Thermoelectric Efficiency of Zero-dimensional Nanocomposites

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Abstract

Thermoelectrics are a promising area of materials research recently revitalised by the introduction of nanocomposites. In this project, we aim to derive a theoretical mechanism, through which new, high efficiency thermoelectric materials can be designed. This will involve a detailed understanding of the fundamental theories of solid-state physics, of which the phonon model plays a critical role. This theoretical project aims to guide experiment, keeping within practical limits and computationally modelling potential designs.

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I Introduction

1.1 Motivation

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

Thermoelectric materials have great potential to revolutionise our energy harvesting methods due to their ability to convert heat directly into electricity. This potential has motivated decades of research, resulting in; radioisotope thermonuclear generators, solid state refrigerators and laser temperature control systems.

The main limitation of thermoelectric materials is their heat to electricity conversion efficiency. In modern applications, this is approximately 7% [1], roughly 4× lower than what is currently possible for internal combustion engines [2].

Recent advances in nano-fabrication have facilitated the development of new nanocomposite materials. Closely resembling metamaterials; nanocomposites are typically periodic arrays of nanoscale sheets, wires or particles. In 2001, it was shown that layering thin-films of thermoelectric materials gave a 2.4× increase in the thermoelectric figure of merit ZT [3]; a key parameter in the conversion efficiency discussed above.

If ZT can be increased to 3, an efficiency comparable to combustion engines could be attained in typical thermoelectric systems [4]. This would open up a wide array of applications such as: solar thermoelectric panels [5], exhust heat recovery systems [6] and high reliability refridgeration systems [7].

It is therefore the goal of this project to understand how nanocomposite structuring effects the electrical and thermal properties of thermoelectric materials and whether a ZT>3 can be achieved.

Figure 1: Normalised thermoelectric properties *versus* doping concentration at 300 K for n-type $Si_{80}Ge_{20}$ [8]. Variables defined as: S the Seebeck coefficient, σ electrical conductivity, k thermal conductivity and ZT the thermoelectric figure of merit (proportional to conversion efficiency). The interrelationships between the variables gives a maximum ZT for a heavily doped semiconductor.

1.2 Approach

Thermoelectricity requires a compromise between 3 variables; S the Seebeck coefficient, σ electrical conductivity and k thermal conductivity. The thermoelectric figure of merit ZT and ultimately the conversion efficiency, is maximised when both S and σ are much greater than k. This is well shown in Figure 1, where a decreasing k and increasing σ produce a maximum in ZT.

The problem therefore lies in the complex interplay between these 3 variables; how do we disentangle their relationships and produce a positive effect on ZT?

In the *CRC Handbook of Thermoelectrics* [9], G. A. Slack proposes a mechanism for enhancing ZT, the phonon glass electron crystal (PGEC). In a PGEC, the material is structured to restrict phonon propagation (PG), but enhance electron propagation (EC). If these two effects are independent, then the resultant increase in electrical conducitivity and decrease in thermal conducitivity will boost ZT as in Figure 1.

In 1993, it was theoretically shown that a nanocomposite of closely packed nanoscale cylinders had the potential to significantly increase ZT [10]. We interpretted these results to be following the PGEC concept; the cylinder boundries are scattering phonons, whilst leaving the electrons unaffected.

Nanocomposites have only been a practical possability for the last 10 years, so the theories describing them are still young and in development.

A core concept for for our project is the idea of **PGEC!** (**PGEC!**) first proposed by G. A. Slack [9]. Slack proposes that developing a material 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 [9]. Some key questions for our project are; How can we achieve **PGEC!**? What are its constraints? How effective is it at increasing ZT?

1.3 Investigation

II Background Theory

All the theories discussed in this report are transport processes. Fundamental to them all are the non-equilibrium statistical mechanics of their particles.

2.1 Boltzmann Equation

2.2 Thermoelectricity

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

$$\mathbf{E_{emf}} = -S\nabla T \tag{1}$$

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 [**?**]:

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

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 **??**), 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.* [8].

2.3 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

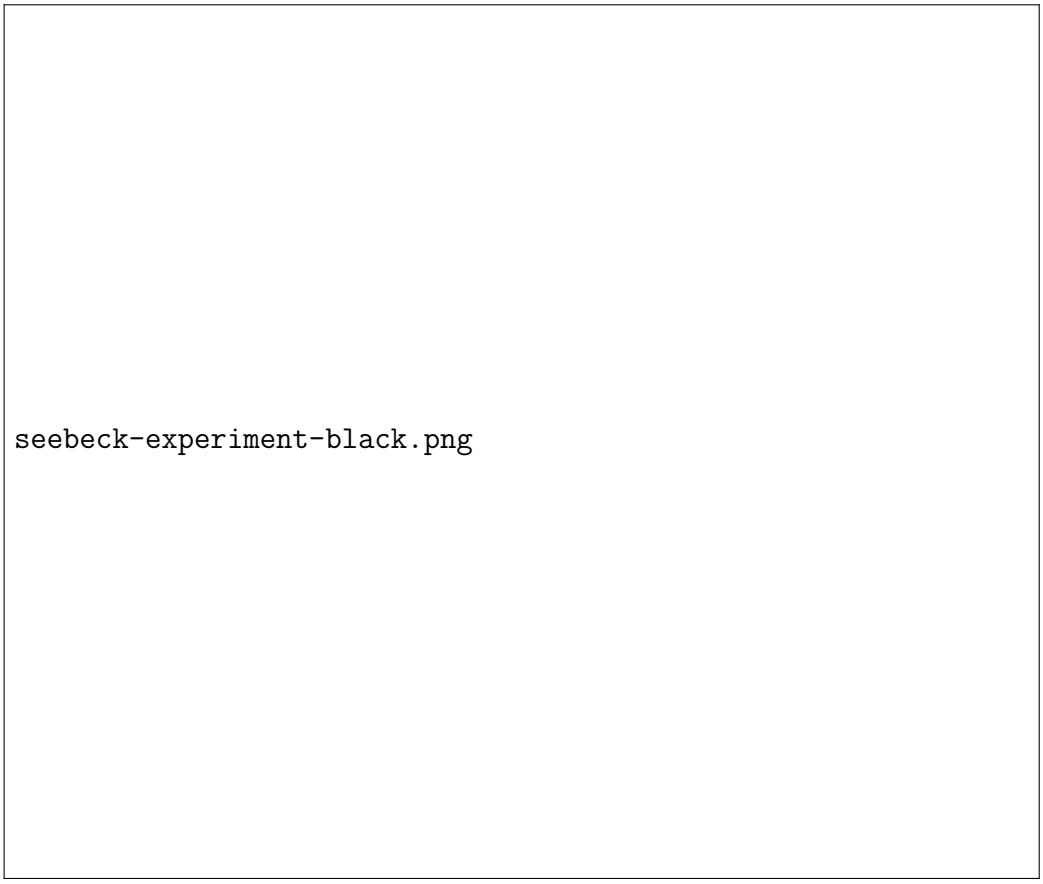

Figure 2: Thomas Seebeck's original thermoelectricity experiment diagram [**?**]. A compass needle lies on top of one metal, underneath a bridge of a different metal (K), connected by two junctions and heated at one of these junctions.

graphene-superlattice.eps

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

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 th0e 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.

2.4 Kinetic Theory

Assumptions

III Specific Theory

3.1 Thermoelectric Theory

Assumptions

IV Results and Analysis

V Conclusion and Potential Development

`https://github.com/kahlos/thermoelectrics`

References

[1] D. M. Rowe, *Modern Thermoelectrics*, September 1983, Holt-Technology, ISBN:978-0835945936 **Page 12**

[2] M. L. Baglione, *Development of System Analysis Methodologies and Tools for Modeling and Optimizing Vehicle System Efficiency*, 2007, University of Michigan, DOI:2027.42/57640 **Pages 52-54**

[3] R. Venkatasubramanian *et al.*, *Thin-film thermoelectric devices with high room-temperature figures of merit*, October 2001, Nature, vol. 413, pp. 597-602, DOI:10.1038/35098012

[4] W. Liu *et al.*, *Recent advances in thermoelectric nanocomposites*, January 2012, Nano Energy, vol. 1, iss. 1, pp. 42-56, DOI:10.1016/j.nanoen.2011.10.001

[5] D. Kraemer *et al.*, *High-performance flat-panel solar thermoelectric generators with high thermal concentration*, May 2011, Nature Materials 10, pp. 532-538, DOI:10.1038/NMAT3013

[6] X. Liu *et al.*, *A case study on compatibility of automotive exhaust thermoelectric generation system, catalytic converter and muffler*,

March 2014, Case Studies in Thermal Engineering, vol. 2, pp. 62-66, DOI:10.1016/j.csite.2014.01.002

[7] L. E. Bell, *Cooling, Heating, Generating Power, and Recovering Waste Heat with Thermoelectric Systems*, September 2008, Science 12, vol. 321, no. 5895, pp. 1457-1461, DOI:10.1126/science.1158899

[8] A. J. Minnich *et al.*, *Bulk nanostructured thermoelectric materials: current research and future prospects*, Feburary 2009, Energy Environ. Sci. 2, pp. 466-479, DOI:10.1039/B822664B

[9] G. A. Slack, ed. D. M. Rowe, *CRC Handbook of Thermoelectrics*, 1995 CRC Press, ISBN:978-0849301469 **Pages 407-440**

[10] L. D. Hicks, M. S. Dresselhaus, *Thermoelectric figure of merit of a one-dimensional conductor*, June 1993 Phys. Rev. B 47, 16631 DOI:10.1103/PhysRevB.47.16631

Appendix

A Further Questions and Thoughts

B List of Assumptions

C Further Reading

D Tools and Software

E Physical Data

F Program Code