OPTIMIZED DESIGN OF NANOFIBERS FOR LOW THERMAL CONDUCTIVITY IN NANOCOMPOSITES

by

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A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering

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ABSTRACT

The design of efficient thermoelectric materials involves the reduction of thermal conductivity without degradation of electrical conductivity. While electronic carriers is responsible for the electrical performance of thermoelectrics, much of the thermal conductivity is attributable to heat conduction by thermally generated elastic waves called phonons. Improved scattering of phonons can be attained by introducing a small volume fraction of elastodynamic inhomogeneities inside a semiconductor matrix material in the form of embedded nanoparticles. In order to make optimal use of such impurities, it is necessary to understand the relationship between their shape, size, and elastodynamic contrast and the performance characteristics such as phonon scattering cross-section and the resulting thermal conductivity tensor.

Calculating the thermal conductivity tensor from microscopic principles requires knowledge of the scattering cross-sections spanning all possible incident elastic wave orientations, polarizations and wavelengths including the transition from Rayleigh to geometric scattering regimes.

In this thesis, analytical continuum mechanics is used to construct the scattering cross-section of incident elastic waves from embedded nanofibers where the waves have arbitrary orientation, polarization, and wavelength. The model is then incorporated using Boltzmann transport theory to predict the thermal conductivity tensor. The thermal model is used to study optimal methods of producing low thermal conductivity nanocomposites. We consider the specific case of $Si_{0.5}Ge_{0.5}$ alloy matrix

materials as the active thermoelectric component and nanoparticle scatterers including Ni, Co, and Pt silicide compounds.

The thermal conductivity tensor is studied as a function of fiber size, elastodynamic contrast, and the degree of orientation (aligned, random 2D, and random 3D) in an effort to minimize thermal conductivity for a given volume fraction of nanoparticles. The optimal fiber size is found to be quite small, corresponding to fiber diameters of only ~2nm. For the range of practical materials studied, the anisotropy of the thermal conductivity tensor is found to be <2 for aligned fibers. PtSi was found to be the most effective silicide material due to its high density and elastic contrast. Compared to an unnanostructured Si-Ge alloy, the addition of 3.4% volume fraction of PtSi is found to reduce the thermal conductivity by a factor of 9 for fully aligned and optimally sized fibers with heat flow perpendicular to the fiber axis. This is found to be more effective than an equivalent amount of PtSi utilized in the form of optimally sized spherical nanoparticles. In some cases like NiSi and CoSi₂, we find two locally optimal nanofiber sizes due to the separate optima associate with each phonon mode.

This thesis helps in understanding the transversely isotropic nature of thermal conductivity attained by embedding nanofibers in the nanocomposite. While the results obtained assist in choosing optimal nanofiber size and orientation for low thermal conductivity, a multimodal distribution of nanofiber sizes can be observed to be optimal.

Chapter 1

THERMOELECTRICITY AND NANOCOMPOSITES

1.1 Thermoelectric Materials and the Need for Reduced Thermal Conductivity

Thermoelectric effects are comprised of three phenomena: the Seebeck effect, the Peltier effect and the Thomson effect. The Seebeck effect is the observation that a potential difference is developed between two junctions of a conducting material when a temperature difference is maintained between them at open circuit. The voltage and temperature gradient are related by a linear coefficient called the Seebeck coefficient. The Seebeck coefficient, S is a function of composition of conducting material and temperature. The Peltier effect is a related phenomenon where an electric current moving from one material to another causes heat to be either emitted or absorbed at the junction between them. This effect occurs because electrons have different average energy levels in different materials; hence when they move from one material to another they must either release or absorb energy to reach the equilibrium energy state of the second material. The Peltier coefficient, Π , is the linear coefficient that relates the heat flux with the electric current. While investigating the Seebeck and Peltier effects, William Thomson (aka Lord Kelvin) predicted a third thermoelectric effect now called the Thomson effect, in which he stated that when a temperature gradient is maintained in a material through which an electric current is passed, heat is either absorbed or emitted. While thermoelectric material convert heat to electricity, they do not necessarily do so efficiently.

The maximum possible conversion efficiency of a thermoelectric device is limited by the performance of the active thermoelectric material. The performance of a thermoelectric material is quantified by the non-dimensional thermoelectric figure-ofmerit, ZT defined as

$$ZT = \frac{S^2 \sigma T}{k} \tag{1.1}$$

Here, S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature and k is the thermal conductivity. For optimally designed devices, the device efficiency monotonically increases with ZT; in refrigeration mode, the maximum achievable temperature difference is also an increasing function of ZT. S and σ are electronic properties of the material, while k has both electronic contributions and contributions from the vibration of atomic nuclei, called "phonons," to be discussed in detail shortly. It is evident from the figure-of-merit that an efficient thermoelectric material should be one that reduces the thermal conductivity without degradation of the electrical transport properties. The term, $S^2\sigma$, appearing in ZT is called the power factor because the maximum power density and heat removal rate (W/m^2) in power generating and refrigeration mode respectively are proportional to $S^2\sigma$. Seebeck coefficient and electrical conductivity can both be controlled by extrinsic carriers ("doping"), but generally have opposite doping trends: S decreases approximately logarithmically with doping, while σ increases approximately linearly with doping. In practice, all semiconductors have an optimal doping level for maximum power factor, and this doping level generally corresponds to the crossover to degenerate doping.

Thermoelectric devices can be divided into two major functional groups refrigerators and power generators. The efficiency of a thermoelectric device depends on its functionality.

(1) Thermoelectric refrigerator: The coefficient of performance of a refrigerator is calculated as:

$$\phi = \frac{Q_c}{W_e} \tag{1.2}$$

where Q_c is cooling power and W_e is the electric power consumed for cooling. There are 3 ways of measuring the performance of a thermoelectric refrigerator: (a) the maximum coefficient-of-performance for a given temperature difference (ϕ_{max}), (b) the maximum cooling power (Q_{max}) or (c) the maximum temperature difference that can be obtained(ΔT_{max}). The ϕ_{max} and ΔT_{max} are both limited by ZT, according to the expressions on the left hand side of Table 1.

(2) Thermoelectric power generator: The efficiency of a power generator can be calculated as:

$$\eta = \frac{W_e}{Q_h} \tag{1.3}$$

where Q_h is the heat supplied and W_e is the power generated. There are two ways of measuring performance of a power generator: (a) maximum efficiency or (b) maximum power obtained when external load resistance is matched with the electrical resistance of the device. The η_{max} is limited by ZT, according to the expression on the right hand side of Table 1.

Refrigeration	Power Generator	
$\phi_{\max} = \frac{T_c}{T_h - T_c} \left(\frac{\sqrt{1 + ZT_{avg}} - T_h / T_c}{\sqrt{1 + ZT_{avg}} + 1} \right)$	$\eta_{\max} = \frac{T_h - T_c}{T_h} \left(\frac{\sqrt{1 + ZT_{avg}} - 1}{\sqrt{1 + ZT_{avg}} + T_c / T_h} \right)$	
$Q_{\rm max} = \frac{S^2 \sigma T_c}{L} \left(\frac{T_c}{2} - \frac{\Delta T}{ZT_c} \right)$	$W_{\rm max} = \frac{1}{2} \frac{S^2 \sigma}{L} \Delta T^2$	
$\Delta T_{\rm max} = \frac{1}{2} Z T_c^2$		

Table 1:Thermoelectric Device Efficiencies1

State-of-the-art materials have ZT between 1 and 2, which according to the table above yields a maximum device efficiency that is only ~30-40% of the Carnot efficiency. Due to the low efficiency of thermoelectrics compared to grid level generation, thermoelectric generation applications have garnered interest mostly in niche sectors like space missions and waste energy harvesting². However, thermoelectric applications in refrigeration are environment friendly as they do not use CFC or other refrigerant gas and can function in environments that are too severe, too sensitive or too small for conventional refrigeration³. They are light weight, reliable and operate well even for low grade heat applications. Thermoelectric materials have applications in thermoelectric generators and localized air conditioning⁴. Thermoelectric materials have also garnered some interest in the semiconductor industry, for spot cooling of electronic devices³.

1.2 Phonon Scattering by Nanoparticles

Nanostructured thin films first attracted the interest of the scientific community when Hicks and Dresselhaus⁵ calculated an increase of ZT by a factor of 13 over bulk

when Bi_2Te_3 was used in a quantum well structure. Hsu et al.⁸ investigated AgPb_mSbTe_{2+m} and found epitaxially embedded nanostructured regions in the material which were rich in Ag-Sb and 2nm to 4nm in size, with the surrounding material depleted of Ag and Sb (i.e. just PbTe). The acoustic impedance of these AgSbTe₂ nanodots were different from the matrix and this caused a scattering of phonons which led to enhancement of ZT to ~1.8. Hsu⁸ found that the enhanced ZT was directly influenced by reduced thermal conductivity due to the scattering of phonons.

For understanding the reason behind these improvements in thermal conductivity, a brief section has been included to help the reader understand microscopic origin of thermal conductivity. Heat conduction through any solid material is facilitated by electrons and/or by the oscillation of the atoms in the material. A metal has a large number of free electrons which can carry thermal energy. These free electrons are the dominant heat carriers in metals. However, not all materials have free electrons (or enough of them), in which case, heat can still be transferred through the vibration of atomic nuclei called phonons. Every atom in a solid material is bonded to other atoms. The vibration of any one atom thus causes vibration in the adjacent atoms, and so on. Thus, vibrations propagate as waves throughout this system of bonded atoms. When one side of the solid is hotter than the other, the atoms on the hotter side will statistically have larger vibrational amplitudes, which will be transferred toward the atoms on the colder side of the system via the propagation and exchange of phonons. We will consider the mathematics behind this in Chapter 2.

In semiconductors, the free electron density is lower than in a metal and the dominant heat carriers are typically phonons. The electrons and holes carry charges, while lattice vibrations (phonons) drive heat transport. Phonons have two length scales associated with their transport - the wavelength and the mean free path. Mean free path is the average distance that a phonon travels between scattering events. The mean free path of phonons in a semiconductor can be reduced by introducing impurities and this has the effect of reducing the thermal conductivity.

There are five common phonon-scattering mechanisms depending upon the kind of scatterer. We will describe them qualitatively here and give a more quantitative description in chapter 2.

- (1) Phonon-phonon scattering Phonon-phonon scattering can involve two processes. The normal process is where the total momentum of the colliding phonons is conserved after collision. Hence the net energy and the direction for the colliding phonons is conserved. But in the Umklapp process, an extra lattice wavevector changes the net direction of the phonon propagation after collision. This change in the net momentum of the phonons after collision causes a resistance to the heat flow. Umklapp phonon-phonon scattering is the dominant mechanism in the case of low-defect crystals.¹
- (b) Alloy disorder scattering An alloy whose components have widely differing lattice constants usually contains a large concentration of highly strained regions which scatter phonons effectively.⁹
- (c) Boundary scattering This is the scattering of phonons from surfaces.
- (d) Phonon-electron scattering Phonon-electron scattering is only relevant when the material is highly doped. This is the dominant mechanism in pure metals, although phonons carry little heat in metals.
- (e) Nanoparticle scattering:

Qualitatively, the response of an elastic wave that interacts with a nanoscale impurity depends upon the wavelength (λ) of the phonon and the size (a) of the discontinuity on which the phonon scatters. Defining a dimensionless quantity called the scattering parameter, $ka = (2\pi / \lambda)a$, there are three general regimes (1) Rayleigh scattering (ka<1), (2) geometric scattering (ka>1) and (3) Mie scattering (ka \sim 1). In the Rayleigh scattering regime, were the wavelength of the phonon is much greater than the radius of the particle it collides with, the interaction between the wave and the structure is weak, albeit stronger for shorter wavelengths. There is no possibility of constructive/destructive interference in the diffracted waves. An example of this is the Rayleigh scattering of sunlight in the atmosphere: the wavelength of light is much greater than the size of the molecules in the atmosphere, but the molecules can still weakly scatter some of the shortest wavelengths of light, and this causes the blue hue of the sky in daytime. Geometric scattering occurs when the size of the particle is greater than the wavelength of the phonon (ka>>1), in which case the wave is able to feel the full geometry of the particle, and scatters effectively. In the intermediate regime called Mie scattering waves may travel through the impurity and return either in-phase or out-of-phase with the incident wave, leading to either constructive or destructive interference. In this regime the scattering effectiveness thus may oscillate as a function of wavelength.

For thermoelectric applications, alloys are generally utilized because atomic substitution distributes mass and elastic contrast (scatterers) on the atomic level. However, alloy disorder and phonon-phonon scattering preferentially scatter short wavelength phonons while doing little to impede the transport of mid to longwavelength phonons (several nanometers in wavelength). In contrast, nanoparticle impurities can help scatter the mid and long wavelength phonons which dominate the heat transfer in alloys¹⁰. If particles can be placed such that their spacing is larger than the mean free path of electrons, but smaller than that of bulk phonons, then it is possible to reduce thermal conduction by phonons without impeding the transport of electrons. To do this as effectively as possible, it is imperative to understand the effect of elastodynamic contrast and geometry on the scattering performance of nanoimpurities.

Attempting to understand the relationship between embedded discontinuities and elastic wave scattering is not a new problem. Ying (1956)¹¹ formulated an analytic approach to obtain the scattering cross-section for a plane longitudinal wave incident on a spherical obstacle in an isotropically elastic medium and developed explicit analytic expressions for scattering cross-section at long wavelength using continuum mechanics by applying displacement and stress boundary conditions for elastic sphere, rigid sphere and spherical cavity. He observed that the scattering cross-section was directly proportional to sixth power of radius of the sphere and inversely proportional to fourth power of the wavelength. In this detailed work, although Ying¹¹ covered the scattering of a variety of spherical nanoparticle cases, the computations were laborious and regular approximations like Rayleigh approximation cannot be used for high frequencies. Later, Johnson (1965)¹² used a computational approach on an IBM 7070 computer to evaluate Ying's model for arbitrary wavelength. From these computations, they could conclude that the scattering cross-section was very close to the Rayleigh approximation for ka < 0.1 and then levels off, asymptotically approaching a value of 2 for higher frequencies. Greater differences in the velocities of the compressional and shear waves caused a higher maximum cross-section at $ka \sim 1$. They associated the oscillatory nature of the scattering cross-section outside the Rayleigh regime, to a resonance phenomenon and speculated that the maximum scattering would occur when the frequency of the incident wave is the close to the resonant frequencies of the system of matrix and discontinuities. Eisenspruch (1960)¹³ formulated the analogous problem for transversely polarized waves, and gave explicit analytic expressions for the scattering cross-section for a void and fluid-filled cavities, and rigid and elastic spheres at long-wavelength. Neither Ying's nor Einspruch's model appears to have been implemented in the context of heat transport modeling in nanostructures.

While scattering of phonons on spherical obstacles has been studied extensively, not much attention has been given to scattering of phonons from nanofibers in the context of heat transport. That is the purpose of this thesis. Scaling laws for long-wavelength phonon scattering are different and generally stronger for cylinders, which we hypothesize should be beneficial for TE applications. In addition, elastic wave scattering models for cylindrical impurities are easier to implement within thermal models than the models of Ying and Einspruch for spheres. This work is thus meant as a first step to understanding the role of coherent wave scattering effects in the Mie regime on the thermal transport properties. Nanofiber systems are also interesting because they admit the possibility of anisotropic transport, a phenomena that has not been studied for semiconductors with embedded nanostructures. The goal of this thesis is to model the thermal conductivity tensor of semiconductors with embedded nanofibers, and to use the model to understand whether there are optimal composite design parameters which would achieve low thermal conductivity using less filler material than existing approaches.

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1.3 Layout

Chapter 2 will describe how thermal transport properties are modeled using Boltzmann transport theory and its application to phononic thermal conduction. In particular, the current work focuses on fiber composites, which generally have anisotropic transport properties, a situation not generally encountered in introductory Boltzmann transport theory treatments. The treatment given in Chapter 2 will allow this. In order to simulate thermal conductivity from microscopic principles, the phonon scattering rates must be known, and in this work the principle challenge is to calculate the increase in phonon scattering rates due to the addition of nanofibers. Thus, in Chapter 3 an analytical continuum model is developed for the scattering cross-section of incident elastic waves on embedded cylinders. As required for use in Boltzmann transport theory, the model allows for arbitrary incident angle, polarizations and wavelength on cylindrical elastic discontinuities embedded in an elastic matrix material. The model is yields generally accepted results over the entire range of possible wavelengths, spanning from the Rayleigh scattering regime to the geometric scattering regime without resorting to perturbation theory. In Chapter 4, the scattering model is utilized in the context of Boltzmann transport theory to simulate the anisotropic thermal conductivity tensor for semiconductor alloy materials with embedded nanofibers. The thermal transport properties are studied as a function of nanofiber radius, fiber composition, and degree of fiber alignment, specifically for the case of Si-Ge alloys with embedded silicide metals. Chapter 5 provides potential areas for future research.

Chapter 2

BOLTZMANN TRANSPORT THEORY

Although early research by Hsu⁸ showed increase in the thermoelectric figureof-merit in nanostructured materials, Kim¹⁰ provided theoretical and experimental evidence for reduced thermal conductivity and corresponding enhancement of ZT by embedding ErAs nanoparticles in In_{0.53}Ga_{0.47}As alloy. Thermal conductivity measurements conducted using the method showed that thermal conductivity in the alloy sample with embedded nanoparticles are lower than that in the pure alloy sample. Theoretical evidence was provided by predicting thermal conductivity using the Callaway model which confirmed that ErAs nanoparticles scatter the mid and long wavelength phonons while the alloy disorder caused scattering of the short wavelength phonons. Mingo¹⁴ analytically predicted the existence of an optimal size of an embedded spherical nanoparticle that minimizes the nanocomposite's thermal conductivity. Mingo found that the optimal nanoparticle size was located between the Rayleigh and the geometric regimes, called the Mie scattering regime. However, while calculating the phonon-nanoparticle scattering cross-section he has only considered the mass mismatch between the alloy and the nanoparticle material. In this thesis, we have considered both mass and stiffness mismatch for calculating the phononnanoparticle scattering cross-section. Zhang (2015)¹⁵ used a numerical optimization method called Particle Swarm Optimization algorithm to find that a broad spectrum of thermal phonons can be most effectively scattered by nanoparticles of neither a unique size nor a broad distribution of size, but one with a few distinct peaks at well-chosen

radii. The algorithm optimizes a multi-dimensional function by iteratively improving candidate solutions among a large number of variables according to a fitness function and thus approaching the best solution in the search space of exhaustively large number of possibilities. Zhang¹⁵ has used his theory of best distribution of discrete peaks to obtain calculated thermal conductivities of 0.89 W/(K.m) for 0.8% volume fraction of Ge in Si_{0.5}Ge_{0.5} matrix.

In this section, we derive the expressions for thermal conductivity of a material using nanoscale energy transport and Boltzmann transport theory.

2.1 Boltzmann Transport Theory

It can be shown that phonons are waves that are solutions of the quantum mechanical Schrödinger equation subject to a harmonic potential. The most important result of this is that phonons can only exist at a series of discrete energy levels, separated by energy $\hbar \omega$, where $\hbar = 1.054 \times 10^{-34} \text{ J} \cdot \text{s}$ is a universal constant called Planck's constant and ω is the frequency of vibration in rad/s. The energy of a phonon state is specified by the quantum number n as, $E_n = \hbar \omega (n+1/2)$ where (n = 0, 1, 2, 3...). The frequency of vibration is uniquely determined once the wavevector and polarization of the phonon is specified; the correspondence between wavevector and frequency is called the dispersion relation, and the procedure for calculating $\omega(k)$ is given in most undergraduate solid-state physics books^{16,17}. A key result is that for small magnitudes of wavevector (wavelengths much larger than the distance between atoms), the correspondence is linear and the constant of proportionality is the speed of sound (i.e. $\omega = c |\underline{k}|$); this is equivalent to what one would find for waves traveling in a continuous medium in the framework of linear elasticity. The situation is more complicated for short wavelength-phonons, since the

dispersion becomes non-linear and anisotropic even in cubic materials, and because there is a restriction on the shortest wavelengths that are possible. For the purposes of this thesis, we will treat phonon dispersion as linear and isotropic, and we will be able to judge the limitations of this only after determining which phonons are responsible for thermal transport.

There is no restriction on the quantum number n. However, according to statistical thermodynamics, at thermodynamic equilibrium the value of n will fluctuate with an average value given by the Bose-Einstein distribution:

$$n_0 = f_0 = \frac{1}{\frac{\hbar\omega}{e^{\frac{k_B T}{k_B T}} - 1}}$$
(2.1)

Boltzmann transport theory is a method of calculating what happens once the system is perturbed from this equilibrium. The core idea is that at non-equilibrium (i.e. if transport is occurring), there is a probability distribution describing the average state of the system for various wavevectors and polarizations (p), denoted as $f(t, \tilde{x}, \tilde{k}, p)$, but it will differ from the equilibrium distribution, f_0 . Then, f will not be an even function of \tilde{k} , since transport requires states to be biased toward a particular propagation direction. Taking the time derivative of f gives,

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \left(\frac{\partial x_i}{\partial t}\right) \frac{\partial f}{\partial x_i} + \left(\frac{\partial k_i}{\partial t}\right) \frac{\partial f}{\partial k_i}
= \frac{\partial f}{\partial t} + v_{g,i} \frac{\partial f}{\partial x_i} + \frac{F_i}{\hbar} \frac{\partial f}{\partial k_i}
= \frac{\partial f}{\partial t} + \tilde{v}_{g,i} \nabla f + \frac{\tilde{F}}{\hbar} \nabla_k f$$
(2.2)

We have used the fact that, for phonons, the group velocity, $\tilde{v}_{g,i} = \frac{d\omega}{dk_i}$, is the speed

that wave energy moves. \tilde{F} is the external force on the phonon which is zero since no external force is acting on the system. The particle in this single size distribution

function interacts with other particles in the system. The rate of phonons entering state \underline{k} at location \underline{r} , must be the result of scattering process that brings other carriers into the state.

$$\frac{df}{dt} = \left(\frac{df}{dt}\right)_{scattering}$$
(2.3)

It is generally difficult to calculate the rate of scattering on a state-by-state basis, so the usual approach is to simplify the process by considering the fact that the overall effect of scattering is to bring all particles toward equilibrium. This idea leads to the Relaxation Time Approximation (RTA), where the scattering rate is modeled as:

$$\left(\frac{df}{dt}\right)_{scattering} = -\frac{(f - f_0)}{\tau(\tilde{k}, p)}$$
(2.4)

Thus the scattering rate is proportional to the separation of each state with respect to thermodynamic equilibrium. Here, τ is the relaxation time, which is the time required for a perturbed system to return to equilibrium. This can be shown by neglecting the spatial non-uniformity of the function and considering no external forces, in which case we get

$$\frac{\partial f}{\partial t} = -\frac{f - f_0}{\tau(\tilde{k}, p)}$$
(2.5)

The solution for this equation is

$$f = f_0 + f_{t=0} e^{\left(-t/\tau(\tilde{k}, p)\right)}$$
(2.6)

Now, if the temperature in a material varies with space, but not time as typically occurs in heat conduction, then $\frac{\partial f}{\partial t} = 0$. Let us continue with the assumption that the external force, $\tilde{F} = 0$. Then the Boltzmann transport equation in the relaxation time approximation is

$$V_{g,i}\frac{\partial f}{\partial x_i} = -\left(\frac{f-f_0}{\tau(\tilde{k},p)}\right)$$
(2.7)

If $f - f_0$ is small compared to f_0 then $\nabla f \approx \nabla f_0$. Then the equation above can be easily solved for f.

$$f = f_0 - \tau(\tilde{k}, p) v_i^g \frac{\partial f_0}{\partial x_i}$$
(2.8)

2.2 Thermal Conductivity

The heat flux in a material can be calculated using f.

$$q_{j}"(\tilde{x}) = \sum_{all \ k \ and \ p} (\hbar \omega_{k,p}) / V \cdot (V_{j}^{g}) \cdot (f)$$
(2.9)

where $(\hbar \omega_{k,p})/V$ is the quantum of energy of each mode (distinct wavevector and polarization) per unit volume, f is the average quantum number, and (V_j^g) is the group velocity of the phonon. Although the allowed wave-vectors are technically discrete, they are extremely closely spaced compared to the maximum allowable size ($\Delta k / k_{max} \approx a/L$) where L is the length of the sample and a is the lattice constant, so it is helpful to treat them as a continuum. Replacing the summation over k by integration and by integrating across all k coordinates we get

$$q_{j}''(\tilde{x}) = \sum_{p} \int_{all \quad \tilde{k}} \hbar \omega_{k,p} v_{j}^{g} f \frac{1}{V} \left(\frac{V}{(2\pi)^{3}} \right) d^{3} \tilde{k}$$

$$= \frac{1}{(2\pi)^{3}} \sum_{p} \int_{all \quad \tilde{k}} \hbar \omega_{k,p} v_{j}^{g} f d^{3} \tilde{k}$$
(2.10)

Plugging in the solution for f, we get

$$q_{j}''(\tilde{x}) = \frac{1}{(2\pi)^{3}} \sum_{p} \int_{all} \hbar \omega_{k,p} v_{j}^{g} \left(f_{0} - \tau(\tilde{k}, p) v_{i}^{g} \frac{\partial f_{0}}{\partial x_{i}} \right) d^{3}\tilde{k}$$
(2.11)

The integral involving f_0 must work out to be zero because there can be no transport at equilibrium. Physically, the gradient of f_0 is only non-zero because the temperature is spatially dependent. So, heat flux can be expressed as,

$$q_{j}''(\tilde{x}) = -\left[\frac{1}{\left(2\pi\right)^{3}}\sum_{p}\int_{all}\int_{\tilde{k}}\left(\hbar\omega_{k,p}v_{j}^{g}\tau(\tilde{k},p)v_{i}^{g}\frac{\partial f_{0}}{\partial T}\right)d^{3}\tilde{k}\right]\frac{\partial T}{\partial x_{i}}$$
(2.12)

Let us represent the heat flux in spherical k-coordinates. In order to convert the cartesian vectors of \tilde{k} into spherical coordinates, we use the following substitution.

$$\tilde{k}_x = \tilde{k}_r \sin\phi\cos\theta$$
; $\tilde{k}_y = \tilde{k}_r \sin\phi\sin\theta$; $\tilde{k}_z = \tilde{k}_r \cos\phi$ (2.13)

The Jacobian matrix for this coordinate transformation can be given as $\tilde{z} = \tilde{z}$

$$\frac{\partial(k_x, k_y, k_z)}{\partial(\tilde{k}_r, \theta, \phi)} = -k_r^2 \sin \phi$$
(2.14)

Therefore, a differential volume in k-space is given by

$$d^{3}\tilde{k} = k_{r}^{2}\sin\phi d\tilde{k}_{r}d\theta d\phi \qquad (2.15)$$

So, we can write equation (2.12) as

$$q_{j}''(\tilde{x}) = -\left[\frac{1}{\left(2\pi\right)^{3}}\sum_{p}\int_{0}^{k_{\max}}\int_{0}^{2\pi}\int_{0}^{\pi}\left(\hbar\omega_{k,p}v_{j}^{g}\tau(\tilde{k},p)v_{i}^{g}\frac{\partial f_{0}}{\partial T}\right)\tilde{k}_{r}\sin\phi d\phi d\theta d\tilde{k}_{r}\left[\frac{\partial T}{\partial x_{i}}\right] (2.16)$$

By comparing it to $q_i = -\kappa_{ij} \frac{\partial I}{\partial x_j}$, we can identify the thermal conductivity tensor as

$$\kappa_{ij} = \frac{1}{(2\pi)^3} \sum_p \int_0^{k_{max}} \int_0^{2\pi} \int_0^{\pi} \int_0^{\pi} \left(\hbar \omega_{k,p} v_j^g \tau(\tilde{k}, p) v_i^g \frac{\partial f_0}{\partial T} \right) \tilde{k}_r \sin \phi d\phi d\theta d\tilde{k}_r$$
(2.17)

Note that by definition, the group velocity $v_j^{g} \equiv v_g \cdot \hat{e}_j$ where \hat{e}_j is the unit vector in direction j. For isotropic group velocity, $v_g = v_g \hat{e}_\rho$ where \hat{e}_ρ is the unit vector in the direction of k. Expressed in cartesian coordinates

$$\hat{e}_{\rho} = \sin(\phi)\cos(\theta)\hat{e}_x + \sin(\phi)\sin(\theta)\hat{e}_y + \cos(\phi)\hat{e}_z$$
(2.17)

Thus, the term v_j^g depends on the spherical polar angles ϕ and θ as well as the value of j = x, y, or z.

2.3 Relaxation Time

As introduced in Chapter. 1, the effective phonon scattering rate experienced by any particular state is the result of all possible scattering mechanisms including anharmonic scattering, alloy/point defect scattering, boundary scattering, and nanoparticle scattering. It is usually assumed that these processes act independently so that the total scattering rate is the sum of all the rates of the individual mechanisms. This is summarized by Matthiessen's rule as

$$\frac{1}{\tau} = \frac{1}{\tau_{u}} + \frac{1}{\tau_{a}} + \frac{1}{\tau_{b}} + \frac{1}{\tau_{np}}$$
(2.18)

One of the most important aspects of the different mechanisms is that they have different scattering rates for different frequencies of phonons. τ_u is the relaxation time due to Umklapp phonon-phonon scattering. Empirically, it is given by

$$\tau_u^{-1} = AT\omega^2 e^{-B/T} \tag{2.19}$$

where A and B are parameters specific to the material. Note that high frequency phonons are scattering far more quickly than low frequency phonons.

 τ_a is relaxation time due to alloy disorder scattering. Abeles has derived a phenomenological model for alloy scattering based on principles from continuum mechanics and finds that the form of the scattering rate is⁹

$$\tau_a^{-1} = \frac{Fx(1-x)\omega^4}{v_p^3}$$
(2.20)

where F is a constant for the given material system and x is the ratio of different elements constituting the alloy. In principle, F can be estimated from knowledge of the lattice constants, atomic masses, and elastic constants of the individual alloy components⁹, but it is usually treated a phenomenological constant and determined by fitting to experimental data; this is the approach we take.

 au_b is relaxation time due to boundary scattering given by

$$\tau_b^{-1} = v_p / L_b \tag{2.21}$$

where L_b is the boundary scattering length of the alloy. This form expresses the time it takes a phonon to travel ballistically over a length of L_b at speed of sound v_p .

We denote τ_{np} as the relaxation time due to nanoparticle impurities. This can be calculated from the scattering cross-section of phonons. The scattering crosssection of any wave is defined based on the rate at which an incident wave carrying energy at rate P (units W/m²) loses energy to a single scatterer at rate Q (units W); the scattering cross-section is defined as $\sigma = Q/P$. If there are many nanoparticles present the scattering rate for energy is given by $\tau_{NP}^{-1} = \eta_{NP}v_p\sigma$ where η_{NP} is the number density (units #/m³) of nanoparticles. If the size and shape of the nanoparticles are known, then the number density of particles can be calculated in terms of their volume fraction, f_{vol} in composite material as

$$\eta_{NP} = f_{vol} / V_{NP} \tag{2.22}$$

where V_{NP} is the volume of each nanoparticle.

The primary difficulty in modeling thermal transport in nanocomposites is determining the value of the scattering cross-section, σ , using an appropriate model. In this thesis we wish to investigate the thermal conductivity of fiber-based nanocomposites for which scattering cross-sections for phonons are not generally available. Note that unlike spherical particles, fibers have inherently anisotropic scattering cross-section. To capture the anisotropic physics, it is thus required that the Boltzmann transport equation not be directionally averaged as has been done in most previous modeling efforts. Due to the lack of symmetry, evaluating the Boltzmann integral requires that the phonon scattering cross-section be calculated for all possible incident angles, polarizations, and wavelengths.

The next chapter is dedicated to determining the scattering cross-section for phonons incident on an embedded cylinder in a composite material using a continuum mechanics approach.

Chapter 3

SCATTERING OF PHONONS BY EMBEDDED NANOCYLINDERS

Since thermal conductivity in a semiconductor material is directly driven by phonons, it becomes pertinent to promote phonon scattering to reduce the thermal conductivity of the material. One of the methods to accomplish this, that has been studied extensively has been the introduction of embedded nanoparticles, thereby locally modifying elastodynamic properties resulting in improved phonon scattering at these discontinuities.

Kim¹⁰ has derived the scattering cross-section for spherical nanoparticles from quantum mechanical perturbation theory. However, Kim¹⁰ found that short wavelength evaluation of the perturbation theory result does not reproduce the known geometric limit. Concluding that this was an error due to the use of perturbation theory, he proposed patching the perturbation obtained Rayleigh limit together with a neargeometric model for compressional wave scattering that was instead obtained through analogy with the van der Hulst solution, which is technically valid for scalar waves. Although Kim¹⁰ reports Mie-like oscillations near the transition from the Rayleigh to geometric regimes, it should be noted that the model is not exact near the transition for either compressional or transverse waves; additional shortcomings include (1) that perturbation theory prevented Kim from treating force constant contrast and density contrast simultaneously, and thus cross-correlations could not be taken into account. The unintended result of this is that materials with matched elastic impedance but different density would be predicted to have high scattering cross-section. (2) In the Rayleigh limit, the model does not differentiate between compressional and transverse wave scattering cross-sections, (3) the model does not specify which "elastic constant" it is referring to when evaluating the cross-section, (4) the van der Hulst solution is only strictly valid for scalar waves, but is applied to vector waves. Kim also extended the calculated scattering cross-section to include the effect of a distributed range of nanoparticles sizes by taking the effective scattering cross-section to be a weighted average of the monodisperse result with the particle size distribution function.

Mingo $(2009)^{14}$ used a model for calculation of scattering cross-section for nanospheres by considering the mass missmatch between the matrix and fiber materials, while ignoring the stiffness missmatch. Such an assumption enabled him to simplify the scattering cross-section calculation into the following expressions: $\sigma_{LW} = 4\pi/9 (\Delta M / M)^2 k^4 a^6$ in the Rayleigh regime and $\sigma_{sW} = 2\pi a^2$ in the geometric regime, where $\Delta M / M$ is the mass missmatch, *k* the wave number of the phonons and *a* is the nanosphere radius. Thermal conductivity of nanoparticle-in-alloy systems with silicide nanoparticles embedded in SiGe alloy were modeled using this scattering cross-sections. However, this model proves inefficient when there is significant stiffness missmatch between the materials.

White (1958)¹⁸ has developed an analytic model for scattering of incident elastic waves of arbitrary incident angle and polarization from cylindrical discontinuities in an elastic medium, which is exactly the solution that is needed for the current modeling effort. White showed that the results of the model compare favorably to direct experimental observations of scattering phase function for normal incidence. However, we have found that White's formulation contains a number of errors when applied to the oblique angles of incidence needed to apply Boltzmann transport modeling.

In particular, the potential functions for normal and tangential parts of the vector potentials used to formulate the scattered shear wave expressions were incorrect.

As a result, White's expressions for displacement and stress components contain many non-trivial errors which we will rectify in this thesis. In particular, in White's paper we have found that in Table I, following components are incorrect for oblique incidence: (1) the incident z-polar shear wave displacements u_r and u_z , and incident z-polar shear wave stress components T_{rr} , $T_{r\theta}$ and T_{rz} , (2) the scattered compressional wave stress components T_{rr} , $T_{r\theta}$ and T_{rz} , the scattered shear wave displacements, u_r , u_{θ} and u_z . In addition, White's expressions for scattering crosssection and mode-conversion are only valid for normal angles of incidence. For many applications, oblique angles of incidence are important. For example, the thermal conductivity of a composite material with embedded fibers is the result of contributions of many different phonon frequencies, polarizations, and angles of incidence even for composites with randomly distributed fiber orientations. The mode conversion efficiencies are also anticipated to change with incidence angle analogous with electromagnetic scattering. Apart from formulating the oblique incidence equations, which contained the errors discussed above, White did not present any results or simulations associated with oblique incidence. In addition, the wavenumber dependence of scattering was not investigated either for normal or oblique incidence.

Here, we have redeveloped the analytic formulation for scattering of an incident elastic wave of arbitrary polarization and angle of incidence from an

embedded cylindrical discontinuity, and derived expressions for scattering crosssection and mode-conversion that apply for the entire range of possible conditions. For the purpose of simplicity, we will be denoting the tangential shear wave as y-polar wave and the normal shear wave as z-polar wave. The scattering cross-section is calculated as a ratio of the time average energy flux generated by the scattering wave with the time averaged rate of work done by the incident wave. We have generated plots of scattering efficiency for NiSi₂ material. The scattering efficiency, σ/a (where a is the normal area of wave incidence), is shown to be proportional to $(kr)^3$ in the Rayleigh scattering regime, while it attains a constant value of 2 at the geometric regime. An optimal value of kr can be found in between the Rayleigh and the geometric regimes just as the scattering efficiency attains a constant value of 2 which would be ideal for efficiently reducing the thermal conductivity of the doped alloy material.

3.1 Scattering Cross-section - An Analytic Approach

In developing the analytical formulation, we follow the same general procedure as White. We will consider the scattering of a plane compressional or shear wave of a single frequency incident obliquely on an infinitely long elastic cylindrical discontinuity embedded in a different elastic medium. Figure 1 shows the orientation of the cylinder and the incident wave with coordinate axes. The general formulation proceeds as follows.



Figure 1: Cylinder orientation

Referring to the figure above, an incident wave of a single frequency and polarization travels through an outer region (denoted as region 2), with propagation direction in the x-z plane, given by unit vector \tilde{a} ,which has an oblique incidence relative to the x-y plane. The angle between \tilde{a} and the x-y plane is denoted by ϕ , for incident compressional waves and or by ψ for shear waves. The incident wave encounters a cylindrical scattering medium at radius 'a' from the z-axis denoted as region 1. This produces both a scattered wave in region 2 and excites an internal wave in region 1. The total wave displacement in region 2 is a combination of the incident and scattered waves. For continuity, both the displacements and the traction must be continuous at the interface between regions 1 and 2.

If both mediums are linearly elastic with isotropic elastic tensors, then the equation of motion for each material is given by

$$\rho \frac{\partial^2 \underline{u}}{\partial t^2} = (\lambda + 2\mu) \nabla (\nabla \cdot \underline{u}) - \mu (\nabla \times \nabla \times \underline{u})$$
(3.1)

Where ρ is the density of the material, and λ and μ are the Lamé constants.

If the displacements are temporally sinusoidal, then any spatial portion of the displacement field which satisfies (3.1) can be expressed as the superposition of displacements derived from scalar functions (Φ , Θ , and χ) which satisfy Helmholtz equations. In particular (1) if $(\nabla^2 + k^2)\Phi = 0$ then $\underline{L} = \nabla\Phi$ is a solution representing a longitudinal wave, (2) if $(\nabla^2 + k_s^2)\Theta = 0$ then $\underline{M} = \nabla \times (\hat{z}\Theta)$ is a solution representing a transverse wave with polarization orthogonal to the plane containing the \tilde{z} axis of the cylinder and (3) if $(\nabla^2 + k_s^2)\Theta = 0$ then $\underline{N} = \nabla \times \nabla \times (\hat{z}\chi)$ is a solution representing a transverse wave with polarization parallel to the plane containing the \tilde{z} axis of the cylinder.

3.2 Incident Wave Expressions

The displacement associated with the incident plane compressional wave is of the form,

$$\tilde{u} = \tilde{a}u_0 e^{-i\omega t} e^{ik_2(x\cos\phi_2 + z\sin\phi_2)}$$
(3.2)

It can be easily verified from $\tilde{u} = \nabla \Psi$ that the scalar potential function for this displacement can be expressed as

$$\Psi = \frac{u_0}{k_2} e^{-i\omega t} e^{ik_2(x\cos\phi_2 + z\sin\phi_2)}$$
(3.3)

where $k_2 = \omega/c_2$, where c_2 is the velocity of propagation of the compressional wave through the region 2. The velocity of propagation for a compressional wave can be given by,
$$c_2^{\ 2} = \frac{\lambda_2 + 2\mu_2}{\rho_2} \tag{3.4}$$

Similarly, the vector potential functions for displacement for an incident shear wave can be expressed as

$$\Lambda = \frac{u_0}{ik_{II}} e^{-i\omega t} e^{ik_{II}(x\cos\psi_2 + z\sin\psi_2)}$$
(3.5)

where $k_{II} = \omega / c_{II}$, where c_{II} is the velocity of propagation of the shear wave through the region 2. The velocity of propagation of a shear wave can be given by,

$$c_{II}^{2} = \frac{\mu_{2}}{\rho}$$
(3.6)

We wish to do the calculation in cylindrical coordinates. In order to write the $e^{ik (x\cos\psi)}$ terms in cylindrical coordinates, we can implement a substitution with Bessel functions, which can be derived as follows ¹

$$e^{ik(x\cos\psi)} = e^{ik(r\cos\theta\cos\psi)} = e^{ik'r\cos\theta}$$

where $k' = k\cos\phi$ (3.7)

Let us consider the Laurent series expansion of a term $e^{z(t^2-1)/2t}$ which has an essential singularity at t=0¹⁹

$$e^{z(t^2-1)/2t} = \sum_{n=-\infty}^{\infty} t^n J_n(z)$$
(3.8)

Substituting $t = ie^{i\theta}$ and z = k'r on the left hand side of (3.8) we get

$$e^{z(t^2 - 1)/2t} = e^{ik' r \cos\theta}$$
(3.9)

The same substitutions on the right hand side of (3.8) leads to

$$\sum_{n=-\infty}^{\infty} t^{n} J_{n}(z) = J_{0}(kr) + \sum_{n=1}^{\infty} (i)^{n} J_{n}(kr) \left(e^{in\theta} + e^{-in\theta} \right)$$
(3.10)

Note that the left hand side is a sum from $-\infty < n < \infty$, but on the RHS we exploit the symmetry to make the sum run from $0 < n < \infty$. Using the complex definition of $cos(z) = (e^{iz} + e^{-iz})/2$, we get

$$e^{ik'r\cos\theta} = \sum_{n=0}^{\infty} e_n(i)^n J_n(kr)\cos(n\theta)$$

$$e_n = \begin{cases} 1 & \text{if } n = 0\\ 2 & \text{if } n \ge 1 \end{cases}$$
(3.11)

If we neglect the harmonic time-dependence term in the expressions (3.3) and (3.5) the potential functions become

$$\Psi = \frac{u_0}{k_2} \sum_{n=0}^{\infty} e^{iKz} e_n(i)^n J_n(k_2'r) \cos(n\theta)$$
(3.12)

$$\hat{\Lambda} = \frac{u_0}{ik_{II}} \sum_{n=0}^{\infty} e^{iKz} e_n(i)^n J_n(k_{II}'r) \cos(n\theta) \hat{e}_z$$
(3.13)

where
$$k_2' = k_2 \cos \phi_2$$

 $k_1' = k_1 \cos \phi_1$
 $k_{II}' = k_{II} \cos \psi_2$
 $k_1' = k_1 \cos \psi_1$
 $K = k_2 \sin \phi_2$

$$(3.14)$$

(All terms with subscript 1 or 2 refer to the corresponding region, while the Roman numeral subscripts are used for shear waves and Arabic numeral subscripts are used for compressional waves. Note that both polarizations of shear wave are derived from the same potential function.)

Note: From the above expressions, we can see that the correct expressions for the potential functions for shear waves mentioned in White's paper are as follows:

Region 1:

$$V_{\text{tangential}} = \sum_{n=0}^{\infty} E_n \left\{ grad \left[J_n(k_I \,' r) \frac{\sin}{\cos} \, (n\theta) \exp(iKz) \right] \right\} \times \tilde{z}$$
(3.15)

$$V_{normal} = (1/k_I) \sum_{n=0}^{\infty} F_n \left\{ curlcurl \left[\tilde{z} J_n(k_I'r) \sup_{\sin}^{\cos} (n\theta) \exp(iKz) \right] \right\}$$
(3.16)

Region 2

$$V_{\text{tangential}} = \sum_{n=0}^{\infty} B_n \left\{ grad \left[H_n(k_{II} ' r) \cos^{(n\theta)} \exp(iKz) \right] \right\} \times \tilde{z}$$
(3.17)

$$V_{normal} = (1/k_{II}) \sum_{n=0}^{\infty} C_n \left\{ curlcurl \left[\tilde{z}H_n(k_{II}'r) \frac{\cos}{\sin} (n\theta) \exp(iKz) \right] \right\}$$
(3.18)

From here on we will be using the following substitutions for simplicity of expression. r - k r

$$x_{i} - k_{i}'$$

 $x_{i}' = k_{i}'r$ (3.19)
where $i = 1, 2, I, II$

Let us express the amplitude for the incident waves by the term K_n , such that

$$K_{n} = \frac{u_{0}}{k_{2}} \quad incident \quad compressional$$

$$K_{n} = \frac{u_{0}}{ik_{II}} \quad incident \quad shear$$
(3.20)

The expression for displacements can be derived from the potential functions by using the following expressions

$$u_c = \nabla \Psi$$
 for compressional wave (3.21)

$$u_{sy} = -\nabla \times \hat{z}\Lambda$$
 for $y - polar$ shear wave (3.22)

$$u_{sz} = (1/k_{II}) \cdot (-\nabla \times \nabla \times (\hat{z}\Lambda)) \quad for \quad z - polar \quad shear \quad wave \qquad (3.23)$$

Stress components expressed in cylindrical coordinates can be derived from the displacement components as follows,

$$T_{rr} = \lambda \left[\frac{1}{r}\frac{\partial}{\partial r}(ru_r) + \frac{1}{r}\frac{\partial}{\partial \theta}(u_\theta) + \frac{\partial}{\partial z}(u_z)\right] + 2\mu \frac{\partial}{\partial r}(u_r)$$
(3.24)

$$T_{r\theta} = \mu \left[r \frac{\partial}{\partial r} \left(\frac{u_{\theta}}{r} \right) + \frac{1}{r} \frac{\partial}{\partial \theta} (u_r) \right]$$
(3.25)

$$T_{rz} = \mu \left[\frac{\partial}{\partial r}(u_z) + \frac{\partial}{\partial z}(u_r)\right]$$
(3.26)

The displacement and stress components for the incident waves have been given in Table 2. The incident displacement and stress components in this paper are different from those used by White¹⁸, which were clearly incorrect because they were not dimensionally consistent. However, his expressions would not have impacted the

predicted scattering cross section since this involves taking the ratio of the incident and scattered waves, each of which was proportional to the square of the displacement.

Table 2:Incident wave components

1. Compressional Wave	
$\frac{u_r}{(1/r)} = \sum_{n=0}^{\infty} K_n e^{iK_z} \left[-x_2 J_n (x_2) \right] \cos(n\theta)$	(3.27)
$\frac{u_{\theta}}{(1/r)} = \sum_{n=0}^{\infty} K_n e^{iK_z} \left[\pm nJ_n(x_2') \right] \sin(n\theta)$	(3.28)
$\frac{u_z}{(1/r)} = \sum_{n=0}^{\infty} K_n e^{iKz} \left[-i(Kr) J_n(x_2') \right] \cos(n\theta)$	(3.29)

$$\frac{T_{rr}}{(\mu_2 / r^2)} = \sum_{n=0}^{\infty} K_n e^{iK_z} \left[-2(x_2')^2 \left(J_n''(x_2') - \left(\frac{x_2}{x_2'}\right)^2 \left(\frac{\lambda_2}{2\mu_2}\right) J_n(x_2') \right) \right] \cos(n\theta) (3.30)$$

$$\frac{T_{r\theta}}{(\mu_2/r^2)} = \sum_{n=0}^{\infty} K_n e^{iKz} \left[\pm 2n \left((x_2') J_n'(x_2') - J_n(x_2') \right) \right] \quad \sin(n\theta)$$
(3.31)

$$\frac{T_{rz}}{(\mu_2/r^2)} = \sum_{n=0}^{\infty} K_n e^{iKz} \left[-2i(x_2')(Kr) J_n'(x_2') \right] \cos(n\theta)$$
(3.32)

2. y-polar Shear Wave

$$\frac{u_r}{(1/r)} = \sum_{n=0}^{\infty} K_n e^{iK_z} (\pm n J_n (k_{II} 'r)) \quad \cos(n\theta)$$
(3.33)

$$\frac{u_{\theta}}{(1/r)} = \sum_{n=0}^{\infty} K_n e^{iKz} (-(k_{II}'r) J_n'(k_{II}'r)) \quad \sin(n\theta)$$
(3.34)

$$\frac{T_{rr}}{(\mu_2/r^2)} = \sum_{n=0}^{\infty} K_n e^{iKz} \left[\pm 2n \left(x_{II} \,' J_n \,' \left(x_{II} \,' \right) - J_n \left(x_{II} \,' \right) \right) \right] \quad \cos(n\theta)$$
(3.35)

$$\frac{T_{r\theta}}{(\mu_2 / r^2)} = \sum_{n=0}^{\infty} K_n e^{iKz} \left[-(x_{II}')^2 (2J_n''(x_{II}') + J_n(x_{II}')) \right] \quad \sin(n\theta)$$
(3.36)

$$\frac{T_{rz}}{(\mu_{2}/r^{2})} = \sum_{n=0}^{\infty} K_{n} e^{iKz} (Kr) [\pm inJ_{n}(x_{H})] \cos(n\theta)$$
(3.37)
3. z-polar Shear Wave

$$\frac{u_{r}}{(1/r)} = \sum_{n=0}^{\infty} K_{n} e^{iKz} \left[i(Kr) \left(\frac{x_{H'}}{x_{H'}} \right) J_{n}'(x_{H'}) \right] \cos(n\theta)$$
(3.38)

$$\frac{u_{\theta}}{(1/r)} = \sum_{n=0}^{\infty} K_{n} e^{iKz} \left[\mp in \left(\frac{Kr}{x_{H'}} \right) J_{n}(x_{H'}) \right] \sin(n\theta)$$
(3.39)

$$\frac{u_{z}}{(1/r)} = \sum_{n=0}^{\infty} K_{n} e^{iKz} \left[\frac{(x_{H})^{2} J_{n}(x_{H'})}{x_{H}} \right] \cos(n\theta)$$
(3.40)

$$\frac{T_{rr}}{(\mu_{2}/r^{2})} = \sum_{n=0}^{\infty} K_{n} e^{iKz} \left[2i \left(x_{H'} \right)^{2} \left(\frac{Kr}{x_{H}} \right) J_{n}''(x_{H'}) \right] \cos(n\theta)$$
(3.41)

$$\frac{T_{r\theta}}{(\mu_{2}/r^{2})} = \sum_{n=0}^{\infty} K_{n} e^{iKz} \left[\mp 2i n \frac{Kr}{x_{H}} (x_{H'} J_{n}'(x_{H'}) - J_{n}(x_{H'})) \right] \sin(n\theta)$$
(3.42)

$$\frac{T_{rz}}{(\mu_{2}/r^{2})} = \sum_{n=0}^{\infty} K_{n} e^{iKz} \left[\frac{2(x_{H'})^{3} J_{n}'(x_{H'})}{x_{H'}} \left(1 - \frac{1}{2\cos^{2} \psi_{2}} \right) \right] \cos(n\theta)$$
(3.43)

3.3 Scattered Wave Expressions

The potential functions used to generate scattered wave components must satisfy the Helmholtz equation. In addition, the scattered waves in region 1(inside the cylinder) pass through the origin and must remain finite there; this places an addition restriction on the allowable components. The potential functions which satisfy these conditions for region 1 can be expressed as:

$$\Psi_{1} = -e^{iK_{z}} \sum_{n=0}^{\infty} D_{n} J_{n} (k_{1}'r) \frac{\cos}{\sin} \quad n\theta$$
(3.44)

The scattered waves in region 2 must be outgoing traveling waves, but the potential function need not be finite at the origin since the waves do not physically exist for r<a. Thus, in region 2 Hankel functions of the second kind are used instead of Bessel functions:

$$\Psi_2 = -e^{iK_z} \sum_{n=0}^{\infty} A_n H_n (k_2'r) \frac{\cos}{\sin} n\theta \qquad (3.45)$$

where $H_n(kr) = J_n(kr) + iY_n(kr)$ is the Hankel function. Here, we are using arbitrary constants A_n and D_n for the scattered in region 2 and region 1 respectively. We have used two angular functions (cosine and sine) in each potential equation as both of these satisfy the Helmholtz equation. However, it will later become clear that the upper angular function denotes the potential to be used for an incident compressional wave and the lower angular function denotes an incident shear wave because of the need to match terms with the respective incident wave.

The scattered wave displacement, \hat{V} can be constructed as the superposition of all possible compressional and shear waves.

$$\hat{V} = \hat{L} + \hat{M} + \hat{N} \tag{3.46}$$

where

$$\hat{L} = \sum_{n=0}^{\infty} A_n (\nabla \Phi_n)$$
(3.47)

$$\hat{M} = \sum_{n=0} B_n (\nabla \times (\hat{z} \Theta_n))$$
(3.48)

$$\hat{N} = 1/k_{s} \sum_{n=0} C_{n} (\nabla \times \nabla \times (\hat{z} \chi_{n}))$$
(3.49)

where the potential functions in Eqs. (3.46), (3.47), (3.48) and (3.49) are given as

$$\Phi_n(r,\theta,z) = e^{ik_2 \sin(\phi_2)z} H_n(k_2 \cos(\phi_2)r) \qquad \begin{array}{c} \cos(n\theta) \\ \sin(n\theta) \end{array}$$
(3.50)

$$\Theta_n(r,\theta,z) = e^{ik_{II}\sin(\psi_2)z} H_n(k_{II}\cos(\psi_2)r) \qquad \frac{\sin(n\theta)}{\cos(n\theta)}$$
(3.51)

$$\chi_n(r,\theta,z) = e^{ik_{II}\sin(\psi_2)z} H_n(k_{II}\cos(\psi_2)r) \qquad \frac{\cos(n\theta)}{\sin(n\theta)}$$
(3.52)

 \hat{L} represents the longitudinal part of \hat{V} , \hat{M} is the part of the transverse vector field normal to the surface, while \hat{N} is the part tangential to that surface.

Using the expressions above, it is possible to analytically obtain the displacements and stresses due to the scattered waves. The stress and displacements on the boundary of the cylinder must be matched for a self-consistent solution. This provides the 6 conditions (for each value of n) that will be necessary to determine the unknown coefficients, A_n , B_n , C_n , D_n , E_n , F_n . The derivations of these expressions are quite lengthy. While symbolic manipulation software (MAPLE) was employed to perform some of the calculation, certain simplifications, such as recursion formula's for Bessel and Hankel functions were not recognized by the software and were performed by hand to obtain the final expressions. The non-dimensionalized results for stress and strain evaluated at the cylinder surface due to the scattered wave in region 2 are summarized in Table 4. The corresponding expressions due to scattered waves in region 1 can be obtained from Table 4 by making the substitutions noted in Table 3.

Importantly, we have discovered that the expressions used by White for displacements for shear waves as well as the radial-stress component for compressional waves contained non-trivial errors for oblique angles of incidence. The refraction and reflection angles for the compressional and scattered waves in both regions can be related by Snell's law and used to determine the angle of the scattered waves from knowledge of the angle and type of incident wave:

$$\frac{\sin\phi_1}{c_1} = \frac{\sin\psi_1}{c_I} = \frac{\sin\phi_2}{c_2} = \frac{\sin\psi_2}{c_{II}}$$
(3.53)

Table 3:Substitutions for expressions for region 1

Region 2	Region 1
H_n	J_n
Subscript 2	Subscript 1
Subscript II	Subscript I
A_n	D_n
B_n	E_n
C_n	F_n

1. Compressional Wave	
$\frac{u_{r,L}}{(1/r)} = \sum_{n=0}^{\infty} A_n e^{iKz} \left[-x_2 H_n'(x_2) \right] \frac{\cos(n\theta)}{\sin(n\theta)}$	(3.54)
$\frac{u_{\theta,L}}{(1/r)} = \sum_{n=0}^{\infty} A_n e^{iKz} \left[\pm nH_n(x_2') \right] \frac{\sin(n\theta)}{\cos(n\theta)}$	(3.55)
$\frac{u_{z,L}}{(1/r)} = \sum_{n=0}^{\infty} A_n e^{iKz} \left[-i(Kr)H_n(x_2') \right] \frac{\cos(n\theta)}{\sin(n\theta)}$	(3.56)
$\frac{T_{rr,L}}{(\mu_2/r^2)} = \sum_{n=0}^{\infty} A_n e^{iKz} \left[-2(x_2')^2 \left(H_n''(x_2') - \left(\frac{x_2}{x_2'}\right)^2 \left(\frac{\lambda_2}{2\mu_2}\right) H_n(x_2') \right) \right] \cos(nx_2) \sin(nx_2)$	$\left(\begin{array}{c} \theta \\ \theta \end{array} \right) $ (3.57 $\left(\begin{array}{c} \theta \end{array} \right) $
$\frac{T_{r\theta,L}}{(\mu_2/r^2)} = \sum_{n=0}^{\infty} A_n e^{iK_z} \left[\pm 2n \left((x_2') H_n'(x_2') - H_n(x_2') \right) \right] \frac{\sin(n\theta)}{\cos(n\theta)}$	(3.58)
$\frac{T_{rz,L}}{(\mu_2/r^2)} = \sum_{n=0}^{\infty} A_n e^{iKz} \left[-2i(x_2')(Kr)H_n'(x_2') \right] \frac{\cos(n\theta)}{\sin(n\theta)}$	(3.59)
2. y-polar Shear Wave	
$\frac{u_{r,M}}{(1/r)} = \sum_{n=0}^{\infty} B_n e^{iKz} (\pm nH_n(k_{II}'r)) \frac{\cos(n\theta)}{\sin(n\theta)}$	(3.60)
$\frac{u_{\theta,M}}{(1/r)} = \sum_{n=0}^{\infty} B_n e^{iKz} \left(-\left(k_{II} 'r\right) H_n '\left(k_{II} 'r\right)\right) \frac{\sin(n\theta)}{\cos(n\theta)}$	(3.61)
$\frac{T_{rr,M}}{(\mu_2 / r^2)} = \sum_{n=0}^{\infty} B_n e^{iKz} \left[\pm 2n \left(x_{II} ' H_n ' (x_{II} ') - H_n (x_{II} ') \right) \right] \frac{\cos(n\theta)}{\sin(n\theta)}$	(3.62)
$\frac{T_{r\theta,M}}{(\mu_2/r^2)} = \sum_{n=0}^{\infty} B_n e^{iKz} \left[-\left(x_{II}\right)^2 \left(2H_n \left(x_{II}\right) + H_n\left(x_{II}\right)\right) \right] \frac{\sin(n\theta)}{\cos(n\theta)}$	(3.63)

$\frac{T_{rz,M}}{(\mu_2/r^2)} = \sum_{n=0}^{\infty} B_n e^{iKz} (Kr) [\pm inH_n(x_{II}')] \frac{\cos(n\theta)}{\sin(n\theta)}$	(3.64)
3. z-polar Shear Wave	
$\frac{u_{r,N}}{(1/r)} = \sum_{n=0}^{\infty} C_n e^{iKz} \left[i(Kr) \left(\frac{x_{II}}{x_{II}} \right) H_n'(x_{II}') \right] \frac{\cos(n\theta)}{\sin(n\theta)}$	(3.65)
$\frac{u_{\theta,N}}{(1/r)} = \sum_{n=0}^{\infty} C_n e^{iKz} \left[\mp in \left(\frac{Kr}{x_{II'}}\right) H_n(x_{II'}) \right] \frac{\sin(n\theta)}{\cos(n\theta)}$	(3.66)
$\frac{u_{z,N}}{(1/r)} = \sum_{n=0}^{\infty} C_n e^{iKz} \left[\frac{(x_{II})^2 H_n(x_{II})}{x_{II}} \right] \frac{\cos(n\theta)}{\sin(n\theta)}$	(3.67)
$\frac{T_{rr,N}}{(\mu_2/r^2)} = \sum_{n=0}^{\infty} C_n e^{iKz} \left[2i \left(x_{II} \right)^2 \left(\frac{Kr}{x_{II}} \right) H_n''(x_{II}) \right] \frac{\cos(n\theta)}{\sin(n\theta)}$	(3.68)
$\frac{T_{r\theta,N}}{(\mu_2/r^2)} = \sum_{n=0}^{\infty} C_n e^{iKz} \left[\mp 2in \frac{Kr}{x_{II}} (x_{II}'H_n'(x_{II}') - H_n(x_{II}')) \right] \frac{\sin(n\theta)}{\cos(n\theta)}$	(3.69)
$\frac{T_{rz,N}}{(\mu_2/r^2)} = \sum_{n=0}^{\infty} C_n e^{iKz} \left[\frac{2(x_{II}')^3 H_n'(x_{II}')}{x_{II}} \left(1 - \frac{1}{2\cos^2 \psi_2} \right) \right] \frac{\cos(n\theta)}{\sin(n\theta)}$	(3.70)

Although the expressions used by White¹⁸ for displacements and stresses when waves are normally incident on the cylindrical discontinuity are correct, we found certain discrepancies in the scattered wave components in the region outside the scatterer when the incident wave is obliquely incident. Therefore, we have rectified the expressions to incorporate all angles of incidence of the incident wave.

3.4 Boundary Conditions

For the most general case of an elastic scatterer in an elastic medium, at the boundary of the cylinder both the displacement vector u and the traction vector T, are continuous across the boundary. So, there are six boundary conditions that will apply at the surface of the cylindrical discontinuity at r=a. They can be given as follows:

$$((T_{ij})_{2} + (T_{ij})_{II}' + (T_{ij})_{II}'' - (T_{ij})_{1} - (T_{ij})_{I}' - (T_{ij})_{I}'')_{scattered} = -(T_{ij})_{incident}$$
(3.71)

$$((\mathbf{u}_{ij})_{2} + (\mathbf{u}_{ij})_{II} + (\mathbf{u}_{ij})_{II} - (\mathbf{u}_{ij})_{1} - (\mathbf{u}_{ij})_{I} - (\mathbf{u}_{ij})_{I})_{scattered} = -(\mathbf{u}_{ij})_{incident}$$
(3.72)
$$ij = rr, r\theta, rz$$

Here, unprimed terms are for compressional waves, single primed are for y-polar shear waves and double primed terms are for z-polar shear waves. Further simplification can be made in the special cases of cylindrical voids or completely rigid cylinders. For a void scatterer, at the boundary the total traction vectors T must be zero at the boundary but there is no restriction on the total displacement. So, there are three boundary conditions that will apply at the surface of the cylindrical discontinuity at r=a. They can be given as follows:

$$((T_{ij})_{2} + (T_{ij})_{II} + (T_{ij})_{II}'')_{scattered} = -(T_{ij})_{incident}$$

$$j = rr, r\theta, rz$$
(3.73)

For a rigid scatterer, at the boundary the total displacement vector u is zero (considering a cylinder immobilized externally) at the boundary and there is no restriction on the traction vector. So, there are three boundary conditions that will apply at the surface of the cylindrical discontinuity at r=a. They can be given as follows:

$$((\mathbf{u}_{ij})_{2} + (\mathbf{u}_{ij})_{II}' + (\mathbf{u}_{ij})_{II}'')_{scattered} = -(\mathbf{u}_{ij})_{incident}$$

$$ij = rr, r\theta, rz$$
(3.74)

The solutions of these equations give us the ratio of scattered wave amplitudes to incident wave amplitudes, A_n', B_n' and C_n' , where

$$A_{n}' = \frac{A_{n}}{K_{n}}$$
, $B_{n}' = \frac{B_{n}}{K_{n}}$ & $C_{n}' = \frac{C_{n}}{K_{n}}$ (3.75)

3.5 Cross-section Calculation

From the displacement and stress components, we can calculate the energy flux in both incident as well as scattered waves. The time-averaged energy flux passing through a surface, A, can be calculated as: ²⁰

$$F = \left\langle \iint \left[\Sigma_{ij} \cdot \frac{\partial S_{ij}}{\partial t} \right] \cdot dA \right\rangle_{t}$$
(3.76)

where the outer bracket denotes a time-averaging of the flux. Σ_{ij} and S_{ij} are the stress and displacement components in their harmonic form. Up until now displacement and stress have been treated as complex quantities, but for calculation of energy fluxes, we are interested in real displacements leading to real stresses. To utilize our results, we will simply substitute $\frac{1}{2} \left(\Sigma_{ij} + \overline{\Sigma}_{ij} \right)$ instead of Σ_{ij} and $\frac{1}{2} \left(\frac{\partial S_{ij}}{\partial t} + \frac{\partial \overline{S}_{ij}}{\partial t} \right)$ instead of $\frac{\partial S_{ij}}{\partial t}$.

$$F = \left\langle \frac{1}{4} \iint \left[\Sigma_{ij} \cdot \frac{\partial S_{ij}}{\partial t} + \Sigma_{ij} \cdot \frac{\partial \overline{S}_{ij}}{\partial t} + \overline{\Sigma}_{ij} \cdot \frac{\partial S_{ij}}{\partial t} + \overline{\Sigma}_{ij} \cdot \frac{\partial \overline{S}_{ij}}{\partial t} \right] \right\rangle_{t}$$
(3.77)

If we substitute the displacement and stress terms with known dependencies,

$$\Sigma_{ij} = T_{ij}e^{i\omega t}$$

$$S_{ij} = u_{ij}e^{i\omega t}$$
(3.78)

$$F = \left\langle \frac{1}{4} \iint [i\omega(T_{ij}u_{ij}e^{2i\omega t}) + i\omega(\overline{T}_{ij}u_{ij}) - i\omega(T_{ij}\overline{u}_{ij}) - i\omega(\overline{T}_{ij}\overline{u}_{ij}e^{-2i\omega t})] \cdot dA \right\rangle_t$$
(3.79)

The sinusoidal terms vanish upon taking the time average and we are left with

$$F = \frac{i\omega}{4} \iint \left[(\overline{T}_{ij} u_{ij}) - (T_{ij} \overline{u}_{ij}) \right] \cdot dA \tag{3.80}$$

Let us consider the incident wave in Cartesian coordinates for ease of calculation. The area associated with an infinitely extended plane wave is not defined, but we can still do the calculation on a per-unit-area basis to obtain an incident energy flux with units W/m^2 . If we consider the time-averaged intensity of the incident compressional plane wave, it can be expressed as follows⁹:

$$\left(\frac{dW}{dt}\right)_{avg} = \left(\frac{i\omega}{4}\right) \left(T_{xz}\overline{u}_x - \overline{T}_{xz}u_x + T_{yz}\overline{u}_y - \overline{T}_{yz}u_y + T_{zz}\overline{u}_z - \overline{T}_{zz}u\right)$$
(3.81)

For an incident compressional wave, displacement is only in the x-direction,

$$u_x = u_0 \exp\left(-ik_2 x\right) \tag{3.82}$$

$$u_y = u_z = 0 \tag{3.83}$$

and

$$T_{xx} = \lambda_2 \frac{\partial u_x}{\partial x} + 2\mu_2 \frac{\partial u_x}{\partial x}$$

= $(\lambda_2 + 2\mu_2)(-ik_2) \exp(-ik_2 x)$ (3.84)

From these expressions we can derive that, for an incident compressional wave,

$$\left(\frac{dW}{dt}\right)_{avg} = \left(\frac{(\lambda_2 + 2\mu_2)u_0^2}{2}\right)(k_2\omega)$$
(3.85)

Similarly, for an incident y-polar shear wave, using

$$u_{y} = u_{0} \exp\left(-ik_{II}x\right)$$

$$u_{x} = u_{z} = 0$$
(3.86)

and

$$T_{xy} = \mu_2 \left[\frac{\partial u_y}{\partial x} + \frac{\partial u_x}{\partial y} \right]$$

= $\mu_2 (-ik_{II}) \exp(-ik_2 x)$ (3.87)

we get, for an incident y-polar shear wave,

$$\left(\frac{dW}{dt}\right)_{avg} = \left(\frac{\mu_2 u_0^2}{2}\right) (k_{II}\omega)$$
(3.88)

Similarly, for an incident z-polar shear wave,

$$\left(\frac{dW}{dt}\right)_{avg} = \left(\frac{\mu_2 u_0^2}{2}\right) (k_{II}\omega)$$
(3.89)

For the scattered wave, the energy flux leaving a cylindrical control volume of radius b can be given as,

$$\dot{P}_{avg} = \left(\frac{i\omega}{4}\right) \int_{-\pi}^{\pi} \left(T_{rr}\overline{u}_{r} - \overline{T}_{rr}u_{r} + T_{r\theta}\overline{u}_{\theta} - \overline{T}_{r\theta}u_{\theta} + T_{rz}\overline{u}_{z} - \overline{T}_{rz}u_{z}\right)_{r=b} bd\theta$$
(3.90)

Let us substitute the values for the displacements, stresses and their complex conjugate components from Table 4. We can also use the following asymptotic expressions for Hankel functions considering $x \to \infty$ to simplify the expression.

$$H_n(x') \to \left(\frac{2}{\pi x'}\right)^{1/2} e^{i(x' - (n+1/2)\pi/2)}$$
 (3.91)

$$\overline{H}_{n}(x') \rightarrow \left(\frac{2}{\pi x'}\right)^{1/2} e^{-i(x'-(n+1/2)\pi/2)}$$
 (3.92)

$$H_n'(x') \to iH_n = i \left(\frac{2}{\pi x'}\right)^{1/2} e^{i(x' - (n+1/2)\pi/2}$$
 (3.93)

$$\overline{H}_{n}'(x') \to -i \left(\frac{2}{\pi x'}\right)^{1/2} e^{-i(x'-(n+1/2)\pi/2)}$$
(3.94)

$$H_n''(x') \to -H_n = -\left(\frac{2}{\pi x'}\right)^{1/2} e^{i(x'-(n+1/2)\pi/2)}$$
 (3.95)

$$\overline{H}_{n}''(x') \to -\left(\frac{2}{\pi x'}\right)^{1/2} e^{-i(x'-(n+1/2)\pi/2)}$$
 (3.96)

From these, we can derive the expressions for the energy flux of the scattered waves (units of W/m)

1. Scattered compressional wave

$$\dot{P}_{c} = A_{n} \overline{A}_{n} \left(-\omega k_{2}^{2} \left(2\mu + \lambda_{2} \right) - \omega \frac{2\mu n^{2}}{b^{2}} \right)$$
(3.97)

If we consider a cylindrical discontinuity with a control volume of infinitely large radius b, the expression will simplify to

$$\dot{P}_{c} = A_{n} \overline{A}_{n} \left(-\omega k_{2}^{2} \left(2\mu_{2} + \lambda_{2} \right) \right)$$
(3.98)

$$\dot{P}_{c} = \frac{A_{n}' \overline{A}_{n}'}{K_{n}^{2}} \left(-\omega k_{2}^{2} \left(2\mu_{2} + \lambda_{2} \right) \right)$$
(3.99)

2. Scattered y-polar Shear Wave (considering a cylindrical discontinuity with a control volume of infinitely large radius b)

$$P_{S_y} = B_n \overline{B}_n \left(\mu \omega k_{II}^2 \cos^2 \psi_2 \right)$$
(3.100)

$$P_{S_{y}} = \frac{B_{n}'B_{n}'}{K_{n}^{2}} \left(\mu\omega k_{II}^{2}\cos^{2}\psi_{2}\right)$$
(3.101)

3. Scattered z-polar Shear Wave (considering a cylindrical discontinuity with a control volume of infinitely large radius b)

$$P_{S_{z}} = C_{n} \overline{C}_{n} (\mu \omega k_{II}^{2} \cos^{2} \psi_{2})$$
(3.102)

$$P_{S_z} = \frac{C_n' \bar{C}_n'}{K_n^2} (\mu \omega k_{II}^2 \cos^2 \psi_2)$$
(3.103)

The scattering cross-section associated with each scattered component can be calculated as follows:

$$Q_{cs} = P_{cs} / W_c \tag{3.104}$$

where P_{cs} is the energy flux generated by a scattered shear wave when compressional wave is incident on the scatterer and W_c is the work done by the incident compressional wave. The same expression can be used to calculate the scattering cross-sections for each combination of compressional and shear waves. From this expression, we get,

$$Q_{CC} = \frac{2}{k_2} \left(2 \|A_0\|^2 + \sum_{n=1}^{\infty} \|A_n\|^2 \right)$$
(3.105)

$$Q_{CS_{y}} = \frac{2}{k_{2}} \cos^{2} \psi_{2} \left(2 \|B_{0}\|^{2} + \sum_{n=1}^{\infty} \|B_{n}\|^{2} \right)$$
(3.106)

$$Q_{CS_z} = \frac{2}{k_2} \cos^2 \psi_2 \left(2 \left\| C_0 \right\|^2 + \sum_{n=1}^{\infty} \left\| C_n \right\|^2 \right)$$
(3.107)

$$Q_{SC} = \frac{2}{k_{II}} \left(2 \|A_0\|^2 + \sum_{n=1}^{\infty} \|A_n\|^2 \right)$$
(3.108)

$$Q_{SS_y} = \frac{2}{k_{II}} \cos^2 \psi_2 \left(2 \|B_0\|^2 + \sum_{n=1}^{\infty} \|B_n\|^2 \right)$$
(3.109)

$$Q_{SS_z} = \frac{2}{k_{II}} \cos^2 \psi_2 \left(2 \|C_0\|^2 + \sum_{n=1}^{\infty} \|C_n\|^2 \right)$$
(3.110)

These are the expressions for calculating the scattering cross-section for a cylindrical elastic scatterer when a compressional or shear wave is obliquely incident on it. Note that these are equivalent to the results given by White only for normal incidence where $\psi_2 = 0$.

3.6 Results and Discussion

Scattering efficiency plots have been calculated for a $NiSi_2$ cylindrical nanoparticle discontinuity embedded in a $Si_{0.5}Ge_{0.5}$ matrix for size parameters ranging from the Rayleigh regime up to the geometric regime. The elastic properties for these materials along with their sources have been detailed below:

Table 5:Elastic Properties of Si, Ge and NiSi2 (The numbers in round brackets in
the top right corner denote sources of data)

Parameters	Silicon ²¹	Germanium ²²	NiSi2 ²³
C11 (GPa)	166	126	199
C44 (Gpa)	79.6	44	53
Density (kg/m ³)	2329 (24)	5323 (24)	4803 (25)

Fig. 2a, 2b, and 2c show the scattering efficiency, Q/2a for incident compressional, y-polar, and z-polar elastic waves respectively plotted as a function of the non-dimensional incident wavenumber ranging from the Rayleigh regime to the geometric regime. In each plot the total scattering cross-section is given (black) and the relative contributions of scattering into particular modes is shown (compressional=blue, y-polar = green, z-polar = red). For each figure, the angular dependence is also given. Normal incidence is given in Fig. 3a, 3b, 3c.

3.6.1 Scattering efficiency v/s size parameter

Figure 2a shows that incident compressional waves are scattered mostly into other compressional waves. It can be noticed that in all cases the scattering efficiency has a slope proportional to $(ka)^3$ (indicated in figure 2a) in the Rayleigh region (ka<<1). The scattering efficiency can be seen to approach the value of 2 (indicated in figure 2b) in the geometric regime when the elastic waves of all polarizations are normally incident on the cylinder surface. But as the angle of the incidence increases, the scattering efficiency can be seen to fall below 2. This can be verified by comparing the values with the figures 3a, 3b and 3c where the scattering efficiency is shown for varying angle of incidence. These figures show that the maximum scattering efficiency can be achieved when the nanoparticles are aligned perpendicular to the direction of the incident wave. The relation stated by White, $Q_{sc} / Q_{cs} = c_{ii} / c_2$ is found to be satisfied as well. A distinct curve in the 2b and 2c figures is the scattered compressional wave which shows a certain degree of instability in the case of scattered compressive wave when the angle of incidence of the shear wave is 45 deg, while the curve is completely absent in the case of angle of incidence for shear waves being 60 deg. But that can be associated to the fact that at those of angles of incident

shear waves, the scattered compressive waves is nearing their angle of internal reflection or past it. In the latter case, we may see the development of evanescent waves, which do not play a role in heat transfer, so have not been taken into consideration for the scattering cross-section calculations in this work.

These cross-section calculations, have improved our understanding about the scattering of phonons. From these results, we can decide the orientation of the cylindrical discontinuity that would enable us to attain maximum phonon scattering and thus reduced thermal conductivity.



Figure 2a: Scattering efficiency for incident compressional wave incident at various incidence angles. The increasing z-polar shear wave cross-section can be seen as the angle of incidence increases (Legend description provided on Page 42)



Figure 2b Scattering efficiency for incident y-polar shear wave incident at various incidence angles. The decreasing compressional wave cross-section can be seen as the angle of incidence increases, which completely disappears at 60 deg because of total external reflection (Legend description provided on Page 42)



Figure 2c: Scattering efficiency for incident z-polar shear wave incident at various incidence angles. The decreasing compressional wave cross-section can be seen as the angle of incidence increases, which completely disappears at 60 deg because of total external reflection (Legend description provided on Page 42)



3.6.2 Scattering efficiency v/s angle of incidence

Figure 3a: Scattering efficiency for incident compressional wave with a variety of size parameters ranging from the Rayleigh regime to the start of the geometric regime. In the Rayleigh regime, it can be seen that the scattering due to scattered z-polar shear waves for angles greater than 45 deg is significant



Figure 3b: Scattering efficiency for incident y-polar shear wave with a variety of size parameters ranging from the Rayleigh regime to the start of the geometric regime. Unlike the compressional wave, scattering due to scattered y-polar shear waves are dominant scattering mode at all incidence angles. This is mainly because, with varying incidence angles, the amplitude of the scattered compressional waves get transferred to z-polar shear waves due to the cylinder orientation



Figure 3c: Scattering efficiency for incident z-polar shear wave with a variety of size parameters ranging from the Rayleigh regime to the start of the geometric regime.

Chapter 4

THERMAL CONDUCTION IN SEMICONDUCTORS WITH EMBEDDED NANOFIBERS

In Chapter 2, the basic procedure for calculating the thermal conductivity of a material from microscopic principles, Boltzmann transport theory, was given. The formulation was general enough to simulate anisotropic conduction if the directional dependence of the scattering rate was known. Chapter 3 was devoted to calculating the directional dependence of the scattering rate for nanofibers embedded in a host material. Now that we have established the underlying principles, we will make detailed calculations of the anisotropic thermal conductivity tensor for some representative cases.

As far as we know, there has not been any previous effort to compare the thermal conductivities obtained by a variety of nanoparticle shapes and nanofiber orientations. By modeling the thermal conductivity of embedded nanofibers in the aligned, 2D random and 3D random orientations and providing a comparison with the case of embedded nanospheres, we intend to find the optimum shape and nanofiber orientation and optimal fiber radius to obtain the greatest reduction in thermal conductivities for embedded nanofibers, because of their transversely isotropic nature. By modeling the thermal conductivities in two orthogonal directions, we can deduce anisotropy in each case. Mingo [Mingo (2010)] has neglected the effects of elasticity in his model for calculating the thermal conductivity of nanospheres. By including the stiffness

properties in our model, we aim to illustrate the effects of both mass and stiffness mismatch between the matrix and fiber materials which promote the reduction of thermal conductivity, Through his model, Zhang¹⁵ has predicted the necessity of a bimodal distribution of nanospheres to be more effective at reducing thermal conductivity than a single size. We will attempt to provide a justification for this observation.

In particular, we will present the process involved for estimating the scattering parameters for the relaxation time calculations for the specific case of $Si_{1-x}Ge_x$ and present the thermal conductivity results for a variety of silicide nanoparticles. This case is chosen both because $Si_{1-x}Ge_x$ is a traditional high temperature thermoelectric material, and because Mingo has previously modeled this system for the case of embedded spherical particles which facilitates comparison.¹⁴

4.1 Elastic Properties and Fitting Parameters for Si_{0.5}Ge_{0.5}

The basic properties of Si0.5Ge0.5 used for our calculations are:

Properties	Silicon ²¹	Germanium ²²
C11 (GPa)	166	126
C44 (GPa)	79.6	44
Density (kg/m ³)	2329 (24)	5323 (24)
ω _{max} [longitudinal](THz)	77 (26)	44.8 (27)
ω _{max} [transverse](THz)	28 (26)	15 (27)

Table 6:Basic properties of Si0.5Ge0.5 used for our calculations (The numbers in
round brackets on the right top corner are the sources of the data)

4.1.1 Maximum frequency of phonons

While continuum theory places no constraints on the maximum frequency of elastic waves, the discretization of the lattice leads to a minimum wavelength and an associated maximum frequency. In a one dimensional chain the minimum wavelength is two lattice constants. More generally, the maximum wavenumber occurs at the edge of the Brillouin zone. The phonon dispersion relations experimentally calculated by Dolling (1963)²⁶ for silicon and by Weber (1977)²⁷ in the [100] direction at 300K were used to determine the maximum frequency of phonons for the integral in Eqn (2.17) .The integrals are done over wavenumber rather than frequency. Since for the rest of the calculation we assume linear dispersion, we calculate the corresponding maximum wavevector as $k_{max}^p = \omega_{max}^p / v^p$ where p is the index that denotes the polarization.

4.1.2 Temperature fitting for material parameters related to Umklapp scattering

The calculation of Umklapp scattering time, $\tau_u^{-1} = AT\omega^2 e^{-B/T}$ contains two unknown scattering parameters, A and B. In order to find these parameters, thermal conductivity vs. temperature curves for Silicon and Germanium were fit individually to the recommended experimental values suggested by Touloukian (1977)²⁸ in the Thermophysical Properties of Matter data series in the temperature range 100-1000K, where umklapp scattering is the dominate resistive mechanism. The fit was obtained by minimizing the sum of the square of the residuals using MATLAB's built-in fminsearch command. After the fitting process, the calculated parameters A and B the individual materials were found to be:

 Table 7:
 Fitting for material parameters related to Umklapp scattering

Parameter	Silicon	Germanium
A (s/K)	1.407 ⁻¹⁹	2.7005 ⁻¹⁹
B (K)	140.0177	64.7034



Figure 4: Plot used to find the temperature fitting parameters

To calculate the scattering rates at intermediate alloy compositions we used an compositionally weighted average of the individual scattering rates.

4.1.3 Alloy disorder scattering

According to Abeles, the alloy disorder scattering time is given in the form, $\tau_a^{-1} = Fx(1-x)\omega^4 / v_p^{-3}$, where we consider the constant F is an unknown parameter related to the mass, bonding, and strain contrast. F was found by fitting experimentally obtained thermal conductivity vs alloy composition curves. Note that this step also requires accurate modeling of Umklapp scattering rates for which the results of 4.1.2 were used. Experimental results have been obtained from literature²⁹. The calculated value of F was estimated to be 4.9e-30 m³.

4.2 Elastic Properties of Silicide Nanoparticle Impurities

In order to compare results with Mingo, we have considered several possible silicides as the embedded nanoparticle. Silicides are potential candidates for $Si_{1-x}Ge_x$ nanocomposites because they are metallic, commonly used in the semiconductor industry, and in some cases can be epitaxially grown from pure starting materials by annealing. The silicides that we consider here are NiSi₂, NiSi, CoSi₂ and PtSi, for which structure, density, and elastic constants are available from literature and are summarized below. The difficulty involved in considering additional materials is minimal, so long as the elastic constants and density can be obtained. For exotic compounds such as silicides, elastic constants in particular are difficult to obtain from experiment and are often estimated from Density Functional theory (DFT) instead.

Property	NiSi2	NiSi	CoSi2	PtSi
C11(GPa)	199 (23)	285 (30)	228 (32)	298.2 ⁽³⁴⁾
C44(GPa)	53 (23)	64.7034 ⁽³⁰⁾	83 (32)	100.1 (34)
Density(kg/m ³)	4803 (25)	5860 ⁽³¹⁾	4940 ⁽³³⁾	12378 (35)

Table 8:Basic Properties of the silicides (The numbers in round brackets on the
right top corner are the sources of the data)

4.3 Thermal Conductivity Plots

Thermal conductivity calculations have been carried out at 300K for a nanofiber impurity of volume fraction of 3.4% embedded in the Si_{0.5}Ge_{0.5} alloy matrix, again chosen to facilitate easy comparison with related calculations on nanospheres in literature¹⁴. We envision that there are three most likely geometries in which nanofibers could be manufactured into alloy composites in analogy with traditional fiber reinforced composited:

1. Aligned: When all the nanofibers are oriented along in one direction, the orientation of which can be defined using the spherical coordinate angles, θ and ψ (θ is ill-defined for $\psi = 0$, but by symmetry the scattering cross-section and thus the thermal conductivity cannot depend on the value of θ in that case). For simplicity, we calculate the thermal conductivity tensor using

the case $\psi = 0$ with the understanding that the thermal conductivity for any other (aligned) orientation can then be obtained using a tensor rotation.

$$\overset{\kappa'}{\underset{\approx}{}} = \underset{\approx}{R} \overset{\kappa}{\underset{\approx}{}} \overset{R^{T}}{\underset{\approx}{}} \tag{3.111}$$

where $\frac{R}{2}$ denotes the combined rotation matrix

$$R_{z} = R_{z}R_{x} = \begin{bmatrix} \cos\theta & -\sin\theta & 0\\ \sin\theta & \cos\theta & 0\\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0\\ 0 & \cos\theta & -\sin\theta\\ 0 & \sin\theta & \cos\theta \end{bmatrix}$$
(3.112)

which would transform the z-axis unit vector to co-alignment with the desired cylinder orientation using two rotations about the x and z axis, respectively. By symmetry, the thermal conductivity tensor for the $\psi = 0$ case must be transversely isotropic, meaning $\kappa_{xx} = \kappa_{yy} \equiv \kappa_{\perp}$, $\kappa_{zz} \equiv \kappa_{\parallel}$, and all off-diagonal components are zero. We have numerically verified that our simulations obey this symmetry requirement.

2. 2D Random: When the nanofibers lie on one plane but are distributed with a random orientation within that plane (in this case, the xy plane). In this case, each fiber has a unique value of $\psi = \pi/2$ but can take on any random value of θ . There are multiple methods possible for calculating the thermal properties when there are statistically distributed scattering cross-sectional properties. Kim³⁶ has studied the effect of polydispersity of spherical nanoparticles on thermal conductivity and performed the calculation by assuming that the effective scattering cross-sections. We feel that this may be inaccurate because a phonon at any particular location will only scatter with one particular orientation of cylinder (which will be associated with one particular thermal conductivity),

not an average. We take the inhomogeneity in orientation into account by taking the weighted average thermal conductivity tensor over all orientations, rather than the weighted average of the scattering cross-section. Thus,

$$\kappa_{zeff} = \frac{1}{2\pi} \int_{0}^{2\pi} \kappa'(\theta, \phi = \pi/2) d\theta$$
(3.113)

The integration is accomplished by Gaussian quadrature. This has the added computational advantage that we only need to calculate the thermal conductivity tensor once, an important advantage since the simulation necessarily already involves 3-dimensional integration over an integrand which itself contains an "infinite" sum as part of the scattering cross-section solution. We have attempted to compare the two averaging techniques but the computation time for the scattering-cross section approach has proven too long for practical purposes.

By symmetry the resulting thermal conductivity tensor for a 2D mat of embedded fibers must be transversely isotropic and the through-plane value must be equal to κ_{\perp} from case 1.

3D Random: When the nanofiber orientation can take on random values for θ and ψ, such that they are randomly oriented in a 3D space. Thus, the thermal conductivity tensor in this case is calculated as

$$\underbrace{\kappa}_{\widetilde{z}eff} = \frac{1}{4\pi} \int_{0}^{2\pi} \int_{0}^{\pi} \underbrace{\kappa}_{0}'(\theta, \psi) \sin \psi d\psi d\theta \qquad (3.114)$$

which we again perform by 2D Gaussian quadrature. By symmetry the result must be isotropic.

 Spherical Nanoparticle scattering: For the purposes of comparison, we have included simulations of spherical nanoparticle scattering, using the form of the scattering cross-section given by Mingo

(3.115)

$$\sigma_{LW} = 4\pi / 9 (\Delta M / M)^2 k^4 a^6 \quad (ka << 1)$$

$$\sigma_{SW} = 2\pi a^2 \quad (ka >> 1)$$

$$\sigma_{eff}^{-1} = \sigma_{LW}^{-1} + \sigma_{SW}^{-1}$$

and using identical volume fractions to calculate the total scattering rates. There are a several important effects not included by this model: (1) the model does not include any physical effects due to elastic constant mismatch between particle and matrix, in contrast to our cylinder model. (2) the model does not include any information about wave interference. (3) it is not clear which incident phonon modes this is valid for(presumably only compressional) (4) it is not valid in the regime in between the Rayleigh and geometric limits ($ka \approx 1$). Despite these major limitations, the model is simple to apply and is expected to at least provide approximate trends for comparison.

Figures 5-8 show thermal conductivity tensor simulations for the cases of $Si_{0.5}Ge_{0.5}$ embedded with $NiSi_2$ (Fig. 5), NiSi (Fig. 6), $CoSi_2$ (Fig.7), and PtSi (Fig. 8) nanofibers and nanoparticles. In all cases, the volume fraction of nanoparticles is held at 3.4%. In the case of nanospheres, our result is in good agreement with Mingo¹⁴.

4.4 Results



Figure 5: Thermal conductivity of SiGe alloy nanocomposite with NiSi₂ nanofiber impurities embedded in it. Spherical thermal conductivity calculated from [Mingo(2009)]¹⁴



Figure 6: Thermal conductivity of SiGe alloy nanocomposite with NiSi nanofiber impurities embedded in it. Spherical thermal conductivity calculated from [Mingo(2009)]¹⁴


Figure 7: Thermal conductivity of SiGe alloy nanocomposite with CoSi₂ nanofiber impurities embedded in it. Spherical thermal conductivity calculated from [Mingo(2009)]¹⁴



Figure 8: Thermal conductivity of SiGe alloy nanocomposite with PtSi nanofiber impurities embedded in it. Spherical thermal conductivity calculated from [Mingo(2009)]¹⁴

Some general observations can be made. In all cases, the thermal conductivity is significantly reduced below the room temperature bulk (isotropic) thermal conductivity of $Si_{0.5}Ge_{0.5}$ (8.1 W/m-K). As initially observed by Mingo, we find an optimal size for spherical nanoparticles in the several nanometer size range.

The behavior of the embedded cylinders is much more complex. In each case, we find at least one optimal nanocylinder radius, but in some cases we find what appear to be two optimal operating points. For example in the case of embedded NiSi nanofiber (Fig. 6), the thermal conductivity has a weak double minima, which has the effect of broadening the range of optimal conditions. In other cases, there is not a double minima, but inflection points are still present that indicate rapid oscillations of scattering rate (Fig. 5 and 7).



Figure 9: Thermal Conductivity (k_{xx}) of NiSi nanofiber embedded composite contributed by each incident wave polarization



Figure 10: Thermal Conductivity (k_{zz}) of NiSi nanofiber embedded composite contributed by each incident wave polarization

A mechanism that might explain such a double minimum is that there may be different optimal sizes which separately minimize conduction by compressional and transverse waves. The plots in Fig. 5-8 show only the total, so it is conceivable if optimized separately, these would give different minima that when summed give the appearance of a double optima. This might be consistent with a very recent observation by Zhang¹⁵, that show that a bimodal distribution of nanospheres may have lower thermal conductivity than a single size. We have investigated this by

decomposing the thermal conductivity in the Boltzmann integral into the contribution from each polarization for NiSi nanofiber. The results are given in Fig. 9 & 10. Neither Zhang¹⁵ nor Mingo¹⁴ give a separate treatment of the scattering by compressional and transverse waves (they use the same scattering cross-section for both modes). In figures 9 & 10, the thermal conductivities are segregated on the basis of the polarization of the incident wave from which the heat flux originates. It is clearly evident that the optimal nanoparticle radii for the compressional and shear waves are located at different values. Thus, an overlap of the thermal conductivity results, which causes the double optima in the overall thermal conductivity. This bodes well with the results obtained by Zhang¹⁵ who observed multiple optima of nanosphere radius for yielding minimum thermal conductivity. (2) An alternate explanation could be that coherent oscillations in the scattering cross-section lead to this behavior. When the non-dimensional scattering parameter $ka \gtrsim 1$, the scattering cross-section oscillates rapidly through a series of constructive and destructive interference events. This could potentially cause local minima and maxima thermal conductivity in a material that only has a single sized particle (i.e. monodispersed). Note that this physics is completely absent in the recent paper by Zhang¹⁵ because their model does not consider phonon coherence. This might seems like an unlikely explanation since heat is conducted by a broadband range of phonons and coherence behavior should at least be masked by the fact that some phonons would constructively interfere while others would destructively interfere. However, if the frequency range of phonons contributing to transport were sufficiently narrow, and scattering efficiency oscillation are large enough then it may be possible to observe oscillations via the thermal conductivity. In fact, we do see such oscillation in the polarization and decomposed thermal conductivities (Fig 9-10)

We find that the highest performance candidate material studied was PtSi, due to its unusually high mass density and stiffness. 3.4% vol PtSi is predicted to achieve up to a 10-fold reduction in thermal conductivity. The optimal configuration is for aligned cylinders where the temperature gradient/heat flow is applied perpendicular to the axis of the cylinders. The optimal fiber radius is predicted to be ~1nm, several nanometers smaller than the predicted optimal radius of a spherical nanoparticle. From a modeling point of view, these small sizes may not be consistent with our scattering model. In particular, the atomic nuclei of most crystalline materials are only separated by ~0.2-0.3nm, so the assumption that we are dealing with a continuum is questionable. We will comment further on this point in the following chapter.

To our knowledge this is the first attempt anywhere to calculate the anisotropic ratio of the thermal conductivity tensor due to anisotropic nanoparticle scattering. The case of aligned PtSi nanofibers yields the most dramatic anisotropic ratio ($\eta \equiv \kappa_{\parallel} / \kappa_{\perp}$), but even in this extreme case we find that the anisotropic ratio is rather low, $\eta \approx 1.3$. In the 2D random case, the lowest thermal conductivity remains the same as in the completely aligned case, it is not necessary to align the fibers to achieve the lowest possible thermal conductivity. However in the other transport directions the conductivity will not be as low. In 3D the anistropic ratio is zero (as required by symmetry). In the Rayleigh limit, it is not obvious that the anisotropic ratio must be $\eta < 1$ for aligned fibers since the compressional waves actually have a higher scattering cross-section when traveling parallel to the nanofiber. However, the transverse waves do have lower scattering cross-section in that direction and it is those

that dominate transport; the net effect is an anisotropic ratio that is always $\eta > 1$, even for cylinder radii below the optimum.

The question of what determines whether nanospheres outperform nanocylinders remains open. Fig. 5-8 shows that a comparison between the two types of scatterers yields conflicting results. In the best case scenario for nanofibers (PtSi, Fig. 8), optimally sized nanofibers outperform an optimal nanosphere configuration by $\sim 30\%$. In the case of NiSi₂, the performance is about the same (Fig. 5). In the cases of NiSi (Fig. 6) and CoSi₂ (Fig. 7), nanospheres are much better than nanofibers. Since the densities of the materials are not so different from one another (with the exception of PtSi), it is not clear what causes such variation between material combinations. We postulate that elastic constant contrast might play an important role in scattering. In any case, the results would indicate that there is more than one single material property which drives thermal conductivity. Again, we should note that the nanospherical model does not include any physics related to elastic contrast or polarization dependence, and thus the nanosphere results may appear smoother with respect to the material choice than they would be if modeled more rigorously. We have attempted full elastic modeling of spheres¹³, but we have found some inconsistencies within existing literature which will require significant effort to correct and currently prevent us from employing an accurate model.

To understand the relevance of density and stiffness contrasts to scattering, we studied the change in the scattering efficiency as a function of density and stiffness contrasts. The scattering efficiency (Q/2r) is a dimensionless quantification of scattering which makes it dependent on the size parameter (kr) rather than just the radius of the nanofiber (r). Since the density and stiffness contrasts are relevant in the

Rayleigh regime, this model has been prepared at kr=0.001. In the Rayleigh regime, the scattering efficiency (Q/(2r)) scales as $(kr)^3$. The proportionality depends on the density and stiffness contrasts. To determine the effect of density and stiffness contrast, we therefore have prepared contour plots of the quantity $(Q/(2r)) / (kr)^3$ in the Rayleigh regime. We define stiffness contrast $[\Delta C_{11}=(C_{11})_{np}-(C_{11})_a]$ as the difference between the stiffness of the nanoclyinder material $((C_{11})_{np})$ and the alloy material $((C_{11})_a)$. We have considered the ratio between C_{11} and C_{44} as a constant. Similarly, we define density contrast $(\Delta \rho = \rho_{np}-\rho_a)$ as the difference between the stiffness of the nanoclyinder material (ρ_a) .



Figure 11a: Normalized scattering efficiency when a compressional wave is incident on a nanocylinder at 0 deg angle of incidence. Note: C_{11} and C_{44} for the nanocylinder material is taken as the same as alloy matrix material at $\Delta C_{11}/(C_{11})_a=0$ and both are varied proportional to change in ΔC_{11} for the purposes of this graph



Figure 11b: Normalized scattering efficiency when a y-polar shear wave is incident on a nanocylinder at 0 deg angle of incidence. Note: C_{11} and C_{44} for the nanocylinder material is taken as the same as alloy matrix material at $\Delta C_{11}/(C_{11})_a=0$ and both are varied proportional to change in ΔC_{11} for the purposes of this graph



Figure 11c: Normalized scattering efficiency when a z-polar shear wave is incident on a nanocylinder at 0 deg angle of incidence. Note: C_{11} and C_{44} for the nanocylinder material is taken as the same as alloy matrix material at $\Delta C_{11}/(C_{11})_a=0$ and both are varied proportional to change in ΔC_{11} for the purposes of this graph

In Figures 11a, 11b and 11c we can see that when the angle of incidence of the incident compressional wave is 0 deg, scattering cross-section is more sensitive to density contrast than to stiffness contrast. It is interesting to notice that the scattering cross-section can be significantly increased by using an impurity material that is more compliant (low stiffness values (Δ C11<0)) than the matrix material.

The scattering efficiency as a function of density and stiffness contrast was also analyzed for nanofiber oriented obliquely (45 deg) to the direction of the incident wave. These results have been presented in the following figures 12a, 12b and 12c.



Figure 12a: Normalized scattering efficiency when a compressional wave is incident on a nanocylinder at 45 deg angle of incidence. Note: C_{11} and C_{44} for the nanocylinder material is taken as the same as alloy matrix material at $\Delta C_{11}/(C_{11})_a=0$ and both are varied proportional to change in ΔC_{11} for the purposes of this graph



Figure 12b: Normalized scattering efficiency when a y-polar shear wave is incident on a nanocylinder at 45 deg angle of incidence. Note: C_{11} and C_{44} for the nanocylinder material is taken as the same as alloy matrix material at $\Delta C_{11}/(C_{11})_a=0$ and both are varied proportional to change in ΔC_{11} for the purposes of this graph



Figure 12c: Normalized scattering efficiency when a z-polar shear wave is incident on a nanocylinder at 45 deg angle of incidence. Note: C_{11} and C_{44} for the nanocylinder material is taken as the same as alloy matrix material at $\Delta C_{11}/(C_{11})_a=0$ and both are varied proportional to change in ΔC_{11} for the purposes of this graph

Figures 12a, 12b and 12c show an interaction effect between density and stiffness contrast on scattering cross-section, i.e.: change in one factor has an effect on the other. In fact when the angle of incidence is oblique (or the cylinder orientation is oblique) the rate of increase in the scattering cross-section can be achieved by varying both density and stiffness contrast of the nanoparticle impurity along the a-b line

shown in Figures 12a and 12c. From this, we can conclude that scattering crosssection of nanofibers in the Rayleigh regime is dependent on the density contrast, stiffness contrast and their interaction effect. Further, for some materials scattering efficiency may actually increase, if the nanofibers are obliquely aligned as opposed to aligned perpendicular to the direction of incident waves, depending upon their stiffness and density contrast. Note that in this case, we have considered the ratio between C_{11} and C_{44} is a constant. It remains to be seen how the scattering crosssection changes when the stiffness contrasts for C_{11} and C_{44} vary independent of each other.



Figure 13: Thermal conductivity of PtSi (nanofibers of radius 0.89nm, 2 nm and 5nm) embedded nanocomposite in the fiber and matrix direction for a decreases with an increase in volume fraction.

One important variable that contributes to reducing thermal conductivity is the volume fraction of the nanoparticle impurities. As observed in Fig 13, at small volume fractions, it seems fairly obvious that adding more volume fraction will lead to lower thermal conductivity, because the higher volume fraction will increase the number of scatterers and thus the scattering rate. However, there are obvious limitations to this

logic: (1) A higher density of impurities may be detrimental to the electron mobility and reduce the electrical conductivity; it is not currently clear what upper limit this imposes on the current system, and this is likely to be material system dependent as well as doping level dependent. (2) At sufficiently large volume fractions the nanoimpurities cannot simply be thought of as scatterers, but will become active conductors of heat themselves. PtSi for example has a bulk electrical resistivity of ~30 $\mu\Omega$ -cm, which can be translated via the Wiedemann Franz law into an electronic contribution to thermal conductivity of κ ~25 W/m-K. However, at the nanoscale the effective conductivity of metal would be much smaller due to boundary scattering, and the presence of Schottky barriers makes it difficult to estimate the critical volume fraction that would cause this cross-over in behavior.

This research was aimed to finding an optimal embedded nanofiber radius for reduced thermal conductivity in a nanocomposite. To that purpose, the scattering of phonons on a nanocylinder elastic inclusion was studied. Early research by White¹⁸, seemed to have certain discrepancies that have been fixed and the model was improved to include angular orientation of the cylinders. The analytic continuum model provides an insight into the optimal orientation and radius of nanofiber to improve its scattering efficiency.

The thermal conductivity model developed from Boltzmann transport theory uses this phonon scattering model. The results of this study show that the optimal nanoparticle shape and size are distinctly dependent on the mass and stiffness contrast between the matrix and fiber materials. There is clear evidence to show that perpendicularly aligned nanofibers have a distinct advantage over other orientations in thermal conductivity reduction. The observations further confirm that a bimodal dispersion of nanofiber sizes will enable better reduction in thermal conductivity.

Although from a manufacturing point of view, these small nanofiber sizes seem impractical, the model developed provide an insight into the necessary parameters required to reduce thermal conductivity in nanocomposites.

Chapter 5

FUTURE WORK

The results obtained in this research can be further improved upon by finding the optimal size of nanoparticles for a wide range of temperatures and volume fractions. Higher operating temperatures would reduce the thermal conductivity of the nanocomposite and result in a wide minima, which would mean that a smaller volume fraction of nanofibers would be required to achieve the same thermal conductivity reduction. Whereas, if the temperature is maintained as the same and the volume fraction is increased, the optimal size of the nanoparticle can be expected to increase. The reason is that, the same size and higher number of nanoparticles would mean that the distance between the nanoparticles become much smaller than the mean free path of the long wavelength phonons which are effective heat carriers in semiconductors. These phonons will be more effectively scattered by maintaining the distance between the nanoparticle and increasing their size. However, increasing the volume fraction can also adversely affect the electron mobility. As discussed by $Mingo^{14}$, the scattering of electrons are mainly caused by alloy scattering and nanoparticle scattering. The nanoparticle scattering rate, given by $\tau_e^{-1} = \sigma_e v_e / V$, where σ_e is the electron scattering cross-section which is directly influenced by the nanoparticle size, v_e is the electron velocity and V is the volume containing one nanoparticle. So, size and number of nanoparticles play a vital role in electron scattering. However, Mingo calculated that the electron mean free path will not be affected in the case of SiGe if the volume fraction is maintained lower than $f_{vol} < a/30nm$ for spheres. A similar analysis for nanofibers will aid in obtaining an optimal nanofiber radius without affecting the electron mobility in the nanocomposite.

In his paper, Zhang (2015)¹⁵ used an optimization algorithm to find the bimodal distribution of nanosphere sizes. As discussed earlier, this bimodal distribution is most probably related to the dual optimal nanofiber sizes caused due to different wave polarizations Such an optimization analysis can be carried out for nanofibers as well. Since nanofibers are transversely isotropic, there might be as many as six different nanoparticle sizes that might reduce the thermal conductivity.

Just as we have included the mass and stiffness missmatch for analyzing the scattering of both compressional and shear waves on a cylindrical obstacle, a similar analysis can be carried out for a spherical obstacle. Ying¹¹ analyzed scattering of a plane longitudinal wave by a spherical obstacle, but we found certain discrepancies in the expressions for the scattering cross-section. An analysis of the same can be used to formulate expressions for the thermal conductivity of nanocomposite with embedded nanospheres and thus calculate the optimal nanopshere radius for reducing thermal conductivity. The results can also be compared with Mingo¹⁴ and Zhang¹⁵ to assess the effects of the stiffness missmatch in thermal conductivity.

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Appendix

THERMAL CONDUCTIVITY CODE

clearall PropertiesForSiGe T = 300; a = logspace(log10(1e-10),log10(1e-7),200); MatParams.eta_NP = 0;

fori = 1:length(a); MatParams.a_NP = a(i); disp(a(i)); MatParams.eta_NP = MatParams.VolFrac_NP/(pi*MatParams.a_NP^2); %maintains constant Volume Fraction

```
[ktot_align, ktot_inplane, ktot_random] = Get_Kappa_Avg(T,MatParams);
kappa_xx_align(i) = ktot_align(1,1);
kappa_yy_align(i) = ktot_align(2,2);
kappa_zz_align(i) = ktot_align(3,3);
kappa_xx_inplane(i) = ktot_inplane(1,1);
kappa_yy_inplane(i) = ktot_inplane(2,2);
kappa_zz_inplane(i) = ktot_inplane(3,3);
kappa_xx_random(i) = ktot_random(1,1);
kappa_yy_random(i) = ktot_random(2,2);
kappa_zz_random(i) = ktot_random(3,3);
end
```

figure;

loglog(a(1:length(a)),kappa_xx_align,'b-',a(1:length(a)),kappa_yy_align,'g-',a(1:length(a)),kappa_zz_align,'r-','LineWidth',2); xlabel('a'); ylabel('kappa tensor') legend('kappa_{xx} (perp)','kappa_yy (normal)','kappa_{zz} (parallel)') title('Aligned')

figure;

loglog(a(1:length(a)),kappa_xx_inplane,'b-',a(1:length(a)),kappa_yy_inplane,'g-',a(1:length(a)),kappa_zz_inplane,'r-','LineWidth',2);

xlabel('a'); ylabel('kappa tensor') legend('kappa_{xx} (perp)','kappa_yy (normal)','kappa_{zz} (parallel)') title('Random Inplane')

figure; loglog(a(1:length(a)),kappa_xx_random,'b-',a(1:length(a)),kappa_yy_random,'g-',a(1:length(a)),kappa_zz_random,'r-','LineWidth',2); xlabel('a'); ylabel('kappa tensor') legend('kappa_{xx} (perp)','kappa_yy (normal)','kappa_{zz} (parallel)') title('Random')

timestamp = datestr(clock,30); save(strcat('Results_k_vs_a_',timestamp,'.mat')) %PropertiesforSiGe % Build Materials Properties of a Matrix / NP system % Matrix Properties %Silicon MatParams.Si_vs = [8442.3 5846.2 5846.2]; MatParams.Si_omega_max = [77 28 28]*1e12;%from ioffe/Dolling(1963) Si_A = 1.407e-19; Si_B = 140.0177; Si_F = 1; Si_rho = 2329;

%Germanium MatParams.Ge_vs = [4865.3 3566.3 3566.3]; MatParams.Ge_omega_max = [44.8 15 15]*1e12;%rad/s from ioffe/Weber (1977) Ge_A = 2.7005e-19; Ge_B = 64.7034; Ge_F = 1; Ge_rho = 5323;

%% Alloy Property Testing code % These can be used while testing for A,B& K properties for materials that make up the alloy % MatParams.xalloy = 0.0; % alloy percentage % MatParams.vs = [4865.3 3566.3 3566.3]; % sound speeds % % MatParams.A = Si_A; % Anharmonic scattering terms %change back to correct ones % % MatParams.B = Si_B; % Anharmonic scattering terms %change back to correct ones % MatParams.A = Ge_A; % MatParams.B = Ge B; % MatParams.F = 2e-30; % alloy scattering % MatParams.Lb = 300e-6; % boundary scattering / film thickness % MatParams.rho = 2329; % density %% Alloy Code %Alloy Properties MatParams.xalloy = 0.5; %alloy percentage, x: perc Ge in alloy MatParams.vs = MatParams.xalloy.*MatParams.Ge_vs+(1-MatParams.xalloy).*MatParams.Si_vs; %sound speeds MatParams.omega_max = MatParams.xalloy.*MatParams.Ge_omega_max+(1-

MatParams.xalloy).*MatParams.Si_omega_max; %max frequency

MatParams.kmax = MatParams.omega_max./MatParams.vs;

MatParams.A_Si = Si_A; %Anharmonic scattering terms

%change back to correct ones

MatParams.B_Si = Si_B; %Anharmonic scattering terms %change back to correct ones MatParams.A_Ge = Ge_A; MatParams.B_Ge = Ge_B; MatParams.F = 4.9e-30; %alloy scattering MatParams.Lb = 300e-6; %boundary scattering / film thickness MatParams.rho = MatParams.xalloy*Ge_rho+(1-MatParams.xalloy)*Si_rho; %density

%% Nanoparticle Properties NiSi MatParams.a_NP = 10e-9; %nanocylinder radius MatParams.vs_NP_Material = [6436.8, 3321.9, 3321.9]; %nanocylinder sound speeds MatParams.rho_NP_Material = 4803; %nanocylinder density MatParams.VolFrac_NP = 0.034; %volume fraction of nanocylinders %change back to 0.05 MatParams.eta_NP = MatParams.VolFrac_NP/(pi*MatParams.a_NP^2); %number density (#/m2) of nanocylinders.

```
function [k avg1, k avg2, k avg3] = Get Kappa Avg(T,MatParams)
%% Completely aligned
ktot = get_kappa_ij(T,MatParams);
                                     k_avg1 = ktot;
%% Random Inplane
phi_cyl = pi/2;
[\text{theta\_points,w}] = \text{lgwt\_V4}(10,0,2*\text{pi});
k avg2 = zeros(3,3);
for n = 1:length(w)
theta cyl = theta points(n);
th =theta_cyl;
ph = phi_cyl;
Ry=[cos(ph) 0 sin(ph); 0 1 0; -sin(ph) 0 cos(ph)];
Rz = [cos(th) - sin(th) 0; sin(th) cos(th) 0; 0 0 1];
Rnet = Rz^*Ry;
k_inc2 = (Rnet)*ktot*(Rnet');
k_avg2 = k_inc2.*w(n)./(2*pi) + k_avg2;
end
%% Random
[\text{theta_points,w1}] = \text{lgwt_V4}(4,0,2*\text{pi});
[phi_points,w2] = lgwt_V4(4,0,pi);
k_avg3 = zeros(3,3);
for n1 = 1:length(w1)
theta_cyl = theta_points(n1);
k_halfavg3 = zeros(3,3);
for n2 = 1:length(w2)
phi_cyl = phi_points(n2);
th =theta_cyl;
ph = phi cyl;
Ry=[cos(ph) 0 sin(ph); 0 1 0; -sin(ph) 0 cos(ph)];
Rz = [cos(th) - sin(th) 0; sin(th) cos(th) 0; 0 0 1];
Rnet = Rz^*Ry;
k_inc3 = (Rnet)*ktot*(Rnet');
k_halfavg3 = k_inc3.*sin(ph)*w2(n2)./2 + k_halfavg3;
end
k_avg3 = k_halfavg3.*w1(n1)./(2*pi) + k_avg3;
end
end
```

```
functionktot = get_kappa_ij(T,MatParams)
ifnargin==0
PropertiesForSiGe
T = 300;
end
i = 3;
i = 3;
ktot = zeros(3,3);
fori = 1:3
j=i;
%fprintf('%i \t %i\n',i,j)
for p = 1:3 %all polarizations
                                           %change back if needed
         fprintf('%i \t %i \t %i\n',i,j,p)
\%
integrand = @(k,theta,phi)(k.^2.*abs(sin(phi)));
kmax = MatParams.kmax(p);
k_p(p)=integral3(@(k,theta,phi)
thermal_integrand(k,theta,phi,p,T,i,j,MatParams),0,kmax,0,2*pi,0,pi,'method','tiled','R
elTol',1,'AbsTol',1e-4);
end
ktot(i,j) = sum(k_p);
       sum(k_p)
\%
                                   %change back if needed
end
```

```
function result = thermal_integrand(k,theta,phi,p,T,i,j,MatParams)
hbar = 1.05457173e-34;
kb = 1.3806488e-23;
prefactor = 1/(2*pi)^3;
c = MatParams.vs;
%c = [8000,4000,4000];
cp = c(p);
omega = cp*k;
```

```
ifi == 1
vg_i = cp.*sin(phi).*cos(theta);
elseifi==2
vg_i = cp*sin(phi).*sin(theta);
elseifi==3
vg_i = cp*cos(phi);
end
if j == 1
vg_j = cp.*sin(phi).*cos(theta);
elseif j==2
vg_j = cp*sin(phi).*sin(theta);
elseif j==3
vg_j = cp*cos(phi);
end
```

```
vgi_vgj = vg_i.*vg_j;
tau = 1./Get_TauInv_4kij(k,theta,phi,p,T,MatParams); %10e-9/cp;%./sin(phi);
x = hbar.*omega/(kb*T);
f = 1./(exp(x)-1);
```

```
dfdT = f.*(f+1).*x/T;
hbaromega_dfdT = hbar.*omega.*dfdT;
zero_logic = (x==0); %if omega = 0
hbaromega_dfdT(zero_logic) = kb;
dV = (k.^2.*abs(sin(phi)));
result = prefactor.*hbaromega_dfdT.*vgi_vgj.*tau.*dV;
```

functionTauInv_tot = Get_TauInv_4kij(k,theta,phi,p,T,MatParams)

%% ifnargin<5 T = 300; end ifnargin<6 %if MatParams not provided in function call %then we need to input something...lets use properties for Si MatParams.vs = [3970 2770 2770]; MatParams.A=876e-021; %Anharmonic scattering terms MatParams.B=85.6; %Anharmonic scattering terms MatParams.F = 2e-30; MatParams.Lb = 300e-6; MatParams.xalloy = 0; end

%% Unpackage the necessary materials parameters (stored as an object): vs=MatParams.vs; %Sound velocity vector [vL vT1 vT2]

%phonon-phonon scattering parameters: tau^(1) = A*T*omega^2*exp(-B/T) Si_A=MatParams.A_Si; Si_B=MatParams.B_Si; Ge_A=MatParams.A_Ge; Ge_B=MatParams.B_Ge;

% phonon-impurity scattering tau^(1) = F*(1-x)*x*omega^4/vs^3; F=MatParams.F; xalloy = MatParams.xalloy;

%phonon-boundary scattering tau^(1) = vs*Lb; Lb=MatParams.Lb; %Boundary Scattering Length

%phonon-np scattering:-> complicated function of (k, theta, phi, p) %% Calculate the scattering times omega = vs(p)*k; TauInv_phph_Si = Si_A*T.*(omega.^2)*exp(-Si_B/T); TauInv_phph_Ge = Ge_A*T.*(omega.^2)*exp(-Ge_B/T); TauInv_phph = xalloy.*TauInv_phph_Ge+(1-xalloy).*TauInv_phph_Si; TauInv_alloy = F*xalloy*(1-xalloy)*(omega.^4)/(vs(p)^3); TauInv_boundary = vs(p)/Lb; TauInv_np = Get_TauInv_NP(k,phi,theta,p,MatParams); TauInv_tot = TauInv_phph + TauInv_alloy + TauInv_boundary + TauInv_np; end functionTauInv_NP = Get_TauInv_NP(k,phi,theta,p,MatParams)

```
eta_NP = MatParams.eta_NP;
ifeta_NP==0
TauInv_NP = zeros(size(k));
return
end
vs = MatParams.vs;
```

```
%% Completely aligned
phi_cyl = 0;
theta_cyl = 0;
Psi = Get_Psi(phi,theta,phi_cyl,theta_cyl);
sigma_avg = GetSigmaCyl_Parallel(k,p,Psi,MatParams);
```

TauInv_NP = eta_NP*vs(p).*sigma_avg;

end

```
function sigma = GetSigmaCyl_Parallel(k,p,Psi,MatParams, relerr_tol) % this is for the whole thing in 2D (i.e. the wave travels in the plane % perpendicular to the axis of the cylinder)
```

```
ifnargin<5
relerr_tol = 1e-8;
end
```

%unpack some things a = MatParams.a_NP; vs=MatParams.vs; rho_1 = MatParams.rho_NP_Material; vs_NP = MatParams.vs_NP_Material; cL_1 = vs_NP(1); cT_1 = vs_NP(2);

rho_2 = MatParams.rho; cL_2 = vs(1); cT_2 = vs(2);

```
w = warning('off','MATLAB:nearlySingularMatrix');
w = warning('off','MATLAB:illConditionedMatrix');
w = warning('off','MATLAB:SingularMatrix');
```

```
% % ErSb<---legacy code
% rho_1 = 17050*1000;
% cL_1 = 3.2837e+003;
% cT_1 = 1.4196e+003;
```

% In0.5Ga0.5Sb <----legacy code % rho_2 = 5500; % cL_2 = 4.2895e+003; % cT_2 = 2.9970e+003;

C11_1 = cL_1^2*rho_1; C44_1 = cT_1^2*rho_1; mu_1 = C44_1; lambda_1 = C11_1 - 2*mu_1;

C11_2 = cL_2^2*rho_2; C44_2 = cT_2^2*rho_2; mu_2 = C44_2; lambda_2 = C11_2 - 2*mu_2; if p == 1wtype = 'c'; phi_2 = Psi; % for longitudinal $psi_2 = 0$; % for transverse elseif p==2 wtype = 's_axial'; $phi_2 = 0$; % for longitudinal psi_2 = Psi; % for transverse elseif p==3 wtype = 's_perp'; $phi_2 = 0$; % for longitudinal psi_2 = Psi; % for transverse else fprintf('p is not between 1 and 3...not a valid polarization \n') end [phi_1_mat,psi_1_mat,phi_2_mat,psi_2_mat]=get_angles(wtype,cL_1,cT_1,cL_2,cT_ 2,phi_2,psi_2); ifstrcmp(wtype,'c') phi_mat = phi_2_mat; else phi_mat = psi_2_mat; end phi_1 = phi_1_mat(:); psi_1 = psi_1_mat(:); phi_2 = phi_2_mat(:); psi_2 = psi_2_mat(:); phi = phi_mat(:); omega_mat = vs(p)*k; omega_vect = omega_mat(:); QC= zeros(1,length(omega_vect)); QS1 = QC;QS2 = QC;Qtot = QC;kvect = k(:); parfornomega = 1:length(omega_vect) w = warning('off','MATLAB:nearlySingularMatrix'); w = warning('off','MATLAB:illConditionedMatrix');

w = warning('off','MATLAB:SingularMatrix');
omega = omega_vect(nomega); counter_omega = nomega; if omega~=0

%omega = 1e12; k_1 = omega/cL_1; k_2 = omega/cL_2; k_I = omega/cT_1; k_II = omega/cT_2; % a = 5e-9;

 $x_1 = k_1^*a;$ %internal compression wave $x_2 = k_2^*a;$ %external $x_I = k_I^*a;$ $x_{II} = k_{II}^*a;$ $Ka = k_2^*a*sin(phi_2(nomega));$

 $x_1_p = x_1*\cos(phi_1(nomega));$ $x_2_p = x_2*\cos(phi_2(nomega));$ $x_I_p = x_I*\cos(psi_1(nomega));$ $x_{II_p} = x_{II}*\cos(psi_2(nomega));$

```
counter = 0;
    AA = zeros(1,200);
    BB = AA;
    CC = AA;
    DD = AA;
    EE = AA:
    FF = AA;
relerr=Inf;
Qtot\_temp = 0;
    A = zeros(6,6);
    b = zeros(6,1);
while (relerr>relerr_tol)
      n = counter;
counter = counter +1;
       [Trr_inc,Trt_inc,Trz_inc,ur_inc,ut_inc,uz_inc] =
incident_calc_full(n,wtype,phi(nomega),x_1,x_2,x_I,x_II,mu_1,lambda_1,mu_2,lamb
da_2,omega,rho_2,k_2,k_II,a);
```

```
pm_mem = pm(wtype);
```

bh $x_{2p} = besselh(n, x_{2p});$ %reused multiple times bh xIIp = besselh(n,x II p); $bhp_x2p = besselh_prime(n,x_2_p);$ bhp_xIIp = besselh_prime(n,x_II_p); $bhdp_x2p = besselh_doubleprime(n,x_2_p);$ bhdp xIIp = besselh doubleprime(n,x II p); $bj_x1p = besselj(n,x_1_p);$ bj xIp = besselj(n,x I p); $bjp_x1p = besselj_prime(n,x_1_p);$ bjp xIp = besselj prime(n,x I p); $bjdp_x1p = besselj_doubleprime(n,x_1_p);$ $bjdp_xIp = besselj_doubleprime(n,x_I_p);$ $A(1,1) = -2*x_2p^2*(bhdp_x2p - (x_2/x_2p)^2*(lambda_2/(2*mu_2))*bh_x2p); \%$ An, Trr (external) $A(1,2) = pm_mem^2 n^*(x_II_p^*bhp_xIIp_bh_xIIp); \% Bn, Trr (external)$ $A(1,3) = 2i*Ka./x_II.*(x_II_p).^2.*bhdp_xIIp; \% Cn, Trr (external)$ $A(1,4) = -mu_1/mu_2 * (-2)*x_1_p^2*(bjdp_x1p (x_1/x_1_p)^2 (lambda_1/(2*mu_1))*bj_x1p); \% Dn, -Trr (internal)$ $A(1,5) = -mu_1/mu_2*(pm_mem*2*n*(x_I_p*bjp_xIp-bj_xIp)); \%En, -Trr (internal)$ $A(1,6) = -mu_1/mu_2*2i*Ka_x_1*(x_I_p)^2.*bjdp_xIp; \% Fn, -Trr (internal)$ $A(2,1) = pm_mem^2 n^*(x_2_p^*bhp_x^2p_bh_x^2p_b); %An$ $A(2,2) = -x_{II_p^2}(2*bhdp_xIIp + bh_xIIp);$ $A(2,3) = -pm_mem*2i*Ka./x_II.*n.*(x_II_p.*bhp_xIIp-bh_xIIp); \%$ $A(2,4) = -mu_1/mu_2*(pm_mem*2*n*(x_1_p*bjp_x1p-bj_x1p));$ $A(2,5) = -mu_1/mu_2*(-x_I_p^2*(2*bjdp_xIp + bj_xIp));$ $A(2,6) = -mu_1/mu_2.*(-pm_mem*2i*Ka./x_I.*n.*(x_I_p.*bjp_xIp-bj_xIp));$ A(3,1) =-2i*Ka*(x_2_p).*bhp_x2p; A(3,2) =pm_mem*1i*Ka.*n.*bh_xIIp; 2*x_II_p^3/x_II*(1-0.5*(x_II/x_II_p)^2)*bhp_xIIp; A(3,3) = $A(3,4) = -mu_1/mu_2*(-2i*Ka*(x_1_p).*bjp_x1p);$ $A(3,5) = -mu_1/mu_2*(pm_mem*1i*Ka.*n.*bj_xIp);$ $A(3,6) = -mu_1/mu_2*(2*x_I_p^3/x_I*(1-0.5*(x_I/x_I_p)^2)*bjp_xIp);$ $A(4,1) = -x_2_p.*bhp_x2p;$ $A(4,2) = pm_mem^*n^*bh_xIIp;$ $A(4,3) = 1i*Ka.*x_II_p/x_II*bhp_xIIp;$ $A(4,4) = x \ 1 \ p.*bip \ x1p;$ $A(4,5) = -pm_mem*n*bj_xIp;$

 $A(4,6) = -1i^*Ka.^*x_I_p/x_I^*bjp_xIp;$

 $A(5,1) = pm_mem^*n^*bh_x2p;$ $A(5,2) = -x_{II_p}.*bhp_xIIp;$ $A(5,3) = -pm_mem^{1i*}(Ka./x_II).*n.*bh_xIIp;$ $A(5,4) = -pm_mem^*n^*bj_x1p;$ $A(5,5) = x_I_p.*bjp_xIp;$ $A(5,6) = pm_mem^{1i*}(Ka./x_I).*n.*bj_xIp;$ $A(6,1) = -1i^*Ka.^*bh x^{2p}; \% **$ A(6,2) = 0; $A(6,3) = x_{II_p^2/x_{II.*bh_xIIp; \%^{**}}$ $A(6,4) = 1i^{*}Ka.^{*}bj_{x1p};$ A(6,5) = 0; $A(6,6) = -x_I_p^2/x_I.*bj_xIp;$ % figure(1) %spy(A)%nnz(A) b(1,1) = -Trr inc; $b(2,1) = -Trt_inc;$ b(3,1) = -Trz inc; $b(4,1) = -ur_inc;$ $b(5,1) = -ut_inc;$ $b(6,1) = -uz_{inc};$ sol = A b;AA(counter) = sol(1);BB(counter) = sol(2);CC(counter) = sol(3);DD(counter) = sol(4);EE(counter) = sol(5);FF(counter) = sol(6); $QC(nomega) = 2*kvect(nomega)*(abs(AA(1))^2+(AA(:))'*AA(:));$ ifimag(phi_2(nomega))~=0 QC(nomega)=0; end QS1(nomega) =2*kvect(nomega)*cos(psi_2(nomega))^2*(abs(BB(1))^2+(BB(:))'*BB(:)); QS2(nomega) =2*kvect(nomega)*cos(psi_2(nomega))^2*(abs(CC(1))^2+(CC(:))'*CC(:)); Qtot(nomega) = QC(nomega) + QS1(nomega) + QS2(nomega);

```
relerr = abs(Qtot(nomega) - Qtot_temp)/Qtot_temp;
Qtot_temp = Qtot(nomega);
end
AA(isnan(AA))=0;
BB(isnan(BB))=0;
CC(isnan(CC))=0;
else
QC(nomega) = 0;
QS1(nomega) = 0;
QS2(nomega) = 0;
end
end
%Qtot = QC + QS1 + QS2;
%%repackage result from vector -> matrix
  [n,m]=size(k);
sigma = reshape(Qtot,n,m);
end
```

function

```
[phi_1,psi_1,phi_2,psi_2]=get_angles(wtype,cL_1,cT_1,cL_2,cT_2,phi_2,psi_2)
```

ifstrcmp(wtype,'c')
 psi_2 = asin(cT_2/cL_2*sin(phi_2));
 phi_1 = asin(cL_1/cL_2*sin(phi_2));
 psi_1 = asin(cT_1/cL_2*sin(phi_2));
elseif or(strcmp(wtype,'s_axial'),strcmp(wtype,'s_perp'))
 phi_2 = asin(cL_2/cT_2*sin(psi_2));
 phi_1 = asin(cL_1/cT_2*sin(psi_2));
 psi_1 = asin(cT_1/cT_2*sin(psi_2));
else
fprintf('error: to choose between +/- sign, need character assignment:\n')
fprintf('options: c (compression), s_axial (shear, axially aligned), s_perp (shear,perp
to axis)\n')
return
end

```
function [Trr_inc,Trt_inc,Trz_inc,ur_inc,ut_inc,uz_inc] =
incident_calc_full(n,wtype,phi,x_1,x_2,x_I,x_II,mu_1,lambda_1,mu_2,lambda_2,ome
ga,rho_2,k_2,k_II,a)
%UNTITLED12 Summary of this function goes here
% Detailed explanation goes here
```

```
Cphi = cos(phi);
Sphi = sin(phi);
x_2_p = x_2*Cphi;
x_{II_p} = x_{II*Cphi};
k^2 = x 2/a;
kII = x_II/a;
C1 = lambda_2/(2*mu_2);
if n == 0
en = 1:
else
en = 2;
end
ifstrcmp(wtype,'c')
Ka = x_2 sin(phi);
bj = besselj(n,x_2_p);
bjp = besselj_prime(n,x_2_p);
Trr\_inc = -2*x_2_p^2*(besselj\_doubleprime(n,x_2_p)-(x_2/x_2_p)^2*C1*bj);
Trt_inc = 2*n*(x_2_p.*bjp-bj);
Trz_inc = -2i*x_2_p*Ka*bjp;
ur_inc = -x_2_p*bjp;
ut_inc = n*bj;
uz inc = -1i*Ka*bj;
\%f = en*1i^n/(rho_2*omega^2);
  f = en*1i^n/(1i*k2);
elseifstrcmp(wtype,'s_perp')
Ka = x_{II} * sin(phi);
bj = besselj(n,x_II_p);
bjp = besselj_prime(n,x_II_p);
Trr_inc = 2i*(x_II_p).^2*Sphi*besselj_doubleprime(n,x_II_p);
Trt_inc = 2i*Sphi*n*(x_II_p.*bjp-bj);
Trz_inc = 2*x_II_p^3/x_II*(1-0.5*(x_II/x_II_p)^2)*bjp;
ur inc = 1i^*Ka^*x \parallel p/x \parallel^*bip;
ut_inc = 1i*n*Ka/x_{II*bj};
uz_inc = x_II_p^2/x_II*bj;
```

```
\%f = en*1i^n/(rho 2*omega^2);
  f = en*1i^n/(1i*kII);
elseifstrcmp(wtype,'s_axial')
Ka = x_{II} * sin(phi);
bj = besselj(n,x_II_p);
bjp = besselj_prime(n,x_II_p);
Trr_inc = -2*n*(x_II_p.*bjp-bj);
Trt_inc = -(x_II_p).^2.*(2*besselj_doubleprime(n,x_II_p)+bj);
Trz_inc = -1i*Ka*n*bj;
ur_inc = -n*bj;
ut_inc = -x_II_p.*bjp;
uz_inc = 0;
  f = en*1i^n/(1i*kII);
\%f = en*1i^n/(rho_2*omega^2);
else
fprintf('error: to choose between +/- sign, need character assignment:\n')
fprintf('options: c (compression), s_axial (shear, axially aligned), s_perp (shear,perp
to axis)\n')
return
end
Trr_inc = Trr_inc* f;
Trt_inc = Trt_inc* f;
Trz_inc = Trz_inc* f;
ur_inc = ur_inc* f;
ut_inc = ut_inc* f;
uz_inc = uz_inc* f;
```

```
end
```

```
function f = pm(wtype)

ifstrcmp(wtype,'c')
    f = 1;
elseif or(strcmp(wtype,'s_axial'),strcmp(wtype,'s_perp'))
    f = -1;
else
fprintf('error: to choose between +/- sign, need character assignment:\n')
fprintf('options: c (compression), s_axial (shear, axially aligned), s_perp (shear,perp
to axis)\n')
return
end
```

function [x,w]=lgwt V4(N,a,b) % lgwt.m % % This script is for computing definite integrals using Legendre-Gauss % Quadrature. Computes the Legendre-Gauss nodes and weights on an interval % [a,b] with truncation order N %% Suppose you have a continuous function f(x) which is defined on [a,b] % which you can evaluate at any x in [a,b]. Simply evaluate it at all of % the values contained in the x vector to obtain a vector f. Then compute % the definite integral using sum(f.*w); % % Written by Greg von Winckel - 02/25/2004 N=N-1; N1=N+1; N2=N+2; xu=linspace(-1,1,N1)'; % Initial guess y=cos((2*(0:N)'+1)*pi/(2*N+2))+(0.27/N1)*sin(pi*xu*N/N2);% Legendre-Gauss Vandermonde Matrix L=zeros(N1,N2); % Derivative of LGVM Lp=zeros(N1,N2); % Compute the zeros of the N+1 Legendre Polynomial % using the recursion relation and the Newton-Raphson method y0=2; % Iterate until new points are uniformly within epsilon of old points while max(abs(y-y0))>eps

L(:,1)=1; Lp(:,1)=0; L(:,2)=y; Lp(:,2)=1;

for k=2:N1

L(:,k+1)=((2*k-1)*y.*L(:,k)-(k-1)*L(:,k-1))/k; end

Lp=(N2)*(L(:,N1)-y.*L(:,N2))./(1-y.^2);

end

% Linear map from[-1,1] to [a,b] x=(a*(1-y)+b*(1+y))/2;

% Compute the weights w=(b-a)./((1-y.^2).*Lp.^2)*(N2/N1)^2;