IMPACT OF MASS AND BOND ENERGY DIFFERENCE AND INTERFACE DEFECTS ON THERMAL BOUNDARY CONDUCTANCE

by

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Abstract

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ChangJin Choi, Doctor of Philosophy
Utah State University, 2016

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The objective of this study is to use molecular dynamics simulation techniques in order to improve the understanding of phonon transport at the interface of dissimilar materials and the impact of different material properties on thermal boundary conductance (TBC). In order to achieve this goal, we investigated the contributions of mass and bond energy difference and interface defects on TBC at the interface of nanostructured materials using non-equilibrium molecular dynamics (NEMD) simulation and phonon wave-packet (PWP) simulation techniques.

NEMD is used to distinguish relative and combined contributions of mass and bond energy difference on TBC. As a result, it is found that the mass has a stronger contribution than the bond energy on lowering the TBC and that the TBC is dependent on the length of interdiffusion region as well as temperature. In addition, evidence of inelastic scattering is observed with interdiffusion regions especially when two materials differ in the bond energy.

A detailed description of phonon interactions at the interface is obtained performing PWP simulations. A frequency dependence of the TBC based on phonon dispersion relation is observed. As it is expected, minimum scattering occurs when there exists only vibrational mismatch at the interface and inelastic scattering is to take place at high frequency region.
when the bond energy of the two materials is different resulting in the strain at the interface. It is also shown that the level of inelastic scattering is dependent on the length of the interdiffusion region. In addition, the TBC calculated with the results of PWP simulations is compared with that of NEMD simulations as well as theoretical predictions from the acoustic mismatch model and the diffuse mismatch model.

A simple analytical model, which utilizes knowledge of thermal interface resistance and the interface geometry for the prediction of effective thermal conductivity, is developed. This model is generated based on Si-Ge superlattices and embedded nanoparticle and nanowire arrays, and is validated by comparing to existing experimental and computational data. Results shows that the effective thermal conductivity calculated from the analytic model agrees well with that of various systems of different materials and geometries.

(123 pages)
Public Abstract

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Many portions of energy generated in the U.S. are not used and take the form of wasted heat due to a poor heat transfer efficiency. This fact leads research communities to focus on thermoelectrics as a means for using waste heat through direct thermal to electrical energy conversion. One way to enhance thermoelectric efficiency is to reduce thermal conductivity through nanostructuring. In nanostructures, understanding energy transport across the interface of two materials is important because interfaces dominate the resistance to overall thermal transport of the system and can be described by thermal boundary conductance (TBC). Also of note, an understanding of thermal transport cannot be achieved without an understanding of transfer via atomic vibration, known as phonons.

In this study, two different techniques of molecular dynamics (MD) simulation are introduced in order to improve the understanding of the phonon transport at the interface of dissimilar materials and the impact of different material properties on TBC. Non-equilibrium MD simulations are used to study relative and combined contributions of mass and bond energy difference on TBC and phonon wave-packet simulations are used to obtain a detailed description of phonon interactions at the interface. At the end of this study, a simple
analytical model for the prediction of effective thermal conductivity, using knowledge of thermal boundary resistance, an inverse of TBC, and the interface geometry, is developed.
To my wife, Catherine, and my baby, Ian.
And my family... Mom, Dad, and Eugene.
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Chapter 1

Introduction

Heat transfer is defined as an exchange of thermal energy between physical systems, and convection, radiation, and conduction are three fundamental mechanisms for heat transfer. When heat is transferred by a gas or liquid mass movement, it is called convection. Radiation is a transmission of energy in the form of waves or particles through a material medium. Although all matter with a temperature greater than absolute zero emits thermal radiation, it is usually important only at high temperatures. Conduction is heat transfer by molecular or atomic motions, and heat conduction is the dominate mechanism in solid materials. Heat transfer plays a critical role in our daily life, for example when we use cellphones or radiator, and even when we cook. However, about 20% and 80% of the energy generated from industrial and transportation sectors, respectively, in the U.S. takes the form of waste heat due to a poor heat transfer efficiency, and an estimated 60% of energy produced in the U.S. is ultimately not used [1]. This large amount of waste heat leads research communities to focus on thermoelectrics as a means for using this waste heat through direct thermal to electrical energy conversion, improving the overall efficiency by recapturing waste heat. At the atomic scale, an applied temperature gradient in a material causes charge carriers to diffuse from higher temperature to lower temperature, creating a flow of current that is used to generate electric power. Usually the process, however, has a very low efficiency which makes it unrealistic for many applications, even though all materials have a nonzero thermoelectric effect. Thermoelectric efficiency is determined by the dimensionless figure of merit ($ZT$). $ZT$ is defined as $ZT = \sigma S^2 T / k$, where $\sigma$, $S$, $T$, and $k$ are electrical conductivity, Seebeck coefficient, temperature, and thermal conductivity, respectively. Therefore $ZT$ requires a material to have high electrical conductivity, high Seebeck coefficient, and low thermal conductivity in order to have higher thermoelectric efficiency. If $ZT$ is larger than 3,
the thermoelectric device can be competitive with traditional mechanical energy conversion systems. Therefore, either a higher Seebeck coefficient or lower thermal conductivity is needed to increase $ZT$. However, the electrical terms in $ZT$ are typically inversely dependent on each other, for example $S$ decreases while $\sigma$ increases [2], which makes it difficult to enhance one property without an opposing affect from another property. Thus the research community has focused on reducing thermal conductivity of materials in order to have enhanced $ZT$.

In the last several decades, improving thermoelectric efficiency has been done by reducing the thermal conductivity through nanostructuring a material [3–5]. Mingo et al. [6] studied the optimal embedded nanoparticle size in order to minimize the thermal conductivity of a solid, and showed that 5-10 nm nanoparticles in SiGe alloys reduce the thermal conductivity from about 10 to 1-2 $Wm^{-1}K^{-1}$. Hu et al. [7] and Chen et al. [8] showed that the reduced thermal conductivity in silicon-germanium nanowires results in an increased dimensionless figure of merit ($ZT$). Lee et al. [9] and Capinski et al. [10] measured thermal conductivity of SiGe superlattices and thin film using the $3\omega$ method and GaAs/AlAs superlattices using a pump-and-probe technique, respectively. They agreed that the thermal conductivity of superlattice structures is less than that of an alloy of two constituent materials. However, they predicted different trends in thermal conductivity with period length. Lee et al. [9] showed that superlattices with longer periods have smaller thermal conductivity while Capinski et al. [10] found a decrease in thermal conductivity with a reduction of the superlattice period. Chen and Neagu reported that the interface scattering of phonons plays a major role in thermal conductivity of superlattice structures [11]. Nanostructuring (interfaces and boundaries) successfully reduced the thermal conductivity in each of these studies, however the differences in trends still requires a need for more understanding. The ability to predict and control the thermal transport in nanostructures, especially at the interface, is critical in order to fully take advantage of nanostructuring and to use it for improving $ZT$ of thermoelectrics. However achieving this understanding is difficult because thermal transport between two nanostructured materials is obscure due to the complexity
of the phonon reflection mechanisms, such as inelastic scattering and mode conversion, and the roughness created by defects at the interface.

A resistance to the thermal conduction, known as Kapitza resistance [12], occurs at the interface of two different materials due to the structural disorder at the interface or the different material properties on both sides of the interface. Thus there exists a temperature discontinuity at the interface of two different materials when heat is transported across the interface. The thermal transport at the interface of two solid materials can be described as the Kapitza conductance, often called thermal boundary conductance (TBC). The TBC, which is an inverse of Kapitza resistance, is defined as

\[ h_k = \frac{q}{\Delta T}, \]  

(1.1)

where \( q \) is the heat flux across the interface and \( \Delta T \) is the difference in temperature across the interface. It is now important to understand TBC in nanostructures because the energy transport at the interface between two nanostructured materials has a significant importance in determining the performance not only of thermoelectric devices but also in other electronic, photonic, and phononic devices. In many of these nanostructured devices, interfacial resistance dominates the overall thermal resistance of the system. Thus interfacial conductance has been a subject of research with the objective of better understanding and predicting thermal transport in nanostructured materials [13]. Specifically this work will provide knowledge that can lead to materials with tailored thermal properties by investigating the role of different material parameters on TBC at the interface of two dissimilar materials.

1.1 Theoretical Model

The idea that there exists a resistance across the interface between liquid helium and solid was first observed in 1936 [14,15]. However they did not study further on this thermal boundary resistance (TBR), and it was Kapitza who is measured the temperature drop, when heat flows across the boundary, near the boundary between liquid helium and solid in
There are two general theories that account for the phonon transport across the interface of two materials: the acoustic mismatch model (AMM) and the diffuse mismatch model (DMM). It was in 1955 when the first theoretical model, which is known as AMM, was introduced, by Mazo and Onsager, to predict the TBR between liquid helium and solids [16]. The AMM was extended to solid-solid interfaces by Little in 1959 [17]. The AMM is based on the assumption of a perfect interface. In this model, the incident phonons are treated as plane waves and assume no scattering occurs at the interface, therefore, phonons can only reflect, reflect and mode convert, refract or refract and mode convert. Figure 1.1 describes these possibilities.

After the AMM is applied to solid-solid interfaces, many experimental measurements were performed on solid-solid interfaces, especially on metallic contacts and metal-insulator contacts, to validate the AMM. Barnes and Dillinger measured the TBR between copper-lead and copper-tin at 1.3 K, in 1963 and 1966, respectively, and the measured TBR was higher than that of the AMM for copper-lead contacts and lower than AMM for copper-tin contacts [18,19]. They attributed these mismatches to stress and dislocations near the contact area that caused additional phonon scattering, and the electron thermal transport across the interface. The measured TBR of the copper-solder-copper structure at 0.06 K by Steyert [20] was a factor of 4 higher than the AMM value because of the scattering near the interface resulted from the defects at the interface. These experiments and Harrison [21] showed that it is hard to validate the AMM with the metallic contacts due to the phonon scattering of imperfect interface and electron transport.

In order to eliminate these effects at the interface, metal-insulator contacts are studied. The experiment by Holt [22] in 1966 was the first measurement of TBR using thin films. The use of thin films to measure TBR has many advantages, such as reliability and better quality of interface. Holt [22] achieved a good agreement with the AMM prediction at 1.5 K using gold films on sapphire. However, Von Gutfeld et al. [23] found that the TBR between thin films and quartz is predicted a factor of 2 higher than that of the AMM, and this result is attributed to graininess in the film causing reduced contact area. In 1970, Wolfmeyer
et al. [24] soldered indium on sapphire but they failed to eliminate phonon scattering at the interface thus failed to agree with the AMM prediction. Wigmore et al. [25], in 1972, evaporated a thin film heater onto a polished and cleaned MgO substrate, therefore it has high quality interface, and shows that the TBR at temperature above 1 K is consistent with the AMM prediction. This experiment is important because the result firstly showed that the TBR is consistent with the AMM at any temperature above 1 K. In 1977, Matsumoto et al. [26] used epoxide contacts and found that the AMM agreed with the low temperature limit (near 0.1 K).

As it is shown above, the AMM predicts TBR relatively well at low temperatures for the perfect interface. Although remarkable success had been made to predict the TBR using the AMM, at the imperfect interface and at higher temperatures, when higher frequency phonons dominate thermal transport, the AMM becomes not valid. In 1977, Bron and Grill observed a strong frequency dependent scattering above 1 THz which is an evidence of inelastic scattering [27]. Wybourne et al., in 1985, observed a time delay in very short phonon pulse and they attributed this to the phonon scattering in the layer underneath the thin film [28]. Thus Swartz and Pohl, in 1987, measured TBR over the large range of temperature, from below 1 K to over 100 K [29], and suggested the diffuse mismatch model (DMM) [16]. The assumption of the DMM, opposed to that of the AMM, is that all the phonons at the interface are diffusely scattered and are emitted to either side of the
interface. This assumption maximizes the effect of diffuse scattering at the interface on the TBR. Figure 1.2 represents that the AMM is the maximum limit while the DMM is the minimum limit resulted from their assumptions. As it is shown in figure 1.2, experimental measurement of TBR is close to the AMM at lower temperature ranges, and deviates from the AMM by approaching the DMM as the temperature increases. It is also shown that the DMM is not accurate for the prediction of TBR at lower temperature ranges where diffuse scattering does not occur. Additionally, in the DMM, the transmission probability is dependent on the density of states on both sides of the interface and the other selection rules. Duda et al. demonstrated that different assumptions of the principle of detailed balance play an important role in predicting thermal transport using the DMM [30]. Therefore, diffuse scattering is important for imperfect interfaces and at higher temperatures. However Swartz and Pohl showed that the DMM does not predict all transport regimes at the interface [16].

Although the prediction of TBR from the DMM has been shown as a lower limit of the TBR prediction, one can think about the smallest possible TBR occurs when all phonons are transmitted into another side of the interface regardless of the details of the scattering event at the interface. This limit is known as a phonon radiation limit, and is an ultimate lower limit of TBR across the interface. Although it is almost not possible to make it happen in reality, it is obvious that, in some way, high frequency phonons need to be transmitted into low frequency phonons, which would be a role of inelastic scattering.

In summary, the AMM and DMM provide a basis of understanding TBR. Although the basic assumptions of these models are different, they share the idea that the scattering occurring at the interface is elastic, which limits both models to predict TBR at higher temperatures and in highly disordered interfaces. In addition, both models are usually applied under the Debye approximation and do not account for the atomic-level details of the interface which result in a poor prediction of thermal boundary conductance in many cases [31–33]. Therefore, it is necessary to have a better understanding of inelastic scattering in order to accurately predict thermal transport across the interface.
1.2 Lattice Dynamical Model

Lattice dynamics is a study of the vibrations of atom in a crystal with a harmonic approximation. The lattice dynamical model allows for direct consideration of the effects, such as phonon dispersion, the cutoff in the phonon density of states for high frequencies, and the weak bonding at the interface, which are important for phonon transport at high temperatures. In 1978, Lumpkin et al. performed one dimensional lattice dynamical calculation for the Kapitza conductance at the interface between two dissimilar harmonic lattices and compared results with computer experiments [34]. They found that their lattice model does not agree with the values obtained from computer experiments and that the Kapitza conductance is increased as anharmonicity increases. Arimitsu et al. [35], also developed a one dimensional lattice dynamical model to study phonon scattering at a planar interface between two dissimilar materials. They showed that the phonon transmission coefficient becomes small at high frequencies if the force constant is weak which represents that the bonding energy between two materials is an important factor of phonon transport at high frequency ranges. Paranjape et al. [36] extended their previous study [35] using three dimensional model of a homogeneous solid to obtain equations for the relative amplitudes of
the reflected and transmitted longitudinal and transverse waves. They found that there are no reflections at very low frequencies which is in agreement with macroscopic theory. In 1989, Young and Maris showed a spectral dependence of the phonon transmission coefficient and the temperature dependence of the thermal boundary resistance at the interface between two dissimilar solid materials consisting of semi-infinite harmonic FCC lattices with different masses and spring constants [37]. They also found that $T^3$ dependency of the TBC is broken because of high frequency phonons at higher temperature. Each of these studies show the impact of anharmonicity on the TBC either at high frequency range or at high temperatures. However all of these studies assumed that the lattice constant are the same in the two materials. In 1990, Pettersson and Mahan [38] extended lattice dynamical theory for different lattices. Their model can be applied to models that consist of two different lattice constants or of even different crystal structures and to generate more phonons using larger unit cells at the interface. They showed that the phonon transmission coefficient of materials of different lattice constant is much lower than that of lattice matched materials. They also found that the high frequency phonons carry considerable amount of the reflected and transmitted energy. Fagas et al., in 1999, developed lattice model that contains phonon dispersion relations and singularities in the phonon density of states, and presented that phonon transmission probability is a strong function of frequency and the disorder correlation length [39]. The lattice dynamical model is then widely applied to different nanostructured materials, such as thermal transport in semiconductor superlattices [40], single-walled carbon nanotubes [41], and nanotubes and nanowires [42], to predict thermal transport. In 2009, Turney et al. calculated thermal conductivity of solid argon from lattice dynamics calculations and compared them with the results from molecular dynamics simulations [43]. They concluded that the predicted thermal conductivity from lattice dynamics agrees with the molecular dynamics results within 30 % below 40 K and becomes inaccurate at higher temperatures which is resulted from an inherent approximation of lattice dynamics.

As it is discussed, lattice dynamics accounts for more effects, that are not included in
theoretical predictions, in their calculation and has an ability to predict thermal transport accurately. In addition, it has an advantage on the computational effort over molecular dynamics [43]. However, it still requires a low temperature approximation and the assumption of elastic scattering.

1.3 Molecular Dynamics Simulation

Different experimental methods, such as $3\omega$ method, scanning thermal microscopy, optical pump-probe methods, and thermal conductivity spectroscopy, have been developed and optimized in order to measure thermal transport properties [44]. Although these experiment techniques have successfully measured thermal conductivity of nanostructured materials [45, 46] and the TBC at the interface [47], experiments have demonstrated that neither the AMM nor the DMM predict well the phonon transportation across the interface between two dissimilar materials [13, 29, 48–50]. The accuracy of the experimental measurement of thermal properties at the interface is heavily dependent on the condition of the interface. Many experimental measurements have shown that the impact of defects on thermal transport at the interface [50, 51]. However, due to the difficulties in making accurate measurement resulted from the difficulty in fabricating complicated interfaces, it is hard to have an exact experimental data set to validate the AMM and DMM. In addition, calculating phonon transmission probability using AMM and DMM is based on bulk properties of two materials forming the interface, they do not account for the bond strength and phonon dispersion relations [52]. Consequently, molecular dynamics (MD) simulations are used for modeling and simulation of interfacial thermal transport. As the accuracy of interatomic potential function increases, MD simulations become a powerful tool to study the interface effect. Previous research has already shown that MD is a practical method to probe thermal transport in nanostructures [53, 54].

MD simulations trace the time dependent atom displacement based on the numerical solution of Newton’s equations of motion. The forces between atoms are derived from interatomic potentials [55]. Interatomic potential is a mathematical description of the interaction between atoms based on their locations. The two most commonly used methods in
MD simulations to obtain thermal properties, such as thermal conductivity and TBC, are non-equilibrium molecular dynamics (NEMD) and equilibrium molecular dynamics (EMD). NEMD method allows to predict the TBC at the interface while EMD method is able to provide the detailed understanding of the thermal coupling across the interface. Researches have shown that thermal conductivity that is obtained by NEMD and EMD methods are consistent with each other [56], however, Merabia et al. proved that NEMD and EMD show inconsistency of results on TBC [57]. Rajabpour and Volz carried out both NEMD and EMD simulations to calculate TBC, and showed that results of NEMD simulations overestimate the one from EMD simulations, and that results of EMD simulation agree well with the DMM prediction [58].

1.3.1 Equilibrium Molecular Dynamics (EMD)

The most common method in EMD is the Green-Kubo formulation which uses a equilibrium fluctuation of the heat current to calculate thermal properties. While it is simple as it uses fewer atoms in the computational domain, it requires longer simulation time to converge the autocorrelation function and includes a finite size effect. In 1996, Pickett et al. first used EMD simulation to explore the phonon energy transmission at the interface of materials that differed only in mass [59]. They showed that the energy transfer through the interface can be strongly affected by small differences in mass of the two regions. Since then many researchers have used EMD simulation to study the thermal properties in nanostructures [60–63]. Volz et al. showed that the silicon thermal conductivity that is obtained by EMD method compares favorably with the experimental data [60] and they discovered that strain affects the overall thermal conductivity of the superlattices [61]. In 2004, Tretiakov and Scandolo conducted EMD simulations using the Green-Kubo method and a Lennard-Jones (L-J) interatomic potential to calculate the thermal conductivity of solid argon in the classical limit [62]. Results suggest that the thermal conductivity at high temperature region is in good agreement with the experimental data which shows that the EMD simulation with Green-Kubo formalism is a powerful tool to calculate the thermal conductivity. However, the EMD simulations were not successful in the prediction of thermal boundary
resistance of an interface between Lennard-Jones solids when studied by McGaughey and Li in 2006 [63].

1.3.2 Non-equilibrium Molecular Dynamics (NEMD)

NEMD simulations are often called the direct method. This method is comparable with experimental measurements because it imposes a temperature gradient across the system by introducing heat source and sink on each sides of the interface. During the simulation the same amount of heat flux is added and subtracted from the heat source and sink. In that way, the temperature gradient is imposed which is used to calculate the thermal conductivity from Fourier's law, given in equation 1.2, and the TBC is determined from equation 1.1.

\[ q = -kA\frac{\Delta T}{L}, \]  

(1.2)

where \( q \) is the heat flux, \( k \) is the thermal conductivity, \( A \) and \( L \) are the cross-sectional area and length of the material, respectively, and \( \Delta T \) is the temperature difference across the system. NEMD simulations, usually, involve a large temperature gradient results in the nonlinear response near the heat source and sink, and require a completely new system set-up to calculate the thermal conductivity along different crystal lattice directions which is different from EMD simulation where the entire thermal conductivity is computed in one simulation. However, due to the direct calculation of thermal properties from the temperature gradient, NEMD simulations are preferred especially for the calculation of phonon transport behavior at the interface, such as TBC.

Since Maiti et al. [64] first used NEMD simulations, researchers have started to use NEMD method to study thermal transport in various nanostructures. Lukes et al. showed that increases of argon thermal conductivity with increasing film thickness which is consistent with experimental data and theoretical predictions [65]. The increases with the film thickness is attributed to the exclusion of long-wave length phonons at short film thickness. Abramson et al. used NEMD simulations, in 2002, to study how the strain and interface of the superlattices affect thermal conductivity and found that the effective thermal con-
ductivity of nanoscale strained heterostructures with a single interface could be less than that of half of an unstrained thin film [66]. Chen et al. studied the effects of interface scattering and boundary scattering on lattice thermal conductivity of krypton-argon super-lattice nanowires using NEMD method in 2004 [67]. Their results showed that the boundary scattering provides significant resistance to phonon transport, and that the dependence of interfacial thermal resistance on temperature which can be evidence of inelastic scattering. Skye and Schelling explored scattering from mass disorder and found it to be a dominant factor of thermal transport in silicon-germanium alloys using Stillinger-Weber (S-W) potentials [68]. These studies show that the dependence of thermal transport of nanostructures on different scattering at the interface, resulted from the mass difference, strain at the interface and the thickness of the interface.

In addition, NEMD has been widely used to explore interfacial phenomena in nanostructures [69–72]. Theses studies focused the bonding stress across the interface and their impact on TBC, however they have been limited to Si-α-polyethylene [69], self-assembled monolayer (SAM) such as Au-SAM-Si [70], carbon nanotubes-SiO$_2$ [71], and graphene/graphite-polymer interfaces [72]. In order to generalize the effects at the interface research communities began to study the TBC across the interface between solid-solid materials [64,73–78]. Kapitza resistance in heterogeneous solid materials is first calculated by Maiti et al. in 1997 [64]. They proved that NEMD simulation is a practical method to determine thermal properties in solid-solid interface. Stevens and Norris observed a temperature dependence of TBR which is evidence of inelastic scattering by separating two materials with the same L-J interatomic potential parameters but different atomic masses [73]. In 2006, Hegedus and Abramson created heterogeneous systems by modifying L-J potential parameters of argon to predict the influence of interface on thermal conductivity [74]. Their results showed that the introduction of the second material into the argon film leads to a decrease in overall thermal conductivity, and that neither AMM nor DMM can fully predict the thermal boundary effects by comparing with the simulated data. In 2009, Landry and McGaughey assumed the perfect interfaces in a silicon-germanium system.
and predicted TBR in the temperature range between 300 and 1000 K [75]. They found that elastic scattering is observed below 500 K and that the temperature dependence of TBR at higher temperatures can be attributed to inelastic scattering. Shen et al. investigated the effects of bonding strength, which is varied in two different ways, on thermal conductance and suggested that the interfacial bonding dominates the change in thermal conductance for weak interfaces [76]. On the contrary for strong interfaces, thermal conductance is pressure independent. Duda et al. examined the behavior of TBC at interfaces by varying range and cross-species interaction and concluded that the interface condition can be a core factor on temperature dependence of TBC even for the perfect interface [77]. In 2012, English et al. showed that inserting an interfacial film with the vibrational mismatch enhances interface conductance [78].

In general, above studies have focused on either atomic mass or interatomic potential parameters to study the thermal transport at the interface, however, the defects on the interface is also an interesting topic to study [79–85]. Daly et al. [79] and Twu and Ho [80] have done some preliminary work of the impact of imperfect interfaces on the Kapitza conductance. In 2002, Daly et al. presented the addition of roughness to the interface of superlattices resulted in reduced thermal boundary conductance [79]. Twu and Ho, in 2003, studied the impact of imperfect interfaces on the Kapitza conductance by employing interdiffusion and voids [80]. Results show that the Kapitza conductance is a strong function of a degree of the vacancies and the interdiffusion rates. Liang and Sun also created the interface with mixed atoms between two FCC solids and found that the thickness of the mixed region significantly affects to thermal conductivity [81]. Stevens et al. also found that the thermal transport could be improved nearly a factor of two by interface mixing [82]. In 2013, Zhou et al. performed various NEMD simulations to study effects of interfacial morphology and disorder on Kapitza conductance [83]. They found that the Kapitza conductance is dependent on interfacial shape, which is consistent with the result that the Kapitza conductance increases with the total interface area is increased. It is also found that the diffused interface increases Kapitza conductance. They found, in another study,
that the TBC increases with interfacial stiffness and is sensitive to crystal orientations [84]. Shao and Bao studied heat transfer across a disordered thin film, and found that TBR can be reduced only when few layers of alloy region between two materials exists [85].

### 1.3.3 Phonon Wave-packet Dynamics

The majority of thermal energy in dielectric and semiconducting materials are carried by phonons and the analysis of these systems are mainly based on the Boltzmann transport equation (BTE) [43, 86]. Although both EMD and NEMD simulations make it possible to predict thermal properties at the system level, it is hard to get an information about phonons, such as phonon group velocities and lifetimes, that are the required inputs of the BTE [87]. These phonon properties can be obtained from lattice dynamics calculations [88] and MD simulations in the time domain [89]. Larkin et al. showed that phonon velocities and lifetimes can be predicted by the spectral energy method [90]. They used two different spectral energy methods to predict and compare values from each method by testing them using three different MD systems, L-J argon, S-W silicon, and a carbon nanotube that is described by the Reactive Empirical Bond Order (REBO) potential. They found that the phonon lifetimes or thermal conductivity cannot be exactly predicted by the phonon spectral energy density without the phonon mode eigenvector.

In order to provide information on phonon transport at the interface in terms of the individual vibration, phonon wave-packet (PWP) dynamics is proved to be a useful tool [91]. PWP dynamics is a MD based simulation technique which provides a thorough understanding of phonon scattering at the interface of two dissimilar materials. The basic idea of PWP simulation is to propagate a phonon wave-packet of well-defined wavevector and polarization toward the interface, and analyze the reflected and transmitted phonons, when they encounter the interface, by determining a transmission probability [91]. In PWP simulations, the wave-packet is generated and the transmission probability is calculated according to equation 1.3 and equation 1.4, respectively.

\[
u_n = A \exp\left[i k (x_n - x_0)\right] \exp\left[-(x_n - x_0)^2 / \xi^2\right], \quad (1.3)
\]
where $u_n$ is the displacement of the $n^{th}$ atom, $A$ is the amplitude of the displacement, $\epsilon$ is the polarization vector, $k$ is the wavevector, $x_n$ is the location of the atom along the direction of transport, $x_0$ is the center of the wave-packet, and $\xi$ is the width of the wave-packet.

$$\alpha = \frac{E_{tr}}{E},$$

(1.4)

where $\alpha$ is the transmission probability, $E_{tr}$ is the transmitted energy and $E$ is the initial wave-packet energy.

Research has shown that phonon wave-packet dynamics possess an advantage in understanding the phonon transport at the interface [92–94]. In 2002, Schelling et al. performed PWP simulations to investigate a transmission of phonons across an interface between two semiconductors, and they found a good agreement of the transmission coefficient with those predicted by the AMM [91]. They also showed that phonon scattering is dependent on the phonon frequency and grain boundary structures using PWP simulations [95]. Becker et al. studied the scattering from interfaces in semiconductor nanowires in 2006 [96]. They found that the energy transmission depends strongly on both the area of the interface and the frequency of the incident wave. Sun and Murthy, in 2008, used phonon wave-packet simulations to find that the phonon transmission coefficient is a strong function of frequency, roughness, characteristic length and atomic structure, and they observed complex phonon mode conversion and wave interference effects [97]. Yao et al. [98] compared their results from phonon wave-packet simulations with the classic formula derived by Klemens [99] for the scattering strength of point defects. They found that the fraction of transmitted and reflected energies strongly depend on the frequency of the incident phonons and the mass and concentration of defects, and that the Klemens’ theory is valid only when each phonon-defect scattering event is independent. Tian et al. showed that phonon transmission coefficient obtained from the wave-packet method coincide with the thermal conductivity calculated from NEMD method [100]. In addition, they found that the perpendicular interface area plays an important role when calculates the transmission coefficient. In another study, they found a good agreement with the AMM in the low-frequency limit by observing phonon
transport across single-crystal thin films of different thickness [101]. Roberts and Walker investigated the direction and frequency dependence of the phonon transmission probability at the interface of dissimilar materials by performing phonon wave-packet simulations [93]. As a result, they concluded that thermally rectifying materials can be obtained when no or little inelastic scattering occurs. Deng et al., in 2014, performed NEMD and phonon wave-packet simulations to compute the Kapitza resistance of Si-SiO$_2$ interface [102]. They concluded that the energy transmission is decreased with increased thickness of the SiO$_2$ layer, and energy shift and mode conversion occurred when the incident phonon frequency is increased. In addition, they also achieved good agreement in Kapitza conductance calculated from NEMD and phonon wave-packet methods.

Above studies, in general, showed that the frequency dependence of transmission probability and the TBC agrees well with the AMM at low frequencies. However many models did not consider the effect of strain which usually exists at the interface of two materials, such as silicon and germanium. Therefore, this study focuses on the phonon scattering at the interface in which strain and defects are existed as well as the interface where the mass is differed in two materials.

1.4 Introduction of Current Study

Molecular dynamics simulations have been used as a means of understanding thermal properties at the interface of materials since the 1990’s [59, 64]. There have been several theoretical studies on thermal transport at the interface of two solid materials [37–39, 103], analytical analysis of thermal transport at atomic junctions [104–106], and even new theoretical models have been developed [107, 108], but we still lack a complete understanding of thermal transport at the interface. As it is shown in previous sections, the thermal transport in small devices is dominated by the interactions at the interface and is strongly influenced by the strength of the bond at the interface, defects, and the constituent materials forming the interface. Thus the current study begins with focusing on the thermal boundary conductance at the interface between two materials.

In the current study two different MD simulation techniques will be used to investigate
the relative and combined role of mass and lattice difference on TBC. First, NEMD simulations will be used to calculate the effective thermal conductivity of the system and TBC at the interface. The accuracy of an MD simulation is heavily dependent on the quality of interatomic potentials thus it is not the best method to probe specific material properties. However, it is a good method for investigating the trends in material properties which is the focus of the current study. The goal of the NEMD study is to show the contributions of the mass and bond energy to TBC and show the frequency dependence of TBC as well as demonstrate evidence of inelastic scattering at the interface. Next, PWP simulations will be used to attain a thorough insight into the phonon transport at the interface by calculating phonon transmission probability. As a result, we will show that inelastic scattering plays a significant role in thermal transport. In all simulations, solid argon will be the basis material and an argon-like material will be introduced in order to represent the material that differs in mass and bond energy from the solid argon. A Lennard-Jones interatomic potential will be used to describe the interactions between atoms. The results will be generalized by performing the same simulations with practical materials, such as silicon and germanium. Finally, a simple analytical model will be developed in order to calculate the effective thermal conductivity with minimal inputs using the concept of the interface geometry and TBR at the interface.

The remaining portion of this document is organized as follows. The NEMD study is described in Chapter 2, the PWP study is introduced in Chapter 3 followed by introducing a simple analytical model in Chapter 4, and conclusions in Chapter 5.

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Chapter 2
Contributions of Mass and Bond Energy Difference and Interface Defects on Thermal Boundary Conductance

Nomenclature

\( A \) Cross-sectional Area

\( h_k \) Thermal Boundary Conductance

\( K \) Kinetic Energy

\( k \) Stiffness

\( k_b \) Boltzmann’s Constant

\( L \) Length

\( m \) Mass

\( N \) Number of Atoms

\( q \) Heat Flux

\( r \) Interatomic Separation Distance

\( T \) Temperature

\( \Delta T \) Temperature Difference

\( U \) Interatomic Potential Function

\( \epsilon \) Energy Scale of the Potential Function

\( \kappa \) Thermal Conductivity

\( \omega \) Frequency

\( \sigma \) Length Scale of the Potential Function

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2.1 Introduction

As the size of electronic, photonic, and phononic devices becomes smaller there is an increasing need to understand thermal transport across interfaces between two different materials. Interfaces are considered to be a thermal transport bottleneck in nanostructured materials and therefore play a critical role in the effective thermal conductivity. In order for next generation devices to perform at the necessary efficiency and desired performance, predicting thermal transport at the interface is crucial [1, 2]. When heat is transported across the interface between dissimilar materials there exists a resistance to conduction heat transfer creating a temperature discontinuity. This temperature discontinuity can be described by the thermal boundary resistance, or Kapitza resistance [3], which is the inverse of the thermal boundary conductance (TBC). The TBC is given in equation 3.3.

\[ h_k = \frac{q}{\Delta T}. \]  

(2.1)

where \( q \) is the heat flux and \( \Delta T \) is the difference in temperature across the interface.

The first theoretical model to predict the TBC was the acoustic mismatch model (AMM) [4]. The AMM is based on an assumption of a perfect interface, where incident phonons are treated as plane waves and assumes no scattering occurs at the interface, therefore phonons can only reflect, reflect and mode convert, refract or refract and mode convert. This model is valid only at relatively low temperatures (< 20 K) and perfect planar interfaces. In an attempt to capture scattering at the interface, the diffuse mismatch model (DMM) was introduced [5]. In the DMM phonons are diffusely and elastically scattered at the interface and are re-emitted to either side of the interface. The transmission probability predicted by the DMM depends on the density of states of materials on both sides of the interface and the selection rules that assume different scattering at the interface. To understand the role of scattering, Duda et al. [6] studied different scattering mechanisms, including complete diffuse scattering, partial diffuse scattering, elastic scattering, and inelastic scattering, and showed the dependency of transmission probability on the principle of detailed balance, and found that one of their specific cases produces the DMM developed
by Swartz and Pohl [5]. Hopkins and Norris developed the joint frequency diffuse mismatch model (JFDMM) with the assumption of inelastic scattering at the interface, and found that inelastic scattering can contribute to thermal transport at high temperatures [7]. Although these models have advanced the understanding of phonon transmission across interfaces by including scattering, a complete and accurate prediction of thermal boundary resistance at higher temperatures and in highly disordered interfaces is still lacking. In practical applications neither the AMM nor the DMM can exactly describe the phonon transport across the interface.

Over the last several decades, since Pickett et al. [8] first used molecular dynamics (MD) simulations, MD has become a widely used technique to study thermal transport across the interface of dissimilar materials, and a variety of different nanostructures, for example superlattices [9–15], nanowires [16,17], and carbon nanotubes [18,19]. Specifically, studies of thermal transport at interfaces have shown that the mass of constituent materials and bond energy across the interface are dominant factors that affect TBC [20–24]. Skye and Schelling explored scattering from mass disorder and found it to be a dominant factor in thermal transport, while the bond disorder was found to play a minor role in silicon-germanium alloys using Stillinger-Weber potentials [21]. Hu et al. studied the interface of single-crystal solid and amorphous polyethylene and found a strong dependence of Kapitza conductance on interfacial bond energy [22]. This result was attributed to the “graded” interface which is created by soft polymer-polymer bonds and stiff Si-Si bonds. In another study using a system of Au-self-assembled monolayer (SAM)-Si, it was found that the TBC at one interface is dependent on the bond energy of the other interface due to proximity of the 2 interfaces [23]. This research was extended to generalize the role of the interface characteristics on TBC using the interface between solid-solid materials [25–27]. While MD simulations enable researchers to obtain a thorough understanding of the mass and bond energy at the interface on TBC, it is only recently that defects at the interface have been studied [28–31]. Research has shown that interface mixing between two solid materials has a significant effect on TBC [28,29] while vacancies have a negligible impact [30]. Li and
Yang studied the effect of lattice mismatch across the interface of Si and Ge-like materials with defected interfaces and showed that defects reduce the impact of lattice mismatch on TBC [32].

Although previous studies have been performed and found the impact of mass and bond energy between two materials on TBC, they have not distinguished the relative contributions of their impact on TBC. In this study, we perform non-equilibrium molecular dynamics (NEMD) simulations to investigate the relative and combined contributions of mass and bond energy differences on TBC at the interface. Mass and bond energy differences result in a mismatch between phonon dispersions, limiting high frequency phonon transport at the interface. This frequency mismatch is defined by a frequency ratio which is a ratio of the characteristic frequencies of the two materials, presented in the discussion section, and is a reference of the level of the phonon dispersion mismatch. In addition, the impact of defects, such as interdiffusion and vacancies, on TBC is explored. Finally, we propose that it is ultimately the phonon dispersion mismatch and the level of inelastic scattering at the interface that dictate the phonon contribution to TBC.

2.2 Molecular Dynamics Method

Molecular dynamics (MD) is a widely used technique to investigate thermal transport across individual nanoscale features [33–38]. NEMD is especially useful for the study of thermal boundary conductance across interfaces between two materials. In this study we use NEMD simulations of argon and argon-like systems using the Lennard-Jones (L-J) interatomic potential to calculate the effective thermal conductivity of the system and the TBC at the interface. All simulations performed in this work use the LAMMPS molecular dynamics package [39]. An illustration of the computational domain is shown in figure 2.1; $x$ is the direction of transport, and only $y$ and $z$ directions have periodic boundary conditions. The computational domain does not impose a periodic boundary in the direction of transport, but rather has a single interface between two baths. The computational domain consists of 36352 atoms where the system size of $128 \times 8 \times 8$ unit cells (UCs) in $x$, $y$, and $z$ directions, respectively, with an additional 14 UCs (7 on each side) in the direction of heat
Fig. 2.1: Computational domain. Two fixed walls are shown in black, hot and cold baths are shown in red and blue, respectively, and light gray and dark gray represent two different materials, argon and argon-like materials, respectively.

flow for fixed position walls, heat source, and sink. 6 UCs (3 on each side) are assigned to fixed walls to eliminate evaporation and enforce a known constant heat flux across the system and interface, and 8 UCs (4 on each side) are used as heat baths.

A L-J potential is used to describe the interatomic interactions because it provides a realistic description of interactions between two FCC structures. Only the phonon, or lattice vibration, contribution is considered for thermal energy transport within the solid system [40]. The L-J potential is given in equation 2.2.

\[ U(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]. \]  

(2.2)

where \( \epsilon \) and \( \sigma \) are parameters that define the energy and length scales of the potential function, respectively, and \( r \) is the interatomic separation distance. Parameters for argon are taken from Chen et al. [41], and the interactions between the argon and argon-like materials are defined using the Lorentz-Berthelot mixing rules, \( \epsilon_{12} = \sqrt{\epsilon_1 \epsilon_2} \) and \( \sigma_{12} = (\sigma_1 + \sigma_2)/2 \) [42]. The argon-like material properties are chosen relative to argon and are defined in detail later.

Prior to the NEMD simulations, additional simulations are performed in order to find an appropriate time step. Both pure argon and argon-like materials are simulated to check the validity of the time step for the high frequency materials. The maximum time step is chosen where the stable energy distribution for both cases is observed during the simulation. As a result, a time step of 10 fs is used for all NEMD simulations. The zero pressure NPT (constant number of atoms, pressure, and temperature) ensemble is performed for
200 ps under periodic boundary conditions in order to account for temperature dependent equilibrium atom spacing within the system. In the main NEMD simulation, periodic boundary conditions are used in \( y \) and \( z \) directions (see figure 2.1) with the previously calculated lattice constant from the NPT relaxation. The NEMD simulations are run for 200 ps within the NVT (constant number of atoms, volume, and temperature) ensemble to reach an equilibrium energy distribution state at the desired temperature, 10 K, 25 K, and 50 K, followed by 15 ns of the NVE (constant number of atoms, volume, and energy) ensemble while the constant heat flux, between \( 9.0062 \times 10^7 \) and \( 1.2609 \times 10^8 \) W/m\(^2\) for different simulations, is applied across the system. The heat flux is imposed across the material by adding and subtracting an equal and prescribed amount of kinetic energy from the bath regions. The imposed heat flux results in a temperature gradient and the thermal conductivity and TBC are calculated from Fourier’s law and equation 3.3, respectively. As the simulations run, the temperature distribution across the material is calculated for each unit cell length from the kinetic energy based on kinetic theory.

2.3 Simulation Results

2.3.1 Impact of Mass and Bond Energy Difference

In this work the mass and bond energy ratio are varied to study the role of the individual and combined impact on TBC. The mass of the material, \( m \), is varied first while all of the other parameters are fixed. In the second set of simulations the bond energy, defined by the interatomic potential well depth, \( \epsilon \), is the only parameter that is varied. Finally, the combined impact of \( m \) and \( \epsilon \) on TBC is studied by varying both parameters at the same time. The TBC from the mass variation is shown in figure 2.2(a), and the thermal conductivity is shown as an inset. In this simulation the mass of solid argon is fixed on one side of the computational domain, and the mass at the other side is varied. Figure 2.2(b) represents the temperature profiles, showing two different cases at 10 K across the computational domain during the NEMD simulations. The temperature is linearly distributed from the hot bath to the cold bath and the discontinuity is created at the interface of two
dissimilar materials. The thermal conductivity presented here represents an effective thermal conductivity because it is calculated with the full length of the system, however it will be shown as thermal conductivity hereafter. As expected, the maximum TBC and thermal conductivity are obtained when the mass of two dissimilar materials are matched. The TBC decreases and saturates as the mass ratio is varied from unity.

The individual impact of the bond energy on TBC and thermal conductivity is shown in figure 2.3. The maximum TBC is achieved where the bond energy is the same for two materials at low temperatures, which is similar to the case of mass variation, however, the thermal conductivity is not necessarily maximum at that ratio because the contribution of the individual thermal conductivity of the constituent materials (as is demonstrated by the different temperature gradient on the right hand side of the interface in figure 2.2(b) for the bond energy ratio case). Additionally, the maximum TBC at 50 K is not observed at the bond energy ratio of 1, as shown in figure 2.3. The authors believe this behavior indicates the onset of inelastic scattering of high frequency phonons from a combination of strain at the interface and increased vibrational amplitudes at 50 K vs. 10 K. An increase in TBC could be accounted for by inelastic scattering by allowing high frequency phonons (above the maximum acoustic frequencies of the material on the opposite side of the interface) to contribute to transport by scattering into multiple lower frequency phonons. Phonon modal or spectral based techniques are required to confirm this belief. This effect has been observed in another study, and can also result in TBC predictions greater than the DMM and other effects like thermal rectification [43,44].

The combined impact of \( m \) and \( \epsilon \) on TBC and thermal conductivity at 10 K is studied and presented in figure 2.4. Results of the combined impact show that the decrease in TBC is almost equivalent to that from the mass ratio alone. Even though the mass and bond energy differences have their individual contribution to TBC as it is presented above, we observe that the mass difference is the more dominant factor in TBC at the interface of two dissimilar materials. Figure 2.4 is plotted as a function of maximum phonon frequency ratio because the systems in these simulations are treated as simplified mass-spring systems.
Fig. 2.2: (a) Individual impact of $m$ on TBC. The inset shows the impact on thermal conductivity. (b) Temperature distribution of the domain for the case of mass ratio of 2 and the bond energy ratio of 1.25 at 10 K. Dashed lines do not present the trend but show guide lines to help the eye.
Fig. 2.3: Individual impact of $\epsilon$ on TBC. The inset shows the impact on thermal conductivity. Dashed lines do not present the trend but show guide lines to help the eye.

We have assumed a simplistic mass-spring calculation to represent the system, but only do so to demonstrate the impact of mass and bond energy on vibrational properties. A characteristic frequency in the mass-spring system is estimated as $\omega = \sqrt{k/m}$, where $k$ in this system is a function of the potential function near the equilibrium position and will be presented later. The characteristic frequency ratio of dissimilar materials is plotted in figure 2.5 as a function of mass and bond energy difference showing that the differences in mass and bond energy result in different characteristic frequencies in the two materials. Based on this result, the authors hypothesize that transport across an interface between dissimilar materials is a function of the mismatch in phonon vibrational frequencies and the level of inelastic scattering, though further investigation is needed to confirm the rate of inelastic scattering.

2.3.2 Impact of Defects

In order to study the impact of defects across the interface on TBC, interdiffusion regions of widths of 4, 10, 50, and 90 UCs, and vacancies are created at the interface.
Fig. 2.4: Combined impact of mass and bond energy difference on TBC. The inset shows the impact on thermal conductivity. Dashed lines do not present the trend but show guide lines to help the eye.

Fig. 2.5: Frequency ratio as a function of $m$ and $\epsilon$ ratio. Dashed lines do not present the trend but show guide lines to help the eye.
Similar to the previous set of simulations, these simulations focusing on the impact of defects are run at three different temperatures.

As expected the TBC and thermal conductivity at 10 K, shown in figure 2.6, decrease as the width of the interdiffusion region increases. In figure 2.6(a), a small change in the characteristic frequency ratio results in a much more significant change in TBC versus the introduction of the interdiffusion region, although a clear trend of decreasing TBC is still observed with increasing the interdiffusion region. Interestingly the thermal conductivity of the alloy, shown in figure 2.6(c), is greater than that of the system with 90 UCs of inter-diffusion region. Presumably this is due to additional resistances in the form of a thermal boundary resistance between the alloy region and the homogeneous regions on each side of the interdiffusion region. Figure 2.7 shows that the TBC decreases with increasing the interdiffusion region. However, as the width of the interdiffusion increases to 50 UCs and greater, the TBC appears to become temperature independent. This apparent temperature independence could point to alloy scattering beginning to dominate over multiphonon scattering. This could be similar to what is seen in superlattices and nanowires where weaker temperature dependent thermal conductivity is observed due to increased interface and boundary scattering, respectively [45,46].

As with interdiffusion, vacancies are expected to be present and contribute to thermal transport behavior, even in the highest quality single crystalline materials. Thus the impact of vacancy density at the interface is considered by simulating pure argon systems with a variable level of vacancy density. Since only one material is used in these simulations, no interfaces exist, but an impact on thermal transport behavior is established. Figure 2.8 shows that the thermal conductivity is independent of vacancy density and is, therefore, not expected to contribute significantly to TBC, which agrees with the result from Zhou et al. [30].

2.4 Discussion and Conclusion

In this study the stiffness of the “spring” in the mass-spring system, $k$, is obtained by linearization of the L-J interatomic potential. The linearization is performed using a Taylor
Fig. 2.6: (a) Impact of interdiffusion on TBC. (b) Magnification of the result of TBC with interdiffusion. (c) Impact of interdiffusion on thermal conductivity. Dashed lines do not present the trend but show guide lines to help the eye.
Fig. 2.7: Interdiffusion effects on TBC at different temperatures. Dashed lines do not present the trend but show guide lines to help the eye.

Fig. 2.8: Vacancy effects on thermal conductivity. Dashed lines do not present the trend but show guide lines to help the eye.
series expansion of the L-J interatomic potential at the equilibrium separation distance. The result of the linearization of the L-J potential at the equilibrium separation distance is shown in figure 2.9, and the expression for $k$ is given in equation 2.3.

\[
k = 2 \epsilon \left( \frac{156 \sigma}{2^{14}} - \frac{42 \sigma}{2^{5}} \right),
\]

where $\epsilon$ and $\sigma$ are again the energy and length scales from the L-J potential function, respectively. In order to study how the mass and bond energy of the material influence the frequency, the phonon dispersion curve is obtained for different variations of argon with changes in mass and bond energy. Figure 2.10 represents the longitudinal acoustic (LA) phonon branch for these different cases. For the purpose of validation, the phonon dispersion of solid argon is calculated directly from MD simulations using an auxiliary post-process code developed by Kong [47]. This result agrees well with the phonon dispersion of solid argon calculated both analytically [48] and computationally [49]. In the case of using a doubled bond energy, the frequencies above the normalized wave vector of 0.5 are greater than the maximum frequency of the solid argon for the same LA branch. Since these frequencies do not exist in the solid argon, we assume that they cannot contribute to TBC, unless an inelastic scattering event has occurred, and is the reason for large reductions in TBC when even small differences in the mass and/or bond energy exist. We hypothesize that at higher temperatures and in disordered interfaces inelastic scattering begins to occur. If this is the case, higher frequency phonons are disproportionately affected resulting in a deviation in the maximum TBC away from matched materials in some cases, as it is observed in figure 2.3. This study has demonstrated that modifying the mass and bond energy ratios of the constituent interface materials results in changes to the phonon dispersion, and thus a phonon dispersion mismatch between the two different materials and therefore changes in TBC across the interface.

Using the NEMD method with L-J interatomic potential the individual and combined impact of mass and bond energy difference as well as the impact of defects on TBC are presented. Results from the study of mass and bond energy difference show that the maximum
Fig. 2.9: L-J interatomic potential and its linearization at the minimum.

Fig. 2.10: Phonon dispersion curves for different cases. Dashed lines do not present the trend but show guide lines to help the eye.
TBC is achieved when there is no difference in two materials. Some cases deviate from this behavior and the authors believe it is a result of inelastic scattering. The mass and bond energy ratios of 2 result in 97% and 83% reductions in TBC at 10 K, respectively, as a result of increased phonon dispersion mismatch.

Defects at the interface also play a significant role on TBC. TBC is dependent on the length of the interdiffusion region as well as temperature. The temperature dependence becomes less significant with increases in the length of interdiffusion region, presumably due to increased alloy scattering. Figure 2.11 shows that the larger the interdiffusion region is, the greater reduction of TBC is observed with small differences in the characteristic frequency. This result differs from that of Stevens et al. [29] due to the difference in the temperature range of the study, resulting in different phonon scattering behavior at the interface. This result also shows some agreement with recent results from Tian et al. [31], although the current study does not include interdiffusion thicknesses thin enough (below 4 UCs) to demonstrate an increased TBC. The impact of vacancies appears to play an insignificant role in thermal transport.

Fig. 2.11: Impact of interdiffusion on TBC. The inset shows the impact on thermal conductivity. Dashed lines do not present the trend but show guide lines to help the eye.
References


Chapter 3

Prediction of Thermal Boundary Conductance at the Interface using Phonon Wave-packet Simulations: The Role of Mass and Bond Energy and Inelastic Scattering

Nomenclature

\begin{align*}
A & \quad \text{Amplitude of the displacement} \\
a & \quad \text{Lattice Constant} \\
E & \quad \text{Initial wave-packet energy} \\
E_{tr} & \quad \text{Transmitted energy} \\
h & \quad \text{Reduced Planck's constant} \\
h_k & \quad \text{Thermal boundary conductance} \\
k & \quad \text{Wave vector} \\
k_b & \quad \text{Boltzmann constant} \\
n & \quad \text{Bose-Einstein phonon occupation factor} \\
S & \quad \text{Interface area} \\
T & \quad \text{Temperature} \\
u_n & \quad \text{Displacement of } n^{th} \text{ atom} \\
v & \quad \text{Phonon group velocity} \\
x_n & \quad \text{Location of the atom} \\
x_0 & \quad \text{Center of the wave-packet} \\
Z & \quad \text{Acoustic impedance} \\
\alpha & \quad \text{Transmission coefficient} \\
\epsilon & \quad \text{Polarization vector} \\
\omega & \quad \text{Phonon frequency} \\
\xi & \quad \text{Width of the wave-packet}
\end{align*}
3.1 Introduction

The performance of many electronic devices, optical data storage media, and energy harvesting modules is currently limited by their local and effective thermal transport properties. In all of these areas, performance has been improved by decreasing length scales, resulting in increased interface density and therefore a shift from thermal transport properties being dominated by the bulk to the interface. For example, optical switching devices, RF amplifiers, and other wide bandgap semiconducting devices require thermal transport at interfaces, also known as thermal boundary conductance (TBC), which is an inverse of the Kapitza resistance [1], in order to operate at the desired performance level. Specifically, this has been demonstrated as a requirement to enhance the energy flow in optical switching devices and to maintain reasonable operating temperatures in high-electron-mobility transistors (HEMTs) [2, 3]. This shift toward interface dominated thermal transport behavior has resulted in a significant focus on understanding and the developing models to predict thermal boundary conductance [4, 5]. These works have improved the understanding of phonon-dominated thermal boundary conductance, but a complete understanding is lacking, specifically with complex behavior associated with differences in constituent materials or phonon dispersions [6], interface disorder and imperfections [7], and temperature [8].

In order to improve the performance of these applications, a better understanding of phonon transport across interfaces is needed [9]. Many experimental [10, 11] and computational [12–14] studies have utilized an approach that measure cumulative or effective transport properties of the material system or across an individual interface producing values of an effective thermal conductivity or the TBC, respectively. However, there is still a lack of theoretical understanding of thermal transport at the nanoscale [15]. The two most commonly used theoretical models to predict TBC are the acoustic mismatch model (AMM) and the diffuse mismatch model (DMM) which only considers elastic scattering at the interface. Due to this assumption, the TBC obtained through experimental measurement and molecular dynamics simulations deviates from the prediction of AMM and DMM especially at high temperatures. Hopkins et al. and Stevens et al. showed a temperature
dependence of TBC which is evidence of inelastic scattering at the interface [16, 17]. In particular, an experimental measurement showed that the TBC can be affected by inelastic scattering at a disordered interface [18], and a new model, an anharmonic inelastic model, is developed to account for the effect of inelastic scattering on TBC [19]. In addition, it is shown that thermal boundary resistance, which is predicted by molecular dynamics simulations, agrees well with theoretical calculations only under the assumption of elastic scattering [20]. As previous studies show that TBC is significantly influenced by scattering at the interface and temperatures, there is an increasing need for understanding this phenomena. However, traditional molecular dynamics simulations could not provide enough information on phonon interactions at the interface. Therefore, in order to fully understand phonon transport behavior at the interface, methods must be used that directly measure the modal contribution to these values, for example phonon wave-packet dynamics [6,21,22], so that future materials can be designed to behave as desired. By calculating a transmission rate, the phonon wave-packet dynamics makes it possible to directly demonstrate phonon interactions at the interface, therefore enhances the thermal management of electronic, photonic, and phonoic devices. Thus the phonon wave-packet dynamics has become a widely used technique to understand the phonon scattering at the interface of variety structures, such as nanowires [23], nanotube [24], and nanocomposite [25].

This study uses the phonon wave-packet (PWP) method to explore fundamental phonon interface dynamics and their impact on TBC. The impact of differences in the mass and the bond energy of dissimilar materials as well as the impact of interdiffusion and vacancies are studied. In addition, the transmission probability is compared with the AMM and the DMM demonstrating the need for a frequency dependent phonon transmission model. Results show good agreement with a recent NEMD study [26]. Additionally, surprising results are observed that show evidence of frequency dependent inelastic scattering that could be exploited via nanoscale interface modification to tune the TBC.

3.2 Simulation Methods and Models

In order to study the phonon scattering at the interface between two materials this
study uses the LAMMPS [27] molecular dynamics (MD) simulation package to perform PWP simulations. PWP simulations allow the direct observation of phonon behavior at the interface during the simulation, and thus phonon transmission rates can be calculated. The concept of the PWP simulation is to construct a phonon wave-packet from a single branch of the phonon dispersion curve with a narrow frequency range and well-defined polarization [21]. The wave-packet is generated by displacing the atoms according to equation 3.1 [28].

\[
u_n = A \epsilon \exp [ik (x_n - x_0)] \exp \left[ - (x_n - x_0)^2 / \xi^2 \right], \tag{3.1}\]

where \(u_n\) is the displacement of the \(n^{th}\) atom, \(A\) is the amplitude of the displacement, \(\epsilon\) is the polarization vector, \(k\) is the wavevector, \(x_n\) is the location of the atom along the direction of transport, \(x_0\) is the center of the wave-packet, and \(\xi\) is the width of the wave-packet. In this study \(A = 0.02a\), \(\epsilon = 1\), \(x_0 = 250a\), \(k\) ranges from \(0.1 \times (2\pi/a)\) to \(0.9 \times (2\pi/a)\), and \(\xi = 100a\) are used for the simulations. The amplitude of the displacement used in this study is larger than that of other studies [6, 21, 22, 29]. This larger amplitude was used to increase the wave-packet energy and improve the accuracy of the transmission rates. The amplitude of 0.02a shows no sign of anharmonicity behavior within the lattice so we feel the use of this amplitude is justified. Once the wave-packet is formed it is allowed to propagate. When the wave-packet encounters the interface it is either transmitted, reflected, or partial transmitted (partial reflected) and the transmission coefficient, \(\alpha\), is calculated with equation 3.2.

\[
\alpha = \frac{E_{tr}}{E}, \tag{3.2}\]

where \(E_{tr}\) is the transmitted energy and \(E\) is the initial wave-packet energy. The initial wave-packet energy is obtained by subtracting the total minimized energy of the system, which is calculated from pre-simulations, from the total energy of phonon wave-packet simulations. In the pre-simulations the minimized energy of the system is obtained by applying the ‘minimize’ function of LAMMPS. This function performs an energy minimization by adjusting atom coordinates iteratively according to the given criteria and provides the local
potential energy minimum at zero Kelvin (0 K). This energy minimization was confirmed through additional simulations under an NVE (constant number of atoms, volume, and energy) ensemble to confirm the kinetic energy in the system remains zero and the potential energy does not change. An NPT (constant number of atoms, pressure, and temperature) ensemble was also used to perform the energy minimization and achieved the same minimum system potential energy. Since the first method is faster in computational time and the results are the same, this study uses the built-in function of LAMMPS to obtain the minimized energy of the system.

The PWP method requires the system to be long enough so that the phonon is localized, propagates, interacts with the interface, and possesses sufficient energy by itself to calculate the transmission during the interaction. Therefore the system size used in this work is $1000a \times 2a \times 2a$, where $a$ is a lattice constant, similar to other studies [6, 21, 22, 29]. This system consists of FCC crystal structures of argon and argon-like materials with 16000 atoms. The Lennard-Jones (L-J) interatomic potential is used to describe the atomistic interactions between two dissimilar materials, and the potential parameters for argon are defined from the literature [30]. The argon-like materials are chosen relative to argon and are defined in detail later. The interface interactions are defined using the Lorentz-Berthelot mixing rules [30].

### 3.3 Simulation Results

The wave-packet is first generated in the argon material (left side of domain) and is allowed to propagate toward the interface with the argon-like material. Another simulation is performed where the wave-packet is generated in the argon-like material and it is allowed to propagate in the opposite direction. In both simulations, the wave-packet interaction with the interface between dissimilar materials is observed. Since the argon-like material is assigned to have a different mass or bond energy, the phonon dispersion of two materials is different, as shown in figure 3.1. The phonon dispersion of these materials is calculated directly from the MD simulations using an auxiliary post-process code developed by Kong [31]. Based on this difference in phonon dispersion, the impact of differences of these
parameters on the frequency dependent transmission coefficient of energy of the longitudinal acoustic (LA) branch is studied. The maximum frequency for the $2m_{Ar}$ and $2\epsilon_{Ar}$ materials are 1.4 THz and 2.7 THz, respectively, while the maximum frequency of this LA branch of Ar is 1.9 THz, shown in figure 3.1. These maximum frequencies will be critical to behavior discussed in the results and are considered as a cutoff frequency when coupled with a higher frequency material, such as the pure argon coupled with the $2m_{Ar}$ material. We expect that without inelastic scattering, the upper limit of frequency for phonon contributions to thermal boundary conductance will be limited by this cutoff frequency.

In the first set of simulations, the only variation for the argon-like material is mass which is set to have 2 times of the mass of argon. Because the difference in mass does not create any difference in the lattice structure, the interface in between these materials is considered to be a perfect interface with no strain or disorder. Figure 3.2 shows the energy transmission coefficient as a function of the phonon frequency. The maximum frequency of the $2m_{Ar}$ material is lower than that of the Ar as seen in the dispersion plots in figure 3.1. From this we expect the entire range of the phonon frequencies up to the maximum frequency of the $2m_{Ar}$ material can, at least partially, transmit into Ar. For the case of transmission from the Ar to the $2m_{Ar}$ material, we expect that at frequencies above the maximum of the $2m_{Ar}$ material, the wave-packet is completely reflected thus the transmission coefficient is zero. This result has also been seen by Kakodkar et al. using the numerical approach to the solution of elastic phonon-interface scattering [32].

The frequency dependence of the energy transmission coefficient for the case of the bond energy difference is shown in figure 3.3. In this simulation, the two materials only differ in bond energy (depth of the potential well). Varying the depth of the potential well results in a change of the equilibrium lattice spacing thus we have introduced strain at the interface. Similar to the case of the mass difference, figure 3.3 shows that most of the wave-packet energy is transmitted to the other side of the material in the low frequency range (below 1.6 THz), above which the transmission coefficient decreases. In this case, a non-zero transmission is observed above the cutoff frequency for the $2\epsilon_{Ar}$ material compared to
Fig. 3.1: Phonon dispersion relation for the argon and argon-like materials. Only longitudinal acoustic (LA) mode is included. Dashed lines are added to help guide the eye.

Fig. 3.2: Transmission coefficient of materials with different mass as a function of phonon frequency. Dashed lines are added to help guide the eye.
no energy transmission occurred above the cutoff frequency when a mass difference exists. In the bond energy difference case the strain at the interface results in a deviation from the equilibrium lattice spacing and an increase in anharmonic behavior at the interface. Increased anharmonicity results in more inelastic phonon scattering allowing the high frequency phonon energy to at least partially transmit through scattering the high frequency wave-packet to multiple lower frequency phonons.

To study this further, a finite interdiffusion length is introduced to increase strain at the interface. The transmission coefficient of interfaces with different interdiffusion lengths is presented in figure 3.4. The transmission coefficient for the interface without interdiffusion is inserted for the purpose of comparison. Different lengths of the interdiffusion region (2, 4, 6, 10, 50, and 90 unit cells), are generated at the center of the system, and the case of $2m_{Ar}$ and $2\epsilon_{Ar}$ materials are shown in figure 3.4(a) and 3.4(b), respectively. By inserting an interdiffusion region between the argon and argon-like materials, more strain is introduced resulting in increased phonon scattering at the interfaces. As a result, the interdiffusion changes the transmission behavior in multiple ways. Figure 3.4(a) shows the phonon transmission for the entire frequency range, below the cutoff frequency, is suppressed by increasing the interdiffusion length up to 50 UCs, while the phonon transmission above the cutoff frequency is increased at short interdiffusion lengths (below 10 UCs) before decreasing to near zero at longer interdiffusion lengths. It is interesting that the phonon transmission probability at higher frequencies increases with the introduction of a short interdiffusion region, which would not be expected. As the interdiffusion length increases the transmission probability no longer changes, suggesting that a 50 UCs interdiffusion length scatters almost all phonon modes and additional interdiffusion do not change phonon transmission behavior. When the interdiffusion region is introduced between the materials with a bond energy difference additional strain results in a similar behavior. At short interdiffusion lengths only a modification of the high frequency transmission behavior is observed. The transmission probability in the lower frequency region is also affected as the interdiffusion length becomes greater than 10 UCs as shown in figure 3.4(b). In both
cases, as the interdiffusion length is increased, high frequency wave-packets are primarily imparted in the short interdiffusion length cases. As the interdiffusion length increases to longer length, the modification of the transmission rates begin to impact lower frequency phonons resulting in a net reduction in phonon transmission and presumably TBC. Based on these results that show the ability to selectively introduce inelastic scattering in the high frequency phonon range, nanoscale imperfection (interdiffusion, texturing, etc.) could be used to enhance or tune TBC. Additionally, these results validate the hypothesis developed from a recent NEMD study [26] that pointed to inelastic phonon scattering at the interface due to anharmonicity from strain and increased temperature.

The contribution of point defects on the thermal transport is studied by creating a vacancy at the center of the structure. Similar to previous studies [33, 34], it is found that the energy transmission rate is constant at 1 throughout the entire frequency range. Thus the impact of high vacancy concentration on TBC is negligible as it is shown in the previous study [26]. At elevated temperatures vacancies could play a more significant role, especially if diffusion rates are high and dislocations or voids begin to form.
Fig. 3.4: Transmission coefficient of materials with interdiffusion as a function of phonon frequency. (a) Ar to $2m_{Ar}$ material and (b) $2\epsilon_{Ar}$ material to Ar. Dashed lines are added to help guide the eye.
3.4 Discussion and Conclusion

A recent study of TBC of Ar/Ar-like interface using NEMD hypothesized that interdiffusion and increased temperature resulted in increased inelastic scattering when the bond energy differed at the interface [26]. The PWP simulations performed here demonstrate that inelastic scattering does in fact occur in the high frequency region when the bond energy of dissimilar materials is different and is increased when there is interdiffusion at the interface as shown in figures 3.3 and 3.4. In order to compare this work to that of the previous work, this study calculates the TBC using a Landauer-Buttiker formalism based on this expression [35].

\[
h_k = \frac{1}{S} \sum_k \hbar w \frac{\partial w(k)}{\partial k} \frac{\partial n(w(k), T)}{\partial T} \alpha_k, \tag{3.3}
\]

where \( h_k \) is the TBC, \( S \) is the interfacial area, \( k \) is the wavevector, \( h \) is the reduced Planck’s constant, \( w \) is the phonon frequency, \( n(w(k), T) \) is the phonon occupation factor given by the Bose-Einstein distribution, \( T \) is the temperature, and \( \alpha_k \) is the transmission coefficient obtained from PWP simulations. The Bose-Einstein distribution is given by equation 3.4 according to Kittel [36].

\[
n(w(k), T) = \frac{1}{\exp \left( \frac{\hbar w}{k_B T} \right) - 1}, \tag{3.4}
\]

where \( k_B \) is the Boltzmann constant. The TBC, calculated from the NEMD simulations and the PWP simulations, as a function of interdiffusion length is shown in figure 3.5. The solid line in figure 3.5(a) is inserted to present the calculated value of TBC when there is no interdiffusion for different cases of the PWP simulations. We expect that the TBC from two different simulations will not agree well quantitatively because the PWP simulations are performed at 0 K, which suppresses anharmonic scattering behavior at the interface. A temperature of 25 K is used for the calculation of the phonon distribution for calculating the TBC from the PWP result using equation 3.3, while the MD simulations are performed at three different temperatures, 10 K, 25 K, and 50 K, respectively. The decreasing trend in TBC as the interdiffusion length increases is observed for both simulation methods and is
presented in figure 3.5(b). This result shows that the different phonon scattering behavior at
different phonon frequency ranges can directly affect the TBC at the interface. In fact, the
nanoscale disorder at the interface can result in selective high frequency inelastic scattering
of phonons resulting in an enhanced TBC. It is not obvious from figure 3.5, but a slight
increase in the TBC is observed from the interface with no interdiffusion to the case of
2 UCs interdiffusion length. Additionally, an interesting trend is seen from 4, 6, and 10
UCs of interdiffusion. This could be related to the interdiffusion length corresponding to a
significantly contributing phonon wave length.

The transmission coefficient of dissimilar materials using the AMM and the DMM can
be calculated with equation 3.5a and 3.5b, respectively, according to Swartz and Pohl [4].

\[
\alpha_{AMM} = \frac{4Z_1Z_2}{(Z_1 + Z_2)^2},
\]

\[
\alpha_{DMM} = \frac{v_{g,i}(w)n_i(w,T)}{v_{g,i}(w)n_i(w,T) + v_{g,i+1}(w)n_{i+1}(w,T)},
\]

where \(Z_i = \rho_ic_i\), \(\rho_i\) is the mass density of material \(i\), \(c_i\) is the speed of sound of material
\(i\), \(v_{g,i}\), is the phonon group velocity of material \(i\) and \(n_i\) is the phonon occupation number
of material \(i\). Figure 3.6 shows the energy transmission rate and the TBC of the 2\(\epsilon_{Ar}\) to
Ar material with the prediction of AMM and DMM. In the low phonon frequency region,
as expected, the transmission rate agrees with the AMM prediction. It starts to deviate
from the AMM prediction as the frequency approaches the maximum phonon frequency of
Ar, and the transmission rate falls below the DMM prediction above the cutoff frequency.
Since the DMM predictions considers only the phonon group velocity and the frequency,
but not the phonon dispersion relation, it predicts the energy transmission rate even above
the high frequency region where the transmission is expected to be zero without inelastic
scattering.

Using the PWP method with the L-J interatomic potential, the frequency dependence
of the TBC based on the phonon dispersion relation is presented in this study. As expected,
at a perfect interface minimum phonon scattering occurs, therefore no energy transmission
Fig. 3.5: The TBC as a function of interdiffusion depth: (a) from the PWP simulation. (b) comparison of TBC with NEMD simulation. Dashed lines are added to help guide the eye.
Fig. 3.6: (a) Transmission coefficient as a function of phonon frequency. (b) The TBC as a function of interdiffusion depth. Dashed lines are added to help guide the eye.
above the maximum frequency of the $2m_{Ar}$ material is observed. Inelastic scattering begins to occur in the high phonon frequency regions when there is a mismatch in the bond energy of dissimilar materials and the interdiffusion region is short.

References


Chapter 4

Simple Model for Effective Thermal Conductivity of Bulk Nanostructured Materials

Nomenclature

- $k$: Thermal Conductivity
- $k_b$: Boltzmann’s Constant
- $k_{AL}$: Alloy Limit
- $k_{eff}$: Effective Thermal Conductivity
- $k_{Ge}$: Thermal conductivity of Germanium
- $k_{Si}$: Thermal conductivity of Silicon
- $n_{Si}$: Atomic Percentage of Silicon
- $q$: Heat Flux
- $A$: Cross-sectional Area
- $A_{\parallel}$: Interface Area Parallel to the Heat Flow
- $A_{\perp}$: Interface Area Perpendicular to the Heat Flow
- $T$: Temperature
- $\Delta T$: Temperature Difference
- $K$: Kinetic Energy
- $L$: Length
- $N$: Number of Atoms
- $\xi$: Thermal Boundary Resistance caused by Parallel Interface Area
- $\Xi$: Thermal Boundary Resistance caused by Perpendicular Interface Area

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4.1 Introduction

The ability to predict thermal conductivity of bulk nanostructured materials (with the inclusion of nanoparticles, nanowires, interfaces, and core-shell structures) is becoming increasingly important [1–4]. Over the past several decades, extensive research has been focused on understanding thermal transport behavior (electrons and phonons) across individual nanostructures, nanofeatures, or interfaces [5]. These studies have led to an improved fundamental understanding of thermal transport, but has not made the same advancement towards the ability to predict an effective thermal conductivity due to the inclusion of these features. Nan et al. showed, using an effective medium approximation, that the effective thermal conductivity can be significantly altered by the inclusion of interfacial thermal boundary resistance and is dependent on particle shape and size [6]. The effective medium approximation was more recently modified to account for the particle interaction at higher volume fraction to predict the effective thermal conductivity of nanocomposites [7]. However, these studies do not take into account the effect of thermal boundary resistance with respect to the specific interface orientations.

Ideally, a predictive model of this sort would include the multiscale physics that are present in these materials, but the only reasonable approach requires solution of the Boltzmann Transport Equation (or other computationally intensive approach), which is not realistic due to the intensive computational requirements of the solution and the necessary knowledge of the dispersion relation of the energy carriers [8]. This work proposes a simple analytic model for the calculation of an effective thermal conductivity of a bulk nanostructured material by considering the thermal boundary resistance associated with interfaces perpendicular and parallel to the direction of transport. The required information necessary for accurate use of this model is the thermal boundary resistance (or impact of a single interface on the thermal conductivity) of a single interface at each orientation and an estimate of the alloy limit thermal conductivity of the material system. The limitations of this model are that (1) it only applies when wave-effects are not expected to be present (when nanoscale features are greater than the length scales associated with coherent phonon
transport) [9–11] and (2) for systems in which electron contributions to thermal transport can be neglected, (i.e. metals and metal alloys).

The availability of a simple model, like the one presented here, could have a dramatic impact on the development of higher efficiency thermoelectric materials [12,13] allowing for the direct harvesting of a large amount of energy that is typically lost in the form of waste heat [14]. This model would also allow for the continued development of high performance electronic devices, where the thermal conductivity of the material or system could be predicted in advance, saving time, effort, and expenses associated with the “build and test” approach that is commonly applied. The alternatives to this simple model require detailed computational simulation that can also take considerable time and effort. These computational models have a distinct advantage in modeling the atomic and nanoscale physics, but fall well short of being able to model a full device or material [15]. This model takes advantage of the results obtained from simulations, like molecular dynamics (a powerful technique for studying transport behavior across a single or a few nanoscale features), for the prediction of an effective thermal conductivity of the material or system. This model can also take advantage of experimental measurements of individual nanoscale features that have been enabled through techniques like 3−ω, Raman spectroscopy, photothermal radiometry, thermal bridge, and the more recent time-domain and frequency-domain thermoreflectance techniques [16–22].

In this paper, an analytic model is developed from a set of molecular dynamics simulations and presented. The model accounts for the contribution of both perpendicular and parallel interface area on the effective thermal conductivity of a bulk nanostructured material using the popular Si/Ge material system. Many studies have been performed on the Si/Ge material system [23, 24], thus sufficient data is available to validate our analytic model. Additionally, Si/Ge is a commonly used material system for microelectronics and high temperature thermoelectrics. The model is then applied to other material systems using computational and experimental results from the literature. This model provides the ability to predict an effective thermal conductivity with only a limited set of data from
atomistic simulations or experimental measurements therefore saving time and money for the design of thermoelectrics and electronic devices.

4.2 Molecular Dynamics Method

Molecular dynamics (MD) is a common technique used to investigate thermal transport across individual nanoscale features [25–32]. Non-equilibrium MD (NEMD) is especially useful in the study of thermal boundary conductance across interfaces between similar and dissimilar materials. These simulations provide both information about the thermal boundary conductance associated with the interface and the effective thermal conductivity of the material in which the interface exists. A review of NEMD and the other commonly used approach of molecular dynamics for determination of thermal transport properties (equilibrium MD) can be found in ref. [33]. In this study NEMD simulations of Si and Ge systems are performed using the Stillinger-Weber interatomic potential [34–37] to formulate a model for effective thermal conductivity of bulk nanostructured materials. The NEMD simulations are all performed using LAMMPS [38].

The first set of materials used in this study are thin film structures constructed from bulk Si and Ge. The size of these materials are varied in length with a size of $n \times 8 \times 8$ unit cells (UCs), where $n = 32, 64, 128,$ and $256$, with an additional 16 UCs (8 on each side) in the direction of heat flow for fixed position walls and heat source and sink. 4 UCs (2 on each side) are assigned to the fixed wall to ensure no energy transport directly from the heat source to the heat sink, and 12 UCs (6 on each side) are used as heat source and sink. The second set of materials are Si-Ge superlattice structures where the stacking sequences are parallel (in-plane) and perpendicular (cross-plane) to the heat flow direction. The third set of materials are embedded Ge-Si nanowire arrays and embedded Ge-Si nanoparticle arrays, as they are shown in Figure 4.1.

A time step of 0.5 fs is used for all NEMD simulations. The zero pressure NPT (constant number of atoms, pressure, and temperature) ensemble is performed for a minimum of 30 ps under the periodic boundary condition in order to relax the lattice. In the main NEMD simulation, periodic boundary conditions are used in all directions with the previ-
Fig. 4.1: Core-shell wire array (a) Interfacial area of the Ge-Si core-shell structure, (b) Embedded nanoparticle array (top) Embedded NW array (bottom).

Previously calculated lattice constant from the NPT relaxation. The NEMD simulations are run for a minimum of 10 ps within the NVT (constant number of atoms, volume, and temperature) ensemble to reach an equilibrium energy distribution state at the desired temperature, 300 K, followed by a minimum of 10 ns of the NVE (constant number of atoms, volume, and energy) ensemble while the constant heat flux is applied across the system. The heat flux is imposed across the material by adding and subtracting energy from the bath regions. The imposed heat flux results in a temperature gradient and the thermal conductivity is then calculated from Fourier’s law,

\[ q = -kA \frac{\Delta T}{L}, \]  

(4.1)

where \( q \) is the heat flux, \( k \) is the thermal conductivity, \( A \) and \( L \) are the cross-sectional area and length of the material, respectively, and \( \Delta T \) is the temperature difference across
the device. As the simulations run, the temperature distribution across the material is calculated for each unit cell length from kinetic theory,

\[ T = \frac{2}{3} \frac{K}{Nk_b}, \tag{4.2} \]

where \( T \) is the temperature, \( K \) is the kinetic energy, \( N \) is the number of atoms, and \( k_b \) is Boltzmann’s constant.

### 4.3 Model Development

In order to develop an analytic model for interfacial systems the relevant parameters must first be identified. A rule-of-mixtures composite model typically applies the property of interest of each of the constituent materials weighted by a mass, volume, or atomic ratio [39]. This initial assumption would require knowledge of the individual thermal conductivity of Si and Ge and the relative amounts of each. Figure 4.2 displays the temperature profile from simulations of pure Si and pure Ge used to calculate the individual thermal conductivity. This data is shown here to demonstrate the linear temperature distributions obtained when a constant heat flux is applied, validating the use of Fourier’s law. Deviation from a linear temperature distribution is observed close to the baths which is typical of NEMD simulations caused by the enhanced phonon scattering required to maintain a constant temperature [40].

Figure 4.3 shows the inverse thermal conductivity of Si and Ge films as a function of the inverse length of the domain in the heat flow direction. These results are typical for NEMD simulations where the thermal conductivity increases with increasing domain length until the domain is long enough to include contributions from all phonon modes at which point the thermal conductivity remains constant. Extrapolation to the intercept of infinite length of the inverse thermal conductivity vs. the inverse length gives the bulk thermal conductivity. For Si and Ge bulk thermal conductivity values were calculated to be 113.91 W/mK and 90.85 W/mK, respectively, at 300 K. For comparison, experimentally measured values for Si and Ge are 156 W/mK and 60 W/mK, respectively [41, 42]. Although the values
obtained through these simulations only provide some agreement, this is typical of NEMD simulation results. NEMD simulations often include finite size effects that can result in an under-prediction of the thermal conductivity. In addition, NEMD simulations do not include defects such as impurities and vacancies, which can result in an over-prediction of thermal conductivity. Based on these two shortfalls of NEMD simulations, there can be a range of calculated values of thermal conductivity. This range has also been documented by Dong et al. [43]. Additionally, the purpose of this work is not to match experimentally measured thermal conductivity using NEMD, but to develop an analytic model for predicting an effective thermal conductivity of bulk nanostructured materials, therefore for the purpose of this model development, the thermal conductivity obtained through the simulations are expected to be consistent within each material regardless of the composition and organization.

With the constituent thermal conductivities established, the next step is to address the role of the interfaces within the material. Composite models for effective thermal conductivity typically include an orientation dependence even with the simplest equivalent
Fig. 4.3: Inverse length dependence of the inverse thermal conductivity. Extrapolation of the linear fit to zero represents the bulk thermal conductivity.

resistance circuit analysis models, therefore we expect that the model will depend on the orientation of the interface relative to the heat flow direction. As is likely obvious at this point, the interface between the Si and Ge is expected to play a significant role in the effective thermal conductivity. The actual role played by the interface is a current area of interest in micro/nanoscale heat transfer [5, 44–47], but is not the focus of this work. This work is focused on understanding the impact of multiple interfaces on the effective thermal conductivity when the thermal boundary conductance or the impact of a single interface on thermal conductivity is known. In order to quantify the impact of interface area, we begin by studying materials with simple and well-defined interface geometry. These interfaces are oriented both parallel and perpendicular to the flow of heat. We distinguish these for two reasons: (1) equivalent resistance models for estimating effective thermal conductivity in simplified 1-dimensional transport treats these differently and (2) the in-plane and cross-plane thermal conductivity are drastically different in superlattice structures (oriented interfaces), resulting in anisotropic thermal conductivity. The effective thermal conductivity for a material with perpendicular interface is shown in Figure 4.4. A clear exponential
decay is observed from the arithmetic average of the Si and Ge thermal conductivities down to some lower limit, which we assume to be the alloy limit, or minimum thermal conductivity, for the Si/Ge composite. From this data, a simple model is developed for an effective thermal conductivity as a function of perpendicular interface area and is presented in equation 4.3.

\[ k_{\text{eff,\perp}} = [k_{\text{Si}} n_{\text{Si}} + k_{\text{Ge}} (1 - n_{\text{Si}}) - k_{\text{AL}}] \times \exp \left( -\frac{A_{\perp}}{\Xi} \right) + k_{\text{AL}}, \]  

(4.3)

where \( k_{\text{Si}} \) is the thermal conductivity of pure silicon, \( k_{\text{Ge}} \) is the thermal conductivity of pure germanium and \( n_{\text{Si}} \) is the atomic percentage of silicon and is used to weight the thermal conductivity of the composite based on a rule-of-mixtures, neglecting the contribution of the interface. \( k_{\text{AL}} \) is included as a lower limit of the effective thermal conductivity of the composite and is commonly known as the alloy limit associated with the system constituents and geometry. \( A_{\perp} \) is the normalized perpendicular interface area (normalized by the cross-sectional area) and \( \Xi \) is related to the thermal boundary resistance and produces the net impact on thermal conductivity reduction when perpendicular interfaces are present. The exponential behavior is observed in the presented data in figure 4.4 and is commonly seen in the literature, which is the justification for the selection of this functional form.

The simulations focusing on materials with only parallel interface area are also presented in Figure 4.4. The data appears to have a nearly linear dependence with parallel interface area. To satisfy the condition of infinite parallel interface area a lower limit must be maintained, therefore an exponential function was fit as with the perpendicular case and resulted in the model presented below, in equation 4.4. The impact on the effective thermal conductivity as a function of parallel interface area is given by

\[ k_{\text{eff,\parallel}} = [k_{\text{Si}} n_{\text{Si}} + k_{\text{Ge}} (1 - n_{\text{Si}}) - k_{\text{AL}}] \times \exp \left( -\frac{A_{\parallel}}{\xi} \right) + k_{\text{AL}}, \]  

(4.4)

where \( A_{\parallel} \) is the total interface area parallel to the direction of transport, \( \xi \) is related to the thermal boundary resistance and produces the net impact on the thermal conductivity
when parallel interfaces are present, and $k_{AL}$ is again the alloy limit associated with the system constituents and geometry. A direct comparison of the impact of perpendicular and parallel interface area clearly shows that the effective thermal conductivity is dominated by the perpendicular interfacial area.

4.4 Model Validation

4.4.1 Si/Ge Embedded Nanoparticle and Nanowire from NEMD Simulations

In order to apply this simple model to bulk nanostructured materials, systems with combined perpendicular and parallel interfaces need to be considered to ensure the impact on effective thermal conductivity are complementary. To investigate this we again use NEMD simulations to calculate the effective thermal conductivity of embedded nanowire and nanoparticle arrays. In these systems, interfaces with both perpendicular and parallel area are present and vary between the different systems. The combined model is presented in equation 4.5 and accounts for both parallel and perpendicular areas on effective thermal conductivity.

$$k_{eff} = [k_{Si} n_{Si} + k_{Ge} (1 - n_{Si}) - k_{AL}] \times \exp \left(-A_\perp/\Xi\right) \times \exp \left(-A_\parallel/\xi\right) + k_{AL}, \quad (4.5)$$

Table 4.1 presents the average effective thermal conductivity for each case from both analytic and computational calculations along with the total perpendicular and parallel areas. Figure 4.5 shows the effective thermal conductivity for different nanoparticle array systems and that of analytic models for the purpose of the comparison. The atomic percentage of silicon in these systems varied between 75 % and 87.5 % due to the different configurations and is why those two models are plotted with the data. The actual atomic percentage of silicon for each simulation data point is presented in table 4.1 along with the actual calculated value from the model. The models plotted along with the data in figure 4.1 are similar, showing the dominance of the interface and the minimal contribution of the atomic ratio (since the thermal conductivities of silicon and germanium are relatively
close). The effective thermal conductivity calculated from the NEMD simulations of different nanoparticle arrays is presented in figure 4.5. Similar to the perpendicular interface simulations used to generate that portion of the model, the effective thermal conductivity decreases with increasing perpendicular interface area. In this case the model based on the individual perpendicular and parallel interface simulations slightly over-predicts the effective thermal conductivity. This is again due to the fact that a fixed parallel interface area is assumed in the plotted model, where in reality the parallel interface area varies. The actual parallel area for each of the NEMD simulation data points is presented in table 4.1 along with the model calculated value for the effective thermal conductivity.

4.4.2 Ar/Kr Systems from NEMD Simulations

The analytic model is next applied to embedded nanoparticle arrays of argon and krypton in order to confirm the validity of the developed model. In figure 4.6 the symbols represent the effective thermal conductivity of three different Ar/Kr nanostructures, consisting of $n_{Ar} = 0.5$, which are calculated by NEMD in reference [48], and lines show the
Table 4.1: Effective thermal conductivity and interface area for the simple and nanoparticle array systems

<table>
<thead>
<tr>
<th>Configuration</th>
<th>$A_\perp*$</th>
<th>$A_{\parallel}$*</th>
<th>$n_{Si}$</th>
<th>Model $k_{eff}$*</th>
<th>Simulated $k_{eff}$*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perpendicular Interface</td>
<td>1</td>
<td>0</td>
<td>0.5</td>
<td>0.172</td>
<td>0.172</td>
</tr>
<tr>
<td>Perpendicular Interface</td>
<td>3</td>
<td>0</td>
<td>0.5</td>
<td>0.085</td>
<td>0.091</td>
</tr>
<tr>
<td>Perpendicular Interface</td>
<td>5</td>
<td>0</td>
<td>0.5</td>
<td>0.084</td>
<td>0.079</td>
</tr>
<tr>
<td>Parallel Interface</td>
<td>0</td>
<td>1</td>
<td>0.5</td>
<td>0.887</td>
<td>0.898</td>
</tr>
<tr>
<td>Parallel Interface</td>
<td>0</td>
<td>3</td>
<td>0.5</td>
<td>0.700</td>
<td>0.725</td>
</tr>
<tr>
<td>Parallel Interface</td>
<td>0</td>
<td>5</td>
<td>0.5</td>
<td>0.557</td>
<td>0.534</td>
</tr>
<tr>
<td>Embedded Nanowire</td>
<td>0.5</td>
<td>2</td>
<td>0.75</td>
<td>0.446</td>
<td>0.442</td>
</tr>
<tr>
<td>Embedded Nanoparticle</td>
<td>1</td>
<td>1.8125</td>
<td>0.7734</td>
<td>0.313</td>
<td>0.302</td>
</tr>
<tr>
<td>Embedded Nanoparticle</td>
<td>2</td>
<td>1.625</td>
<td>0.7969</td>
<td>0.259</td>
<td>0.255</td>
</tr>
<tr>
<td>Embedded Nanoparticle</td>
<td>4</td>
<td>1</td>
<td>0.875</td>
<td>0.253</td>
<td>0.249</td>
</tr>
</tbody>
</table>

* normalized values

Fig. 4.5: Effective thermal conductivity of embedded nanoparticle arrays.
values calculated from the analytic model. The exponential decay of the effective thermal conductivity is observed from a simple structure that has only parallel and perpendicular interfaces. Also the analytic model predicts the effective thermal conductivity of the block structure well, even though some deviation is observed. In general, however, the analytical model and the computational calculation of the effective thermal conductivity are in good agreement which shows that the analytic model developed with Si/Ge interface simulations can be applied to different nanostructured materials.

Fig. 4.6: Effective thermal conductivity of Ar/Kr nanostructures. Data is taken from reference [48]

4.4.3 Si/Ge Nanostructures from Monte Carlo Simulations and Experiments

Figure 4.7 contains the comparison of analytic model with the effective thermal conductivity of Si/Ge nanostructures obtained by Monte Carlo simulations [49] and experiments [50] in order to further validate the analytic model. Since the atomic percentage of Si and Ge from reference [49] and [50] are not presented, the approximated percentage of Si is used for the analytic model calculation. As shown in figure 4.7, predicted effective thermal conductivity from the analytic model agrees well with that of the Monte Carlo
simulations and experimental measurements on Si/Ge nanostructures. There is a notable difference between the experimental Si/Ge superlattice thermal conductivity behavior and the Monte Carlo Si/Ge nanoparticle array thermal conductivity behavior as well as with the NEMD Si/Ge data that was used to establish this model. The sometimes poor agreement between NEMD simulations and experiments has been discussed previously and can account for the different values obtained for the interface parameters and the minimum thermal conductivity value. Additionally, the assumptions for how phonon-interface scattering occurs in the Monte Carlo simulation also introduces potential differences between the other two techniques. The simulation data acquired from the Monte Carlo study applied a specularity parameter for determining the probability of specular vs. diffuse phonon scattering events when a phonon interacts with an interface. This assumption of the phonon-interface scattering may not accurately represent the behavior in experiments and in NEMD simulations, and thus we would not expect perfect agreement. In order for this model to be successfully applied, a simulation or measurement data point is needed from a system. Optimization can then be performed with the model, but is limited to the prediction of the effective thermal conductivity based on the source data (i.e. MD data can be used to optimize within the MD parameter space and experimental data can be used to optimize within the experimental parameter space).

4.4.4 TiN/TaN Superlattices from Experiments

The model is also validated with experimental thermal conductivity data of TiN/TaN superlattice structures, as shown in figure 4.8. Sood et al. [51] measured the thermal conductivity of TiN/TaN superlattices with different atomic percentage of TiN material and different superlattice periods. Figure 4.8 includes three different model calculations in order to show different atomic percentages of the TiN material. The analytic model calculation shows good agreement with the experimental thermal conductivity of TiN/TaN superlattice structures. The thermal conductivity of the TaN material is obtained from reference [52] and used in the model calculation. Table 4.2 includes the effective thermal conductivity of various systems and parameters that are used to predict the model calculations. In this
Fig. 4.7: Effective thermal conductivity of Si/Ge nanostructures. Data is taken from reference [49, 50].

Fig. 4.8: Effective thermal conductivity of TiN/TaN superlattices. Data is taken from reference [51].
study fitting parameters are used to represent $k_{AL}$, $\Xi$, and $\xi$ in analytic model calculations. Even though saturation regions in plots are assumed to be an alloy limit of each system, the parameters used in analytic model calculations remains the topic of the further study.

Table 4.2: Effective thermal conductivity and parameters for different systems.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>$A^*$</th>
<th>$k_{eff}$*</th>
<th>$\Xi$</th>
<th>$k_{AL}$</th>
<th>$\xi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Embedded Nanowire for SiGe</td>
<td>0.5</td>
<td>0.446</td>
<td>0.425</td>
<td>2.444</td>
<td>7.559</td>
</tr>
<tr>
<td>Embedded Nanoparticle for SiGe</td>
<td>1</td>
<td>0.313</td>
<td>0.425</td>
<td>2.444</td>
<td>7.559</td>
</tr>
<tr>
<td>Embedded Nanoparticle for SiGe</td>
<td>2</td>
<td>0.259</td>
<td>0.425</td>
<td>2.444</td>
<td>7.559</td>
</tr>
<tr>
<td>Embedded Nanoparticle for SiGe</td>
<td>4</td>
<td>0.253</td>
<td>0.425</td>
<td>2.444</td>
<td>7.559</td>
</tr>
<tr>
<td>Embedded Nanoparticle for ArKr**</td>
<td>1</td>
<td>0.804</td>
<td>3.443</td>
<td>0.667</td>
<td>12.264</td>
</tr>
<tr>
<td>Embedded Nanoparticle for ArKr**</td>
<td>3</td>
<td>0.623</td>
<td>3.443</td>
<td>0.667</td>
<td>12.264</td>
</tr>
<tr>
<td>Embedded Nanoparticle for ArKr**</td>
<td>7</td>
<td>0.464</td>
<td>3.443</td>
<td>0.667</td>
<td>12.264</td>
</tr>
<tr>
<td>Embedded Nanoparticle for ArKr**</td>
<td>15</td>
<td>0.399</td>
<td>3.443</td>
<td>0.667</td>
<td>12.264</td>
</tr>
<tr>
<td>Embedded Nanoparticle for ArKr**</td>
<td>31</td>
<td>0.392</td>
<td>3.443</td>
<td>0.667</td>
<td>12.264</td>
</tr>
<tr>
<td>Embedded Nanoparticle for SiGe***</td>
<td>0.2</td>
<td>0.872</td>
<td>0.600</td>
<td>1.198</td>
<td>1.200</td>
</tr>
<tr>
<td>Embedded Nanoparticle for SiGe***</td>
<td>0.65</td>
<td>0.366</td>
<td>0.600</td>
<td>1.198</td>
<td>1.200</td>
</tr>
<tr>
<td>Embedded Nanoparticle for SiGe***</td>
<td>1</td>
<td>0.222</td>
<td>0.600</td>
<td>1.198</td>
<td>1.200</td>
</tr>
<tr>
<td>Superlattices for SiGe****</td>
<td>0.148</td>
<td>0.460</td>
<td>0.081</td>
<td>9.698</td>
<td>-</td>
</tr>
<tr>
<td>Superlattices for SiGe****</td>
<td>0.295</td>
<td>0.355</td>
<td>0.081</td>
<td>9.698</td>
<td>-</td>
</tr>
<tr>
<td>Superlattices for SiGe****</td>
<td>0.593</td>
<td>0.336</td>
<td>0.081</td>
<td>9.698</td>
<td>-</td>
</tr>
<tr>
<td>Superlattices for SiGe****</td>
<td>1</td>
<td>0.335</td>
<td>0.081</td>
<td>9.698</td>
<td>-</td>
</tr>
<tr>
<td>Superlattices for TiNTaN*****</td>
<td>0.149</td>
<td>2.01</td>
<td>0.043</td>
<td>1.521</td>
<td>-</td>
</tr>
<tr>
<td>Superlattices for TiNTaN*****</td>
<td>0.158</td>
<td>1.57</td>
<td>0.048</td>
<td>1.525</td>
<td>-</td>
</tr>
<tr>
<td>Superlattices for TiNTaN*****</td>
<td>1</td>
<td>1.55</td>
<td>0.053</td>
<td>1.528</td>
<td>-</td>
</tr>
</tbody>
</table>


4.5 Conclusion

This work presents a simple analytic model for the prediction of thermal conductivity of bulk nanostructured materials from NEMD simulations. This model provides an efficient means for the calculation of thermal conductivity with the requirement of minimal simulations or experiments and allows for optimization of the design thermal transport properties of nanostructured materials, which are encountered often in microelectronic and thermoelectric applications. The model uses physically significant parameters that are linked to thermal boundary resistance at an interface and the minimum material system thermal con-
ductivity, typically called the alloy limit to calculate an effective thermal conductivity of the system. The developed model is validated and generalized by comparing to additional systems with different constituent materials and geometric configurations and shows good agreement of the behavior associated with the impact of interfaces on the effective thermal conductivity. Overall this model, even with a simplistic form that neglects electron contributions to transport and wave-effects in ultra-short length-scales, could provide significant time and money savings over the current “build and test” approach typically applied in materials discovery and design.

References


Chapter 5
Conclusions

The objective of this work is to improve the understanding of the phonon transport at the interface of dissimilar materials and the impact of different material properties on thermal boundary conductance. In order to achieve this goal, we investigated the contributions of mass and bond energy difference and interface defects on thermal boundary conductance at the interface of nanostructured materials using non-equilibrium molecular dynamics and phonon wave-packet dynamics techniques.

As a result of the non-equilibrium molecular dynamics study, it is shown that a small difference in mass and bond energy of two materials results in a significant decrease in thermal boundary conductance, independently, with a greater effect observed due to mass difference. It is also shown that interdiffusion plays a crucial role with respect to thermal boundary conductance. The thermal boundary conductance decreases as the interdiffusion length increases. However, the temperature dependence of thermal boundary conductance becomes less significant as the length of interdiffusion region increases, presumably due to increased alloy scattering. In general, we have concluded that the difference in frequency caused by material property difference results in different phonon dispersion which plays an important role on thermal boundary conductance.

Phonon wave-packet simulations provided a thorough understanding of phonon transport at the interface by calculating phonon transmission probabilities. The frequency dependence of thermal boundary conductance based on phonon dispersion relations of two materials is presented. As expected, minimum phonon scattering occurs when the mass on either side of an interface is different, therefore observing no energy transmission above the cutoff frequency. Inelastic scattering has been observed when the bond energy of two materials is different at high frequencies, and it is strengthened when there exists a short
interdiffusion length, with the level of inelastic scattering decreasing as the interdiffusion length increases. We have observed qualitatively the same trend in thermal boundary conductance that we obtained from the NEMD study.

In this study, we have isolated the mass and bond energy differences at the interface of two materials to study their role on thermal transport at the interface. However, as it is shown in appendix D.1, performing phonon wave-packet simulations with the nanostructure of silicon and germanium show the combined impact of these parameters on thermal transport, and we confirmed the frequency dependence of transmission probability. Therefore, we can conclude that different material properties result in the different phonon dispersion relations between two materials which play an important role on predicting thermal boundary conductance.

Finally, we have developed a simple analytical model to predict an effective thermal conductivity with the requirement of minimal simulations or experiments that allows for optimization of the thermal transport properties of nanostructured materials by design. This model is developed with thermal boundary resistance at the interface and the alloy limit to calculate the effective thermal conductivity. It has been validated and generalized by comparing to different systems with different constituent materials. Overall this model is expected to provide significant time and money savings over the current “build and test” approach typically applied in materials discovery and design.
Appendices
Appendix A

Lennard-Jones Interatomic Potential Parameters of Argon

Interatomic potential parameters of argon is given in table A.1.

Table A.1: L-J interatomic potential parameters of argon

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon$ (J)</td>
<td>$1.67 \times 10^{-21}$</td>
</tr>
<tr>
<td>$\sigma$ (m)</td>
<td>$3.40 \times 10^{-10}$</td>
</tr>
<tr>
<td>$a$ (m)</td>
<td>$5.39 \times 10^{-10}$</td>
</tr>
<tr>
<td>$m$ (kg)</td>
<td>$6.63 \times 10^{-26}$</td>
</tr>
<tr>
<td>$r_c$ (m)</td>
<td>$8.84 \times 10^{-10}$</td>
</tr>
</tbody>
</table>
Appendix B
Validation of Molecular Dynamics Simulations

B.1 Validation of NEMD Simulations

The NEMD simulation begins with the validation of results from LAMMPS. In this stage, we ran simulations of pure solid argon and calculated the thermal conductivity using equation 1.2. The validation is completed by investigating the change in thermal conductivity of solid argon with a system length, and comparing them with the bulk experimental measurement results from reference [1]. In figure B.1 the dependence of thermal conductivity on the system length at temperatures of 10 K, 25 K, and 50 K is presented. We have achieved some agreement with bulk measurements and the finite size effects can be seen for smaller system length. The under-prediction of thermal conductivity for smaller systems is due to the simulation cells being too small to capture long-wave length phonons. Thus the thermal conductivity increases with increasing system length. There are some deviations from the bulk experimental values at low temperatures that mostly comes from the lack of quantum corrections that are important at temperatures well below the Debye temperature. However, quantum effects are not significant for argon [2] and are not necessary for understanding trends, which are of primary importance in this study. We also expect an over-prediction of thermal conductivity due to our system being free of defects. The bulk thermal conductivity of argon can be obtained from the extrapolation of the inverse of thermal conductivity, as it is shown in figure B.2, and the calculated bulk thermal conductivity of argon for different temperatures is compared in table B.1. Although the values obtained through these simulations only provide some agreement, this is typical of NEMD simulation results due to the reasons discussed above. This trend is also shown in reference [3].
Fig. B.1: Thermal conductivity of solid argon. Dashed lines are added to help guide the eye.

Table B.1: Comparison of thermal conductivity of argon

<table>
<thead>
<tr>
<th></th>
<th>Experiments $\frac{W}{mK}$</th>
<th>NEMD $\frac{W}{mK}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 K</td>
<td>3.7</td>
<td>2.36</td>
</tr>
<tr>
<td>25 K</td>
<td>0.99</td>
<td>1.05</td>
</tr>
<tr>
<td>50 K</td>
<td>0.46</td>
<td>0.53</td>
</tr>
</tbody>
</table>
B.2 Validation of PWP Simulations

The validation of PWP simulations was also performed prior to the main PWP simulations. In this step, a wave-packet is generated, using equation 1.3, at the left-hand side of the computational domain, which is composed of one material, solid argon. The entire range of wavevectors are simulated and the transmission probability is calculated using equation 1.4. The change of energy in the computational domain is shown in figure B.3, and, again, material A and B in this simulation are the same material. Transmission probabilities of 1, which means a perfect transmission, is obtained over the entire range of wavevectors. This result is expected since there is no interface in the computational domain thus only transmission is the possible phonon transport in this system.
Fig. B.3: Energy transport of solid argon.
Appendix C

Contributions of Vacancies at the Interface on Thermal Transport

C.1 Impact of Vacancies at the Interface on Thermal Boundary Conductance

It is shown, in figure 2.8, that the thermal conductivity of solid Ar is independent of vacancy density, and is, therefore, not expected to contribute to TBC. In order to validate this behavior, PWP simulations of pure Ar are performed, and the result is shown in figure C.1. The phonon transmission probability of solid Ar, which is a perfect material system, is inserted for the purpose of the comparison in figure C.1. The phonon transmission probability of Ar with a vacancy in the middle of the structure has a constant value of 1 as is the case of the solid Ar case. This result shows the transmission probability is not dependent on vacancy density, as expected. Therefore, it can be concluded that the impact of vacancies on TBC is negligible.
Fig. C.1: Transmission coefficient of Ar with a vacancy as a function of phonon frequency.
Appendix D
Generalization

D.1 Generalization using Si-Ge Superlattices

The TBC of Si-Ge superlattices is obtained using NEMD simulations and is also calculated using the result of PWP simulations for the purpose of comparison. A Stillinger-Weber (S-W) interatomic potential is used in this study. The original parameters to describe the interactions of Si and Ge are taken from reference [4] and [5] and the potential for the interaction between Si and Ge is obtained by taking the arithmetic mean and geometric mean of the Si and Ge potential [6, 7]. Phonon dispersion relations of Si and Ge are shown in figure D.1 and the result of the PWP simulation is presented in figure D.2. Due to the different phonon dispersion of materials the cutoff frequency is observed around 7 THz, as it is shown in figure D.1. Figure D.2 shows the transmission probability of Si-Ge and Ge-Si superlattices. The phonon transmission of Si-Ge superlattices starts to decrease above the cutoff frequency, however it is still nonzero in the high frequency region due to inelastic scattering. This result is in good agreement with results obtained with Ar and Ar-like materials. The TBC, calculated from the NEMD simulations and the PWP simulations, is compared in table D.1. It is shown that the TBC between two methods are one order of magnitude different. This quantitative disagreement is expected as shown in chapter 3.4, and is attributed to the different simulation temperature for the different methods.

In general, we have observed combined effects of mass and bond energy difference with respect to the TBC using Si-Ge superlattices. The results obtained in this study are very

<table>
<thead>
<tr>
<th>TBC $\frac{GW}{m^2K}$</th>
<th>NEMD</th>
<th>PWP</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.387</td>
<td>3.8181</td>
<td></td>
</tr>
</tbody>
</table>
Fig. D.1: Phonon dispersion relations of Si and Ge. Dashed lines are added to help guide the eye.

Fig. D.2: Transmission coefficient as a function of phonon frequency. Dashed lines are added to help guide the eye.
similar to what we have expected from previous simulations where we isolated mass and
bond energy except more phonon transmission is observed above the cutoff frequency. Thus
we concluded that the TBC is a strong function of frequency for the case where there exists
two materials with different phonon dispersion relations.
Appendix E

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E.1 AIP Advances

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Appendix F
LAMMPS Input Files

F.1  Sample NEMD Input Script

# ---------- Initialize Simulation ---------------------
clear
units metal
dimension 3
boundary p p p
atom_style atomic
neighbor 0.3 bin
neigh_modify delay 0 every 1
echo both

# ---------- Create Atoms -------------------------------
lattice fcc 5.39
region box block 0 142 0 8 0 8
create_box 2 box
create_atoms 1 box
mass 1 39.948
mass 2 39.948

# ---------- Define Interatomic Potential ---------------
pair_style lj/cut 8.84
pair_coeff 1 1 0.0104233206 3.4
pair_coeff 1 2 0.0104233206 3.4
pair_coeff 2 2 0.0104233206 3.4

# ---------- Settings --------------------------------
# size: 142*8*8 (domain length : 128)
region wall1 block 0 2.99 0 8 0 8 units lattice # left boundary
region wall2 block 139.0 142 0 8 0 8 units lattice # right boundary
region bath1 block 3.01 7 0 8 0 8 units lattice # high temp bath
region bath2 block 135.01 139 0 8 0 8 units lattice # low temp bath
region domain block 7.01 135 0 8 0 8 units lattice # domain
region nowall block 3.01 138.99 0 8 0 8 units lattice # nowalls

region left block 0 70.99 0 8 0 8 units lattice
region right block 71 142 0 8 0 8 units lattice

region midl block 70.01 71 0 8 0 8 units lattice # left boundary layer
region midr block 71.01 72 0 8 0 8 units lattice # right boundary layer

group wall1 region wall1
group wall2 region wall2
group bath1 region bath1
group bath2 region bath2
group domain region domain
group nowall region nowall

group left region left
group right region right
group midl region midl

set group left type 1

set group right type 2

fix lbdr wall1 setforce 0.0 0.0 0.0
fix rbdr wall2 setforce 0.0 0.0 0.0

velocity nowall create 10 4928459 dist gaussian

thermo 1000

reset_timestep 0
timestep 0.01 # 10 fs

# ------------------ NVT Equilibration ------------------------------
fix nvt nowall nvt temp 10 10 1

# display thermo
thermo_style custom step ke etotal press vol c_nvt_temp

thermo_modify lost warn

run 20000 # 200 ps

unfix nvt
# ---------------- Direct Method --------------------------
fix heatbath bath1 heat 1 0.012
fix coldbath bath2 heat 1 -0.012

# ---------------- Update Positions --------------------------
fix nve nowall nve
compute 1 nowall temp
compute nowall_ke nowall ke/atom
compute leftloc midl property/atom x # to keep track of x position of mid-layer
compute rightloc midr property/atom x
thermo_style custom step ke etotal c_1
thermo_modify lost warn
variable temp atom c_nowall_ke/(1.5*8.617332478e-5)
fix Tprofile nowall ave/spatial 1 1000 1000 x 0 1 v_temp file T_profile.txt
fix nowalltemp nowall ave/time 1 1000 1000 c_1 file nowalltemp_2.txt
fix l_loc midl ave/spatial 1 1000 1000 x 0 1 c_leftloc file leftloc.txt
fix r_loc midr ave/spatial 1 1000 1000 x 0 1 c_rightloc file rightloc.txt
run 1500001 # 15 ns
F.2 Sample PWP Input script

# ---------- Initialize Simulation ---------------------
clear
units metal
dimension 3
boundary p p p
atom_style atomic
neighbor 0.3 bin
neigh_modify delay 0 every 1
echo both

# ---------- Create Atoms -------------------------------
read_data lattice.xyz
mass 1 28.06
mass 2 72.64

# ---------- Define Interatomic Potential ---------------
pair_style sw
pair_coeff * * SiGe.sw Si Ge

# ---------- Settings --------------------------------
group left type 1
group right type 2
thermo 1000

timestep 0.0005 # 0.5 fs

# ------------------ Update Positions (NVE) -----------------------------

fix nve all nve

compute pe1 left pe/atom
compute pel left reduce sum c_pe1

compute pe2 right pe/atom
compute per right reduce sum c_pe2

compute ke1 left ke/atom
compute kel left reduce sum c_ke1

compute ke2 right ke/atom
compute ker right reduce sum c_ke2

thermo_style custom step c_pel c_per pe c_ke1 c_ker ke etotal temp
thermo_modify lost warn

dump 1 all xyz 10000 sigeposition_*.xyz
dump_modify 1 format "%d %15.10g %15.10g %15.10g"

run 1000000 # 0.5 ns
References


Curriculum Vitae

ChangJin Choi

Career Objective

To obtain a position in mechanical engineering and material science which requires computational simulations, particularly in the area of molecular dynamics, nanoscale thermal transport, nanocomposites, and aerospace materials.

Education

• Ph.D. in Mechanical Engineering
  Utah State University, Logan, UT
  – Dissertation: Impact of mass and lattice difference and interface defects on thermal boundary conductance

• M.S. in Mechanical Engineering
  Utah State University, Logan, UT
  – Emphasis on aerospace engineering

• B.S. in Mechanical Engineering
  Utah State University, Logan, UT
  – Graduate with Cum Laude

Journal Publications

• ChangJin Choi and N. A. Roberts, Contributions of mass and bond energy difference and interface defects on thermal boundary conductance, AIP Advances, 5, 9, 097160, 2015.
• ChangJin Choi and N. A. Roberts, A simple model for the effective thermal conductivity of bulk nanostructured materials, submitted.

• ChangJin Choi and N. A. Roberts, Prediction of thermal boundary conductance at the interface using phonon wave-packet simulations: The role of mass and bond energy and inelastic scattering, submitted.

Conference Publications

• ChangJin Choi and N. A. Roberts, Impact of Mass and Lattice Difference on Thermal Boundary Conductance, MRS Spring Meeting, April 6-10, 2015, San Francisco, CA, USA.

Conference Presentations

• ChangJin Choi and N. A. Roberts, Phonon Wave-Packet Simulation: Prediction of Thermal Boundary Conductance at the Interface, NanoUtah 2015 Nanotechnology Conference and Exposition, October 13, 2015, Salt Lake City, UT, USA.

• ChangJin Choi and N. A. Roberts, Thermal Conductivity Prediction in Bulk Nanostructured Materials from Single Interface Molecular Dynamics Simulations, INTERPACK 2015, July 6-9, 2015, San Francisco, CA, USA.

• ChangJin Choi and N. A. Roberts, Impact of mass and lattice difference on thermal boundary conductance, NanoUtah 2014 Nanotechnology Conference and Exposition, October 13, 2014, Salt Lake City, UT, USA.

Research and Professional Experience

• Nanoscale Thermal Energy Laboratory (nTEL), Utah State University, Logan, UT
  Graduate Research Assistant (August 2013 - Present)
    – Modeling thermal transport properties of nanostructured materials
– Predict thermal boundary conductance especially at the interface of two dissimilar material using molecular dynamics (MD) and phonon wave-packet dynamics

• Fluid/Thermal Laboratory, Utah State University, Logan, UT Teaching Assistant (August 2013 - December 2013)
  – Explained basic theory and the process of the laboratory and graded all written work

• Structural Laboratory, Utah State University, Logan, UT Graduate Research Assistant (August 2011 - May 2013)
  – Updated existed finite element code, Variational Asymptotical Beam Sectional (VABS) analysis, to calculate displacement, strain, and stress of the curved and anisotropic beams with arbitrary materials
  – Compared results from VABS with ANSYS

• Department of Mechanical and Aerospace Engineering, Utah State University, Logan, UT General Graduate Assistant, (August 2009 - May 2011)
  – Graded homework and project for variety classes (Aerodynamics, Flight mechanics, Vibrations, Composite materials, Finite element methods, and Dynamics and vibration)

• Tech Center at Korean Airline, Busan, Korea Engineering Intern (May 2009 - July 2009)
  – Involved in the project of BOEING
  – Researched and developed a part at the wing-tip area to reduce a drag coefficient

• Department of Mechanical and Aerospace Engineering, Utah State University, Logan, UT Design Projects (August 2009 - May 2011)
  – Developed a computer program to calculate stress and strain using classical laminate theory (CLT) in composite materials class
- Replaced given wing with another shape of the wing which has the same characteristics with the original wing in aerodynamics class
- Developed a computer program for the aircraft to be stable both statically and dynamically by modifying a preliminary designed aircraft in flight mechanics class