impurities? Alloys and nanostructures immediately come to mind. The following chapter will investigate the resonant coupling of impurities within silicon germanium alloys and germanium slabs embedded in a silicon host crystal.
Chapter 6

Large Systems of Impurities

Since large systems are generally intractable using perturbation theory, we will consider impurity systems that are limited by computational capability and use these results to infer information regarding the infinite system. As mentioned in the previous chapter, for an $N$ impurity system, scattering information is encoded in an $N \times N$ t-matrix that describes the transition of a phonon from one momentum state to another.

Using multiple scattering theory, we can begin to analyze how phonons propagate in systems with large mass disorder. Consider a binary alloy $A_xB_{1-x}$; one can imagine phonons bouncing around incoherently due to the randomly distributed constituent atoms. Because translational symmetry is broken, it is not necessarily valid to define wavevectors in such a crystalline system. The characteristic length over which coherence is maintained is known as the coherence length. The coherence length, which depends on alloy composition and its components, dictates the validity of replacing a disordered material with an ordered supercell [44]. By using calculations of an ordered supercell, translational symmetry is recovered, allowing for tremendous simplification due to Bloch’s theorem [45].

If we replace our disordered system with an ordered supercell, what configuration
most accurately describes phonon propagation? Given a supercell that is large enough to be considered valid for modeling the disordered crystal, within the disordered macroscopic crystal ($\sim 10^{26}$) there should exist all possible supercell configurations. We shall denote $\langle \rangle$ terms as configurationally averaged quantities. For a set of mass disorders $m_{R_i}$, two conditions allow for valid calculations of finite sized alloyed crystals [46]. Spatial homogeneity requires,

$$\langle m_{R_i} m_{R_j} \ldots m_{R_n} \rangle = \langle m_{R_i+a} m_{R_j+a} \ldots m_{R_n+a} \rangle$$  \hspace{1cm} (6.1)

while the vanishing of correlation requires,

$$\langle m_{R_i+a} \ldots m_{R_j+a} m_{R_k} \ldots m_{R_n} \rangle = \langle m_{R_i+a} \ldots m_{R_j+a} \rangle \langle m_{R_k} \ldots m_{R_n} \rangle$$  \hspace{1cm} (6.2)

as $|a| \rightarrow \infty$. If these two conditions hold, the extensive properties (energy, entropy, heat capacity etc.) are self-averaging. For a large enough sample, extensive property values can be uniquely defined and calculated, thus justifying the use of supercell techniques to model disordered infinite systems.

Despite the validity of the supercell calculation, large enough supercells have too many configurations to average over since the problem scales factorially. Further approximations might be necessary for the purposes of computational feasibility. The simplest approximation of a disordered material is known as the virtual crystal approximation (VCA) [24]. The VCA replaces the constituent components of the alloy with a one-component system that represents the average values of the original alloy. In electronic systems, the VCA averages over the one-electron potential. A pictorial representation of the VCA is depicted in Figure 6.1.

How is the VCA implemented in phonon band structure calculations? Abeles provided the first calculation using the VCA [25]. Analogous to the one-electron potential
averaging, the mass of one of the components of the virtual crystal is calculated as,

$$M = \sum_i M_i x_i$$  \hspace{1cm} (6.3)

where $M_i$ and $x_i$ are the atomic masses and fractional concentrations of the constituent component in the alloy, respectively. The size of the unit cell of the virtual crystal follows Vergard's law,

$$\delta = \sum_i \delta_i x_i$$  \hspace{1cm} (6.4)

where $\delta_i$ is the cube root of the volume of the unit cell of the constituent atom. Modern applications of the VCA use weighted averages over the interatomic force constants,

$$\Phi = \sum_i \Phi_i x_i$$  \hspace{1cm} (6.5)

in addition to Vergard's law. The VCA can be expressed very compactly through the tight-binding Hamiltonian formalism [31],

$$H_{VCA} = \sum_i H_i x_i$$  \hspace{1cm} (6.6)
where $H_i$ is the tight-binding Hamiltonian of one of the components. The VCA ultimately modifies the dispersion relation and group velocities. Since underlying scattering effects are not accounted for, an additional alloy scattering term,

$$\tau_i^{-1} = \sum_i \tau_i^{-1} x_i$$  \textbf{(6.7)}

is introduced to recapture some of the effects due to disorder. Calculations for the $\tau_i$ terms have traditionally used first order results from Tamura theory. Alloy scattering can also incorporate strain disorder which includes an adjustable parameter to empirically match experimental results [5]. Since multiple scattering effects are not included, deviations should be expected at higher frequencies that correspond to the single impurity resonant states.

The configurationally averaged Green’s function can be calculated from,

$$\langle G \rangle = G_0 + G_0 \langle H_1 G \rangle$$  \textbf{(6.8)}

Making the approximation

$$\langle H_1 G \rangle = \langle H_1 \rangle \langle G \rangle$$  \textbf{(6.9)}

and noting, for mass disorder,

$$\langle H_1 \rangle = \langle \Delta m \omega^2 \rangle$$  \textbf{(6.10)}

the perturbed Green’s function can be computed as

$$\langle G \rangle = G_0 + G_0 \langle \Delta m \omega^2 \rangle \langle G \rangle$$  \textbf{(6.11)}

The energy shift due to the VCA can be seen when the Green’s function is expressed
in reciprocal form,
\[
\langle G(m\omega^2) \rangle = \frac{1}{m\omega^2 - H_0 - \Delta m\omega^2}
\]  \hspace{1cm} (6.12)

which equals the unperturbed Green's function when the perturbation goes to zero.

This method allows for computationally effective density of states calculations that forgo the calculation of the dispersion relation.

### 6.1 Alloy Scattering

The density of states of $Si_xGe_{1-x}$ alloy is calculated for various germanium concentrations. Although the atomic mass of germanium is significantly larger (156%), the interatomic force constants are nearly identical. The similarity of the IFCs arises because the lattice constants of silicon and germanium are almost equal. The comparison of the density of states for 1 percent versus 44 percent germanium concentration is shown in Figure 6.2. Because the off-diagonal elements of the tight-binding Hamiltonian remain practically unchanged, increasing the mass of the virtual crystal atom merely shifts the band edges to lower frequencies by a factor of
\[
\frac{1}{[(1 - x)m_{Si} + xm_{Ge})]^{1/2}}
\]  \hspace{1cm} (6.13)

Since the bandwidth is decreased, the density of states scales upwards to ensure,
\[
\int_0^\infty D(\omega)d\omega = 1
\]  \hspace{1cm} (6.14)

The scaling of the density of states due to the VCA allows for an estimation of the group velocity as a function of concentration in the long-wavelength limit [47]. Using $D(\omega) \propto \frac{e^2}{m^*}$, if we define
\[
c \equiv [(1 - x)m_{Si} + xm_{Ge})]^{1/2}
\]  \hspace{1cm} (6.15)
then the rescaled density of states is

\[ cD_{si}(\omega) = \frac{(c^{-1}\omega)^2}{(Av_g)^3} = c^{-2}D_{si}(\omega)A^{-3} \]  

(6.16)

where \( A \) is the rescaling of the group velocity. We can see that

\[ v_{new} \propto v_g \frac{1}{[(1-x)m_{Si} + xm_{Ge})]^{1/2}} \]  

(6.17)

which works quite well to calculate the speed of sound of germanium (5400 m/s) from the speed of sound of silicon (8400 m/s) given a mass ratio of 2.586.

It now seems appropriate to highlight some of the key flaws of the VCA. Since we are attempting to compute self-averaged quantities such as the density of states and conductivity, is it valid to average non self-averaging quantities such as the on-site potential and the wavefunction? Although it is reasonable to average the diagonal
term associated with the mass of the atom at a given lattice site, the interatomic force constants in a real alloyed system depends upon the local configuration. By merely averaging the IFCs of each component without considering the perturbations due to local interactions with an impurity, there will exist deviations in the off-diagonal elements and the second diagonal term of the VCA Hamiltonian from the alloyed system. Since the force constants of silicon germanium alloys are nearly identical, this problem should not be too big of an issue, but it is useful to point this out before embarking on calculations with largely varying IFCs between the constituent components. To tackle more involved problems, cluster expansion techniques have been developed to expand the on-site interactions in terms of N-point functions [48] [49].

Explicit perturbed Green’s function calculations over a finite domain can give an understanding into how the VCA fails at higher frequencies. From a qualitative standpoint, the failure stems from the coarse-graining of the system. Coarse-graining ultimately ignores short length scale information associated with local configurations of a system. An explicit calculation should have agreement with the VCA in the long-wavelength limit. Features such as $\omega^2$ behavior of the density of states should be identical until high frequency multiple scattering phenomena become significant.

To construct the perturbed Green’s function for an alloy within a finite domain, it is assumed that the silicon crystal determines the underlying phonon transport. A domain of 282 atoms with a diamond cubic structure is generated to host the silicon germanium alloy. This domain allows for alloy as well as nanostructure Green’s function calculations. Each atomic site is associated with a coordinate in an array. Each coordinate is labeled from 1 to 282. For alloy calculations, an impurity concentration is given and a random number generator determines the positions in which the impurities are placed.

With the impurity coordinates chosen, the t-matrix is computed for the given
configuration. Using the t-matrix, the perturbed Green’s function can be calculated from (5.9). What relevant information should be extracted from this Green’s function? The local density of states provides intuition regarding the single impurity limit. Because the Green’s function near multiple impurities can be affected by neighboring resonances, the local density of states in the alloy depends heavily upon the local configuration of impurities. Since the dependence is nonlinear with regards to the number and distances between impurities, the best way to move forward is to take the local density of states calculation at every atomic site and average over the entire domain. In other words, the value to be computed is

$$\sum_{x \in D} \frac{1}{\pi} \text{Im} \left[ \langle x | G(\omega) | x \rangle \right]$$

(normalized by the size of the domain.)

The averaged density of states of the acoustic branches for an alloy concentration of one percent is given in Figure 6.3. The one percent concentration is low enough

![Figure 6-3: Alloy averaged density of states for TA1 (blue), TA2 (red), and LA (green) branches for a one percent alloy concentration.](image-url)
to consider the alloy to be in the dilute limit. Since the averaged density of states is a superposition of the resonant states and the silicon bulk, it can be concluded that the impurities are independent of one another. Although small, there is a resonance at 5 THz for the LA branch. The resonance is not (currently) significant because it is located far from the band edge. Increasing the concentration further should introduce significant coupling between impurities as described in the previous chapter.

Figure 6.4 presents the density of states of the acoustic branches for ten percent alloy concentration. The ten percent concentration is clearly a departure from the dilute limit. The effects of the impurity resonance state have broadened over a wider range of frequencies. The LA branch, which did not have significant deviations from the silicon limit for one percent concentration, now has fluctuations in the density of states between three and seven THz. In the high frequency regime near the band edges, the density of states retains the structure from the bulk silicon values. Although similar, the peaks in the DOS at high frequencies are of a lower magnitude because many

Figure 6-4: Alloy averaged density of states for TA1 (blue), TA2 (red), and LA (green) branches for a ten percent alloy concentration.
of the original states have been shifted to lower frequencies due to the germanium resonance.

By choosing a concentration that has almost an equal number of impurities as silicon atoms within the domain, the forty percent alloy concentration limit emphasizes the complete loss of the original band structure. The density of states calculation for a forty percent germanium alloy is depicted in Figure 6.5. The resonances become so strongly coupled that the low frequency states are the predominant feature of the density of states for all branches. Furthermore, there is no semblance of the underlying silicon bulk structure at such high concentrations. The TA1 density of states calculation for various concentrations shown in Figure 6.6 shows the progressive shift of the band structure to lower frequencies. The coupling between the germanium impurities is the mechanism that drives the density of states to lower frequencies. This is fundamentally different to the VCA scaling, which is merely due to mass averaging. Although lower frequency modes become predominant at ten percent, the original structure of the density of states is not shifted to lower frequencies. The VCA would
Figure 6-6: Alloy averaged density of states for TA1 for one percent (blue), ten percent (red), and forty percent (green) concentration.

predict that the peaks of the DOS would push to lower frequency and increase in magnitude to retain proper normalization. In the explicit Green's function approach, the peaks stay at the same frequency, and in fact reduce in magnitude. The comparison of the total DOS for both computational approaches is shown in Figure 6.7. The comparison between the VCA and the explicit density of states obtained from the perturbed Green's function demonstrates the deviations that occur at higher frequencies. Because the VCA ignores high frequency information due to the coarse-graining of the system, multiple scattering effects that result in impurity resonance states are not accounted for. At frequencies of about 2 THz, the largest divergences occur between the VCA and the Green's function method. The aforementioned discrepancy stems from the resonances that occur due to germanium resonance states from the TA1 and TA2 branches. The longitudinal resonance state does not contribute much to the divergence because the frequency is too far away from the band edge. Lower
mass difference perturbations would place the LA resonance closer to the band edge, which could significantly affect modes at even higher frequencies.

Although both the VCA and the explicit calculation captures the band structure shift to lower frequencies with increasing germanium concentration, the frequency shift is overestimated using the VCA. The previous two calculations demonstrate the retention of the original bulk silicon band structures at concentrations below forty percent. By increasing the germanium concentration, the increasing influence on the density of states from the resonances merely shifts the silicon bulk DOS downwards. In other words, the downward shift stems from the resonance and its broadening in the limit of high concentration. On the other hand, when the VCA shifts the frequency downward, the magnitude of the DOS increases to maintain proper normalization.

Despite having an understanding of how the density of states in an alloy is explicitly defined, it is very difficult to acquire dynamical information from these calculations. In order to demonstrate this inherent problem, we must see how the Green’s
function is generated from the dispersion relation. Referring back to (3.9), we can interpret the Green's function as, for a certain parameter \( \omega \), a mapping from a three-dimensional dispersion relation to a complex scalar value. Although the contributions to the Green's function are most significant at frequencies infinitesimally close to the parameter \( \omega \), there may exist various dispersion relations that result in the same value for the Green's function for a given \( \omega \).

To gain even more information about the system, the infinitesimal difference between \( G(\omega) \) and \( G(\omega + d\omega) \) can help determine local deviations in the surface of constant energy. This can be achieved through the off-diagonal elements of the Green's function. The off-diagonal elements introduce a phase change that is weighted by the inner product between the k-points and the off-diagonal elements. By seeing how much the phase changes when changing the parameter \( \omega \) by a small amount, one can gather how the constant energy surface changes in the neighborhood of points in the direction \( k \).

Assumptions about the dispersion relation can greatly simplify this problem for certain wavelength regimes. Consider a long-wavelength phonon, it is reasonable to expect that locally varying disorder does not significantly affect the dynamics compared to the configurationally averaged properties derived from the VCA. We can then say that the long-wavelength dispersion from a disordered alloy should be similar to that of an ordered crystal. Since the dispersion in the long-wavelength limit is linear, the surface of constant energy is spherical. This results in a density of states that is proportional to \( \omega^2 \). In this limit, the group velocity can easily calculated from the density of states calculated from the explicit Green's function. The calculated group velocities from the VCA and the Green's function method agree very well for frequencies below 1 THz due to their overlapping density of states.

As the frequency approaches the dispersive regime, the anisotropies of the constant energy surface make the inverse problem much harder. This ultimately begs the
question, is the dispersion relation valid in this high frequency region? We know that translational symmetry allows for the use of Bloch's theorem to express solutions in terms of wave vectors. For short enough wavelengths, the locally varying field significantly breaks the translational symmetry. If the coherence of high-frequency phonons is valid, then the high-frequency vibrations that are (seemingly) randomly scattering throughout the disordered medium interfere in a way that generates coherent transport.

Although the VCA fails at large frequencies, how significantly do the deviations affect phonon transport? By referring to a cumulative thermal conductivity calculation, one can see how phonons of a given frequency or mean-free path contribute to thermal conductivity. In first-order scattering theory, alloy scattering rates scale proportional to $\omega^4$ while anharmonic processes have $\omega^2$ behavior in the long-wavelength limit. Alloying therefore acts as low-pass filter which scatters high frequency phonons very strongly, leading to limited transport contribution from these modes. This can be seen in silicon calculations, which show that thermal transport is significantly carried by phonons up to 6 THz whereas silicon germanium alloys carry significant heat up to frequencies of about 1.5 THz.

Even though the density of states calculations deviate strongly between the VCA and Green's function method for frequencies around 2 THz, these modes do not contribute much to the thermal conductivity. At room temperature, 68% of the thermal conductivity is due to phonons below 0.7 THz [23]. Because of such an important contribution from long-wavelength modes, the VCA can accurately predict the thermal conductivity of silicon germanium for all concentrations. If, on the other hand, high-frequency scattering is weak compared to anharmonic processes due to multiple scattering events, the VCA will greatly underestimate high-frequency phonon lifetimes. An example of such an incorrect approximation occurs when phonons are scattered by single-impurities that are lighter than the atoms in the bulk crystal
structure. Figure 5.1 highlights the discrepancy between positive and negative mass difference effects at higher frequencies. The reduced scattering from a light impurity stems from the resonance being pushed outside the band edge.

The power of the VCA lies in the self-averaging property of atomic masses for a disordered crystal. Although the interatomic force constants are also averaged in the calculations for silicon germanium alloys, the off-diagonal disorder is not accounted for in the relaxation time associated with alloy scattering. Abeles introduces this term in the alloy scattering rate, but since the mass mismatch between silicon and germanium is so large, it contributes insignificantly to the scattering rate. In order to determine whether or not force constant disorder should be included in the alloy scattering calculation, one should compare VCA results with experimental results of alloys with varying degrees of mass mismatch.

Tian et al. investigated the contributions of optical phonons to anharmonic scattering processes in PbTe and PbSe as well as the PbSeTe alloy [30]. When considering the thermal conductivity of the alloy, the VCA replaces one of the two basis atoms with the virtual crystal atom. The thermal conductivity using first principles methods is not reduced as significantly due to increased concentration as it is in silicon germanium alloys. This is mainly due to the low mass mismatch between Selenium and Tellurium. Unfortunately, subsequent experimental measurements of such alloys demonstrated a much more pronounced thermal conductivity reduction for high alloy concentrations.

These discrepancies can be explained by two possibilities. The first possibility stems from the influence of interatomic force constant disorder. Because of the small impedance mismatch in comparison to the discrepancy of the lattice parameters of PbSe and PbTe, ignoring off-diagonal disorder when calculating alloy scattering rates will overestimate thermal conductivity. Including these terms should add a correction for all values of alloy concentration.
The other explanation can stem from the inaccuracy of merely averaging the IFCs of PbTe and PbSe independently of one another. The Tellurium and Selenium atoms may have coupling between one another that is significantly different than their averaged quantities. Additionally when the alloy concentration exceeds the dilute limit, the local configuration of Tellurium and Selenium might cause large discrepancies in the IFCs. This corresponds to the aforementioned inability to self-average on-site potentials due to interatomic interactions. If the thermal conductivity calculations agree with experiments at low concentrations and diverge for higher concentrations, then the local configurations would need to be considered in ab initio methods. Unfortunately, measurements were not taken for alloy concentrations in the dilute limit.

The necessity of including off-diagonal disorder in the alloy scattering rate calculations seems to be more likely considering thermal conductivity calculations for MgSiSn alloys [50]. Although there exists significant lattice parameter mismatch between the constituent crystals, the relatively large impedance mismatch dominates. The calculations agree very well for all alloy concentrations. Because strain mismatch manifests through IFC disorder, the length scale over which the disorder occurs is very short, albeit not as short as the length scale associated with mass disorder. As a result, IFC disorder should strongly scatter phonons with slightly lower frequencies than those scattered by mass mismatch.

### 6.2 Nanostructure Scattering

The alloy density of states calculations for a finite random domain provides one with an understanding of how deviations from the dilute limit occur. Due to the coupling of resonance states in germanium, the low frequency peaks in the DOS broaden and begin to form impurity bands at around 10% impurity concentration. This transition
should also exist when one considers how phonons interact with germanium nanostructures embedded in silicon. Since nanostructures are the most densely packed set of impurities, one should expect that very high alloy concentrations could describe the behavior of such systems.

In order to perform scattering calculations of embedded germanium nanostructures, a domain of 282 atoms is constructed with a diamond cubic structure. The width and height of the nanostructure can vary from one to five lattice parameters in size. The depth of the nanostructure can vary from one to five atomic layers in thickness. A representation of a nanostructure that is $1 \times 1$ lattice parameters wide and tall with a thickness of one atom is shown in Figure 6.8. The direction normal to this surface is incident to the $[0,0,1]$ direction. Scattering rate calculations are performed with a phonon in a momentum state that is normal to the surface of the nanostructure. Figure 6.9 provides a pictorial depiction of the initial phonon scattering off of the embedded nanostructure.

For a given frequency $\omega$, a k-point in the $[0,0,1]$ direction is linearly interpolated from the $20 \times 20 \times 20$ Brillouin zone mesh. Since the collision is elastic, the momentum of the outgoing phonon is also linearly interpolated for the same value of $\omega$. Because the nanostructure is finite in all three dimensions, a phase function can be computed
as a function of frequency, incoming polarization, outgoing polarization, azimuthal direction, and polar direction. The scattering rate due to the single nanoparticle is computed using the optical theorem, which relates the imaginary part of the forward scattering amplitude with the cross-section. The scattering rate of the largest nanostructure is compared to the single-impurity limit in Figure 6.10. The difference in the mid and high-frequency behavior of the nanostructure and single-impurity scattering rate exemplifies the influence of resonance broadening. The single-impurity resonance allows for strong scattering at high frequencies. The nanostructure, on the other hand, is able to scatter lower frequency phonons more effectively [51] [52] [53]. By including high frequency alloy scattering and mid-frequency nanostructure scattering, phonon transport becomes dominated by long wavelength phonons. Although both structures have significantly different frequency dependence, both systems obey the same scaling behavior in the long-wavelength regime.

The Rayleigh limit corresponds to the scattering of phonons with wavelengths much larger than the size of the impurity. In this regime, the scattering rate is proportional to $\omega^4$. Additionally, the phase function is characterized by an isotropic
scattering profile. This can be physically interpreted as a nanostructure being so small that the internal structure cannot be probed by phonons of large wavelengths; consequently, the phonon scatters as if it were interacting with a point particle.

As the wavelength becomes comparable to the size of the nanostructure, there exists a transition from the Rayleigh limit to the geometric limit. The geometric limit corresponds to the upper bound of the scattering rate. Since the cross-section should never be much larger than the geometric size of the nanostructure, high-frequency interactions can be interpreted as particle-like scattering off of a boundary. Rather than explicitly compute the scattering rate of a given nanostructure, recent literature has utilized an interpolation between the long and short-wavelength regimes [54] [55] [56] [57],

\[
\tau^{-1} = \left( \frac{1}{\tau_s} + \frac{1}{\tau_l} \right)
\]  

(6.19)

Such an interpolation ignores the mid-wavelength fluctuations due to interference.
effects. Fortunately, the previous nanostructure calculation captures the transition between the Rayleigh and geometric limit.

Because the Rayleigh limit is dictated by the size of the nanostructure, it seems elucidating to investigate the frequency dependent scattering rate as a function of the size of the nanostructure. The scattering rate for three different layer thicknesses is shown in Figure 6.11. As the nanostructure increases in thickness, the Rayleigh limit gets pushed to lower frequencies. It is interesting to note that although the low frequency limit has significantly different magnitudes for each value of thickness, the scattering rates approach approximately the same values in the geometric limit. This stems from the fact that each nanostructure has the same incident cross-section. In other words, the nanostructure becomes a hard boundary in the high-frequency limit. The harder the boundary, the less important scattering from the deeper layers becomes. In the limit of large layer thickness, the high-frequency scattering rates should be independent of layer thickness. Figure 6.12 demonstrates the effects of varying the cross-sectional area. While the high frequency behavior is similar for the

Figure 6-11: Scattering rates of nanostructures with atomic thicknesses of one (green), two (red), and three (blue) layers.
Figure 6-12: Scattering rates of nanostructures with cross sections of one (green), two (red), and three (blue) lattice constants.

various cross-section sizes, they differ by a constant proportional to the size of the incident cross-section.

Although the long wavelength behavior exhibits the same scaling behavior regardless of layer thickness, the magnitude of the scattering rate in this regime is nonlinear with respect to the size of the nanostructure. For example, the ratio of the scattering rate of the three-layer nanostructure to the two-layer nanostructure is 2.5 despite the larger nanostructure having 1.5 times as many scattering elements. This effect is even more pronounced if you compare the largest slab, which consists of 282 atoms, to the single impurity. The slab scatters 10,000 times stronger despite having only 282 times more impurities.

The diagonal elements of the perturbed Green’s function within the impurity subspace are also calculated. By summing over the imaginary part of this subspace, the average density of states within the nanoparticle can be computed. The average density of states for various slab thicknesses is shown in Figure 6.13. Analogous to the high alloy concentration limit, the density of states calculation demonstrates a
significantly broadened impurity resonance over a wide range of frequencies. Since the density of states is averaged only within the impurity subspace, there is no semblance of the original silicon band structure. As the nanostructure becomes larger, the resonance broadens to lower frequencies. The lowest frequency modes correspond to the largest collective oscillations. Physically one could argue that as this nanostructure approaches an infinite size, the largest bulk oscillation should approach zero frequency. We can now interpret the Rayleigh limit as the manifestation of the resonance modes becoming strongly coupled and pushing to lower frequencies as the nanostructure increases in size. The transition from the Rayleigh limit corresponds to the phonon frequency that couples to the lowest frequency bulk impurity oscillation. This relationship is ultimately exemplified by the fact the lowest frequency peak in the averaged density of states corresponds to the lowest frequency peak in the scatter rate.

The investigation of the different regimes of scattering theory can be supplemented
through angle dependent scattering amplitude calculations. At low enough frequencies, contributions from higher order processes will contribute very little to the off-diagonal elements of the t-matrix. An essentially diagonal t-matrix should then yield an isotropic scattering phase function. The phase function for intra-polarization scattering of the first transverse branch at 500 GHz is plotted in Figure 6.14. The phase function is essentially identical to that of the single impurity phase function. Because the wavelength is much larger than the geometric size of the slab, the phonon does not see an internal structure. The only difference between the Rayleigh scattering of the slab and the single impurity is the magnitude of the scattering in all directions. As the frequencies become large enough to allow for significant coupling between impurities, the angle dependent scattering assumes a more anisotropic profile. Math-

Figure 6-14: Phase function for TA1 to TA1 scattering at 500 GHz. Zero degrees corresponds to the incident phonon direction.
ematically this corresponds to off-diagonal elements having comparable magnitude to the diagonal elements of the t-matrix. The phase function for intra-polarization scattering of the first transverse branch at 1.8 THz is plotted in Figure 6.15. The most interesting aspect of this phase function is the bi-directional scattering behavior. In this regime, the phonon is more likely to be scattered forwards than backwards. At other frequencies, however, the phase function has a similar structure but rotated by 180 degrees. Although the phonon can be scattered in directions other than forward and backwards, this effect is associated with the edges of the slab. One could surmise that as the incident plane of the slab increases in size, the forward and backward scattering peaks of the phase function should become narrower.

At frequencies closer to the band edge, the scattering can strongly interact with

Figure 6-15: Phase function for TA1 to TA1 scattering at 1.8 THz. Zero degrees corresponds to the incident phonon direction.
the edges of the slab. At 3 THz, the phase function for the first transverse acoustic branch is depicted in Figure 6.16. There is now significant scattering in the direction parallel to the interface of the germanium slab. This angular dependent scattering amplitude corresponds to two distinct types of interactions. The first type corresponds to the interaction with the interface, resulting in forward and backscattering traditionally associated with interfacial scattering. The second type results from the interaction with the edges of the slab, resulting in scattering perpendicular to the initial momentum state. The diffusive broadening of both sets of peaks stems from the atomic roughness of the germanium slab. A larger slab or a continuum description of the scattering at such an object should result in a narrowing of the aforementioned peaks. Similar phase functions have been computed using molecular dynamics.
simulations of embedded spherical and rectangular nanostructures [58].

When inter-polarization scattering is considered, interesting dynamics occur at high frequencies. The phase function describing the scattering from the longitudinal acoustic branch to the first transverse acoustic branch is shown in Figure 6.17 for a frequency of 4.5 THz. Because the collision is elastic, high frequency longitudinal acoustic phonons might only scatter to momentum states in very small regions of the Brillion zone of the other acoustic branches. As the frequency becomes larger, the available phase space becomes smaller and more directionally selective. At lower frequencies, the scattering between different polarizations have many of the characteristic phase function features that have been previously mentioned.

![Figure 6-17: Phase function for LA to TA1 scattering at 4.5 THz. Zero degrees corresponds to the incident phonon direction.](image)
Chapter 7

Conclusion

Multiple scattering theory allows for a more accurate assessment of how mass disorder influences phonon transport in crystal lattices. The higher order calculations require the computation of Green's functions obtained from the dispersion relation of the unperturbed system. With the advent of ab initio methods that obtain interatomic force constants from density functional perturbation theory, reliable dispersion relations are calculated, which ultimately provide reasonable Green's functions.

The mass disorder and Green's functions allow for scattering information to be encoded in the t-matrix. The t-matrix allows for resonant states that are not predicted in first order theory. Heavier impurities push the resonance to lower frequencies whereas lighter impurities allow for resonances to occur outside of the band. The single impurity scattering rate is calculated for various mass differences and demonstrates strong deviations from first order theory due to the resonance states. The local density of states exhibits a resonance at the corresponding frequency since it is related to the scattering rate by a constant of proportionality in the independent impurity limit. When multiple impurities are spaced close enough together, the resonances couple and split into multiple peaks. The strength of the coupling is dictated by the relative magnitude of the off-diagonal elements of the t-matrix.
The resonances at high frequencies can shed insight into the behavior of bulk-disordered systems. The virtual crystal approximation uses a mean-field approach to model alloyed crystal lattices. Because this coarse-graining ignores local configurations, there is an inherent difference in short wavelength phonon behavior derived from the VCA as compared to explicit Green’s function methods. At small alloy concentrations ($\sim 1\%$), the configurationally averaged local density of states exists as a superposition of the independent Germanium resonances and the bulk Silicon band structure. As the impurity concentration increases to high values, the coupling between impurities becomes significant. This coupling broadens the resonance over a wide range of frequencies. At 40% concentrations, the impurity resonances become so strongly coupled that there is little recognition of the unperturbed band structure. Despite such deviations, these high frequency components do not contribute significantly to thermal transport due to their short lifetimes and low group velocities. As high frequency components become more significant to thermal transport in alloyed systems, the VCA will become less accurate. Relevant examples should include mass disorder that is comparable in magnitude to strain disorder.

Nanostructure scattering is investigated using the Green’s function formalism. Since the impurity subspace is so densely packed, the coupling between impurities is at its strongest. Such effects manifest in a broadening of the resonance over the widest range of frequencies. Multiple scattering theory captures the transition from Rayleigh scattering, which exhibits $\omega^4$ scaling, to the geometric limit. The lowest frequency peak in the local density of states corresponds to the transition frequency between the long and short wavelength limit. Angle dependent scattering amplitudes are calculated and demonstrate isotropic scattering at low frequencies. As frequencies depart form the long wavelength limit, the phase function becomes more anisotropic. Mid frequency phonon scattering exhibits forward and backward scattering with broadening due to the finite size and atomic roughness of the slab nanostructures. Frequencies
near the band edge have very directionally dependent phase functions, especially when
the interaction scatters phonons between polarization states.

7.1 Future Work

The previous calculations only incorporate the effects of mass disorder. This approx-
imation is justified in Silicon Germanium alloys because the mass mismatch is so
large. At smaller mass differences, the off-diagonal disorder due to interatomic force
constant mismatch becomes significant. Although previous calculations have included
an adjustable parameter to account for off-diagonal disorder, one could compute the
interatomic force constant of an impurity embedded in a bulk crystal through ab
initio methods. This information could be used to alleviate the discrepancy between
theoretical and experimental thermal conductivity calculations in PbTeSe alloys.

While it is convenient to replace a disordered system with an ordered crystal
and include a compensating scattering rate due to alloy scattering, more elegant
techniques encode the scattering rate into the dispersion relation instead. The Co-
herent Potential Approximation introduces a complex-valued energy shift, known as
the self-energy. Phonons with dynamics adjusted by this self-energy do not scatter,
on average, with the constituent impurities of the alloy [59]. In other words, the
configurationally averaged single impurity t-matrix,

\[ \langle T \rangle = \langle T_A \rangle + \langle T_B \rangle = 0 \quad (7.1) \]

allows for a self-consistent computation of the self-energy. The phonon in this co-
herent potential does not experience the effects of the single-impurity disorder. The
lifetime of the phonon in this coherent potential corresponds to the imaginary part
of the self-energy. While the CPA is a single-site theory, generalizations have been
constructed that compute self-energies that allow for clusters and off-diagonal disor-
der [60] [61]. Such computations allow for the comparison between explicit Green’s function methods and self-consistent mean-field theories.
Bibliography


