

Nanocomposite Thermoelectric Materials Theory

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Contents

1	Introduction	1
1.1	Motivation	1
1.2	Investigation	1
1.3	Approach	1
2	Background Theory	1
2.1	Kinetic Theory	1
2.2	Phonons	1
2.3	TBR	2
2.4	Thermoelectricity	2
2.5	Statistical Mechanics	2
2.6	Nanocomposites	5
3	Specific Theory	6
3.1	Assumptions	6
3.2	Thermoelectric Efficiency	6
3.3	Phonon Glass Electron Crystal	7
4	Project Aims	8

Abstract

This is the abstract

1 Introduction

1.1 Motivation

Energy and its use defines human society. Throughout human history we have seen an upwards trend of energy consumption and with it we are able to transform our environment and our lives.

Thermoelectric materials have the potential to revolutionise our energy harvesting methods due to their ability to convert heat directly into electricity.

1.2 Investigation

1.3 Approach

2 Background Theory

2.1 Kinetic Theory

Fundamental to describing the transport properties as moving particles

Assumptions

2.2 Phonons

Core to primary idea

Assumptions

2.3 TBR

Assumptions

2.4 Thermoelectricity

In 1821, Thomas Seebeck discovered that a circuit made from two dissimilar metals, with junctions at different temperatures would deflect a compass magnet (Figure 2), he had discovered thermoelectricity. The temperature gradient ∇T between the junctions generates an electromotive force:

$$\mathbf{E}_{\text{emf}} = -S\nabla T \quad (1)$$

where S is the Seebeck coefficient, defined as the induced voltage per unit temperature difference, mathematically $\Delta S = \frac{\Delta V}{\Delta T}$ [?]. This coefficient is not only material dependent, but also temperature dependent, i.e., a temperature gradient produces an electromotive force gradient. This electromotive force gradient produces a current density gradient described macroscopically by a modified Ohm's law [?]:

$$\mathbf{J} = \sigma(-\nabla V - S\nabla T) \quad (2)$$

where \mathbf{J} and σ are the current density $\frac{I}{A}$ and electrical conductivity at a given location in the material and ∇T and ∇V are the temperature and resultant voltage gradients across the material. If we were to repeat the experiment conducted by Seebeck (Figure 2), using a probe to measure V between junctions and σ at each junction for one of the metals, assuming steady state, i.e., $I = 0$ so $\mathbf{J} = 0$, the metal's Seebeck coefficient can be determined.

Thermoelectricity, its uses and current nanocomposite research are well summarised by J. W. Bos [?] and A. J. Minnich et al. [2].

2.5 Statistical Mechanics

Using the kinetic theory, with relevant assumptions defined in Section ??, the charge density \mathbf{J} of an arbitrary charge carrier can be described micro-

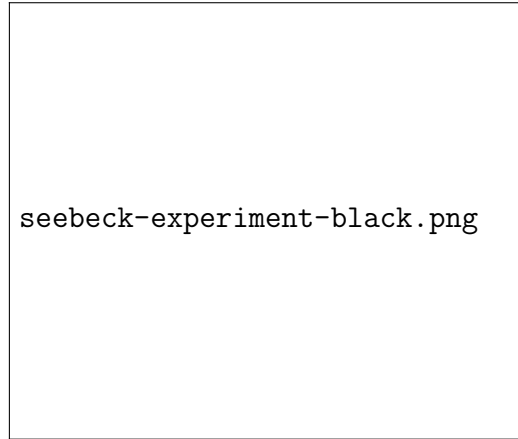


Figure 1: Thomas Seebeck's original thermoelectricity experiment diagram [?]. A compass needle lies on top of one metal, underneath a bridge of a different metal (K), connected by two junctions and heated at one of these junctions.

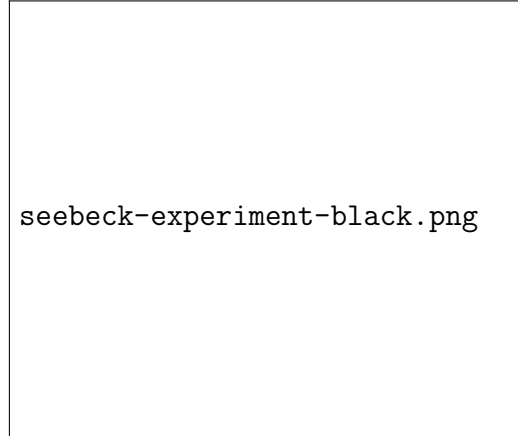


Figure 2: Thomas Seebeck's original thermoelectricity experiment diagram [?]. A compass needle lies on top of one metal, underneath a bridge of a different metal (K), connected by two junctions and heated at one of these junctions.

scopically [?]:

$$\mathbf{J} = \frac{nq^2\mathbf{E}\tau}{m} \quad (3)$$

where n is free charge carrier density, q is the charge of the carrier, \mathbf{E} is the electric field accelerating the carrier, τ is the mean time between carrier collisions and m is carrier mass.

Applying this to solid-state electrical conductivity $\sigma = \frac{ne^2\tau}{m^*}$ it can be shown that [?]:

$$\sigma = \frac{e^2}{m^*} \sum_{\text{spin}} \sum_{\mathbf{k}} n(\mathbf{k})\tau(\mathbf{k}) \quad (4)$$

where e is electron charge, m^* is the electron effective mass, spin refers to electron spin and \mathbf{k} is the electron wavevector over the Brillouin zone. These new concepts are all derived from the nearly free electron model, as described in Kittel [?].

The Boltzmann transport equation “describes the statistical behaviour of a thermodynamic system not in thermodynamic equilibrium” [?] and its general definition is:

$$\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t}\right)_{\text{force}} + \left(\frac{\partial f}{\partial t}\right)_{\text{diff}} + \left(\frac{\partial f}{\partial t}\right)_{\text{coll}} \quad (5)$$

where $\frac{\partial f}{\partial t}$ is time dependence of a system of particles f , the “force” term represents external forces on the particles, the “diff” term is the diffusion of particles through the system and the “coll” term represents forces acting between particles in collisions.

A phonon is the quantisation of vibrational motion of a lattice of atoms at a single frequency, known as a normal mode [?]. These phonons are quasi-particles, free to move around the lattice and they are distributed according to the Bose-Einstein distribution [?]:

$$\bar{n} = \frac{1}{e^{(\hbar\omega)/kT} - 1} \quad (6)$$

where \bar{n} is the probability of a phonon existing with energy $\hbar\omega$.

Electrons can be modelled as quasiparticles in a similar way, with a wavevector and effective mass as in equation (4), leading to the Fermi-Dirac distribution [?]:

$$\bar{f} = \frac{1}{e^{(E-E_f)/kT} + 1} \quad (7)$$

where \bar{f} is the probability of an electron existing with energy E and E_f is the Fermi level.

In the presence of an external fields, phonon and electron distributions ((6) & (7)) both satisfy the Boltzmann transport equation (5) with [?]:

$$\left. \frac{df}{dt} \right|_{field} + \left. \frac{df}{dt} \right|_{collisions} = 0 \quad (8)$$

where function f is $f = \bar{n}$ or $f = \bar{f}$, the Bose-Einstein and Fermi-Dirac distribution functions.

2.6 Nanocomposites

Composite materials are combinations of two or more materials, forming a new structure with significantly different physical or chemical properties than its constituent parts. In a similar way, nanocomposites are the structuring of multiple materials, but at the nanoscale. As our nanocomposites are at a comparable size to the crystal lattices of their constituent materials, we can view nanocomposites as artificial defects in a larger crystal lattice. A simple example of a 2D nanocomposite, a copper-graphene superlattice, is pictured in Figure ?? . Examining one layer of the superlattice, the material in bulk form would be a 3D crystal structure, but by constraining the layer thickness we have introduced a boundary defect. The periodic array of these boundary defects forms a new 3D artificial crystal, which we define as a superlattice, a nanocomposite.

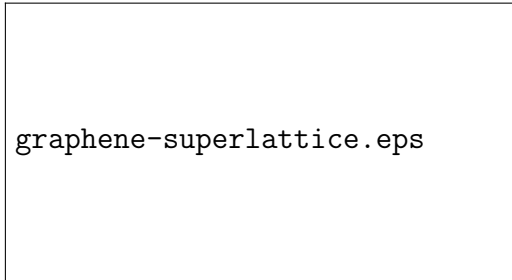


Figure 3: Superlattice of graphene and copper. Alternate layers of nanoscale copper and graphene are sandwiched together.

3 Specific Theory

3.1 Assumptions

For our project we will be using the phonon and nearly free electron models, which bring with them a multitude of assumptions. For the phonon model, our main assumption is that our system consists of at least 50 atomic oscillators [?]; this means we are limited to a $50\text{\AA} = 5\text{nm}$ fabrication size. Current fabrication methods are at best 25nm [2], so our 50 oscillator assumption is well met. For both the phonon and the nearly free electron model, we assume an ideal gas, i.e., particles do not interact with each other and can move freely around the lattice, affected only by lattice perturbations. This is known to be a good assumption for the low temperatures found in solid-state physics [?].

Based on this limited initial analysis, we believe these assumptions should be valid. If it transpires that these assumptions cannot be met, we will seek alternative models.

3.2 Thermoelectric Efficiency

The thermoelectric efficiency is best expressed in the dimensionless parameter ZT with thermal efficiency η which is a function of (ZT, T_h, T_c) , where Z is the figure of merit, $T = \frac{1}{2}(T_h + T_c)$, T_h is the temperature at the hot

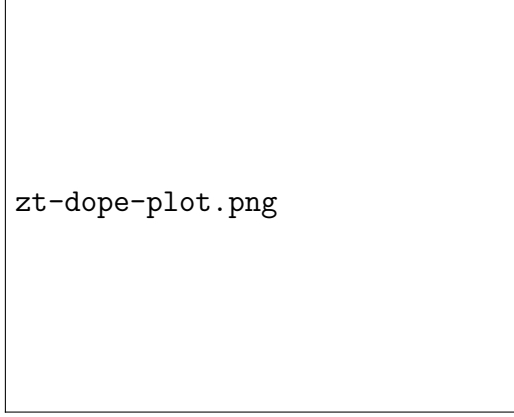


Figure 4: Graph of doping concentration (electron density) against ZT . Insulators are seen up to 10^{19} with semi-conductors occupying the rest of the range. A compromise between variables σ, κ, S^2 , results in heavily doped semi-conductors at the ZT peak [2].

junction and T_c is the temperature at the cold junction. ZT :

$$ZT = \frac{S^2 \sigma T}{\kappa_e + \kappa_{ph}} \quad (9)$$

where S is the Seebeck coefficient from equation (1) & (2), σ is electrical conductivity, κ_e and κ_{ph} are the thermal conductivity due to electrons and phonons respectively. This is derived in D. M. Rowe's Modern Thermoelectrics [?].

Important points to note about ZT are that it is proportional to thermal efficiency η , is increased by a reduction in thermal conductivity and it depends on the square of the Seebeck coefficient. Figure Figure 4 demonstrates the compromise between the variables in equation (9). ZT values of current generation thermoelectric materials have been plotted in figure Figure 5.

3.3 Phonon Glass Electron Crystal

A core concept for our project is the idea of **PGEC!** (**PGEC!**) first proposed by G. A. Slack [1]. Slack proposes that developing a material

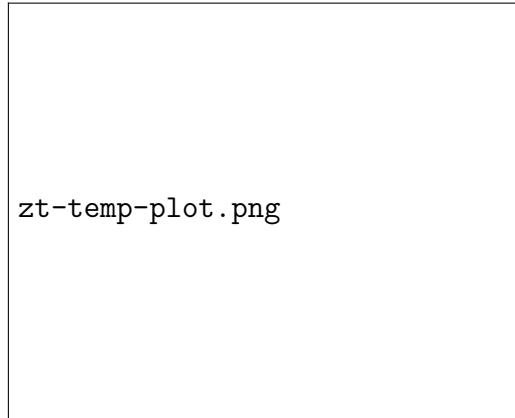


Figure 5: Graph of thermoelectric figure of merit ZT against temperature. The dashed line represents bulk thermoelectric materials, above the dashed line shows current generation nanocomposites [2].

with the properties of both phonon scattering glasses and electron transmissive crystals, will achieve the desired $ZT > 3$. It is thought that the low dimensional systems of nanocomposites introduce the short range disorder of crystal structures common to glasses, yet they maintain the long range order common to electron crystals common [1]. Some key questions for our project are; How can we achieve **PGEC**!? What are its constraints? How effective is it at increasing ZT ?

4 Project Aims

Thermoelectric theory provides a good basis from which we can understand solid-state physics. Using phonon and nearly free electron models together with the Boltzmann transport equation (5) we aim to develop a **PGEC**! inspired mechanism through which ZT can be increased. If such a mechanism is found we will design novel structures and model them computationally. In pursuit of this aim, it is likely that we utilise nanocomposite material design for the introduction of multiple boundary defects.

<https://github.com/kahlos/thermoelectrics>

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References

- [1] G. A. Slack, *CRC Handbook of Thermoelectrics*, 1995, ISBN: 978-0060443849
- [2] A. J. Minnich *et al.*, *Bulk nanostructured thermoelectric materials: current research and future prospects*, Energy Environ. Sci. 2, 466-479 (2009), DOI: 10.1039/B822664B