Using Surface Disorder to Reduce Thermal Conductance and Enhance

Thermoelectric Properties of Nanowires

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Abstract

Thermoelectric devices are designed to generate electrical energy from waste heat. One way to make thermoelectric modules more efficient is to reduce the lattice thermal conductivity without damaging the electrical properties. In this project we compute the lattice thermal conductance for wires with different shaped boundaries ranging from a straight wire, to a wire with a regular zigzag boundary, to wires with random zigzag shaped boundaries. The lowest thermal conductance is obtained for the random zigzag geometry. Because the interior of the wire is still perfectly ordered, this is a promising method to reduce the lattice thermal conductivity while leaving the electrical properties relatively unchanged.
Introduction

Thermoelectricity is used to generate electrical energy from waste heat\(^4\). One potential application is to extract electrical energy from the heat produced by a car’s engine. As much as 75\% of the energy generated by a car’s internal-combustion engine ends up lost to waste heat\(^3\). Thermoelectric units could convert the wasted heat from the engines into electricity, reducing the usage of fossil fuels and lowering carbon dioxide emission\(^4\). Unfortunately, present day thermoelectric materials are not efficient enough to make this cost effective or practical. There have only been a limited number of applications using present day bulk thermoelectric materials\(^3\). One of the main problems of bulk materials is the result of high thermal conductivity, which allows for heat to be transferred from the hot to the cold region without conversion into electrical energy\(^4\).

The performance efficiency of thermoelectric material is measured by the figure of merit:

\[
ZT = \frac{TGS^2}{k},
\]  

where \(G\) and \(k\) are the electrical conductance and thermal conductivity, respectively. \(T\) is the absolute temperature, and \(S\) is the Seebeck coefficient\(^3\). In order to make thermoelectricity effective, the \(ZT\) in Eq. (1), of the material must be larger than one. There are several ways to increase \(ZT\). In this paper we will only be focusing on one of them. The thermal conductivity in Eq. (1) is the sum of two terms, \(k = k_e + k_p\), the electron and phonon contributions, respectively\(^4\). In this research, we will focus on getting the lowest \(k_p\). This will reduce \(k\) and increase the thermoelectric figure of merit, \(ZT\).
The lattice thermal conductivity is determined by how lattice vibrations or phonons are scattered and determining their mean free path. When a phonon encounters a material surface, it is reflects back into the material, which typically impedes heat flow\(^1\). This occurrence depends on factors such as the surface roughness and the boundary scattering because the reflections will decrease when the surfaces are closely structured together, such as in nanowires\(^1\). Aforementioned, reducing the thermal conductivity without affecting the electrical conductance will be the ideal situation for the performance of the thermoelectric material to be efficient\(^4\). Nanostructuring is one of the most promising solutions for making highly efficient thermoelectric devices\(^4\). Through nanofabrication, the elements that are active in the device become comparable in size to the phonon mean free path\(^4\). Nanoscale products have been proposed to enhance the performance efficiency of thermoelectric applications due to their reduced thermal conductivity because of the large surface area to volume ratio\(^4\). Because of the ratio in area to volume, the enhanced scattering of the phonons on the surface of the nanostructured material result in low thermal conductivity compared to bulk counterparts\(^2\).

In this research project, we will be computing the transmission of phonons and thermal conductance through a wire such as a semiconducting wire. To obtain results we will be varying the shape of the wires. The models will only be affecting the surfaces of the wire and not disordered the interior. The shapes of the wire will vary from a straight wire to a rough wire with different patterns to reduce the thermal conductance. The simulations were run in the computer program Matlab on system sizes smaller that
existing nanowires in the interest of computation speed. Nonetheless we expect that our conclusions will apply to larger more realistic systems as well.

**Methods**

The geometry we consider is shown in Figure 1 below. There are two large reservoirs at different temperatures connected by a wire. The 2\textsuperscript{nd} law of thermodynamics states that heat flows from a hot body to a cold body. Thus, heat will be transferred from the hot to the cold reservoir through the wire. The heat current is measured in Watts and resembles:

\[
\text{Heat Current} = \frac{\text{Energy}}{\text{Time}}. \tag{2}
\]

![Figure 1](image)

**Fig 1** Two temperature reservoirs connected by a device, in this research project they will be connected by a wire.

We calculate this heat current using the Landauer formula for phonons:

\[
I_Q = \int \frac{d\omega}{2\pi} \hbar \omega T(\omega) \left( \frac{1}{e^{\hbar \omega/k_B T_L} - 1} - \frac{1}{e^{\hbar \omega/k_B T_R} - 1} \right), \tag{3}
\]
where $\hbar w$ is the energy of a phonon, $T(w)$ is the transmission probability of a phonon through the wire, and the factor in parentheses is the difference in the Bose distributions functions in the left and right reservoirs. Without loss of generality we take the left reservoir to be the hot reservoir and the right one to be the cold one so that the heat flows from left to right. The thermal conductance, $K$, is the heat flow divided by the temperature difference in the reservoirs:

$$K = \frac{dI_Q}{d(T_L - T_R)} = k_B \int \frac{d\omega}{2\pi} \frac{(\hbar \omega)^2/(k_B T)^2}{(e^{\hbar \omega/2k_B T} - e^{-\hbar \omega/2k_B T})^2}. \quad (4)$$

A Matlab computer code calculates the sum of the transmission probabilities, $T(w)$, for all phonons at angular frequency $w$. The scale $w$ is set by the atomic mass, $m$, and the spring constant between atoms, $k$:

$$w_0 = \sqrt{\frac{k}{m}} \quad (5)$$

In the plots shown in the next section frequencies are measured in units of $w_0$, the thermal conductance is measured in units of $k_B w_0$, and the temperature is measured in units of $\frac{k_B T}{w_0}$. The actual computer code uses the recursive green function technique, which is both numerically stable and efficient. The details of this code are beyond the scope of this paper.
Results

The models made in this research project have showed promising results to reduce the thermal conductivity. We have computed different cases during the research, where the different structures that will be displayed show the differences in the energies and thermal conductivity.

Fig 2  $T(w)$ and Temperature vs. Conductance of a straight uniform wire

The straight uniform wire shown in the middle of Figure 2 was programmed into Matlab. The left graph in this figure shows the net transmission as a function of the frequency square. The net transmission is the sum of the transmission probability for each transverse mode in the wire. The net transmission increases and then decreases because the number of allowed vibrational modes increases as one goes to the center of the phonon band. Note that the maximum for the net transmission is approximately 6 or 7 here. The right hand side of Figure 2 plots the lattice thermal conductance as a function of temperature. The maximum at high temperature is approximately 35.
We next examine the cases of ordered zigzag wires in Figure 3 above and Figure 4 below. The transmissions in both cases have sharp peaks that correspond to resonant transmission near specific frequencies. The transmission functions for the two cases are similar, but not identical. Both cases also have a reduced lattice thermal conductance of 8 or 9 down from 35 for the straight wire. The fact that long and short wires have very nearly the same thermal conductance and quite similar transmission functions indicates that we are seeing an interface effect due to the mismatch between the zigzag and the leads. For an interface effect a longer wire would not cause the thermal conductance to go down.
Fig 4 $T(w)$ and Temperature vs. Conductance of a zigzag wire with a long length

Fig 5 $T(w)$ and Temperature vs. Conductance of an evenly distributed zigzag and disordered wire

To further decrease the thermal conductance we will thus need more interfaces. In Figure 5 we show wire that has a zigzag at the top, followed by a rapidly oscillating boundary in the middle, and a slowly varying boundary at the bottom. This has more interfaces, and as the thermal conductance is further reduced from 8 down to 2.5. The peaks in the transmission have become narrower less dense indicating that significant transmission is only occurring in small frequency ranges.
Figures 6 and 7 show wires of the same general structure as that in Figure 5, except longer. In Figure 6, the wire modeled has a straight attachment down the middle of the wire, while in Figure 7 there is no straight attachment down the middle. The wire with no straight attachment down the middle has a lower conductance than the wire with the attachment. Both of these cases have a lower conductance than the case in Figure 5, which is shorter wire.

For our last case we consider a wire with no straight regions and with random zigzags and disorder distributed throughout the wire. This case yields the largest
reduction in the conductance. The conductance is below 0.1; while the previous two cases has conductance of order 21 and the initial straight wire had a conductance of order 10. Thus, we have seen a reduction in the conductance by approximately two orders of magnitude.

In this research project, six different cases were tested to reduce the lattice thermal conductance through a nanostructured wire. In the first case for testing the thermal conductance, presented in Figure 2 and Figure 3, showed the difference in thermal conductance through a straight wire and patterned zigzag wire. The straight wire had a significantly higher thermal conductance. The reduction of the phonon mean free path is the focus to reduce the thermal conductance. In a straight wire, there is a main path where the phonons transmission will collide easily due to inefficiency of boundary scattering. The rougher surface is important because it dictates whether the scattering is mirror like or diffusive. The wire in Figure 3 is more effective at reducing the thermal conductance than the wire in Figure 2.
Another comparison of different models was between wires with the same structure, just longer in length. Here there was no advantage in making the nanowire longer because there were no additional interfaces between the zigzag and straight regions of the wire. Interface disorder occurs when the regions across a common boundary to not match. Length has no benefit in reducing the thermal conductance.

On the other hand, adding disorder to the wire creates more roughness, which benefits in phonon scattering. Our next set of results was a wire that was modeled with roughness and disorder, shown in Figure 5. The thermal conductance was reduced by a significant amount due to the addition of disorder in the wire. Disorder in the wire is efficient in producing the reduction of conductance. As the number of interfaces increases on the wire the thermal conductivity decreases.

The next case to test the thermal conductance refers to Figure 6 and Figure 7. These two figures have relatively the same shape and the same length. The difference is, in Figure 6, there is a path down the middle of the wire for a straight attachment. Figure 7 has no straight attachment down the middle, which creates a more random path for the phonon to travel. This difference shows that the random path for the phonons to travel reduces the thermal conductance. Randomness is a key factor into reducing the thermal conductance.

In this research, Figure 8 had the lowest thermal conductance found during the simulations. The random roughness and disordered wire, in Figure 10, has a thermal conductance lower than 0.1. This wire has disorder through the whole structure and a complete random path for the phonon mean free path. The complete random path allows the phonons to have a greater average to travel as the heat is transferred without
collisions, as previously mentioned. Adding randomness and unlimited amount of disorder to the wire show the most promising results to reducing the thermal conductance for a thermoelectric device to be more efficient.

**Conclusion**

In the simulations presented here a reduction in the thermal conductance by over two orders of magnitude was obtained in going from a straight wire to one with random zigzags. While the zigzag boundary was able to reduce the thermal conductance of a straight wire, increasing the length of the zigzag region did not further reduce the conductance. Only when we considered wires with a random set of zigzag regions did we obtain the largest reduction in the thermal conductance. This research experience confirms that roughness and disorder reduces the thermal conductance through a nanostructured wire. This approach can make thermoelectric devices more efficient by reducing the thermal conductivity and hence enhancing the thermoelectric figure of merit, ZT, which is inversely proportional to the thermal conductivity. The wire considered in this research are smaller than actual nanowires seen in experiments; however, we believe these general conclusions will hold even for larger wires. Further research on larger systems is needed to confirm this.
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References


