A Non-Equilibrium Green Functions Study of Energy-Filtering Thermoelectrics Including Scattering

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Abstract. Thermoelectric materials can convert waste heat into usable power and thus have great potential as an energy technology. However, the thermoelectric efficiency of a material is quantified by its *figure of merit*, which has historically remained stubbornly low. One possible avenue towards increasing the figure of merit is through the use of low-dimensional nanograined materials. In such a system scattering, tunnelling through barriers and other low-dimensional effects all play a crucial role and thus a quantum mechanical treatment of transport is essential. This work presents a one-dimensional exploration of the physics of this system using the Non-Equilibrium Green's Function (NEGF) numerical method and include carrier scattering from both acoustic and optical phonons. This entirely quantum mechanical treatment of scattering greatly increases the computational burden but provides important insights into the physics of the system. Thus, we explore the relative importance of nanograin size, shape and asymmetry in maximizing thermoelectric efficiency.

1 Introduction

Waste heat is created everywhere; in manufacturing, in the engine of an automobile, in the production of power, in the operation of computer chips, and so forth. A thermoelectric material is able to drive a current when an external temperature gradient is applied. Thus, such materials have great potential in turning our abundant heat losses into energy gains. However, the field of thermoelectrics lies on a sort of precipice; although many theoretical schemes for engineering efficient thermoelectrics exist, commercially available thermoelectrics are still too inefficient for most applications.

The efficiency of a thermoelectric material can be effectively encapsulated within a simple quantity, the figure of merit:

$$ZT = \frac{S^2 G}{\kappa} T$$

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where T is the temperature, G is the conductance, S is the Seebeck coefficient, to be described later, and κ is the total heat conductivity, having both electron, κ_e, and lattice, κ_L, components. A material with a high figure of merit is a good thermoelectric. The state of the art in terms of commercial thermoelectrics lies at around ~ 1 with research devices lying in the range 1.5–1.8 [1]. However, it's generally accepted that for thermoelectric technology to find application in places beyond niche industries like arctic and space exploration, values of $ZT > 2$ are required [1]. Thus, current methods for increasing the figure of merit are insufficient should thermoelectric technology ever hope to reach its potential.

The figure of merit, ZT, can be decomposed into two crucial aspects, the denominator, which is the thermal conductivity, and the numerator S^2G which is collectively called the *power factor*. Thus far, the bulk of improvements to ZT have resulted from schemes which minimize the conductivity of phonons, κ_L, without overly harming the electrical conductivity. This approach then seeks to minimize the denominator of the ZT function. It is much rarer to find schemes which seek to maximize the power factor. The reason for this is that the Seebeck coefficient S and the conductance G are highly interdependent and inversely related, and generally when one improves one they tend to erode the other. However, this need not always be the case.

The Seebeck coefficient is defined as $S = -\Delta V/\Delta T$ and thus intuitively encapsulates the ability of a material to separate charge given a certain temperature gradient. Within linearized transport theory it can be written as

$$S = \int \left(-\frac{\partial f_{FD}(E,T)}{\partial E} \right) T(E) \left(\frac{E - \epsilon_F}{k_B T} \right) dE$$

where f_{FD} is the Fermi-Dirac distribution, T is a conductance or transmission function which is also related to the density of states and ϵ_F is the Fermi level. Similarly, the conductance is defined as

$$G = \int \left(-\frac{\partial f_{FD}(E,T)}{\partial E} \right) T(E) dE.$$

Thus, the key difference between the two components of the power factor is only the factor of $(E - \epsilon_F)/k_B T$. This factor means that symmetric transmission above and below the Fermi level acts to cancel each other out and produce a Seebeck coefficient of zero. Thus, to enhance the power factor one seeks to maximize conductance at energies above the Fermi level but minimize conductance at energies below it. In light of this it was generally considered that insulators/semiconductors with asymmetric valence and conduction bands and a Fermi level lying between them were good materials for thermoelectric applications. Similarly, a typical band in three dimensions has a density of state whose shape is approximately $\propto \sqrt{E - E_0}$ where E_0 is the band edge, thus metals whose Fermi level lies deep in a band where the density of states, and thus the transmission, is effectively constant/flat, were deemed to be poor thermoelectrics.

Contrary to this initial assessment, it has been argued [4,5] that a metal can be made a good thermoelectric if a sequence of potential barriers can be added. If the system has a series of potential barriers whose height is near the height of the Fermi level above the conduction band (or below the valence band) then the material will have a high conductivity, as it is a metal, for energies above the Fermi level, and for energies below the Fermi level transport is effectively blocked by the barriers. Further work along this line [7] would argue that scattering with optical and acoustic phonons, which allowed carriers to mix energy and momentum in the regions between barriers, would further heighten this filtering effect.

This system of barrier filtering is not just an abstract contrivance but does indeed occur in real systems. Two prime examples of this are superlattices, where layer-by-layer varying material properties can create a series of transport barriers, and nanograined systems (i.e. polycrystalline systems where the grain size is on the order of nanometers) where grain boundaries can act as potential barriers [6]. However in terms of modelling and theory, such systems offer considerable challenges. As potential barriers and scattering play a large role in the physics, both quantum tunnelling and phonon scattering must be included if any physical model is to be accurate. The standard method for numerically describing quantum transport is the non-equilibrium Green's function method (NEGF). However, the inclusion of electron-phonon scattering within this model results in a substantial computational burden. Thus, the implementation of such a method is necessarily an exercise in high-performance algorithm design.

The issue of ideal barrier shape has been addressed before by authors of this paper, though at the semi-classical level in a system where ionized impurity scattering was the primary source of scattering [6]. An NEGF calculation taking into account scattering to the issue of energy filtering has also been done before [3] with an eye for optimal barrier spacing and height. In this work we consider a fully quantum mechanical study of the effect of barrier shape on the thermoelectric power factor.

The purpose of this work is to use an NEGF algorithm with electron-phonon scattering incorporated to study the effect of barrier height, width and shape on the power factor. A plausible potential barrier shape will be posited and their forms generalized. The ideal barrier shape will be determined as well as the potential loss for non-ideal shapes quantified.

2 Methods

The NEGF method is a robust and accurate method for simulating quantum transport [2]. The numerical crux of the method involves an inversion of a matrix of the form

$$G(E) = [E \pm i\epsilon - H - \Sigma(E, E')]^{-1}$$

where H is the systems Hamiltonian and Σ is a matrix which accounts for both the effect of the contacts and for electron-phonon scattering. The Green's function must be evaluated for every value of the energy considered

(typical $\sim$ 1000 values). If scattering is not considered then the Green's functions at each energy are independent. In such a case the computation can be parallelized in energy provided each processing node has sufficient memory to hold both the Hamiltonian (which is sparse) and two versions of the Green's function; the retarded Green's function G^R which holds static information and the greater-than Green's function $G^>$ which holds dynamic information (see [2]).

When scattering is included into the NEGF method then the Σ matrix acquires a dependence on other energies. This is because the process of inelastic scattering causes a carrier and a phonon with an energy E and E' to scatter and end with energies of E'' and E''' where $E + E' = E'' + E'''$. It is important to note that only the energy of the carrier, and not the phonon, is tracked. Thus carriers can scatter between energies and the Green's functions are no longer independent. This means that all Green's functions must then be determined self-consistently. The parallelization of the NEGF method then becomes less straightforward. However, optical phonon energies are often approximated to be constant ($E = \hbar\omega$) and thus the mixing of energy only occurs between energies that are $\pm\hbar\omega$. This allows one to still parallelize in energy space with only minimal communication between nodes.

The simulations performed in this paper were done using the effective mass model with $m_{eff} = m_0$, a lattice constant of 0.5 nm and a channel length of 120 nm. The channel contained six barriers with a 20 nm separation between each. The optical and acoustic phonon coupling strengths are taken to be the same with a value of $1.6 \times 10^{-3}\text{eV}^2$. The Fermi level was chosen to maximize ballistic conductance and was fixed at 0.14eV above the conduction band. These parameters, though plausible for a silicon-like structure, are effectively arbitrary and though quantitative behaviour will be dependent on them it is believed that qualitative insights will be general.

3 Results

The type of barrier explored in this work is an exponentially decaying square barrier. Such a barrier profile may realistically appear in structures where a square barrier is intended but some level of diffusion, possibly due to annealing, has occurred and thus are a good prototypical shape. In a reality a perfectly square barrier cannot be obtained and such tails are thus a more natural shape. The first part of the considered barrier shape is a square barrier of height h_b and width w_b. At the edges of the square portion the potential then decays exponentially according to the function

$$f(x) = \exp\left(-C_b x\right)$$

where C_b is the *curvature* of the exponential decay. A sample set of barriers can be seen in Fig. 1. In addition to the properties of the barrier one must also specify the separation between barriers. A cursory exploration of both barrier separation and barrier height found that the optimal values for an entirely square barrier were determined to be 20 nm and 0.17 eV respectively. The fact that the

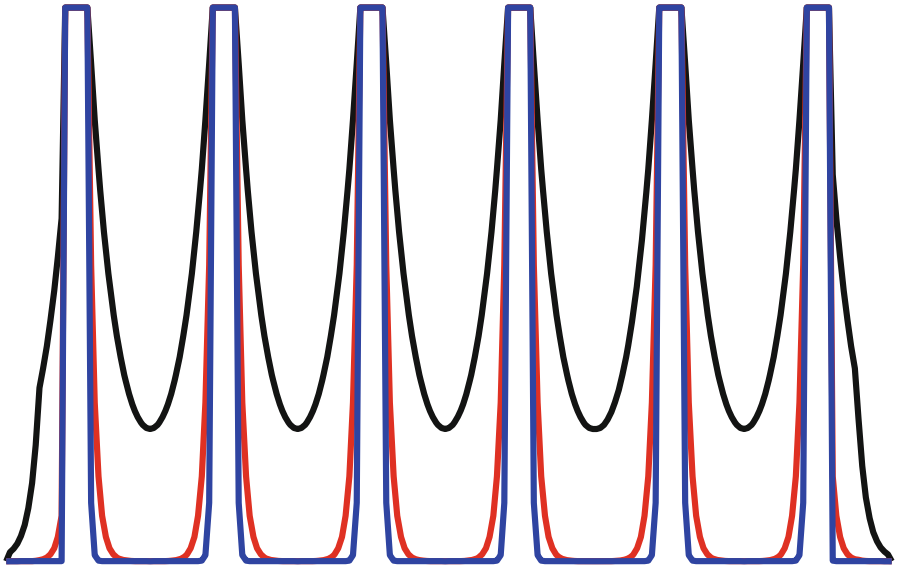

Fig. 1. A schematic diagram of an exponentially decaying square well. The parameter which describes the overall shape is the curvature, C_b. A small C_b corresponds to a very broad, bowl-like, structure (see black line) where a very large C_B corresponds to a square well (see blue line). For reference the curve in red has a curvature of 25.0 (color figure online).

optimal barrier separation corresponds to the specified mean free path suggests the approach taken here is valid.

With the barrier separation and height fixed the power factor dependence on barrier width and curvature were explored. Figure 2 shows the dependence of barrier width on power factor for various curvatures. It is clear that there is a pronounced peak in the power factor at a value of 3 nm. However, the value of the peak is merely an artifact of the chosen system parameters, of greater interest is the loss in power factor associated with deviation from the ideal. For barriers thinner than 3 nm the power factor can be reduced by up to $\sim$ 31 %. The reason for this is fairly intuitive, as the barriers become thinner the amount of tunnelling through the barriers increases. If the purpose of the barriers is to maximize the power factor by blocking conductance through the barrier than tunnelling erodes the power factor gains resulting from this blockage. It is also interesting to note that barriers thicker than the ideal can cause losses of approximately $\sim$ 15 % if one ignores the red and black data (curvatures of 5 and 10), a point to be discussed later. Though this loss is less than the previous case it is still significant. This loss likely results from the poor conductivity of the barrier regions themselves. Since a barrier height of 0.17eV is above the Fermi level of 0.14eV the barrier region is approximately an insulating region. Thus, the thicker the barriers the greater the fraction of the total system volume is comprised of "insulating" material. Thus, conductance drops.

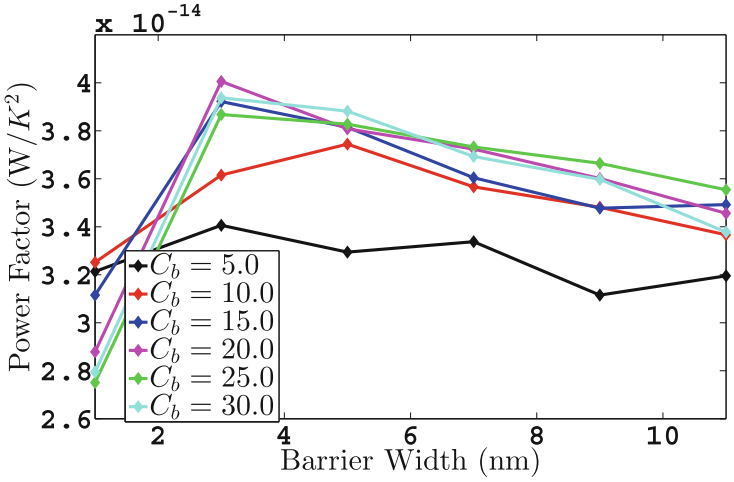

Fig. 2. Power Factors (S^2G) vs. Barrier Width w_b: The above reflects a barrier height of 0.17 eV and separation of 20 nm. There is a clear and pronounced peak at a width of 3 nm with deviations from the ideal causing a loss of $\sim 30\,\%$ in the power factor. Additionally, for curvatures greater than ~ 15.0 the affect on power factor is minimal.

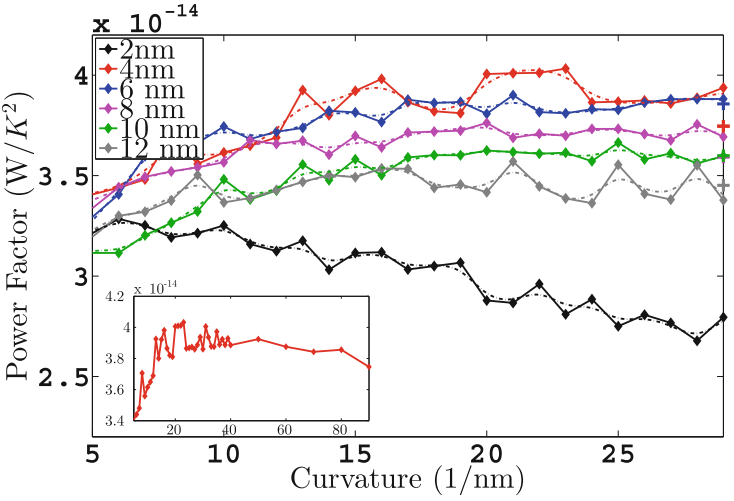

Fig. 3. Power Factor (S^2G) vs. Curvature: The above reflects a barrier height of 0.17 eV and separation of 20 nm. Power factor can be seen to plateau at high curvatures. Lower curvatures have power factors of approximately $\sim 18\,\%$ lower. The inset shows the power factor of a barrier of ideal width, 3 nm, for curvatures tending towards infinity.

Looking at Fig. 2 it is clear that the low curvature data (the red and black lines) has much worse thermoelectric behaviour than the higher curvature data. A plot of power factor versus curvature can be found in Fig. 3. Looking at this figure it is important to stress that higher values of the curvature reflect increasingly square like wells with an infinite curvature being a square well. Thus, the black line in Fig. 3 represent a barrier of width 1 nm and confirms the earlier statement about tunnelling eroding transport with larger curvatures resulting in thinner barriers. However, for all other widths it is clear that overly curved well shapes have worse power factors than square wells, the difference being $\sim 18\,\%$. At curvatures (C_b) of approximately 15.0 it appears that the power factor effectively saturates. From this it can be concluded that the square barrier is the ideal barrier shape.

4 Conclusions

In this work an NEGF study including electron-phonon scattering of the effect of barrier shape and width on the thermoelectric power factor was explored. It was determined that a square barrier of optimized width is ideal for maximizing energy filtering. Furthermore, it was determined that deviations from ideal width can erode the power factor by $\sim 31\,\%$ and deviations from ideal shape can erode by $\sim 18\,\%$.

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