

Molecular Dynamics Simulation of Thin Films with Rough and Asymmetric Interfaces

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Abstract—Thermal rectification is a phenomenon in which thermal transport is preferred in one direction over the opposite. Though observations of thermal rectification have been elusive, it could be useful in many applications such as thermal management problems at the micro/nano scale for electronics cooling. The current work explores the possibility of thermal rectifying devices with the use of interfaces and shows that pristine, imperfect and asymmetric interfaces in thin films can result in a difference in the effective thermal conductivity when the temperature gradient is reversed. The asymmetric geometries investigated in the device include hemispherical and ellipsoidal shapes. The rectifying behavior originates from the difference in the frequency content between two temperature reservoirs. More massive elements will produce different frequencies that reflect preferentially at a nanostructured interface whose features are of the order of the phonon wavelength. At a constant temperature difference of 20K we calculate a different heat flux or effective thermal conductivity depending on the direction of the temperature gradient. Results show a difference of approximately 70% in the effective thermal conductivity for opposite directions.

Key Words: rectification, thermal transport, molecular dynamics

I. INTRODUCTION

Thermal rectification is a phenomenon where transport through a material is dependent on the direction, and though its observations in solids have been rare, rectifying behavior could have wide spread applications in thermal management problems. Records of rectification date back as early as 1935 when Starr [1] found that copper/cuprous oxide systems showed thermal as well as electrical rectification. Walker [2] presented evidence and several candidate theoretical models for rectification behavior. Most models suggest that rectification could be exploited with our improved ability to manipulate materials at the nanoscale. In 2002 Terraneo et al. [3] demonstrated rectification behavior using a nonlinear one-dimensional chain of atoms between two thermostats at different temperatures with a constant temperature difference where they were able to change the chain from a normal conductor to a nearly perfect insulator. In a similar study in 2004, Baowen et al. [4] simulated a nonlinear lattice and calculated a difference in conduction between the two directions to be 100 times that of [3]. In 2006 Chang et al. [5] suggested that solitons were responsible for rectification and showed that greater conduction resulted in the direction of decreasing mass density in

an engineered material having non-uniform mass distribution along the carbon and boron nitride nanotubes. In 2008, Roberts and Walker [6] showed theoretically that if the boundaries in a wire could be made to have a directional dependence a self-biasing device could be created. The difference between the current work and these is that the mechanism for rectification is due to phonon scattering at an interface between two materials.

The current work involves a molecular dynamics study of the rectification effects of a single interface within a thin film. The inspiration of this work came from Walker 2006 [2], which proposed a possible model for rectification due to phonon scattering at the interface. The effects of a pristine interface should be different than that of a rough or asymmetric interface. In this work we have compared the perfect interface to rough interfaces by varying the degree of roughness and asymmetry of the interfaces. Many studies, both experimental and theoretical, have been performed and reported for thermal transport in low-dimensional solids including thin films and nanowires [7–11]. The theoretical studies typically seen are based on the Boltzmann Transport Equation (BTE) or molecular dynamics simulations. These methods have been very effective in explaining thermal transport, specifically in nanoscaled structures.

The goal of this work is to show theoretical evidence of the existence of thermal rectification using Walker’s phonon model [2] and to explain why its effects are not regularly measured experimentally by comparing a pristine interface to interfaces of typically roughnesses present in devices that are fabricated and experimentally measured.

II. SIMULATION METHOD

The devices studied in this work are half argon and half krypton (excluding the ellipsoidal interface) with a single interface located near the center. The types of interfaces investigated include pristine interfaces, rough interfaces and asymmetric interfaces, each of which is shown in Figure 1.

An FCC crystalline lattice is assumed with a Lennard-Jones inter-atomic potential given as

$$U = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

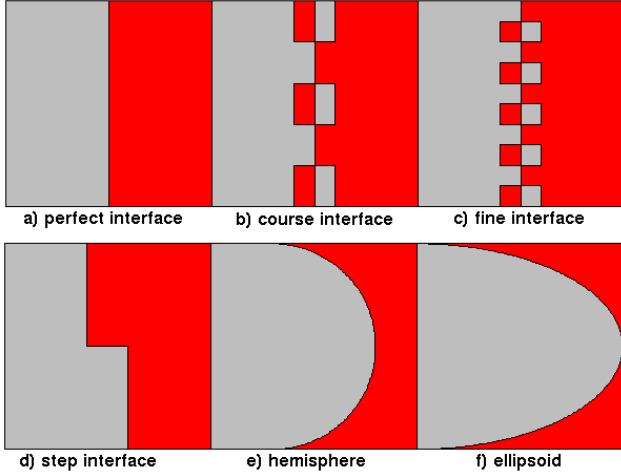


Fig. 1. Schematic of the interfaces studied via molecular dynamics simulations

TABLE I
PARAMETERS USED FOR THE DIFFERENT MATERIALS IN THE SIMULATIONS [12]. FOR POTENTIALS BETWEEN DIFFERENT ATOMS, THE ENERGY PARAMETER $\epsilon_{12} = \sqrt{\epsilon_1 \epsilon_2}$ AND THE LENGTH PARAMETER $\sigma_{12} = (\sigma_1 + \sigma_2)/2$.

Material	Parameter	Value
Kr	ϵ (J)	2.25×10^{-21}
	σ (m)	3.65×10^{-10}
	a (m)	5.69×10^{-10}
	m (kg)	1.39×10^{-25}
	r_{cut} (m)	9.49×10^{-10}
Ar	ϵ (J)	1.67×10^{-21}
	σ (m)	3.4×10^{-10}
	a (m)	5.3×10^{-10}
	m (kg)	6.63×10^{-26}
	r_{cut} (m)	8.84×10^{-10}

As mentioned previously, the devices contain argon and krypton whose properties are given in Table I.

XMD, an open source, general purpose molecular dynamics code [13] is used for the computations in this work. Small modifications were made to the code to extract the information necessary to calculate the thermal conductivity of the device by recording the energy added and subtracted to each temperature bath throughout the simulation. The system is composed of 6 unit cells (3 on each side) of fixed position walls, 8 unit cells (4 on each side) for the high (60 K) and low (40 K) fixed temperature baths and a varying number of unit cells for the simulation domain where the interface is located. This configuration was used because 4 planes of fixed atoms at the ends of the device are sufficient to effectively simulate an infinite wall because of the short range of the inter-atomic potential [14]. The interfaces studied in this work include a pristine interface where the two constituent materials are perfectly divided at the center of the device, a rough or diffused interface where the two constituent materials have atoms on both sides of the interface with two different levels of coarse-

ness, an imperfect interface that includes one step also used to model a fabricated interface, and two asymmetric interfaces which include hemispherical and ellipsoidal geometries. Each of these interfaces will result in some level of rectification, but we expect that the pristine interface will result in the greatest rectification due to the difference in the inter-atomic potential at this interface. Experimentally this effect is generally not seen because of the inability to fabricate a perfect interface where the mass and potential differences can be observed.

The simulation is initialized at a temperature of 50 K and allowed to run for 5000 time steps with a $\Delta t = 3.2 \times 10^{-15}$. The temperature gradient is then applied and allowed to run for until 195,000 time steps which is a total simulation time of 0.64 ns. Throughout the simulation the energy added and subtracted to and from each constant temperature bath is recorded. During the early stages of the simulation these energies fluctuate rapidly. After which they reach a near constant value. At this point the simulation is in steady-state and the energy added to the high temperature bath is equal that of the energy subtracted from the low temperature bath. This value is the total heat flux of the system at the given temperature difference of 20 K. With the computed flux, the thermal conductivity is then calculated using Fourier's law for steady conduction,

$$k = -\frac{q}{A} \frac{dx}{dT} \quad (2)$$

where dx is the domain length between the baths and A is the cross sectional area of the device. Fourier's law is a phenomenological law where the thermal conductivity is considered a proportionality constant or "effective" property. In the current work we calculate and record the energy required to maintain fixed temperatures at each bath. This energy is then divided by the time step to obtain the heat transfer q in equation 2. Since all other values in equation 2 are fixed and the heat transfer is averaged over long times [14], Fourier's law is not a bad approximation.

In all simulations a fixed ratio of argon and krypton are maintained at 50% each except for the ellipsoidal interface, which should help to isolate the effects of the interfaces and allow for a direct comparison of the resulting thermal conductivities of each system. To examine the rectifying behavior of the interfaces we will now introduce a parameter ϵ , which is given by

$$\epsilon = \frac{k_{H-C} - k_{C-H}}{\min(k_{H-C}, k_{C-H})}, \quad (3)$$

where k_{H-C} and k_{C-H} are the thermal conductivities from the hot to cold and cold to hot baths, respectively. A value of $\epsilon = 0$ means there is no difference when the temperature gradient is reversed and no rectification.

III. SIMULATION RESULTS

Results of the molecular dynamics study for each of the symmetric interfaces are shown in Figure 2. Here it can be seen that the rectification effect is negligible for device lengths below 32 unit cells and becomes quite large at lengths of 96 unit cell. The reason rectification is negligible at short

domain lengths is because the phonons from the high temperature and lighter weight atoms do not differ much from the phonons from the lower temperature and heavier atoms due to confinement of the phonon wavelengths [15]. As the device becomes longer, the difference in the frequency of the phonons from each of the baths becomes greater and results in different thermal conductivities when the temperature gradient is reversed. This effect is greatly exaggerated in the case with a perfect interface. As the quality of the interface is degraded (coarse to fine interface) the rectification effect is reduced. This reduction in rectification is a result of the scattering of the phonons at the interface. This scattering has the effect of eliminating the phonon wavelengths which would exist if not for the roughness at the interface. Presumably if we were to increase the roughness at the interface even more than what has been shown it would result in $\varepsilon = 0$ for any device length and this roughness should be obtained by simulating a physically manufactured interface.

Results of the asymmetric interface simulations are shown in Figure 3. Based on these results, the impact of the asymmetrical interfaces is also a form of degradation as they are not perfect. The amount of interfacial area is also greater in these cases resulting in increased scattering. In these asymmetric interfaces we also see a reduction in the rectification. In the case of the ellipsoid there is also the confounding effect of an unequal fraction of argon and krypton which also has an impact on the thermal conductivity [15] and also rectification when the geometry or temperature gradient is reversed.

The simulations labeled ArKr are designed so that the material to the left of the interface is argon and that to the right is krypton and the simulations labeled KrAr are the opposite. It is expected that the difference in the ArKr simulations and the KrAr simulations should have the same magnitude but different sign since the geometries are reversed, which is what is seen in Figures 2 and 3 with some statistical variation.

These results differ from those from Chang et al. [5] which found that the rectification was due to solitons or a difference in mass density through the device. In this case it appears that the rectification is both a result of the difference in mass and the interface. When the interface is pristine we find maximum rectification (approximately 70% difference) with a device length of 96 UC and results show that the preferred direction of transport is from the argon bath to the krypton bath which is low mass and softer potential to high mass and stiffer potential. These results can be understood by looking at the acoustic and diffuse mismatch models. In the case of the perfect interface we are in the limit of the acoustic mismatch model (AMM). The thermal boundary resistance in the AMM is a result of the difference in atomic spacing which results in phonon reflection at the interface [16]. Since the thermal boundary resistance in the pristine interface is due to reflections, the transport is dominated by the difference in phonon frequencies that exist in the constituent materials. This difference in phonon frequencies appears in the definition of the phonon transmission at the interface which increases with increasing phonon frequency [16]. Based on the

mass and stiffness of the potential for argon and krypton we have obtained a ratio of the dominate phonon frequencies of $\frac{\omega_{Ar}}{\omega_{Kr}} \approx 1.25$, which implies that rectification will occur at a pristine interface between argon and krypton. As the interface is degraded (rough and asymmetric interfaces) a combined AMM and diffuse mismatch model (DMM) is required. In the combined model diffuse or mass-difference scattering occurs at the interface [16]. The addition of this type of scattering reduces the difference in transmitted phonons and reduces the observed rectification when the temperature gradient is reversed. As the interface is further degraded the interface approaches the limit of the pure DMM which will result in no rectification.

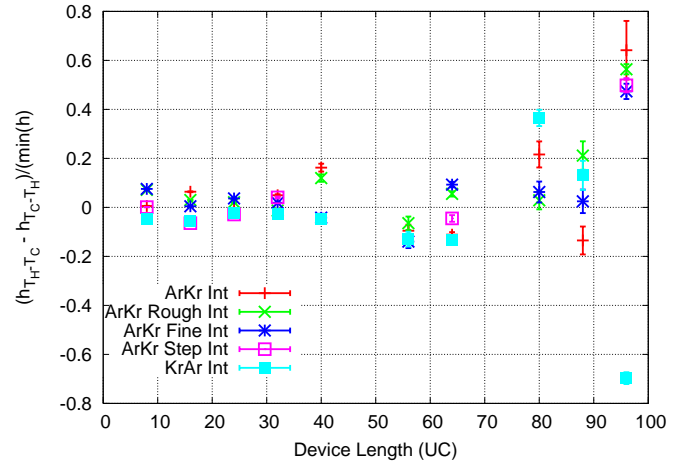


Fig. 2. Rectification as a function of device length for symmetric interfaces

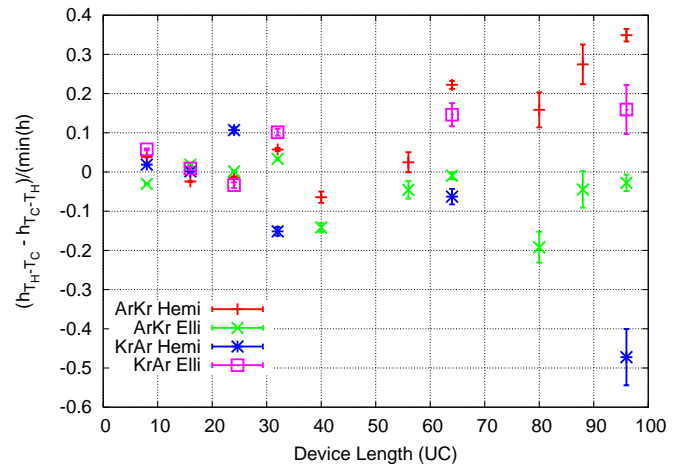


Fig. 3. Rectification as a function of device length for asymmetric interfaces

IV. CONCLUSION

Thermal rectification was observed theoretically and the effect was reduced as the quality of the interface was degraded with the addition of somewhat randomly distributed atoms of each of the constituent materials at the interface. A reduction

in rectification from the perfect interface was also seen with the introduction of the asymmetric interfaces with greater interfacial area. The results suggest that the reason thermal rectification has not been observed in many cases is due to the poor quality of interfaces in devices consisting of only two materials. In this work we have observed that thermal transport is preferred in the direction of lower mass and softer potential to higher mass and stiffer potential. This effect is due to the difference in the dominant phonon frequencies that exist in each of the constituent materials and the transmission of those frequencies at the interface. As the interface is degraded scattering will increase and result in no rectification. In the case of the perfect interface, the acoustic mismatch model, which ignores scattering and results in maximum rectification, can be used to approximate the level of rectification by including frequency dependent coefficients. As the surface is degraded, scattering then occurs as a result of the diffusion of materials at the interface and the difference in the transmitted phonon frequencies is reduced. In the limit of a purely diffuse interface no rectification will be observed.

NOMENCLATURE

a	lattice constant (m)
k	thermal conductivity (W/m ² K)
l	device length (m)
T	temperature (K)
w	device width (m)
ε	rectification effectiveness
ω	phonon frequency (Hz)

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