Thermal rectification mechanisms including noncontinuum effects

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1 Abstract

Thermal rectification is a physical phenomenon where the resistance to heat flow is dependent on the sign of the temperature difference across a solid. This effect could be a useful phenomena to many industries if it could be controlled and optimized. However, experimental evidence shows that thermal rectification is dependent on a large number of competing factors. In addition, theoretical models that allow thermal rectification do not match measurements well largely because of the complexity of the effect and the immaturity of the models. Nevertheless, several mechanisms (geometric, electronic, electron-phonon scattering and anharmonic lattice vibrations) have been identified as possible means to control interface conductance at interfaces. Currently no evidence exists that suggests that the difference in conductance can reach one order of magnitude, which is an arbitrary limit required to deem the effect useful for engineered systems.

2 Nomenclature

A	thermionic constant
C	heat capacity ($\mathrm{J/m^3K}$)
D_o	optical deformation potential (eV)
E	electron energy (eV)
F	Fermi level (eV)
G	coupling rate ($\mathrm{W/m^3}$)
h	thermal conductance ($\mathrm{W/m^2K}$)
J	electron current density ($\mathrm{A/cm^2}$)
k	thermal conductivity ($\mathrm{W/m^2K}$)
k_b	Boltzmann's constant ($\sim 1.38 \times 10^{-23}$ J/K)
m^*	electron effective mass
N	phonon occupation number
p	electron momentum
q''	heat flux ($\mathrm{W/m^2}$)
R	thermal resistance (W/K)
r	radius (m)
S	transition rate (1/s)
T	temperature (K)
U	potential (eV)
β	phonon wavevector (1/m)
ε	rectification effectiveness
ϕ	work function (eV)
ξ	electron transmission
τ	scattering rate
ω	phonon frequency

3 Introduction

Observation of strong thermal rectification in solids has been elusive. However, applications for a material that has different thermal properties in opposite directions would be widespread. For example, one might envision a cooking pot that allows heat to flow from the stove top to the contents of the pot easily but restricts heat flow from the contents to a person's hand. In microelectronics, we can imagine an interface that separates logic circuits from power circuits on an integrated chip (using SOI technology, for example). The thermally rectifying interface would allow heat from the logic side to flow toward the power side, which is more tolerant of excessive heat, but heat would not flow from the power side to the logic side easily.

Although the implications for such a material would be profound, investigation of this effect has been limited in the past perhaps because the problem has been anecdotally and unfairly characterized as Maxwell's demon. In Maxwell's thought experiment, a fictitious event to regulate the transfer of energy was devised so that heat preferentially moved only in one direction. As a result, heat moved from a cold reservoir to a warm reservoir, which violates the second law of thermodynamics for macroscopic systems (Landauer, 1961). Thermal rectification, however, does not violate the second law. For example, consider the fact that the heat flow across a gas-filled gap heated from below is much greater than the heat flow across the same gap heated from above at the same temperature difference. In this scenario, the buoyancy induced convection breaks the symmetry of the problem to allow a different effective conductance in the direction of gravity compared to the direction opposite gravity. In other words, physical grounds for dismissal of thermal rectification based on second law arguments are falla-

cious (Van den Broek et al., 2005). However, the question concerning thermal rectification in a practical device remains.

Esoteric discussions of theoretical curiosities aside, practical pursuit of a thermal rectifier usually consists of creating an asymmetry at a material interface. A junction can conceivably provide different transport properties based on which side the transport originates. Study of this phenomenon is primarily concentrated in the aerospace community when high heating loads of aerospace structures required precise understanding and prediction of contact resistance between materials.[1] For purposes of the present discussion, the mechanisms that may produce rectification can be classified into two groups. Electronic effects are those that rely on the behavior of charge carriers to explain the dynamics of thermal energy. These effects are exclusive to metals because the carrier density of non-metals is far too small to affect thermal transport. Geometric effects rely on the particular conformation of an interface contact to provide varying conduction, convection and radiation loads across a junction. The geometric effects are further classified in the literature into macroscale and microscale effects. This characterization is largely semantic but indicates the different hypotheses used to explain observed rectification. The macroscopic term was used to describe large scale influences such as warping; the microscale term was used to describe smaller scale effects such as the actual contact area resulting from surface roughness. Realize that despite the term used to describe the phenomenon, all effects are continuum in nature. In other words, the hypotheses are based on equilibrium thermodynamics.

The present effort attempts to explore the possibility of thermal rectification in solids in the context of non-continuum thermal transport. Non-continuum effects offer new physical phenomena that may provide the mechanism to break the symmetry normally enjoyed by bulk or continuum heat transfer models. For example, lattice vibrations modeled as waves can reflect at nanoscale structures differently depending on the geometric configuration of the structure. Waves from different directions could be reflected, then, at different rates providing a rectification behavior. In addition, transport across metal-insulator interfaces are governed not only by phonon transport across the interface but also by electron-phonon scattering in the metal. Quantum mechanics gives us a mechanism to prefer energy loss over energy gain by electrons, which may also provide a level of rectification.

4 Historical evidence

Several attempts have been made to measure thermal rectification, but irrefutable success has been scarce. Any claim of observed thermal rectification always involves an interface between materials—usually, but not necessarily, of different materials. Perhaps the first record of thermal rectification is from Starr (1935) who was investigating the electrical rectification properties of a copper/cuprous oxide system. In addition to the electrical rectification behavior, the sample was tested for thermal conductance, and the results indicated that thermal rectification occurred as well. This finding was explained using an argument equivalent to the Wiedeman-Franz law. Electronic current flows more readily in one direction than in the other due to an energy barrier at the material interface. Now if electrons can carry thermal current, then a higher thermal conductance would appear in the direction of larger electrical conductance. This argument is well understood today, but is likely only satisfactory for metals. Cuprous oxide is a semiconductor, so phonons are the primary thermal carrier. As a result, the electronic hypothesis may not completely explain the thermal rectification behavior. In fact, most devices that demonstrate strong electrical rectification are made of semiconductors. Therefore, strong thermal rectification using this electronic effect is probably unlikely, although some rectification is possible. Starr also suggested that the temperature at the interface could affect the magnitude of the thermal conductance but could not explain the asymmetry. Later, Horn (1951) criticized Starr's conclusions suggesting that the Thomson effect possibly lead to errant thermocouple readings.[2]

At the beginning of the aerospace era, when flight vehicles began to experience extremely large heating loads due to re-entry, researchers began to consider thermal resistance at metallic interfaces. New aerospace structures were being made of a combination of metals to provide strength and light weight. New configurations and new thermal requirements lead to some of the early work in thermal contact conductance. Barzelay et al. (1955) is cited as the first to observe rectification in metal/metal interfaces.[3] Although others had considered Barzelay's Aluminum/stainless steel system, none apparently checked the directional dependence of the thermal conductance. Barzelay found that the conductance from Aluminum to steel was significantly larger than the conductance from steel to Aluminum. Rogers (1961) subsequently performed the same experiments in vacuum to eliminate the contribution of conduction or convection in air in the micro-gaps at the interface. He found that the heat flux for each configuration was nominally 16% greater for the Aluminum to steel direction compared to the steel to Aluminum direction for a range of interfacial temperatures as did Barzelay. As a result, he concluded that the effect was electronic in nature but provided no further explanation. Moon and Keeler (1962) provided a detailed explanation of how the band structure of metal/oxide/metal interface could produce rectification. Here, it was assumed that the Aluminum, although well cleaned in Rogers' experiment, quickly produced a nanometer-scale layer of oxidation between the cleansing

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[1]In the 1950s and 1960s, aerospace vehicles were subjected to heating loads previously not experienced by low-speed aircraft. Therefore a tremendous amount of work went into describing the thermal performance of composite structures including interface conductance (Rogers, 1961).

[2]The author was not able to locate the actual work by Horn (1951) and, therefore, was not able to verify this claim that was originally made by Moon and Keeler (1962).

[3]This reference appears repeatedly in the literature, but has been elusive.

step and drawing down the vacuum. This analysis will be revisited in a subsequent section. Note that Rogers also performed directional experiments on other combinations of metals to eliminate thermoelectric effects such as those proposed by Horn (1951) and found that other materials showed no rectification behavior. This can be explained by Moon's model because of the high potential barrier at the interface between the metals investigated.

Despite the apparent success of the electronic model, many researchers claimed that the effect was largely geometric in nature. For example, Powell et al. (1962) thought that the difference in heat flow was driven in large part by macroscopic warping because their experiment performed on similar samples with much smaller cross-sections showed no rectification. They hypothesized that if the samples were not perfectly flat in Rogers (1961), the contact area would be less than expected. In addition, thermal cycling and thermal expansion could change the contact area producing an apparent rectification effect. Williams (1961) on the other hand dismissed the effects as resulting from surface contamination and the variability of microcontact areas inherent to smooth surfaces. However, most researchers in the geometric camp used an argument based on microscopic contact area. Clausing (1966) proposed that the resistance at an interface is the sum of three resistances;

$$R_{\text{tot}} = R_L + R_l + R_f, \tag{1}$$

where the total interface resistance is comprised of a macroscale resistance R_L , microscale R_l and a film resistance R_f. The macroscopic resistance arises from non-flat surfaces or spherical cap surfaces (Clausing and Chao, 1965). In this case the actual contact area is less than the apparent contact surface. The microscopic contact resistance is a result of surface roughness. For nominally flat surfaces, the microscopic contact area dominates the total resistance at an interface (Yovanovich and Fenech, 1966). The film resistance is essentially a result of surface contamination of oxidation. In terms of rectification behavior, asymmetry can occur is each of the three resistances identified above.

For macroscopic resistance, if heat is flowing from a material whose coefficient of expansion is small to a material whose coefficient of expansion is large ($A \rightarrow B$ in Figure 1), then the heat flux through the interface will be less than the heat flux in the opposite direction Clausing (1966). This feature results from the temperature gradient adjacent to interface. If the temperature decreases from the interface into material B, then thermal expansion will result in a decrease contact area, which will decrease the amount of heat transfer. If the gradient is in the opposite direction, the thermal expansion will increase the contact area, resulting in a larger heat transfer and thermal rectification behavior. Jones et al. (1975) provides a demonstration of this global effect.

To study thermal rectification at microcontacts, Clausing (1966) generated an empirical expression involving the modulus of elasticity, contact pressure, and actual and apparent contact areas. However, this model is only applicable in the absence of thermal strain, and agreement is not very good. The experiments merely demonstrate
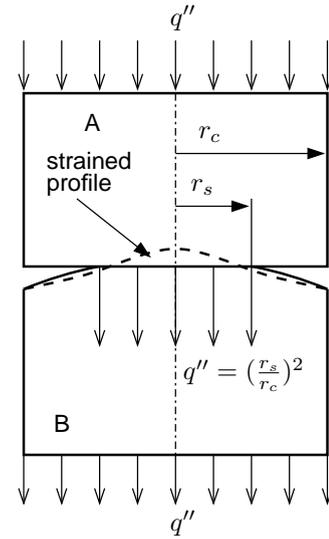

Figure 1: Exaggerated macroscopic constriction due to thermal strain. The actual area available for heat transfer is less due to warping.

that thermal rectification exists and is likely due to thermal strain, but does not offer a relationship between the thermal strain and amount of rectification. Later Somers II et al. (1987) showed that thermal rectification was at least mathematically possible based on a thermal strain relation for two spheres in frictionless contact. Lewis and Perkins (1968) performed careful investigations of microscopic roughness on flat interfaces and found rectification that could be explained by applying the Clausing model to local features, except he found that the direction of rectification was opposite from the macroscopic model. In other words, grooves (not protrusions) that might result from milling behave opposite to non-flat macroscopic surface and on a smaller scale. Thomas and Probert (1970) also confirmed this effect for microscale contacts by examining interfaces with different surface preparations. However, Thomas and Probert (1970) also performed tests at cryogenic temperatures and between similar materials. Their results suggested that the rectification was purely an electronic effect as proposed by Moon and Keeler (1962), where the difference in material workfunction allows the net transfer of thermal energy without a net transfer of charge. The rectification behavior at interfaces of similar materials (similar to Thomas and Probert, 1970) was reportedly also found by Williams (1966). Interestingly, O'Callaghan et al. (1970) found that the rectification behavior disappeared after cyclic loading, suggesting that the microcontacts are primarily responsible for the directional effect. However, additional tests of the same samples after exposure to the atmosphere suggested that surface contamination (oxidation) was also responsible for the rectification behavior and loading simply broke down the surface coating by thermal expansion processes.[4] Although not directly stated in the conclusions from O'Callaghan et al. (1970),

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[4]This is the same effect that Williams (1961) noted about Rogers (1961) data.

the oxide effect could conceivably suggest electronic rectification as well. However, Dundurs and Panek (1976) proposed a model that demonstrated a directional bias based on geometric considerations alone.

A tremendous amount of work has been performed in the field of thermal contact resistance (for a recent review, see Savija et al., 2003), the bulk of which is not concerned with a directional effect. Because of the number of factors that effect contact resistance (mechanical load, surface preparation, mechanical and thermal properties, surface contamination, surface geometry, and temperature to list a few), it is difficult to consider thermal rectification, which is usually considered a secondary effect. However, the lack of definitive evidence in thermal rectification by the 1970's is largely due to the apparent discrepancies between observed measurements from different research groups. Therefore, the validity of relationships describing the direction, magnitude and factors affecting thermal rectification are dubious.

5 Theoretical models

Despite the controversy of the existence and nature of thermal rectification, two simple models have demonstrated success in predicting directional effects at interfaces. The electronic model was proposed by Moon and Keeler (1962) and the geometric model was proposed by many but was eventually refined by Somers II et al. (1987). A third model that involves non-equilibrium between electrons and phonons will be introduced and described in a subsequent section. This new approach, however, is limited to systems where electron-phonon scattering is important (i.e. metal/insulator systems). Finally a brief discussion of rectification considering phonon transport at interfaces will be presented.

5.1 Geometric model

The geometric model is applicable to macro or micro-contacts and is based on a change in contact area due to thermal strain. If the contact area is characterized by a radius r_o, the change in contact area can be calculated as function of the applied heat load across the interface as (Somers II et al., 1987)

$$\frac{\partial r_o}{\partial q} = \frac{\kappa}{3} \left[\frac{1}{R_1 R_2 (R_1 + R_2)^2} \right]^{2/3} \left[R_2^2 \frac{dR_1}{dq} + R_1^2 \frac{dR_2}{dq} \right],$$
(2)

where R_1 and R_2 are the radii of two smooth spheres in contact. The load and mechanical properties of the two spheres are contained in the factor κ. The possibility of thermal rectification, which is represented by a sign change in $\partial r_o / \partial q$, lies in the last term of equation. The change of the radii of either sphere is a function of the thermoelastic materials of the constituent materials, but will change sign depending on the direction of the heat flux. As in Figure 1, a heat flux entering a sphere will cause the radius to decrease (Barber and Wright, 1967). Not shown in Figure 1, a heat flux in the opposite direction will cause the surface to flatten and increase the ef-

fective radius. Consequently, the two derivatives in equation 2 will have different signs. Depending on the difference in material properties, one will dominate and rectifying behavior should be observed. Realize that this theory does not account for surface roughness (friction at the surface), non-spherical surfaces or non-circular contact areas. Nor does this theory allow thermal rectification at an interface composed of a single material, yet measurements have indicated rectification between similar materials (Thomas and Probert, 1970).

5.2 Electronic Model

The electronic model does not depend on the contact area and therefore provides an alternate explanation. However, the electronic model assumes a thin dielectric layer exists between two metallic surfaces. The layer is traditionally surface oxidation due to exposure in air but could easily be extended to an air or vacuum gap where the surfaces do not mate exactly. If the theory is extended in this way, then the contact area and gap distance will affect the amount of rectification. Therefore, the electronic effect could also be sensitive to loading and mechanical properties of the constituent materials as the geometric model is.

When metals are in contact (or near contact) electrons will flow between the two materials due to random migration. The thermal energy transferred by the electrons traveling over the barrier is simply the current density times the average energy of the electrons. Electrons flow over the barrier shown in Figure 2 because of a favorable temperature gradient ($T_A = T_H$ and $T_B = T_C$), and the current from A to B is given by Richardson's equation (Lawrence, 1926),

$$J_{A \to B} = \xi A_o T_H^2 \exp[-(\phi_A - \phi_d)/k_b T_H], \quad (3)$$

where k_b is Boltzmann's constant, A_o is a thermionic constant that is material dependent, ϕ_A and ϕ_d are the work functions of metal A and the dielectric respectively, and ξ is the transmission coefficient. In equilibrium (no applied bias), the net charge transfer across the interface must be zero, which means that the $J_{A \to B} = J_{B \to A} = J$. The electronic heat flux is then given by the difference of the thermal energy carried by the random migration of electrons

$$q_{ef}'' = J_{A \to B} E_A - J_{B \to A} E_B = J(E_A - E_B). \quad (4)$$

If the average energy is calculated as $E_i = E_o + 2K_b T_i$ (Moon and Keeler, 1962), where E_o is the height of the potential barrier, then the electronic heat transfer for a favorable temperature gradient is

$$q_{ef}'' = \xi A_o T_H^2 \exp \left[\frac{-(\phi_A - \phi_d)}{k_b T_H} \right] 2k_b (T_H - T_C). \quad (5)$$

The electronic heat flux resulting from a reversed temperature ($T_A = T_C$ and $T_B = T_H$) can similarly be calculated by swapping the temperatures that appear in equation 5. If the ratio of equation 5 to the reverse direction
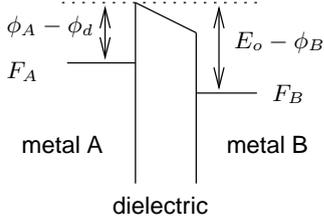
Figure 2: Energy band diagram of a two metal contact separated by a dielectric. E_d is the barrier height of the dielectric d. ϕ and F represent the work function and Fermi level respectively.

is not equal to one, then the model indicates that thermal rectification is possible in the electronic component of heat transfer. The ratio is given as

$$\frac{q''_{ef}}{q''_{er}} = \frac{T_H^2}{T_C^2} \exp\left[\frac{-(\phi_A - \phi_d)}{k_b} \frac{T_H - T_C}{T_H T_C}\right], \quad (6)$$

where the subscripts f and r refer the to favorable and reverse temperature differences respectively. In the foregoing expression, we have assumed the transmission ξ and the material constant A_o are independent of temperature.

5.3 Metal/Insulator Model

In metals, thermal energy is transported primarily by electrons; in insulators, thermal energy is transported by phonons. Therefore, at metal/insulator interfaces, thermal energy must be transferred between electrons and phonons. Because an insulator has no free electrons, the transport across the interface is presumed to occur via phonon exchange. Consequently, electron-phonon scattering must occur in the metal giving rise to two characteristic series thermal resistances that comprise the bulk "contact resistance" (Majumdar and Reddy, 2004).

$$R_{\text{contact}} = R_{e-p} + R_{pt} \quad (7)$$

The first component R_{e-p} is characterized by electron-phonon scattering in the metal near the interface, and the second component R_{pt} is characterized by phonon transmission across the boundary. The localization of these resistances gives rise to a temperature jump at the interface. In contrast to the previous models, this approach assumes that the mechanical contact is perfect.

This simplified model of thermal transport across a metal/insulator interface could conceivably be challenged. For example, the extent of the penetration of the electron wavefunctions into the insulator layer is uncertain. As such, it is possible for the electrons to scatter directly with insulator phonons bypassing the flow path described by equation 7. Based on tests performed on extremely thin oxide layers in MOSFETs () and ability to match experimental data reasonably well (Majumdar and Reddy, 2004), we expect the penetration to be minimal.

The resistance due to electron-phonon scattering in the metal is governed by scattering rates that in general are not symmetric meaning that energy transfer from phonons to electrons is different than energy transfer

from electrons to phonons for similar energies. In fact, Fermi's golden rule provides an estimate of scattering rates for electrons with various modes and polarizations of phonons. As electrons scatter with phonons inelastically, the scattering rates differ for phonon emission and phonon absorption. This break in the symmetry suggests that thermal rectification is possible. The proposed non-equilibrium transport model at the interface used to predict directional resistance follows that of Majumdar and Reddy (2004); the scattering rate prediction follows that of Lundstrom (2000). Refer to Figure 3 for a depiction of the different temperatures considered in the model.

Although the electron-phonon system is out of equilibrium, we assume that Boltzmann moments with an energy exchange term is adequate to model the non-continuum effects. This assumption leads to a coupled system of two Fourier-like carriers

$$k_e \frac{d^2 T_e}{dy^2} - G(T_e - T_p) = 0; \quad (8)$$

$$k_p \frac{d^2 T_p}{dy^2} + G(T_e - T_p) = 0, \quad (9)$$

where k_e and k_p are the electron and phonon thermal conductivities in the metal and G is related to the rate of energy transport between electron and phonons. This metallic system is coupled to the phonon system in the insulator such that the phonon heat flux is matched on both sides of the interface.

$$k_p \frac{dT_p}{dy}\bigg|_{y=0} = -k \frac{dT}{dx}\bigg|_{x=0}. \quad (10)$$

Note that the insulator temperature T and thermal conductivity k are identified without a subscript. Furthermore, the coordinate system for each material is different for convenience as shown in Figure 3. To conserve energy, the metal heat flux must be insulated such that

$$k_e \frac{dT_e}{dy}\bigg|_{y=0} = 0. \quad (11)$$

These boundary conditions combined with a jump condition for the interface to represent the interface phonon resistance,

$$k_p \frac{dT_p}{dy}\bigg|_{y=0} = h[T_p(y=0) - T(x=0)], \quad (12)$$

provide sufficient conditions at the interface for a solution. The final boundary (at $y \to 0$) is provided by assuming equilibrium in the metal such that $T_e - T_p = 0$. A sketch of the solution is provided in Figure 3, which is solved to within an integration constant. Assuming $k_e \gg k_p$ (which is valid for metals), the solution for the interface conductance is given as (Majumdar and Reddy, 2004)

$$h = \frac{h_{ep} h_p}{h_{ep} + h_p}, \quad (13)$$

where $h_{ep} = \sqrt{Gk_p}$, and the subscripts refer to electron-phonon scattering conductance and phonon interface conductance respectively. To estimate the interface conductance, a value for the coupling rate G is needed. The coupling is often expressed in terms of the electron-phonon scatting rate and electron specific heat as $G = C/\tau$.
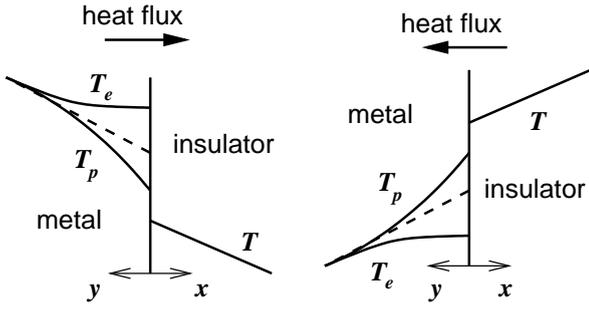
Figure 3: Electron and phonon temperature distributions at a metal insulator interface for opposing temperature gradients.

The foregoing model is also applicable when bulk thermal transport is in the opposite direction as that shown in Figure 3. If the temperature of the insulator is higher than the temperature of the metal (far from the interface) the form of the temperature distributions is the same, but now the sign of the electron-phonon transfer rate presumably changes sign. However, the magnitude of G can also change based on the direction of the net energy exchange between carriers. If $G = C/\tau$, where τ is the energy dependent scattering rate, then we can predict that the scattering rate for phonon emission τ_e is different than the scattering rat for phonon absorption τ_a. Consequently, $G_a \neq G_e$, and the system exhibits thermal rectification.

The scattering rate can be found from Fermi's golden rule where the transition rate is given as

$$S(\mathbf{p}, \mathbf{p}') = \frac{2\pi}{\hbar}|H_{\mathbf{p},\mathbf{p}'}|^2 \delta(E(\mathbf{p}') - E(\mathbf{p}) - \Delta E), \quad (14)$$

where $\mathbf{p}$ and $\mathbf{p}'$ are the electron momenta before and after a scattering event, respectively. ΔE is the change in energy caused by the scattering event. We can evaluate the matrix element $H_{\mathbf{p},\mathbf{p}'}$ by assuming parabolic spherical bands so that the overlap integral is unity, resulting in

$$H_{\mathbf{p},\mathbf{p}'} = \frac{1}{\Omega} \int_{-\infty}^{\infty} e^{-i\mathbf{p}'\cdot\mathbf{r}/\hbar} U_S(r) e^{i\mathbf{p}'\cdot\mathbf{r}/\hbar} \, d^3r, \quad (15)$$

where plane waves are used instead of Bloch functions without loss of generality. The integral of the random potential $U_S(r)$ is over volume Ω. If we introduce the lattice displacement given by

$$u(x,t) = A_\beta e^{i(\beta x - \omega t)} + A_\beta^* e^{-i(\beta x - \omega t)}, \quad (16)$$

where the phonon wavevector is β and the coefficients A_β represents the amplitude, then the perturbing potential is some linear combination of perturbations as

$$U_S = D_o u_\beta, \quad (17)$$

where D_o is the deformation potential. The integral in equation 15 can be evaluated to give the matrix element

$$|H_{\mathbf{p}'\mathbf{p}}|^2 = D_o^2 |A_\beta|^2 \delta_{\mathbf{p}',\mathbf{p}\pm\hbar\beta}, \quad (18)$$

where the δ-function is a statement of conservation of momentum. Now we can replace the matrix element in

equation 14. The double δ-function, which represents conservation of energy and momentum, can be replaced by a single function so the transition rate can be expressed as

$$S(\mathbf{p}, \mathbf{p}') = \frac{2\pi m^*}{\hbar^2 p\beta} D_o^2 |A_\beta|^2 \delta\left(\pm\cos\theta + \frac{\hbar\beta}{2p} \mp \frac{m^*\omega_\beta}{p\beta}\right),$$
$$(19)$$

where m^* is the electron effective mass. The coefficient $|A_\beta|^2$ can be found from the maximum kinetic energy of an oscillator. The time derivative of the displacement (equation 16) gives the kinetic energy as

$$E = \frac{1}{2}M\left|\frac{du}{dt}\right|^2 = \frac{1}{2}\rho\Omega\omega_\beta^2 4|A_\beta|^2, \quad (20)$$

where ρ is the mass density. We equate this with a quantum oscillator to recover the amplitude as

$$|A_\beta|^2 = \frac{N_\omega \hbar}{2\rho\Omega\omega_\beta} \quad (21)$$

for phonon absorption and

$$|A_\beta|^2 = \frac{(N_\omega + 1)\hbar}{2\rho\Omega\omega_\beta} \quad (22)$$

for phonon emission. Here, N_ω is the occupation number described by the Bose-Einstein distribution. This variation in the absorbed and emitted phonons gives a directionality to the effective interface resistance. The question is whether this effect can be significant.

To obtain the scattering rate, we integrate the transition probability over all possible electron momenta. Equivalently, we can integrate over all possible phonon wavevectors because the mapping from $\mathbf{p}'$ to β is unique. Considering the optical branch the integral of equation 19, after considerable manipulation, becomes (Lundstrom, 2000)

$$\frac{1}{\tau} = \frac{\pi D_o^2}{2\rho\omega_o}\left(N_o + \frac{1}{2} \mp \frac{1}{2}\right)g_C(E \pm \hbar\omega) \quad (23)$$

Where the electron density of states g_C is dependent on whether a 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 foregoing development is abbreviated, but presented to demonstrate from where the '$\pm$' originates and to identify the difference between emission and absorption. The energy relaxation rate is then found by scaling the simple scattering rate as

$$\frac{1}{\tau_E} = \frac{\hbar\omega}{E(p)}\frac{1}{\tau}. \quad (24)$$

5.4 Phonon models

The phonon resistance is largely governed by the geometry of the interface. However, unlike the previous geometric model, the area change is not of concern here. If the interface is rough, the reflections will be diffuse, otherwise, the reflections will be specular. In either case, the phonon transmission is similar regardless of the preferred direction of the transport. Therefore, we might conclude

that the thermal rectification is not possible for phonons across an interface in intimate contact.

Recent study of discrete vibrational systems has shown that certain configurations and levels of anharmonicity can produce a thermal rectification effect. Terraneo et al. (2002) and Li et al. (2004)[5] have shown through one-dimensional molecular dynamics simulations using an anharmonic potential that thermal rectification is possible. The system presumably does not model a real system and the possibility of measuring this kind of rectification is dubious. However, Segal and Nitzan (2005) have developed an analytic solution from an anharmonic Hamiltonian that spans the entire domain instead of a contrived scenario. While the demonstration does not match any known physical system, they show that structural asymmetry and nonlinear dynamics are required to achieve rectification from purely phonon transport. In particular, their system is realistically only applicable to an unknown nanoscale structure.

6 Discussion

It is interesting to compare the relative strengths of the mechanisms responsible for rectification behavior. However, a direct comparison is often not possible because the multiple parameters involved confound a comparative analysis. Nevertheless, we can examine the directional performance of some measured systems. If we define the effectiveness of the rectification as a ratio of conductances

$$\varepsilon = \frac{h_{\text{large}} - h_{\text{small}}}{h_{\text{small}}}, \quad (25)$$

then the magnitude of the effect can be compared. Here the ratio varies from zero (no rectification) to something arbitrarily large (significant rectification). Some experimental results are listed in Table 1 with the caveat that many of the results listed here are dependent on contact pressure, oxidation time, or surface preparation, so direct comparison is difficult. Nevertheless, the data demonstrate the variability of the effect in the literature, the variety of possible mechanisms and the magnitude of the strength. A value of zero, of course indicates no effect, and the largest value reported here is slightly above unity. Therefore, in the best case, the conductance has been increased by a factor of $2 \sim 3$. Based on the scattering model for metal/insulator systems, we can theoretically calculate the rectification behavior. If we substitute equation 13 into equation 25 and write G in terms of the scattering rate, the effectiveness becomes

$$\varepsilon = \frac{\sqrt{Ch_p} + h\sqrt{\tau_+}}{\sqrt{Ch_p} + h\sqrt{\tau_-}} - 1, \quad (26)$$

where the scattering rate depends on the direction of heat transfer as in Figure 3. Using values for parameters following Majumdar and Reddy (2004), $C \approx 2 \times 10^6 \, \text{J/m}^3 \, \text{K}$, $k_p \approx 10 \, \text{W/m K}$, and $h \approx 3 \times 10^8 \, \text{W/m}^2 \, \text{K}$. Next we assume that the scattering rate

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[5]These are the same groups and there is little difference between the approach.

Table 1: Comparison of experimental evidence of thermal rectification. In most cases the rectification is a function of some parameters such as heat load, mechanical load, etc. Therefore, these values represent an average or are reported for a particular condition.

system	ε
Cu→Cu$_2$O (Starr, 1935)	1.1
Al→SS (Rogers, 1961)	0.2
Al→SS (Powell et al., 1962)	0
SS→Al (Clausing, 1966)	0.5
Al→SS (Lewis and Perkins, 1968)	1.4
smooth→rough (O'Callaghan et al., 1970)	0.3
rough→smooth (Stevenson et al., 1991)	0.52

is of the order of femtosecond photoexcitation of electrons in metals ($0.1 - 1 \, \text{ps}$) (**??**). This value corresponds well with predicted scattering rates from Fermi's golden rule (equation 23) using $D_o = 1 \times 10^{-8} \, \text{eV/cm}$ for a $100 \, \text{meV}$ electron, the scattering times for phonon emission and absorption respectively become $\tau_- = 2.56 \times 10^{-13} \, \text{s}$ and $\tau_+ = 7.76 \times 10^{-13} \, \text{s}$. Using these values in equation 26, the rectification effectiveness becomes $\varepsilon = 0.03$, which is essentially negligible. However, this value is calculated for a temperature of $300 \, \text{K}$. As the temperature decreases, the effect increases slightly until extremely low temperatures are reached where the effect is dramatic ($\varepsilon = 2.8$ at $T = 50 \, \text{K}$). However, at these low temperatures the analysis is dubious because the properties assumed above are no longer valid.

The foregoing analysis has made many simplifying assumptions about the transport across an interface such as Boltzmann moment transport and lack of wavefunction penetration into the insulator. In addition, the energy of the electron is assumed to be $100 \, \text{meV}$ when in fact an energy distribution should be assumed. Furthermore, the scattering is assumed to be of a single mechanism and only in one direction. Therefore, these assumptions should be investigated before thermal rectification can be ruled out or verified.

7 Conclusions

The paucity of systematic observation and measurement of thermal rectification casts doubt on its potential. However, enough evidence and theoretical mechanisms exist that suggest the effect is real. More often rectifying behavior is the result of other design and manufacturing constraints and not an intentional or an optimized effect. With the ability to manipulate the properties of materials and devices on the nanoscale, effects such as electron/phonon scattering and anharmonicity of lattice vibrations may be leveraged to design thermal rectification into films and devices. Current evidence, however, suggests that the effect is not likely to reach an order of magnitude without other ground-breaking discoveries in the field.

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