A Review of Thermal Rectification Observations and Models in Solid Materials

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Abstract

Thermal rectification is a phenomenon in which thermal transport along a specific axis is dependent upon the sign of the temperature gradient or heat current. This phenomenon offers improved thermal management of electronics as size scales continue to decrease and new technologies emerge by having directions of preferred thermal transport. For most applications where thermally rectifying materials could be of use they would need to exhibit one direction with high thermal conductivity to allow for efficient transport of heat from heat generating components to a sink and one direction with low conductivity to insulate the temperature and heat flux sensitive components. In the process of understanding and developing these materials multiple mechanisms have been found which produce thermally rectifying behavior and much work has been and is being done to improve our understanding of the mechanisms and how these mechanisms can be used with our improved ability to fabricate at the nanoscale to produce efficient materials which have high levels of thermal rectification.

1. Introduction

Thermal rectification is a phenomenon in which thermal transport along a specific axis is dependent upon the sign of the temperature gradient or heat current. Thermal rectification has been a topic of interest dating back to its initial experimental observation in 1936 by Starr [1]. Since then, there have been several experimental and theoretical studies performed in an attempt to understand what mechanisms cause thermal rectification. With an improved understanding of how thermal rectification is achieved, devices like thermal transistors, thermal logic circuits and thermal diodes could be developed and utilized in micro/nanoelectronic cooling as well as thermal memory and computations. In a recent meeting of the thermal management community it was mentioned that devices like thermal switches will be necessary for our ability to cool electronics effectively in the future as device sizes become smaller and as we move towards stacked chip designs and more complicated thermal management problems [2]. Currently several mechanisms for

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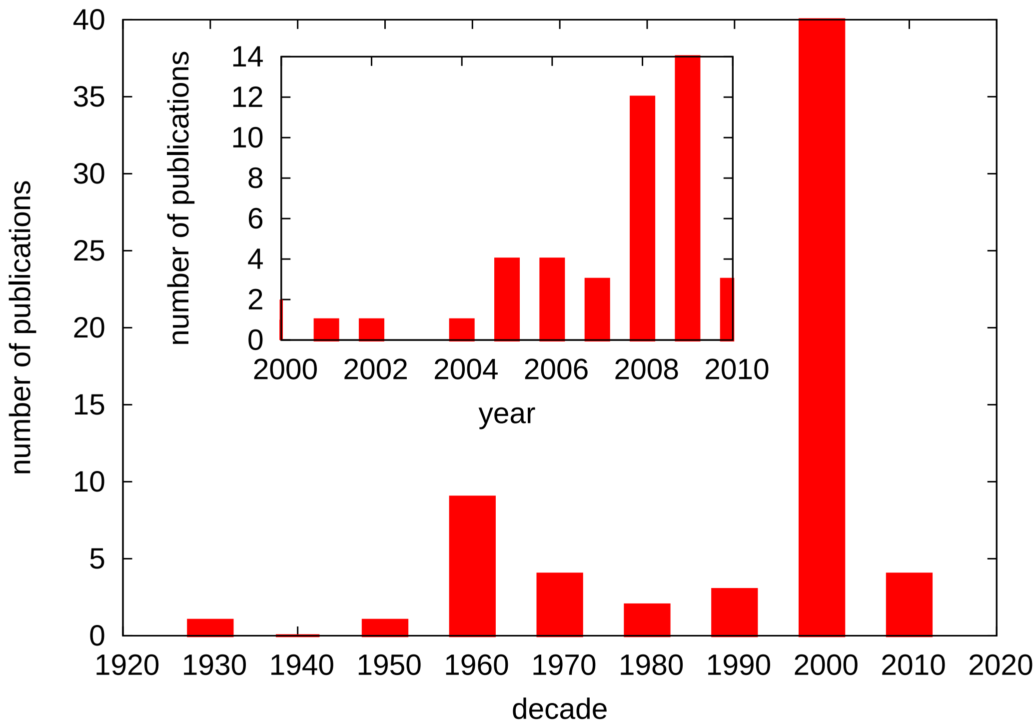

Figure 1: Number of publications on thermal rectification per decade since 1936

thermal rectification have been proposed including surface roughness/flatness at material contacts, thermal potential barrier between material contacts, difference in temperature dependence of thermal conductivity between dissimilar materials at a contact, nanostructured asymmetry (ie. mass-loaded nanotubes, asymmetric geometries in nanostructures, nanostructured interfaces), anharmonic lattices (typically 1D) and quantum thermal systems. Each of these mechanisms will be examined in detail.

Since the first known observation of thermal rectification activity in the area has been sporadic with a very large increase in interest in the last decade. Figure 1 shows the number of publications related to thermal rectification since the original observation in 1936. In the 1960s and 70s interest in this area was advanced because of the studies of composite materials that were of great interest in the aerospace industry [3]. In the 2000s we see an explosion of interest mostly due to the 1D nonlinear lattices initially presented by Terraneo [4] and the experiments of non-uniformly mass loaded nanotubes by Chang et al. [5]. These works along with our improved ability to model, synthesis and characterize systems at the nanoscale have led to an increasing trend in thermal rectification research in the latter part of the 2000s and into the current decade which is shown in the inset of Figure 1.

At first look, thermal rectification may appear to violate the 2nd Law of Thermodynamics, but we can provide common simple examples where rectification is indisputable. A difference in the Nusselt number is observed in natural convection when two parallel plates are oriented horizontally relative to gravity and

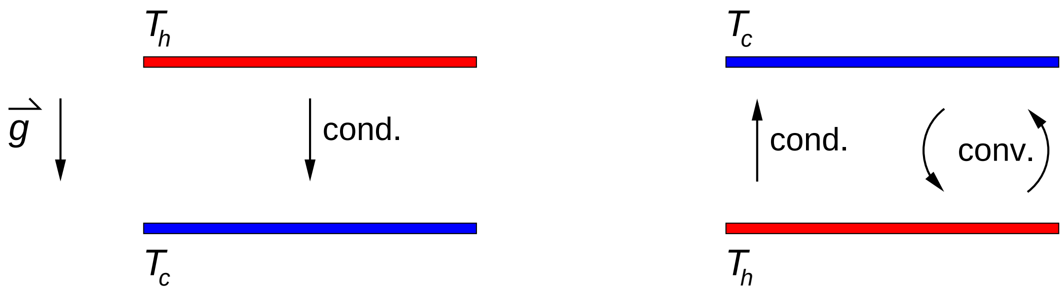

Figure 2: Schematic of rectification in natural convection

separated by a gas as shown in Figure 2. When the lower plate is heated, the heat transfer is driven by buoyancy induced flows and is governed by Rayleigh-Bernard convection in addition to conduction if the Rayleigh number is greater than the critical value of $\mathrm{Ra_{cr}} = 1708$ which is given by [6]

$$\mathrm{Ra_L} \equiv \frac{\mathrm{g}\beta(\mathrm{T_H} - \mathrm{T_C})\mathrm{L}^3}{\alpha\nu}, \tag{1}$$

where g is the gravitational constant, β is the volumetric thermal expansion coefficient, T_H is the temperature of the bottom plate, T_C is the temperature of the top plate such that $T_C < T_H$, α is the thermal diffusivity and ν is the fluid viscosity. We can then calculate the Nusselt number using [7]

$$\overline{\mathrm{Nu}}_L = 0.069\mathrm{Ra_L^{1/3}}\mathrm{Pr}^{0.074}, \tag{2}$$

for $3 \times 10^5 < \mathrm{Ra_L} < 7 \times 10^9$ where $\overline{\mathrm{Nu}}_L$ is the average Nusselt number, $\mathrm{Ra_L}$ is the Rayleigh number and Pr is the Prandtl number. If the upper plate is heated there is no fluid motion and the transport is governed by conduction through the gas and the Nusselt number is 1 [6]. In general the transport in the bottom-heated case will be greater than the top-heated case for the same temperature difference as long as the Rayleigh number is greater than 1708. Figure 3 shows the Nusselt numbers for the two configurations in the natural convection system when the participating fluid is air and water. Thermal rectification is possible in this system because the gravitational acceleration breaks the symmetry.

Another demonstration of thermal rectification can be observed in radiation exchange between two emitters separated by a material that absorbs and re-emits radiation of all wavelengths - a black body. A schematic of this system is shown in Figure 4. If both emitters are black then their emitted radiation is exactly the same when the temperature difference is reversed. If the emitting surfaces are not black and have different emissivities with respect to wavelength then rectification is possible when these emitters are separated by a thermal coupler, in this case a black body. In Figure 4 the emitting surface on the left has an emissivity of one for low wavelength photons while the emitting body on the right has the opposite. The material between the two bodies is a black body. Based on this scenario we would expect to see all the

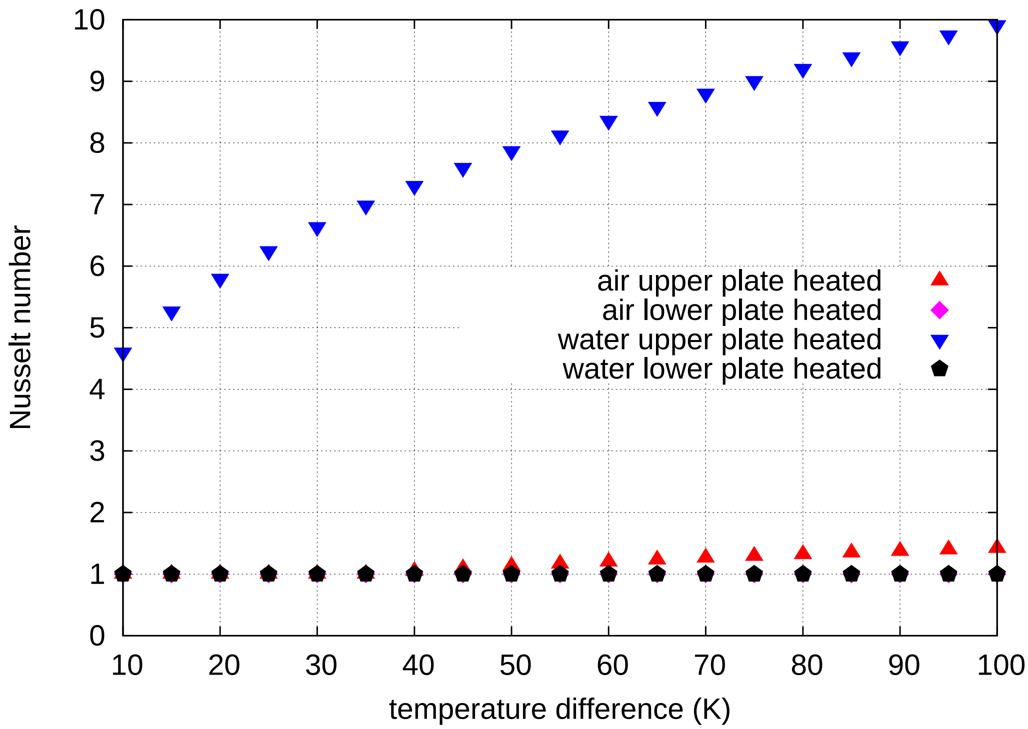

Figure 3: Level of rectification in the natural convection system with air and water

radiation emitted from both emitters to be absorbed and re-emitted by the black body. The re-emitted radiation from the black body will either be absorbed, reflected or a combination of absorbed and reflected, depending on the wavelength of the radiation and the absorptivity of the surface, from the emitters in which case it would be re-absorbed by the black body. To calculate the rectification in this case we perform an energy balance on the black body to give [8]

$$E_l + E_{ref,l} - E_b = E_r + E_{ref,r}, \tag{3}$$

where E_l and E_r are the incident radiation from the left and right emitters, respectively, $E_{ref,l}$ and $E_{ref,r}$ are the reflected radiation originally emitted from the black body and E_b is the radiation emitted from the black body. Figure 5 shows the level of rectification for the system in Figure 4 where the temperatures of the emitters are 1000 K and 500 K with opposite emissivities separated by a single black body. This system exhibits thermal rectification because the symmetry is broken by the difference in emitter properties and is coupled by the black body in between. This system exhibits similar characteristics as some of the solid systems that will be discussed in this paper, specifically the nanostructured interfaces in §2.2.3 and the 1D nonlinear chains in §2.2.4.

A thermal rectifier that exhibits high transport properties in one direction and insulating properties in the opposite would be beneficial for electronics cooling applications specifically at the nanoscale if they could be

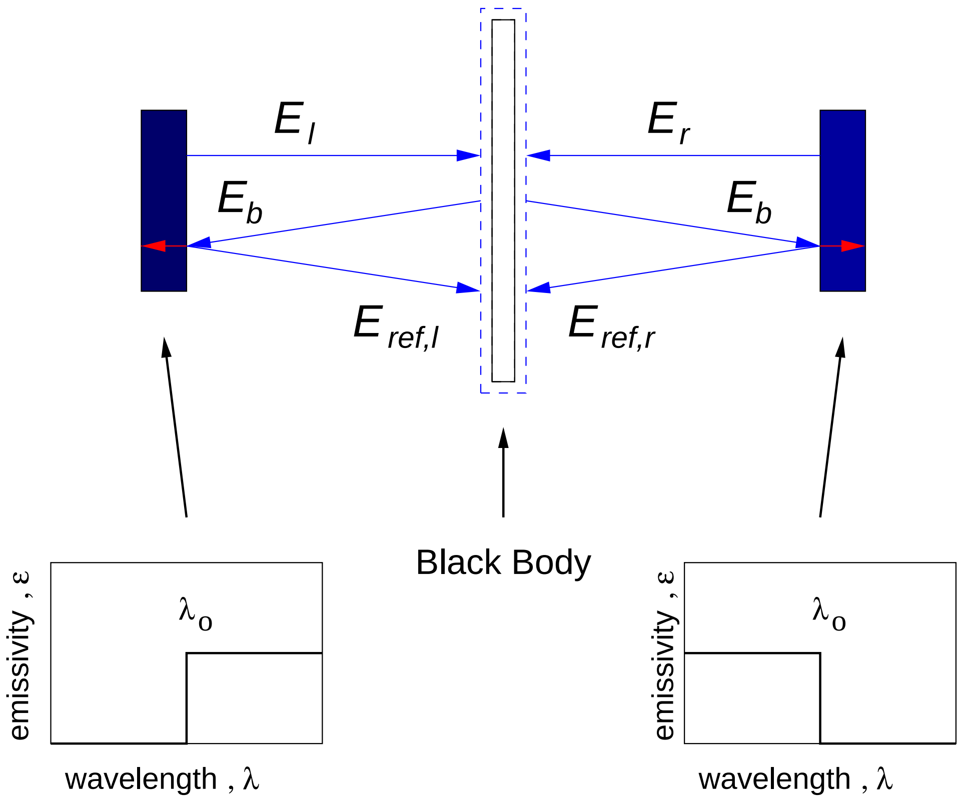

Figure 4: Schematic of rectification in radiation heat transfer

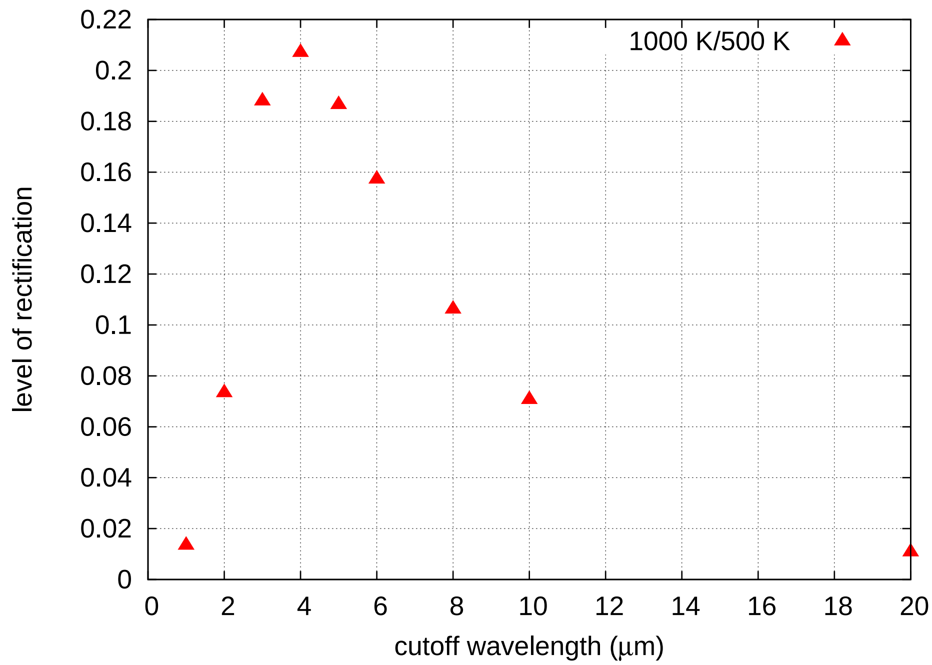

Figure 5: Level of rectification as a function of the cutoff wavelength for the system shown in Figure 4 with the temperatures of the emitters at 1000 K and 500 K

incorporated into the design of the component. Imagine a device that was composed of materials that were capable of transporting heat along a specific path with extremely high transfer rates (high conductivity) while at the same time insulating the components along that same path that are sensitive to high temperatures and heat flux. Thermally rectifying materials exhibit these properties and are therefore the ideal candidate material for future electronics cooling applications. Researchers have also proposed the use of thermally rectifying materials in the design of thermal logic circuits, transistors and memory [9].

This paper will discuss the different known mechanisms of thermal rectification in solid systems. This paper will also look back at the literature and attempt to support or reject the hypothesis/mechanisms proposed in the past with our modern knowledge of thermal transport. This paper begins by looking at bulk thermal rectification mechanisms followed by nano and atomic scale thermal rectification mechanisms. Finally this paper will report the level of rectification in theoretical and experimental studies found in the literature and propose a direction for thermal rectification research based on these results.

2. Thermal Rectification Mechanisms

Thermal rectification has been observed experimentally and predicted theoretically in several different systems, and different mechanisms are responsible for thermal rectification depending on geometry, materials, surface preparation and contamination to list a few.

In this paper the level of rectification will be defined as

$$\varepsilon = \frac{\kappa^{+} - \kappa^{-}}{\kappa^{+} + \kappa^{-}}, \tag{4}$$

where κ^{+} is the thermal conductivity in the forward direction and κ^{-} is the thermal conductivity in the reverse direction. In this definition of rectification we assume that $\kappa^{+} > \kappa^{-}$ meaning we assume that the conductivity in the forward conduction is greater than the conductivity in the reverse conduction direction. Similarly we can define the rectification as the ratio of the difference in heat flux between the two directions over the sum of the two heat fluxes as long as the applied temperature difference is equivalent for the forward and reverse cases. We define the level of rectification this way similarly to some other researchers [10, 5]. In the case of no rectification we have no difference in any of the parameters (eg. $\kappa^{+} = \kappa^{-}$) and the level of rectification is zero ($\varepsilon = 0$). This definition also gives a value of unity for an ideal rectifier where one direction would be a perfect insulator ($\kappa = 0$) or a conductor of infinite conductivity ($\kappa = \infty$). Other definitions of rectification have been a ratio of the larger heat flux or thermal conductivity to the smaller heat flux or thermal conductivity (κ^{+}/κ^{-} or q^{+}/q^{-}). This definition leads to a value of one when the values of each of these are equal and no rectification occurs which could be confusing.

2.1. Bulk Mechanisms

The first observations of thermal rectification were in bulk systems typically composed of metals or metal oxides. In these systems the mechanism was debated and appeared to be very dependent on surface characteristics (ie. roughness and flatness) as well as bulk material properties.

2.1.1. Metal/Insulator Effect

The first observation of thermal rectification was by Starr in 1936 [1]. He was investigating electrical rectification characteristics of Copper/Cuprous Oxide interfaces and also noticed thermal rectification. The measurements showed that thermal conductance was greater in the direction of greater electrical conduction, which was from the metal to oxide (copper to cuprous oxide). Starr attributed this effect to asymmetric electron transport in the system resulting in asymmetric thermal transport, which is expected from the electron theory of heat conduction. The level of thermal rectification in this system was a maximum of $\varepsilon = 0.39$, which suggests that the forward conductivity is about 130% greater than the reverse direction.

In these systems the thermal energy is transported primarily by electrons in the metal and phonons in the insulator or oxide. Since these two materials transport thermal energy with different carriers there must be transfer between the electrons and phonons. Near the interface in the metal, the electrons must scatter with phonons which can then be transmitted into the insulator or reflected back into the metal at the interface. This electron-phonon scattering and the phonon transmission lead to an effective contact resistance at the interface which is given by

$$R_c = R_{e-p} + R_{pt}, \tag{5}$$

where R_{e-p} is the resistance due to electron-phonon scattering and R_{pt} is the resistance due to phonon transmission/reflection. In these systems the materials are assumed to be in perfect contact, but because of the localized resistances, a temperature jump exists at the interface. The resistance due to electron-phonon scattering in metal is governed by scattering rates that are not in equilibrium, which means that the energy transfer from electrons to phonons can be different than that from phonons to electrons. This suggests that thermal rectification is possible in these systems. In 2006 Walker [10] developed a non-equilibrium transport model based on Majumdar and Reddy's work [11] and scattering rates from Lundstrom [12], which is presented here. Figure 6 shows the temperature distributions achieved when the direction of the thermal bias is switched. Although the electron-phonon system is in non-equilibrium, Boltzmann moments with an energy exchange term are assumed to be adequate to model the non-continuum effects [10]. This assumption leads to a system of two coupled Fourier-like carriers given by

$$\kappa_e \frac{d^2 T_e}{dy^2} - G(T_e - T_p) = 0; \tag{6}$$

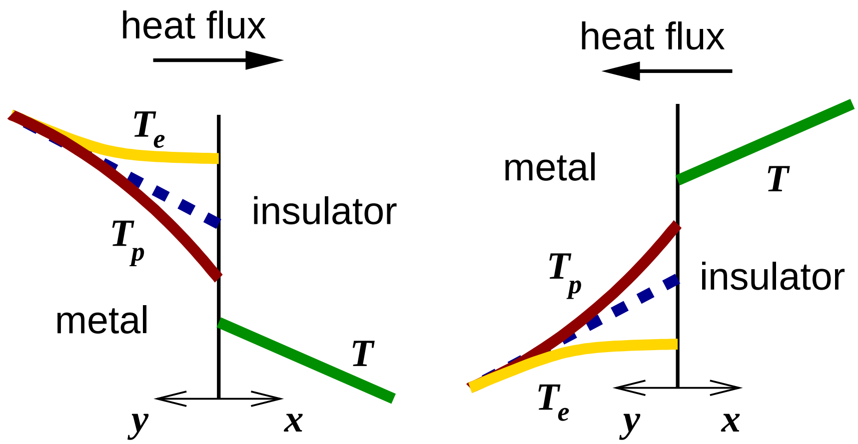

Figure 6: Electron and phonon temperature distributions through a metal/insulator system with reverse temperature gradients

$$\kappa_p \frac{d^2 T_p}{dy^2} + G(T_e - T_p) = 0, \tag{7}$$

where κ_e and κ_p are the electron and phonon thermal conductivities in the metal and G is related to the rate of energy transport between electrons and phonons. At the interface the metal and insulator are coupled such that the phonon heat flux is matched and the electron heat flux is zero. These conditions are given by

$$\kappa_p \frac{dT_p}{dy}|_{y=0} = -\kappa \frac{dT}{dx}|_{x=0}; \tag{8}$$

$$\kappa_e \frac{dT_e}{dy}|_{y=0} = 0. \tag{9}$$

Additionally a temperature boundary condition must exist for the temperature jump at the interface. This boundary condition is given by

$$\kappa_p \frac{dT_p}{dy}|_{y=0} = h[T_p(y=0) - T(x=0)]. \tag{10}$$

Finally, we must also assume that away from the interface in the metal, equilibrium exists and $T_e = T_p$. If we assume that $\kappa_e \gg \kappa_p$, which is true for metals, we obtain a solution for the interface conductance given by [11]

$$h = \frac{h_{e-p} h_{pt}}{h_{e-p} + h_{pt}}, \tag{11}$$

where $h_{e-p} = \sqrt{G\kappa_p}$. In this case G is dependent on the electron-phonon scattering rate, usually expressed as $G = C/\tau$ where C is the electron specific heat and τ is the electron-phonon scattering rate.

This model is, in general, not dependent on the direction of thermal transport through the interface. The difference in directional conductance comes from the energy dependence of the electron-phonon scattering rates. The scattering rate from Fermi's Golden rule is given by [12]

$$\frac{1}{\tau} = \frac{\pi D_o^2}{2\rho\omega_o} \left(N + \frac{1}{2} \mp \frac{1}{2} \right) g_C \left(E \pm \hbar\omega \right) \tag{12}$$

where the electron density of states g_C is dependent on whether the phonon is emitted (+) or absorbed (-), $\hbar\omega$ is the phonon energy, ρ is the material density and D_o is the optical deformation potential. The energy relaxation rate is found by scaling the scattering rate as

$$\frac{1}{\tau_E} = \frac{\hbar\omega}{E(p)} \frac{1}{\tau}. \tag{13}$$

The fact that τ varies depending on the direction of transport suggests that G is also dependent on direction. Therefore the Gregorian model allows for thermal rectification.

2.1.2. Thermal Strain/Warping at Interfaces

Interfaces that are composed of materials that exhibit properties with different temperature dependencies will results in different effective contact areas when the temperatures at each side of the interface change. Experimental and theoretical results have shown that surface roughness and flatness can result in thermally rectifying interfaces when the roughness or flatness is of a specific type and the materials possess the desired relationship. An exaggerated strain or warping is shown in Figure 7 which is described by [13]

$$\frac{\delta r_0}{\delta q} = \frac{\Gamma}{3} \left[\frac{1}{r_1 r_2 (r_1 + r_2)^2} \right]^{2/3} \left[r_2^2 \frac{dr_1}{dq} + r_1^2 \frac{dr_2}{dq} \right], \tag{14}$$

where r_1 and r_2 are the radii of the two smooth spheres in contact. The load and the mechanical properties of the two spheres are contained in the factor Γ. The possibility of thermal rectification, which is represented by the sign of $\delta r_0/\delta q$, lies in the last term of the equation where the change of the radii of either sphere is a function of the thermoelastic properties of the constituent materials, but will change sign depending on the direction of the heat flux. As shown in Figure 7, a heat flux entering a sphere will cause the radius to decrease [14], but a heat flux in the opposite direction will cause the surface to flatten thereby increasing its radius of curvature. Experimental results have been difficult to predict using models based on thermal strain and warping at an interface, but with a well known surface roughness and flatness some predictability has been achieved for the boundary conductance and rectifying effect.

In 1955 Barzelay et al. performed measurements of the thermal contact resistance between similar and dissimilar metals under different loads [15]. Their results showed that the thermal contact resistance decreased with increased pressure with a large change occurring at lower pressures but a leveling off at higher pressures. Their results also showed that the boundary resistance was smaller in the direction of aluminum to stainless steel. Barzelay et al. also showed that the rectification increased with increasing pressure in the

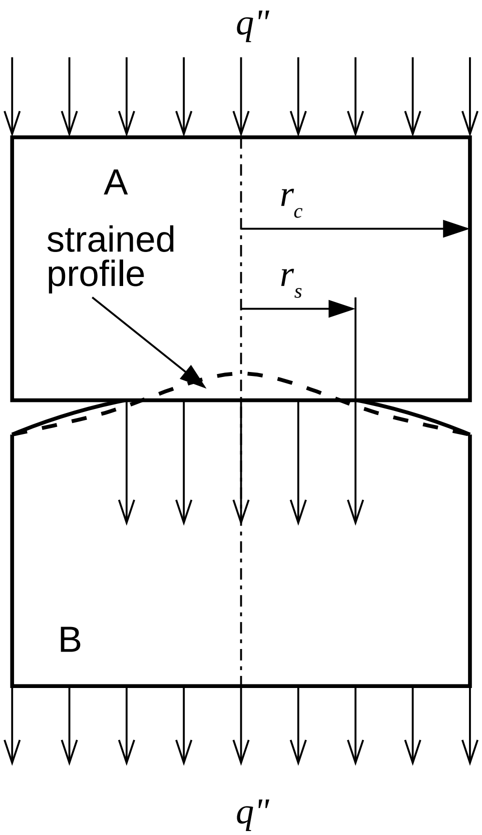

Figure 7: Change in thermal contact area due to strain or warping

ranges they studied (0-400psi) in which the boundary conductance from the stainless steel to the aluminum did not change greatly with pressure while the boundary conductance from aluminum to stainless steel increased roughly linearly in this pressure range (see Figure 9 of ref. [15]). The authors attributed these results to differences in warping of the interface when the heat current is reversed because of a difference in the temperature dependence of the mechanical properties (ie. stiffness, thermal expansion coefficient) of the materials making up the interface resulting in area changes. The level of rectification observed in this study was approximately 0.67. The explanation of the rectification observed was later improved and elaborated by Wheeler [16].

In 1961 the work of Rogers argued that the effect seen by Barzelay et al. was a result of a thermal potential barrier and not the result of the change in the contact resistance with the direction of heat flow [17]. In a response to the work of Rogers, Williams [18] stated that the pressures under which Rogers conducted his experiments were to low to eliminate any effects of the changing contact resistance and that his results were not sufficient to discount a change in contact area due to the difference of material properties at the interface [18]. In 1962 Powell et al. followed the proposed improvement by Williams and found that with the increased pressure loading, a specified contact geometry and a controlled film thickness the directional effect seen by Rogers was eliminated which supported the theory of Williams[19]. Powell et al. also stated that the mechanism proposed by Barzelay et al. could possibly result in rectification when the contacting surface area was large. The rectification in all of these works, excluding Rogers, was believed to be a result of a change in contact resistance due to a change in contact area, which was dependent on the direction of heat flow because of thermal warping at the interface. A schematic of this effect is seen in Figure 7.

In 1966 Clausing discovered an additional mechanism for thermal rectification due to a difference in material properties at an interface [20]. Clausing developed a macroscopic model to explain the rectification being observed, which he argued was a result of thermal strain at the interface in the material with lower thermal conductivity. In his experiments and model, the interface was composed of aluminum and stainless steel with a spherical end with a large radius of curvature in which the contact area could easily be defined. With his model rectification would only exist if the heat flux was large enough and the thermal conductivity of one of the materials was low enough, otherwise there would not be thermal strain and the effect would vanish. The experiments conducted by Clausing showed the opposite results of previous experiments with the same materials [15]. His measurements showed an increased contact conductance or a decreased contact resistance from the stainless steel to the aluminum by a factor of 3 or a level of rectification of 0.5. This directional effect being the opposite of previous works was attributed to thermal strain in the stainless steel when large heat currents were used. The directional effect disappeared when the heat flux was reduced because the reduction of thermal strain in the stainless steel. To eliminate any effect of the surface roughness in these experiments, the surfaces of each sample were polished.

In 1967 Lewis and Perkins conducted experiments in order to determine which effect, either the surface warping or thermal strain, was responsible for the directional effect that was observed and why differences have been reported between Barzelay et al. [15] and Clausing [20] where the experiments were both conducted with aluminum and stainless steel [21]. They performed experiments with samples that had varying levels or surface roughness and surface flatness. They presented two models for the rectifying effect. The first model, which we will call the Thermal Strain Model, was based on the mechanism of thermal strain at the interface proposed by Clausing and the second model, which we will call the Thermal Warping Model, was based on the mechanism of warping at the interface proposed by Barzelay et al. In the cases where the surfaces were flat and the roughness was the same level as the flatness, the results followed that of the Thermal Warping Model, which was based on warping at the interface and conductance was greater from the high thermal conductivity to the low thermal conductivity material (aluminum to stainless steel). In these samples the rectification was eliminated when the surface roughness was decreased by high speed buffing. The rectification effect was then reversed when the surfaces were lapped which resulted in smoother, but rounded surfaces which followed the Thermal Strain Model. In all of these cases the boundary conductance in both directions increased with increasing pressure loading. The results of Lewis and Perkins showed that both the Thermal Warping Model and the Thermal Strain Model can result in thermal rectification, but in opposite directions. In order to predict the level of rectification in these systems the surface conditions of the samples must be known. In 1976 Hudson also concluded that spherical cap surfaces can result in non-uniform isothermal surfaces leading to thermal strain at the interface in the material with lower thermal conductivity [22]. He showed theoretical evidence that this strain could result in thermal rectification. In 1987 Somers et al. developed a model for thermal rectification that accounted for the change in contact area of two spherical surfaces in contact [13]. In 1991 Stevenson et al. developed a more detailed model that could be applied to similar and dissimilar spherical metal contacts for several different metals [23]. Their data matched experimental results reasonably well and showed thermal rectification, which generally increases with loading.

In 1971 Jones et al. performed experiments on a system of 100 stainless steel discs in series with an aluminum expansion element [24]. Their experiments showed thermally rectifying behavior due to the expansion of the stainless steel discs. The authors claimed that their system was more robust, showed a higher and more predictable level of rectification and was more useful for lower thermal resistance systems than the rectification systems previously discussed in this section, though the authors did not justify all of these conclusions.

2.1.3. Thermal Potential Barrier at Interfaces

Electronic effects at interfaces are not only observed in Metal/Oxide interfaces, but they are also seen in Metal/Metal interfaces. In 1961 Rogers [17] argued that the rectifying effect he observed in aluminum/steel interfaces was due to a difference in the work functions of the two materials. A schematic of this effect is shown in Figure 8. Rogers found that materials with differences in the work function (aluminum and steel) produced a thermally rectifying effect. To eliminate the possibility of this being a result of a thermoelectric phenomena Rogers also tested a similar system which consisted of two materials which had very different thermoelectric potentials (Chromel and Alumel) and found no rectifying effect. Rogers also devised an experiment that he felt would test the validity of the argument of warping at the interface due to non-uniform temperature distributions over the cross-section. He did this by replacing the aluminum with copper which results in a greater difference in thermal conductivity between the two materials. His theory was that a larger difference in thermal conductivity should produce greater warping (if that is the mechanism) and therefore result in greater rectification than in the aluminum/steel system. The copper/steel system produced only little rectification, below that of the aluminum/steel system which weakens the argument for warping from non-uniform temperature distribution because of a difference in thermal conductivity. This result could also support the hypothesis that a contact potential between the two materials results in asymmetric electron transport. In the copper/steel system an oxide layer in the copper could result in the elimination of this potential and therefore thermal rectification. This potential barrier that exists is believed to be associated with the work function of the materials in contact. To test this hypothesis further Rogers repeated the measurements with the aluminum and steel with a thin section of mica inserted between them to act as a barrier for electrons, similar to the oxide layer assumed to exist in the copper, in both directions. These measurements resulted in no rectifying effect which supported the hypothesis that the heat transport due to phonons in this system was symmetric and the heat transport due to electrons in the system of just aluminum and steel was asymmetric due to the difference in work function of the two materials. Their measurements of the aluminum/steel system showed greater transport from the aluminum to the steel by about 20% or a level or rectification of $\varepsilon = 0.1$. This work was criticized because the low pressure loading of the interface which could lead to rectifying effects due to a change in surface geometry [18] which was discussed in §2.1.2.

In 1962 Moon and Keeler developed a theoretical model based on Rogers work which showed that a difference in material work functions could result in thermal rectification [25]. Their model predicts greater transport in the direction of decreasing work function (step down) as opposed to increasing work function (step up) when a thin oxide layer is present in between the two metals (Figure 8). Their model for rectification

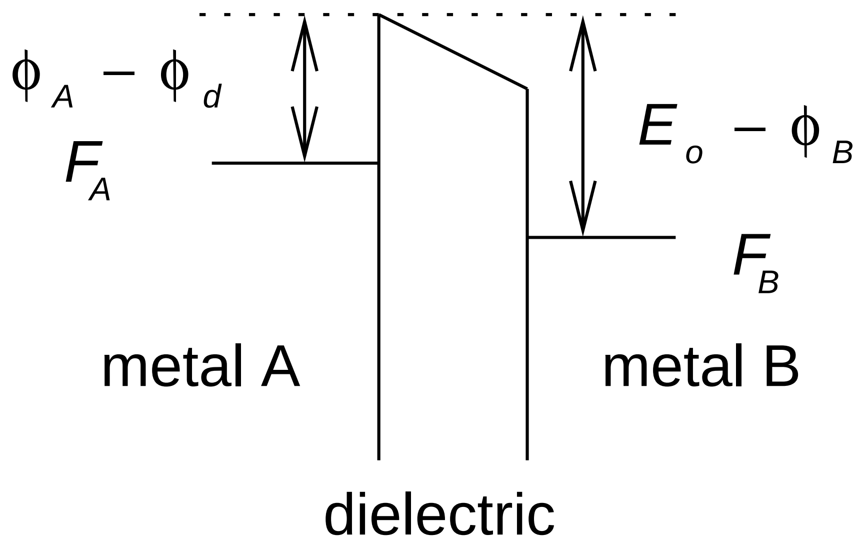

Figure 8: Energy band diagram of two dissimilar metals in contact via a dielectric

is given by

$$\frac{q_{e12}}{q_{e21}} = \frac{A_{a12}}{A_{a21}} \frac{T_{12}}{T_{21}} \frac{T_A^2}{T_B^2} \exp\left[\frac{E_{w1} - E_{w2}}{k} \frac{T_A - T_B}{T_A T_B}\right], \tag{15}$$

where A_{a12} and A_{a21} are the interface area and usually close to being equal, T_{12} and T_{21} are the interface temperatures and usually close to being equal, T_A and T_B are the temperatures of the reservoirs and different and E_{w1} and E_o are the material work functions of the first metal and oxide, respectively[25]. For the systems studied in this work, which were the same as those investigated by Rogers[17], a level of rectification of $\varepsilon = 0.13$ was predicted which compares well to the value measured by Rogers.

In 1970 Thomas and Probert [26] conducted a series of experiments between similar and dissimilar materials and observed thermal rectification. They stated that the mechanism likely responsible for the results in their specimen pair labeled C, which was composed of steel and aluminum, was likely the difference in work function [25], though the lack of knowledge of material work functions of contacting surfaces was an obstacle [26]. Also in 1970 O'Callaghan et al. [27] performed measurements of systems composed of many interfaces. Based on their measurements of directional effect over a full range of pressure loading they found that the directional effect would increase under low loading for freshly assembled stacks up to a certain point and then the directional effect would decrease with increased loading until at some critical value there would be no directional effect. These experiments could be repeated after a re-cleaning process to result in the same measurements. They also observed that if the system was not loaded to the critical value and the loading was reduced the directional effect would return. Based on their results the authors argued that this directional effect in these systems was a result of the formation and buildup of oxide layers and the elimination of the directional effect was due to the compression of the oxide and the welding of the existing contacts of the metals. The electrical rectification of these systems was also measured, but the levels obtained with those measurements were very small therefore the authors suggested that the thermal rectification was due to the phonon contribution to the thermal transport which is contrary to Moon and Keeler's hypothesis [27].

This mechanism has possibly been verified experimentally and has a strong basis in theory, but could also be affected by many of the parameters which affect the level of rectification seen in the geometrical models discussed in §2.1.2 where the contact area and pressure at the interface are important. The results that have been presented to support this mechanism for thermal rectification could also support the geometric model of either strain or warping of the interface resulting in changes of contact area.

2.1.4. Temperature Dependence of Thermal Conductivity at Interfaces

In the mechanisms discussed thus far there has always existed an asymmetry in the system in the form of either dissimilar materials or a geometric asymmetry. In this section we present an additional mechanism for thermal rectification in bulk materials. The asymmetry in this mechanism is due to the difference in the temperature dependence of thermal conductivity between two materials composing an interface. For these systems to result in thermal rectification a distinct difference in the temperature dependence of the thermal conductivity is necessary (ie. material A has low thermal conductivity at low temperature and high thermal conductivity at high temperature while material B is the opposite). This mechanism was initially proposed by Marucha et al. when they performed experiments on inhomogeneous GaAs and found a directional dependence of the thermal conductivity [28]. Marucha et al. later analyzed the system using the one-dimensional Fourier equation and found that this temperature dependence of the thermal conductivity would result in thermal rectification [29]. The experimental and theoretical work by Marucha et al. showed promise for thermally rectifying systems, but later work by Hudson in 1976 showed that their results may not entirely be a result of the effect of the thermal conductivity and may be enhanced by non-uniform isotherms over the cross-section of the specimen [22]. In 1978 Jezowski and Rafalowicz performed experiments of quartz and graphite (differing temperature dependence of thermal conductivity) in series [30]. Unlike the inhomogeneous GaAs system investigated by Marucha et al. this system possessed only two sections of the differing materials instead of four. Quartz and graphite were chosen due to the different signs of the slope of the thermal conductivity. Jezowski and Rafalowicz found a difference in heat flow of 70% or a level of rectification of $\varepsilon = 0.26$ when the temperature difference was 40K. Greater heat flow was observed in the graphite to quartz direction. The graphite has a high thermal conductivity at high temperatures and a lower thermal conductivity at low temperatures while the quartz has a high thermal conductivity at low temperatures and a lower thermal conductivity at higher temperatures. Also in 1978 Balcerek and Tyc performed experiments and theoretical studies of tin and α-brass systems [31]. Their experimental results agreed extremely well with the theoretical prediction based on Fourier's law, which showed that there was no effect due to the interface geometry. Their results also showed that larger thermal rectification was possible and was dependent on the properties of the materials composing the interface. In this case greater transport was observed from α-brass to tin. The rectifying effect increased with temperature difference where the maximum observed rectification was around 0.4 at a temperature difference of 9K. The theoretical calculations showed a rectifying effect of 0.59 at a temperature difference of 40K. In 1984 Kokshenev et al. developed a model for thermal rectification in solid-solid systems based on the Acoustic Mismatch Model [32]. Their model showed that when the boundary or interface resistance was small rectification could exist in systems in which the materials exhibited different temperature dependent thermal conductivity, specifically different signs of the slope of the thermal conductivity with respect to temperature. Kokshenev et al. found good qualitative agreement with the work of Jezowiski and Rafalowicz [30] and Balcerek and Tyc [31].

In 1985 Hoff showed theoretical results that a system with a temperature and spatial dependent thermal conductivity like an inhomogeneous material was a necessary condition for thermal rectification based on this mechanism [33]. In 1993 Hoff verified his own work through experiments and found excellent agreement in a system composed of aluminum and brass where transport was greater in the direction of brass to aluminum [34].

More recently there have been some more rigorous models for the prediction of thermal rectification in systems with materials that have different temperature dependence of thermal conductivity. In 2001 Sun et al. developed a model which suggested that when the thermal conductivity of two contacting solids is different thermal rectification will occur [35]. Previous models have suggested a difference in temperature dependence is needed, but do not show a difference in the value will result in thermal rectification. Their model is based on Fourier's law and the interface temperature. The model presented is flawed however because it assumes the system has an overall effective thermal conductivity while the interface is calculated assuming each component of the material has it's own thermal conductivity. Assuming the materials they use maintain a constant thermal conductivity thermal rectification will not occur. In 2006 Hu et al. proposed a design for a macroscale thermal rectifier based on the same mechanism that has been discussed in this section [36]. They use non-equilibrium molecular dynamics (NEMD) simulations to demonstrate the rectifying behavior of a system of quartz and diamond. In 2009 Dames presented a single algebraic equation for thermal rectification in systems of dissimilar materials with different thermal conductivities [37]. His model made the assumption that the material thermal conductivities followed the power law in order to maintain it's simplicity. This work investigated many combinations of materials which had opposite signs of the power (ranging from -3.5 to +5.4). The power law matched experimental measurements very well in the temperature ranges used in this work. In the low-bias limit the level of rectification was shown to be proportional to the dimensionless thermal bias $\Delta T/T_o$, the difference in power law exponents $n_1 - n_2$ and a simple function of the thermal resistance ratio ρ. The expression for rectification presented by Dames is given by

$$\gamma = \frac{(n_1 - n_2)}{(\rho^{1/2} + \rho^{-1/2})^2}\Delta, \tag{16}$$

where $\Delta = 2\Delta T/(T_H + T_c)$, $\rho = R_{0,2}/R_{0,1}$ and $R_{0,i}$ is the thermal resistance of leg i at uniform temperature T_0. Beyond the low-bias region ($\Delta > 0.1$) a second order theory showed to be extremely close to the full theory that also fit experimental data from Jezowski and Rafalowicz [30] very well. This model also showed good agreement with Balcerek and Tyc [31]. The work of Dames highlights the ability of this mechanism to result in thermal rectification, but also points out a limitation. In order to achieve larger thermal rectification (greater than $\varepsilon = 0.5$) larger temperature gradients are required (of the order of the average temperature). Later in 2009 Kobayashi et al. experimentally demonstrated thermal rectification in a system of two materials with different temperature dependent thermal conductivities which fit well with a theoretical model based on Fourier's law [38]. Their results also showed that conduction was greater in the direction of high to low thermal conductivity.

In 2010 Go and Sen stated that a necessary condition for thermal rectification in a material or a structure is that the thermal conductivity must be a function of both temperature and space and this function must be non-separable [39]. Their results showed that rectification did not always occur when the thermal conductivity was a function of temperature and space and non-separable, but that this property of the thermal conductivity was required for the possibility for the material or system to exhibit thermal rectification. This property of thermal rectification can potentially be achieved in a single material, but this work is mentioned here because it can more thought of more easily as a composite system.

2.2. Molecular Mechanisms

The previous section discussed the major mechanisms for thermal rectification in bulk materials. Recently, as was shown in Figure 1, there has been a large increase in interest in thermal rectification in nanostructured materials. There have been very few experimental reports of thermal rectification in nanostructures, but there has been a large increase in theoretical studies recently that show promising results for future thermally rectifying devices taking advantage of nano and atomic scale asymmetries. The lack of experimental results of thermal rectification in nanostructured systems is a result of our lack of understanding about thermally rectifying mechanisms as well as our inability to fabricate devices or structures with the tolerances necessary to produce rectification at this time. Increased experimental investigations of nanostructure thermal rectifiers is expected as our abilities are improved in both of these areas.

2.2.1. Non-uniform Mass-loading

In 2006 Chang et al. observed thermal rectification in the measurements of non-uniformly mass-loaded carbon and boron nitride nanotubes [5]. The nanotubes were non-uniformly loaded externally with Trimethylcyclopentadienyl platinum ($C_9H_{16}Pt$) along the length of the tube and the thermal conductivity was measured along each direction using the system designed by Shi et al.[40]. The system resulted in a level of rectification of $\varepsilon = 0.01$ in the carbon nanotube and a maximum of $\varepsilon = 0.034$ in the boron nitride nanotube. In both of these cases the greater thermal conductivity was observed in the direction of high-mass to low-mass. The authors concluded that the effect was not a result of phonon transport or due to an impedance mismatch at the contacts, but actually due to presence of solitons which are nonperturbative solutions of nonlinear systems. They result in rectification because they are particle-like entities that can collide with each other without changing shape giving rise to asymmetric heat flow in an inhomogeneous material [5]. However, rigorous analysis has not been performed an additional finding in this work was that the rectification was not only a result of decreased thermal transport in one direction, but also an increase in the higher conductivity direction. An alternative hypothesis was suggested by Otey et al. [41] who pointed to surface polaritons as a likely candidate. Although they computed a maximum rectification effect of $R = 0.4$, the never defined what R is so we have not included these data in Table 2.

In nearly all of the other mechanisms of thermal rectification that have been discussed now and in later sections the rectifying effect is due entirely to the reduction of thermal conductivity in one direction and no increase in the other direction.

In 2009 Alaghemandi et al. performed non-equilibrium molecular dynamics simulations of carbon nanotubes where an asymmetry was present due to a non-uniform mass distribution [42]. In the first case the mass of the carbon atoms were varied along the length resulting in a mass or density gradient along the tube. In the second case additional carbon atoms were added to the exterior of the tube also adding mass to one end of the tube. In this work the Muller-Plathe method [43] was used for the calculation of thermal conductivity in both directions. This method restricts kinetic energy exchange to atoms with the same mass therefore the hot and cold baths were of the same mass, which added an additional interface between the heavy and light carbon atoms in the non-uniform mass distribution case. This restriction did not impact the externally loaded cases, but the added atoms were also of carbon unlike the work of Chang et al. [5]. This work produced results of the same magnitude as that of ref. [5], but with the opposite preferred direction of transport. The non-equilibrium molecular dynamics simulations showed that transport was greater in the direction of low-mass to high-mass with an effective rectification between 0.015 and 0.074 depending on temperature and the mass gradient. In 2010 Alaghemandi et al. performed additional non-equilibrium simulations of non-uniform mass distributed carbon nanotubes and found the same result as their previous work [44]. In this work they found that the addition of anharmonic effects perpendicular to the longitudinal phonon modes acted to increase the contribution of the longitudinal modes to the vibrational energy and transport which does not occur in symmetric systems of the 1D systems that will be discussed in §2.2.4.

2.2.2. Asymmetric Nanostructured Geometry

The recent work involving carbon and boron nitride nanotubes have led researchers to look theoretically at other nanomaterials for possible rectifying behavior. Materials that have become extremely popular in addition to the carbon nanotube include asymmetric graphene sheets and carbon nanocones or nanohorns formed from graphene sheets [45, 46, 47, 48, 49].

In 2008 Roberts and Walker performed a theoretical study of nanowires with an asymmetric boundary roughness using the Monte Carlo method for phonon transport [45, 50]. This work was motivated by the Monte Carlo work performed by Saha et al. and Moore et al., which investigated phonon transport in nanowires that had a sawtooth boundary roughness resulting in phonon backscattering [51, 52]. Roberts and Walker found that devices which had an atomically smooth boundary in one direction and a rough boundary in the opposite were thermally self-biasing and rectifying. To achieve a device like this an asymmetric sawtooth geometry was assumed where phonons traveling in one direction observed a rough boundary while phonons traveling in the opposite would observe a smooth boundary. The phonons scattering with the boundary in the rough direction would reflect diffusely while phonons scattering with the boundary in the smooth direction would reflect specularly. This difference in phonon boundary scattering resulted in a collection of phonons at the boundary in which emitted phonons would travel in the rough direction. When thermalizing boundaries were included in this work high levels of rectification would result at low temperatures, but as the temperature of the device increased multi-phonon scattering would eliminate the observed rectification effect. In a similar study Miller et al. performed ray-tracing simulations [53] and later used the Landauer-Buttiker formalism constrained by the 2nd Law of Thermodynamics along with Monte Carlo simulations [54] to investigate thermal rectification in devices with nanostructured asymmetric inclusions and voids. These voids were of pyramidal geometry. They found rectification levels of around 0.43 due to the asymmetric phonon scattering at the interface of the host material and the voids. The level of rectification in this work increased with the applied temperature bias, though extremely large thermal bias was necessary for rectification levels above 0.025.

In 2009 Yang et al. performed molecular dynamics simulations of asymmetric graphene ribbons and found a rectifying effect of around 0.64 [48]. Their simulations involved graphene sheets with two different angular asymmetries. The first of these asymmetries was a triangular shape where the graphene sheet had a triangular shape and the width of the sheet decreased linearly along the length of the sheet. The second asymmetry was a rectangular shape where the graphene sheet maintained a different, but uniform width on each half of the sheet. Their results showed rectification in both systems with the triangular system having a greater rectifying effect. In both cases transport was greater from the larger section to the smaller section. In the case of the triangular geometry the rectifying effect increased with the angle of width reduction and decreased with the length of the device even when the angle was held constant. The change in the level of rectification as a function of the length of the device appears to be a result of phonon confinement because at lengths greater than about 10 nm the level of rectification remained at approximately 0.33 (a doubling of thermal conductivity). At smaller device lengths a change in rectification is occurring because increased length allows for additional longer wavelength phonon modes to contribute to the thermal transport. In 2009 Hu et al. also performed molecular dynamics simulations of graphene nanoribbons of single and double layer triangular and trapezoidal geometry [49, 55]. They also included verification simulations of rectangular geometries and asymmetric void geometries. Their results showed that the rectification was maximized in the single perfect triangle simulations. The rectification effect and thermal conductivity was reduced at short device lengths in the single layer triangle with the addition of a roughness at the boundary which resulted in diffuse phonon scattering at the boundary. At longer device lengths the rectification of the single perfect interface was reduced drastically while the single rough triangle remained essentially constant. The conductivity of the double layer triangle was greater in both directions, which resulted in the reduced rectification even though the difference in the conductivities remained the same as in the single layer case because of how the level of rectification is defined in equation 4. Rectification still occurred in the trapezoidal case, but was much lower than that of either of the triangular cases due to a reduced level of asymmetry in the system. No rectification was observed in any of the symmetric geometries. In these systems the rectifying effect is a result of the constant change in the phonon spectra along the length of the ribbon in the triangular and the trapezoidal cases and an abrupt change in the phonon spectra in the rectangular ribbons. An interesting point to note about the rectification in the graphene nanoribbons is that the rectification is not necessarily limited by the length of the ribbon as with interfaces which will be discussed in §2.2.3 and §2.2.4.

In 2007 Wu and Li performed molecular dynamics simulations of carbon nanotube intramolecular junctions where two nanotubes of differing diameters were joined at an interface in the center of the system [56]. In these systems there were defects present at the interface between the two nanotubes. By looking at the power spectra on each side of the interface when the temperature gradient was in both directions the authors noticed a change in the overlap of the power spectra. This result is similar to what has been reported in theoretical studies of 1D non-linear lattices which will be discussed in §2.2.4. By looking at the overlap of the phonon spectra in the work by Wu and Li we see that the largest changes occur in the optical phonon modes with low wave vector. Shiomi and Maruyama showed that optical modes with low wave vector were shown to contribute significantly to non-Fourier heat conduction when the length of the tubes was finite [57]. Shiomi and Maruyama also presented the phonon dispersion for the carbon nanotube superlattice structures which showed the phonon group velocity for the optical branches had comparable group velocities to the acoustic branches. Wu and Li showed that the phonons in the frequency range of 400 to 1000 cm^{-1} (optical phonons) had a much greater contribution to transport and thermal rectification because they had relatively large group velocities and a directional dependence. The phonons above that frequency range had much smaller group velocities reducing their contribution to transport and the phonons below that frequency range did not exhibit a directional dependence. The lower frequency phonons are not changed in this system because of the relative small size of the connecting region that was used in the simulation when compared to their wavelength. With this knowledge of how the interface results in rectification the authors performed additional simulations to optimize the rectifying effect. Through their optimization simulations they found that when the tube radius increases to a sufficiently large value the vibrational density of states approaches that of a graphene sheet (curvature effects are becoming less obvious) therefore when the diameter is large in both of the tubes there is little difference between the phonon spectra resulting in little rectification. At small tube diameters the thermal conductivity becomes large and the relative difference between the two can be large, but when normalized by them the percent change becomes smaller. The authors in this study found an optimized rectification effect when the tubes had a diameter ratio of 2 with non-axial alignment. They also investigated the effect of defects at the interface and found the maximum rectification occurred when a minimum of defects existed at the interface (can not have 0 defects because of the change in diameter). Since the authors only found a difference in conductivity of around 20% between the two directions, or $\varepsilon = 0.1$, they performed simulations where the tubes were strained with tensile and torsional stresses. They found that torsional loads had no impact on the rectifying effect while tensile loads resulted in an enhancement of the thermal rectification up to approximately 35% or $\varepsilon = 0.15$. The tensile stress results in an elongation of the tube, which reduces the potential energy between atoms and therefore a reduced thermal conductivity in both directions. Again, based on how the level of rectification is defined, with the same difference in directional thermal conductivity, a greater level of rectification will result in a system with lower directional thermal conductivities. In all the cases reported the system exhibited greater transport in the direction of larger to smaller tube diameter.

In 2008 Wu and Li also performed molecular dynamics simulations of deformed carbon nanohorns which are carbon nanotubes which have a varying diameter along the length of the tube [46]. Carbon nanohorns or nanocones are formed by taking a graphene sheet, cutting a slice of a specified angle out of it and connecting the ends of the removed section which will form a cone or a horn. This work by Wu and Li investigated the angle of the nanohorn, the tensile load applied to the nanohorn along the axis of transport and the temperature gradient applied to the nanohorn. In all cases the nanohorn exhibited a preferred direction of transport in the direction of decreasing radius (and also mass) which was similar to what has been seen in other nanotube and graphene studies [56, 47, 49, 55]. Under no tensile loading the rectification was greater with a larger horn angle when the length of the horns were roughly equivalent. One device was simulated with the larger angle, but only half the length which resulted in a lower level of rectification. Under tensile loading the rectification effect is initially increased due to the decreased force between atoms and the resulting decrease in thermal conductivity, but once the tensile loading reaches a critical value which is dependent on the angle and the length of the horn the effect will be reduced. This change in rectification can be explained in a similar way as in ref. [56] where it was shown that a difference in phonon spectra is the mechanism for thermal rectification. In this work the end of the horn with a large radius resembles a graphene sheet while the end of the horn with a small radius resembles a small carbon nanotube in which the phonon spectra of the two ends becomes very different. As the tensile load is increased the thermal conductivity is decreased resulting in an increase in rectifying effect. If the tensile stress is increased the difference in phonon spectra begins to be reduced as the angle of the horn is reduced resulting in a reduced rectifying effect. Wu and Li also showed that the rectifying effect was also increased with increasing temperature gradient applied. This is also explained by the difference in phonon spectra at the two ends because of the temperature dependence of the phonon spectra. When the applied temperature gradient becomes very large (on the order of the system average temperature) a phenomenon called negative differential thermal resistance is observed in which the resulting net heat flux is reduced [58]. This effect results in a reduced thermal rectifying effect. This effect is extremely interesting because it is essential for thermal transistors which are mentioned, but not discussed here [59]. The maximum thermal rectification reported by Wu and Li in the work involving nanohorns was approximately 0.55 with the largest horn angle at a high temperature gradient ($\Delta T = 0.8T_0$) and under no tensile loading.

In 2008 Yang et al. performed molecular dynamics simulations of carbon nanocones to investigate their thermally rectifying effects as a function of the applied temperature gradient, average system temperature and the length of the nanocone [47]. In this work a fixed cone angle was used which was greater than that of ref. [46]. The rectifying effect was enhanced with increasing temperature gradient with a maximum rectification of about 0.44 under a temperature gradient normalized by the average system temperature of 0.7 at 300K. This work did not report results with temperature gradients greater than 0.8; therefore no negative differential thermal resistance was reported. The rectifying effect was shown to decrease with increasing temperature gradient due to the author's definition of the level of rectification. While the difference in resulting heat flux was effectively the same for the temperature range studied, the heat flux of each direction increased with increasing temperature which resulted in a reduction of the rectifying effect. The rectifying effect nor the heat flux changed greatly with varying cone length. The authors attributed this to ballistic energy transport in the system in which the transport is not dependent upon length. Since transport is ballistic in the nanocone and nanohorn - unlike systems which contain interfaces - the nanocone and nanohorn show the desirable characteristics of thermal rectifiers since longer device lengths do not eliminate the rectifying effect.

In 2009 Noya et al. performed heat pulse molecular dynamics simulations of Y junction carbon nanotubes [60]. These Y junction nanotubes are single nanotubes where one end has a specific diameter and at the other end has two nanotubes which have a smaller diameter. These Y junction nanotubes have already shown electrical current rectification both experimentally [61, 62] and theoretically [63, 64, 65]. In the heat pulse simulations atoms near the end of one side of the nanotube is heated to 800 K during a 0.1 ps followed by 0.8 ps of free equilibration of the system and finished with a 0.1 ps quenching of the heated atoms. The heat pulse is then monitored throughout the system for 4 ps in addition. Their results showed asymmetric thermal transport that was dependent on the lattice structure of the nanotubes. No rectification was observed in the (10,10) to (5,5)X(5,5) system, but transport was preferred from the single tube (stem) to the two tubes (branches) in the (14,0) to (7,0)X(7,0).

In 2010 Alaghemandi et al. performed molecular dynamics simulations of asymmetric systems composed of carbon nanotubes connected by a single graphene layer normal to the axial direction of the carbon nanotubes [66]. The asymmetry of the system came from having different numbers of carbon nanotubes on either side of the graphene layer. Their results showed that the 1D systems could not be mapped to larger, more realistic systems. Their results also showed a preferred direction of transport from the higher mass side to the lower mass side. Similarly in 2010 Varshney et al. performed molecular dynamics simulations of pillared-graphene-CNT nanostructures and mention the possibility of using structures of this architecture as improved thermally rectifying devices [67].

Another asymmetric nanostructure that has shown thermal rectification is a CNT with geometric variations of doped nitrogen introduced by Chein et al. [68]. They showed thermal rectification from molecular dynamics simulations of CNTs with an asymmetric distribution of doped nitrogen along the axial direction of the tube. Rectification only occurred when both a geometric and mass distribution asymmetry existed within the system. The preferred direction of transport in these systems was in the direction of increasing atomic density of nitrogen and increasing geometric size of the doped nitrogen.

2.2.3. *Nanostructured Interfaces*

Thermal transport at solid-solid interfaces has been a topic of great interest because of the necessary understanding in designing smaller and smaller electronics devices because of the increasing effect of the interfaces [69, 70]. In 1959 Little developed the first model for predicting the thermal transport at a solid-solid interface at low temperatures called the Acoustic Mismatch Model (AMM) [71]. The AMM is only valid for perfect interfaces at temperatures below 7 K and the transmission is based on the acoustic impedance of the two materials. In 1989 Swartz and Pohl extended the temperature range for which transport between two dissimilar solids could be predicted with the Diffuse Mismatch Model (DMM) [72]. The DMM transmission is based on the ratio of the materials' density of states and the phonon group velocity. A special case of the DMM known as the Phonon Radiation Limit (PRL) is the case in which the transmission probability is unity resulting in perfect transmission at the interface. The PRL is assumed to be the maximum boundary conductance at an interface when inelastic scattering is not present. Since then a few additional models that take into account inelastic scattering have been developed and will be discussed later.

Phonon transport at nanoscale interfaces in thin films or nanowires has also become interesting for thermal rectification. Materials that have different phonon spectra can exhibit phonon transmission in one direction and reflection in the opposite due to the availability of phonon frequencies in the materials. This effect has also been seen in one-dimensional systems and asymmetric carbon nanotubes and graphene sheets as well (see §2.2.4). Although a rectifying effect has been seen at interfaces in bulk systems where the temperature dependence of thermal conductivity of the two materials is different, the spectral effect is different. In the works reported here the researchers minimized the impact of rectification due to different temperature dependencies of thermal conductivity by using small temperature gradients in comparison to the average system temperature and also using materials with similar temperature dependent thermal conductivities in the temperature ranges investigated.

In 2008 Roberts and Walker performed molecular dynamics simulations of planar, diffuse and asymmetric interfaces between two dissimilar materials and showed the possibility of thermal rectification [73]. Their results showed a nearly 30% difference in transport, or $\varepsilon = 0.13$, which favored the argon to krypton direction over the krypton to argon direction at 25 K in the perfect planar interface system. The rough or diffuse interfaces resulted in a reduced rectification effect as a result of increased inelastic scattering at the interface. The asymmetric boundaries in this work also resulted in a reduction of the rectifying effect as a result of inelastic scattering. The authors still believe the asymmetric boundaries can enhance the rectifying effect, but in the simulations the finite size of the asymmetric shape resulted in a roughness similar to the rough or diffuse interfaces. In 2010 Roberts and Walker continued their investigation of thermal rectification at interfaces, which involved simulations of longer devices and at a range of temperatures [74]. The authors found that inelastic scattering at the interface was important for thermal rectification. At low temperatures and perfectly planar interfaces no inelastic scattering and a small level of rectification was shown with a preferred direction of transport being from the lower frequency material to the higher frequency material because the limited contribution of phonon modes in the higher frequency material. At higher temperatures or slightly diffuse interfaces some inelastic scattering occurred allowing additional modes in the higher frequency material to contribute to the overall transport and results in higher levels of rectification with the preferred direction of transport now being from the higher frequency material to the lower frequency material. At even higher temperatures or very diffuse interfaces no rectification was observed because of high levels of inelastic scattering. Their results showed that inelastic scattering can help to produce thermal rectification though high levels will eliminate the rectifying effect.

In thermal transport at interfaces, inelastic scattering allows for thermal rectification by allowing phonons in the higher frequency material at frequencies that are not present in the lower frequency material by scattering them into multiple lower frequency phonons, allowing them to transmit. Inelastic scattering at interfaces is shown to increase with temperature and imperfections (ie. diffused atoms) at interfaces. The thermal interface conductance/resistance models mentioned previously (AMM and DMM) do not consider inelastic scattering, but they assume no anharmonic interactions and only consider the lower frequency material in their formulation. These assumptions eliminate the possibility of predicting thermal rectification in solid-solid interfaces between dissimilar materials. In 2008 Hopkins and Norris developed the Joint Frequency Diffuse Mismatch Model (JFDMM) which partially considered the effects of inelastic scattering by assuming that the interface possesses joint frequency modes which are weighted fractions of each of the two materials creating the interface which would allow frequencies above the maximum frequency in the lower frequency material to be transmitted into that material. Similar to the PRL, the JFDMM has a special case in which all phonons transmit which is called the Inelastic Phonon Radiation Limit (IPRL) in which all phonons regardless of their frequency transmit at the interface which is the upper limit for thermal boundary conductance possible. Though these models have been shown to predict well known interfaces somewhat accurately, they are not able to predict thermal rectification due to the assumption of no anharmonic or non-linear interaction [75]. To develop a better understanding of the rectifying effect observed in the non-equilibrium molecular dynamics simulations Roberts and Walker performed phonon wave-packet simulations [76] of perfect planar and diffuse interfaces in which a single frequency wave-packet is formed by displacing that atoms at one end of the system and allowing it to propagate through the device, interact with the interface and propagate to either end of the device while observing the wave-packet [77]. Roberts and Walker observed asymmetric phonon transmission probabilities in the argon and krypton system and observed increased inelastic scattering at the interface with an increase in the diffusion region. From the transmission probabilities obtained from the wave-packet simulations the conductance was then calculated and a temperature and interface roughness dependence was observed for thermal rectification.

In 2008 Hu et al. performed molecular dynamics simulations of silicon-amorphous polyethylene interfaces and observed thermal rectification due to a mismatch of phonon density of states [78]. They found that a mismatch of phonon vibrational properties of the materials forming the interface resulted in asymmetric phonon transport across the interface. This mismatch resulted in a directional dependence on the thermal boundary resistance. In all of their simulations they found greater transport in the direction of the amorphous polyethylene to silicon with a maximum difference occurring at the largest applied heat flux giving a level of rectification of 0.18. The rectifying effect is increased with heat flux in this case because the increased heat flux results in a greater difference between the vibrational properties of the two materials in the reverse direction while maintaining similar vibrational properties in the forward direction. In 2009 Hu et al. performed more molecular dynamics simulations of water-functionalized silica interfaces and found a rectifying effect of 0.21 [79]. This work is reported here because of the level of rectification and the mechanism of rectification, but is outside the scope of this paper as this is a liquid-solid interface.

2.2.4. Anharmonic/Nonlinear Lattices in 1D Chains

In 2002 Terraneo et al. presented a model for a thermal rectifier using a nonlinear 1D lattice connecting two thermal reservoirs at different temperatures [4]. The lattice is a chain of N particles with a harmonic coupling and a Morse on-site potential. The Morse potential is a highly anharmonic soft potential in which the the frequency decreases drastically with increasing amplitude. Using idealized materials their theoretical study showed that they could control the heat flow from insulator to a good conductor just by varying the Morse potential constant from 0.5 to 1.2. By taking this lattice and inserting it between two weakly anharmonic regions a thermal rectifier can be devised. Terraneo et al. showed that a doubling of conductivity could be achieved from the parameters investigated in their theoretical study of the thermal rectifier. In 2005 Casati performed a similar study where he found that if the separation of the two phonon bands was larger than twice the harmonic constant in the middle region there would be no transport [80].

In 2004 Li et al. performed a theoretical study similar to that of Terreano et al. except in their work they used two nonlinear segments coupled together by a constant harmonic spring using the Frenkel-Kontorova (FK) model [81]. This work again involved two idealized materials in series which were optimized to produce large levels of rectification by having phonon spectra overlap in one direction of heat current and no phonon spectra overlap in the opposite. In their system they choose material A so that it would only exhibit a high frequency spectra at low temperatures and a broad spectra high temperatures while material B had only a low frequency spectra at low temperatures and a broader, but still low frequency spectra at high temperatures. Their results showed a conduction direction that was 100 times as large as the opposite insulating direction. When a temperature gradient was applied from material A to material B good conducting behavior was observed because of the large phonon spectra overlap. When the gradient was reversed (material B to material A) there was almost no phonon spectra overlap because of the narrow range and high frequency spectra in material A which resulted in insulating behavior. For a thermal rectifier to be realized experimentally using this mechanism, materials must be selected that possess similar properties though it is unlikely to find materials which would result in levels of rectification near that of the idealized system. In 2005 Casati proposed that a prototype of this device could be a disordered harmonic lattice. In 2005 Hu and Yang modified the design of Li et al. [81] with the FK model and showed a change in conductivity of 10000 times [82]. This modification was that the two FK sections had the same interparticle potential, but different external potentials. Their results also showed a reduced rectifying effect with increasing device length.

In 2005 Segal and Nitzan presented an analytical study with a simplified model from that of Terraneo et al. which showed that a nonlinearity and a structural asymmetry results in thermal rectification [83]. Their model was a generalized spin-boson model where the nonlinear lattice is coupled to two different thermal baths at different temperatures with different coupling strengths. An additional model presented by Segal and Nitzan that implied nonseperable coupling also resulted in thermal rectification. The authors stated that asymmetric coupling at the thermal baths could be originated from chemical bonding, by using reservoirs with different Debye temperatures or from different spatial organization of vibrational states if one were to design a thermal rectifier for an experiment. Segal and Nitzan extended this work by highlighting the features of these two models and presented results of rectification in a system of identical anharmonic oscillators connecting asymmetrically two heat baths at different temperatures using classical Langevin dynamics and internal asymmetry of anharmonic molecular models [84]. In the original model (the generalized spin-boson model where the nonlinear lattice is coupled to two different thermal baths at different temperatures with different coupling strengths) the authors reported that (a) in the deep quantum limit rectification decreases exponentially with frequency and in the inverse temperatures, (b) in the highly classical limit the asymmetry increases linearly with the square of the temperature difference and frequency, (c) in the intermediate regime rectification decreases with frequency and (d) the current is larger when the bridge links more strongly to the colder reservoir than when it links more strongly o the hotter one. The maximum rectification observed with this model was 0.05. The major difference observed in the second model presented (nonseperable coupling) was that strong dependence on the coupling strength was observed. The maximum rectification observed with this model was 0.27. The study of the anharmonic systems showed that rectification through asymmetric chains was a general property and the level of rectification increased with an increase in anharmonicity. The rectification was also shown to increase with system length in the range investigated in this study. The maximum rectification observed with this model was 0.04. In the internal asymmetry of anharmonic molecular models work showed rectification levels up to nearly 0.15. In all of this work rectification was observed in asymmetric systems although the conductivity in either direction remained low which is not ideal for most applications that could be exploited with a thermal rectifier.

In 2006 Peyrard proposed a slightly different model for a thermal rectifier where he proposed a system composed of two regions which exhibited different temperature dependent thermal conductivities (like the bulk mechanism presented in §2.1.4) [85]. To create a region with this temperature dependence Peyrard use a method similar to Terraneo et al. [4] for a composite material of alternating layers which exhibited a low thermal conductivity at low temperature and a high thermal conductivity at high temperature. The changing of thermal conductivity of the composite material was due to the overlap (high thermal conductivity) or separation (low thermal conductivity) of the phonon spectra of the different layers.

In 2006 Hu et al. performed a theoretical study of a 1D lattice using the FK model and found that the direction of greater transport in a thermal rectifier composed of two FK segments was dependent on the properties of the interface and the system size [86]. As the harmonic spring constant coupling between the two FK chains becomes larger, their results agree with those from Li et al. [81], but when it is small the phonon band overlap theory no longer applies due to a mixing of phonon bands because of interactions between phonons of the two sections induced by the nonlinearity in the chain. The role of the harmonic spring constant here is similar to what would be observed with an impurity in the chain, which could drastically impact the level and the direction of rectification. This is an interesting finding which is similar to a problem at the bulk level when the surface characteristics of two material samples forming an interface varied [21]. Hu et al. also showed that length plays a role in the rectification level and direction as well. As the length of the system increases, the impact of the harmonic spring constant (treated as an impurity) becomes less significant and the results are what is expected from the phonon band overlap theory. In weakly coupled systems the results should agree with that predicted by phonon band overlap theory, but when the segments are well coupled and the device is sufficiently long, phonon band mixing will become important and opposite to the prediction from phonon band overlap theory.

In 2007 Lan et al. performed a theoretical study of thermal rectification in a 1D lattice composed of two segments, one an FK model and the other a Fermi-Pasta-Ulam (FPU) model [75]. Results showed that a difference in transport of around 2000 times was observed with the preferred direction being the FK to FPU direction.

In 2008 Zeng and Wang investigated the influence of phonon frequency, asymmetry and nonlinear interactions relating to thermal rectification [87]. They studied the impacts of each with a 1D chain of atoms. Their results showed a difference in the transmission probability in one direction and not the opposite when comparing a constant mass system to one in which the left and right boundaries differed considerably in mass. Additionally the authors investigate asymmetric thermal transport at an interface. This is similar to what was discussed earlier in the nanostructured interface section, but is located here because of the dimensionality of the system. The authors argue that nonlinear interactions at the interface allow higher frequency phonons (phonons with frequency higher than the maximum frequency of the lower frequency material) to contribute to transport and without this contribution no rectification could occur. These nonlinear interactions result in inelastic scattering which, as we discussed previously, has a contributory effect on thermal transport at interfaces due to the contribution of additional phonon frequencies.

In 2008 Li et al. performed simulations of an asymmetric lattice composed of one segment of an FK nonlinear lattice and one segment of a harmonic lattice of equal lengths weakly coupled at the center without a constant thermal bias [58]. Instead of a constant thermal bias the bath temperatures are varied over time. By varying the bath temperatures a ratcheting effect is shown to occur which can reverse the heat flux, cause heat to flow from cold to hot against an average thermal bias and turn a regime with a negative differential thermal resistance into one with a positive differential thermal resistance. The ratcheting system was able to produce a non-uniform temperature distribution with no net flux applied which is a self biasing device. The device did not exhibit this when constant bath temperatures were used.

In 2009 Hopkins and Serrano performed a non-equilibrium Green's function study of asymmetric harmonic chains [88]. The asymmetry in this work comes from a doubling of the mass (doubling of the number of silicon atoms) at the right bath of the system which results in a different phonon distribution from the left bath. In small systems no rectification and no difference in the phonon spectra is observed from the mass-loading of one of the baths. By adding a impurity in a location other than the center of the lattice rectification can be produced. This occurs by making the lattice inhomogeneous and acts to manipulate the Fabry-Perot phonon oscillations. The rectification here requires both an asymmetry at the contacts or baths as well as the impurity asymmetry in the lattice. The maximum rectification reported was about 0.29 in a device that was only 10 atoms long. Rectification in a system like this would likely not be observed in longer devices because the effects of the asymmetric impurity would become negligible (similar to the effect seen in interface rectification).

In 2010 Pereira performed an analytical study of a quantum mass graded system [89]. His results showed that thermal rectification occurs in an inhomogeneous quantum model if a phonon scattering mechanism or effective anharmonicity is present. This work does not exclude the rectifying effect that is observed in real anharmonic potentials through numerical studies, but do state that these graded mass systems could be constructed and could be experimentally reliable.

These 1D systems have shown incredible rectification properties in simulations, but realizing these devices experimentally will be challenging and will result in a greatly decreased rectifying effect from what is seen from simulations. Fabrication of a 1D chain with materials that exhibit the exact properties is not possible and even if it were, the systems would need to be scaled up, which has been shown to decrease the rectification in many of the studies. This work is still important at this time because it allows us to peak at the possibilities that may become available down the road as we improve our ability to manipulate and synthesize materials at the atomic level. My proposal for the researchers working in this area is to continue to study the idealized systems, but also follow the lead of Hopkins and Serrano [88] where they used silicon as the material composing the lattice and used impurities and mass-loading to construct a 1D thermal rectifier. Dual path studies of this nature will inspire researchers to think and study the possibilities and push the limits of what we can do while the grounded studies of current capabilities allows us to improve and possible discover effects that could have large impacts in the near future.

2.2.5. Quantum Thermal Systems

Models for thermal rectifiers as well as thermal circuits which exhibit rectification have also been studied. In this section we will discuss some of the quantum thermal rectifiers and systems like switches that have recently been explored. These rectifiers are different from what we have discussed to this point. Some of these devices require external control (similar to gate control) for operation which gives rise to thermal circuits and other devices like that.

In 2006 Eckmann and Mejia-Monasterio [90] showed thermal rectification in a billiardlike system where two differently sized disks in a left and right cell of a device are used to drive the particles into collisions at the junction between the two cells. In this system the transport in the preferred direction was shown to be up to 3 times that of the lower transport direction ($\varepsilon = 0.5$).

In 2008 Segal discussed the control of energy flow between electronic conductors in a single mode heat rectifier [91]. In this system, which is similar to the 1D chain systems, electron transfer is considered where one of the metals is required to have a nonlinear dispersion for thermal rectification to result. The system was designed to model energy transfer through vibrating link and radiative heat transfer. The rectifying effect in this system is increased when the density of states varies strongly with energy or the system-bath couplings are energy dependent. This effect is inevitable in energy transport between metals and dielectric surfaces due to the anharmonic interactions, but likely small due to electron tunneling at high voltages or thermal gradients. In 2009 Wu and Segal continued this study by looking at two specific cases [92]. These cases were one where the baths were dissimilar and one where the baths were identical and they were coupled by unequal strengths and an anharmonic lattice. In this work they were able to achieve a sufficient condition for thermal rectification in hybrid structures in an open quantum system. Their conditions are that the baths must be dissimilar or their statics must differ from the coupling of the two baths.

Quantum dots have also been given some interest as thermal rectifiers. In 2008 an experimental study by Scheibner et al. showed thermally rectifying behavior in quantum dots when high in-plane magnetic fields are present as a result of the presence of a high orbital momentum state in the dot [93]. Their analysis showed a stronger coupling to the drain than the source when not in the ground state. A theoretical study by Chen et al. was in agreement with Scheibner et al. when they showed the thermally rectifying effect was dependent on the coupling between the quantum dot and the electrode [94]. In 2009 Ruokola et al. investigated thermal rectification in nonlinear quantum thermal circuits where the coupling between the baths and the nonlinear resonator circuit were mutual inductances [95]. Their results showed levels of rectification up to 0.11. In there system they found a strong dependence on the bath coupling as well as the temperature range in which the device operated. The operating temperature could effect the direction of preferred transport in the device. In a similar study Ojanen also found rectification in a quantum system where the selection of bath coupling and the properties of the central quantum system were key to the result and level of rectification [96]. Zhang et al. also showed a change in the preferred direction of transport in a quantum system, but their dependence was on on the operating temperature alone [97]. The sign of the level of rectification in their study was dependent on the magnetic field in the chain, temperature and the level of anisotropy in the spin chain.

In each of these works there have been mentions of thermal devices, but the design of such a device has never really been investigated for an actual application. In 2006 Li et al. again described the effect of the negative differential thermal resistance and how it could be used in creating a thermal transistor [98, 99]. This thermal transistor is a three terminal device which consists of a source, a drain and a gate that is temperature controlled. At low gate temperatures the switch is off resulting in no heat current because of the insulating properties, but at higher gate temperatures the switch acts like a conductor and is therefore on which allows heat current to flow. This switch also has a semi-on region where the heat current is about half that of the on state. The temperature dependence of the gate region uses the same effect that has been discussed in the previous section (§2.2.4).

The reader may notice the dearth of experimental evidence of nanostructured systems. Chang et al. [5] is essentially the only report that makes thermal rectification claims. This deficit of evidence is not an indication of the lack of rectification as much as it is an underscore on the uncertainty in experimental measurements, the uncertainty in the theoretical mechanisms and immaturity of the field. Researchers are only now starting to think about what devices can be fabricated, what quantities can be measured and whether the theoretical

Table 1: Table of reported rectification using equation 4 from experimental studies

Investigators	System	Mechanism	ε
Starr[1]	Cu/Cu_2O	electronic	0.39
Barzelay[15]	Al/SS	thermal warping	0.67
Rogers[17]	Al/SS	thermal potential barrier	0.1
Powell et al.[19]	Al/SS	thermal warping	0
Clausing[20]	SS/Al	thermal strain	0.2
Lewis and Perkins[21]	Al/SS	thermal warping	0.41
O'Callaghan et al.[27]	varied	thermal warping	0.13
Stevenson et al.[23]	varied	thermal warping	0.21
Chang et al.[5]	CNT and BNNT	non-uniform mass loading	0.034
Kobayashi et al.[38]	varied	bulk thermal conductivity	0.18

Table 2: Table of reported rectification using equation 4 from theoretical studies

Investigators	System	Mechanism	ε
Terraneo et al.[4]	1D chain	nonlinear lattice	0.33
Li et al.[81]	1D chain	nonlinear lattice	0.98
Hu et al.[82]	1D chain	nonlinear lattice	1.0
Lan et al.[75]	1D chain	nonlinear lattice	1.0
Hopkins and Serrano[88]	1D chain	asymmetric mass loading and defect	0.29
Yang et al.[48]	graphene	asymmetric ribbons	0.6
Hu et al.[49, 55]	graphene	asymmetric ribbons	0.47
Alaghemandi et al.[42, 44]	CNT	non-uniform mass loading	0.17
Hu et al.[79]	water/silica	interface transmission	0.21
Roberts and Walker [74]	argon/krypton	interface transmission	0.13
Wu and Li[46]	CNH	asymmetric CNT	0.55
Yang et al.[47]	CNC	asymmetric CNT	0.46
Wu and Li[56]	CNT	CNT interface	0.39

systems can be realized in the lab. In fact, experimental study of thermal rectification is said to be ongoing in quite a few research labs.

3. Summary of Thermal Rectification Measurements and Predictions

In this section we summarize the results from all the reports of each of the mechanisms discussed previously and use them to propose the future direction of thermal rectification research that should get us to improved levels of rectification and a possible future with available rectifying materials. Tables 1 and 2 show the levels of rectification using equation 4 reported from both experimental and theoretical studies, respectively.

Based on the previous sections and Tables 1 and 2 it is clear that thermal rectification can occur and the difference in transport in the two directions can be quite different. One important aspect with many of the applications for thermal rectifiers would be that they exhibit good conducting properties in the greater transport direction. Unfortunately in many of these reports the mechanism that causes thermal rectification does so by reducing the transport (in one direction more than the other), which can make it difficult to maintain high levels of conduction. In some of these studies, specifically the work with the asymmetric CNTs and graphene [5, 56, 47, 46, 49, 55, 42, 44, 48], the transport appears to be increased in one direction and decreased in the opposite which makes these ideal materials for thermal rectification applications.

4. Conclusions

This paper explored the past, current and future of thermal rectification in solid materials. Thermal rectification exists at the macro and micro scales and a better understanding is being developed in both, which will eventually lead to efficient thermal rectifiers. Currently the many mechanisms that are known to exist in solid systems have shown only small levels of rectification and are not predictable, but theoretical and analytical models have predicted large rectification possible and are becoming more and more accurate. Experimental validation and realization of some of these mechanisms is crucial to the future applications involving thermal rectifiers even if only a fraction of the predicted levels of rectification are achieved.

Nomenclature

A	area (m^2)	g_C	electron DOS	q	heat rate (W)
C	heat capacity (J/K)	h	convect. coeff. (W/m^2-K)	R	therm. res. (K/W)
D_o	deformation pot. (J)	$\hbar$	Planck's constant	Ra	Rayleigh number
E	radiation (W/m^2)	N	occupation number	r	radius (m)
F	Fermi energy (J)	Nu	Nusselt number	T	temperature (K)
G	rate of energy transfer (W)	n	power law exponent		
g	gravitational accel. (m/s^2)	Pr	Prandtl number		

Greek Letters

α	thermal diffusivity (m^2/s)	ε	level of rectification	ϕ	work function (J)
β	thermal exp. coeff. (m^3/K)		emissivity	ρ	therm. res. ratio
Γ	load/mech. properties coeff.	κ	thermal cond. (W/m-K)		mass density (kg/m^3)
γ	effective rectification	λ	wavelength (m)	τ	scattering rate (1/s)
Δ	normalized temp. diff.	ν	fluid viscosity (m^2/s)	ω	frequency (Hz)

Subscripts

$_{A,B,1,2}$	material type	$_e$	electron	o	origin
$_b$	black body		emitted	p	phonon
$_c$	cold	$_{e-p}$	electron-phonon	$_{pt}$	phonon trans.
	contact	$_h$	hot	$_r$	reflected
$_E$	energy	$_l$	left		right

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