



UNIVERSITY OF EXETER

MPhys PROJECT

Thermoelectric Efficiency of
Zero-dimensional Nanocomposites

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Abstract

Thermoelectrics are currently limited by their heat to electric conversion efficiency. If their efficiency can be improved $3\times$ then a wide array of technological applications can be developed. Nanocomposite structuring is a potential technique for achieving this. We utilise an effective medium approximation to calculate the thermoelectric efficiency of a zero-dimensional SiGe nanocomposite. We find that silicon spheres of 10nm diameter densely packed in a germanium host medium, improves the thermoelectric efficiency $2.6\times$ compared to bulk SiGe. This gives good indication that further theoretical and experimental research should be conducted.

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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 the 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 precise thermal control systems.

The main limitation of thermoelectric materials is their heat to electricity conversion efficiency. In modern applications, this is approximately 7% [1], roughly $4\times$ 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 $2.4\times$ increase in the thermoelectric figure of merit ZT [3]; a key parameter in the conversion efficiency discussed above.

If ZT can be increased $3\times$, 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], exhaust heat recovery systems [6] and high reliability refrigeration 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.

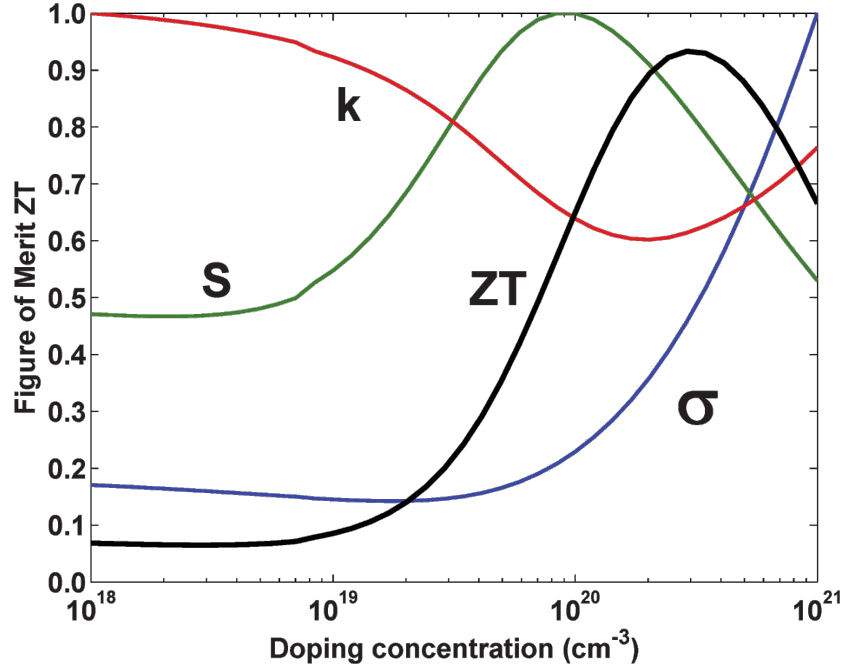


Figure 1: Normalised thermoelectric properties *versus* doping concentration at 300 K for n-type Si₈₀Ge₂₀ [8]. Variables defined as follows: S Seebeck coefficient, σ electrical conductivity, k thermal conductivity and ZT the thermoelectric figure of merit (proportional to conversion efficiency). The 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 the electrical conductivity and k the 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 conductivity and decrease in thermal conductivity will boost ZT, as in Figure 1.

In 1993, Hicks and Dresselhaus theoretically showed that a nanocomposite of closely packed nanoscale cylinders had the potential to significantly increase ZT [10]. We interpreted their findings to be in agreement with the PGEC concept; the cylinder boundaries are scattering phonons, whilst leaving the electrons unaffected. Therefore nanocomposite structuring may offer a possible technique for developing a PGEC material.

As a relatively new field, nanocomposites and its conceptual framework is still young and in development. In the context of thermoelectrics, theories for S , σ and k all need to be explored. We hypothesised that the main reason for the increase of ZT in nanocomposite structuring, is the scattering of phonons. So for our project, we decided to focus on k , specifically the phononic contribution k_{ph} .

Of the literature reviewed, two theories for k_{ph} were of note, the effective medium approximation (EMA) [11] and the phonon hopping model (PHM) [12]. The EMA considers a homogeneous host material whose phonon thermal conductivity is perturbed by a regularly arranged nanostructure. Whereas the PHM considers a linear chain of host atoms regularly perturbed by nanoparticles and calculates the probability of a phonon hopping past or interacting with these nanoparticles. We evaluated both models in detail and decided that the PHM neglected crucial thermoelectric properties, so we adopted the EMA for our calculations.

Our final consideration is which nanocomposite structure to investigate. Originally, we had planned to test multiple structures and compare their effects. However, as we were studying the EMA theory, it became clear that the optimum structure would have a high density of interfaces, with maximal gaps between these interfaces. This made closely packed spheres an ideal choice, as there is minimal contact between the spheres and a large surface area exposed to the host material. This structure is illustrated in Figure 2.

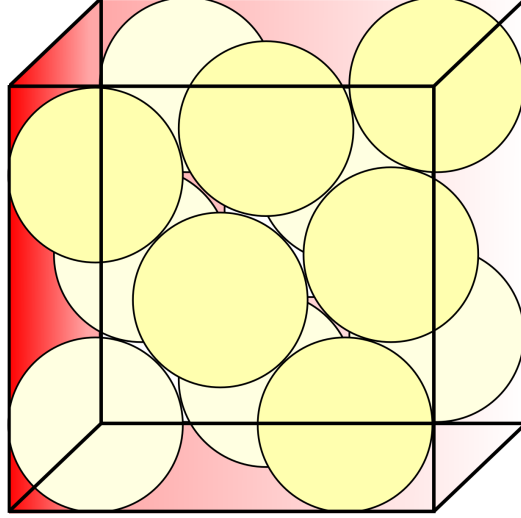


Figure 2: Zero-dimensional nanocomposite structure. Nanoscale spheres are densely packed with a homogeneous host material filling the voids. A temperature gradient is shown, to illustrate use as a thermoelectric.

1.3 Investigation

With the components discussed in the previous section

II Background Theory

All the theories discussed in this report are transport processes. Therefore fundamental to them all are the non-equilibrium statistical mechanics of their quasiparticles, so this is where we will start.

2.1 Boltzmann Equation

The Boltzmann equation describes the statistical behaviour of a thermodynamic system of particles not in thermodynamic equilibrium and its general definition is:

$$\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t} \right)_{\text{force}} + \left(\frac{\partial f}{\partial t} \right)_{\text{diff}} + \left(\frac{\partial f}{\partial t} \right)_{\text{coll}} \quad (1)$$

where $\frac{\partial f}{\partial t}$ is the time dependence of the distribution function of the 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.

From this general definition we can find how a particular system of particles or quasiparticles are distributed across a material and therefore find their average motion. We use this in the electrical conductivity σ (Section ??) and phonon thermal conductivity k_{ph} (Section ??) derivations.

So we have a way of finding the distribution of our quasiparticles, but what exactly are the quasiparticles we are dealing with? And how are they important in the context of thermoelectrics?

2.2 Phonons

A phonon is the quantisation of vibrational motion of a lattice of atoms at a single frequency, known as a normal mode [13]. These phonons are quasiparticles, free to move around the crystal lattice and they are distributed according to the Bose-Einstein distribution [13]:

$$\bar{n} = \frac{1}{e^{(\hbar\omega)/kT} - 1} \quad (2)$$

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

Phonons are carriers of acoustic and thermal energy through a material. They follow two types of dispersion curve; optical and acoustic. Of these

Assumptions

- Acoustic phonons
- The second item

- The third etc ...

Electrons can be modelled as quasiparticles in a similar way, with a wavevector and effective mass as in equation (??), leading to the Fermi-Dirac distribution [13]:

$$\bar{f} = \frac{1}{e^{(E-E_f)/kT} + 1} \quad (3)$$

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 ((2) & (3)) both satisfy the Boltzmann transport equation (1) with [?]:

$$\left. \frac{df}{dt} \right|_{field} + \left. \frac{df}{dt} \right|_{collisions} = 0 \quad (4)$$

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

2.3 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:

$$\mathbf{E}_{\text{emf}} = -S\nabla T \quad (5)$$

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 [?]:

$$\mathbf{J} = \sigma(-\nabla V - S\nabla T) \quad (6)$$

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].

2.4 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.

Assumptions

III Specific Theory

From a qualitative understanding, there must be strong boundary and interface effects; by definition nanocomposites contain numerous transi-

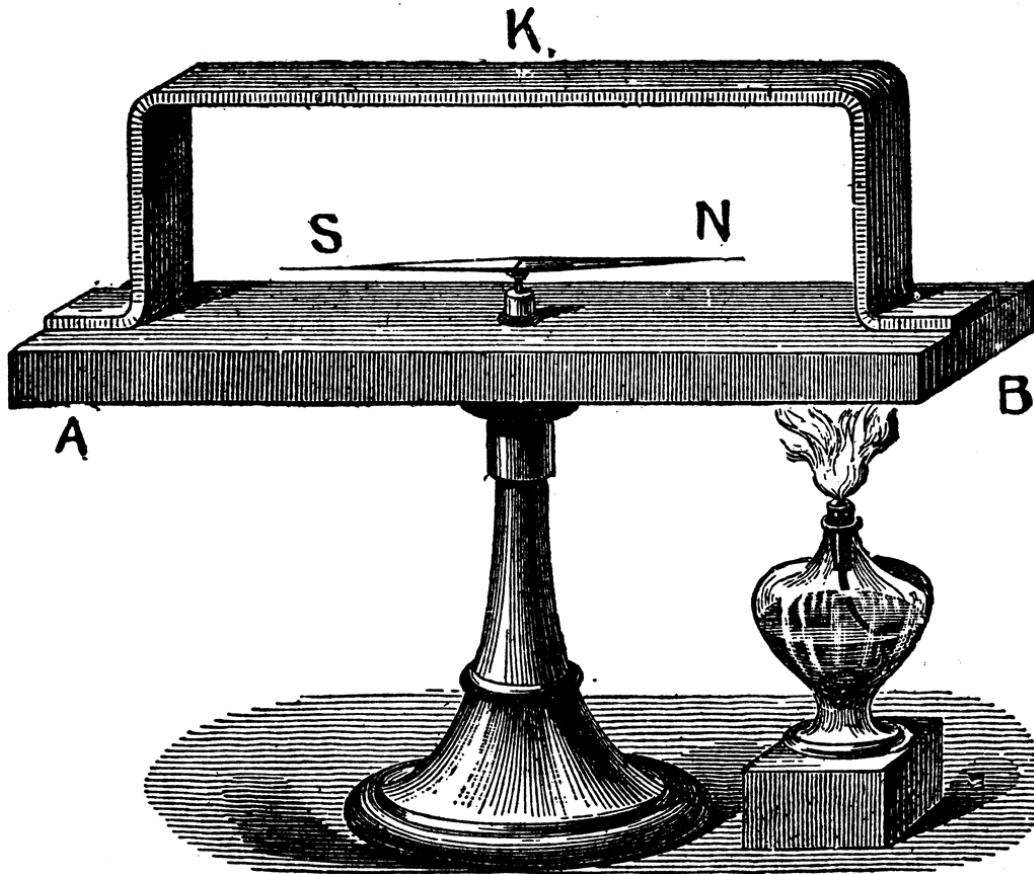


Figure 3: Thomas Seebeck's original thermoelectricity experiment diagram [?]. A compass needle lies on top of one metal, underneath a bridge of a different metal (K), connected by two junctions and heated at one of these junctions.

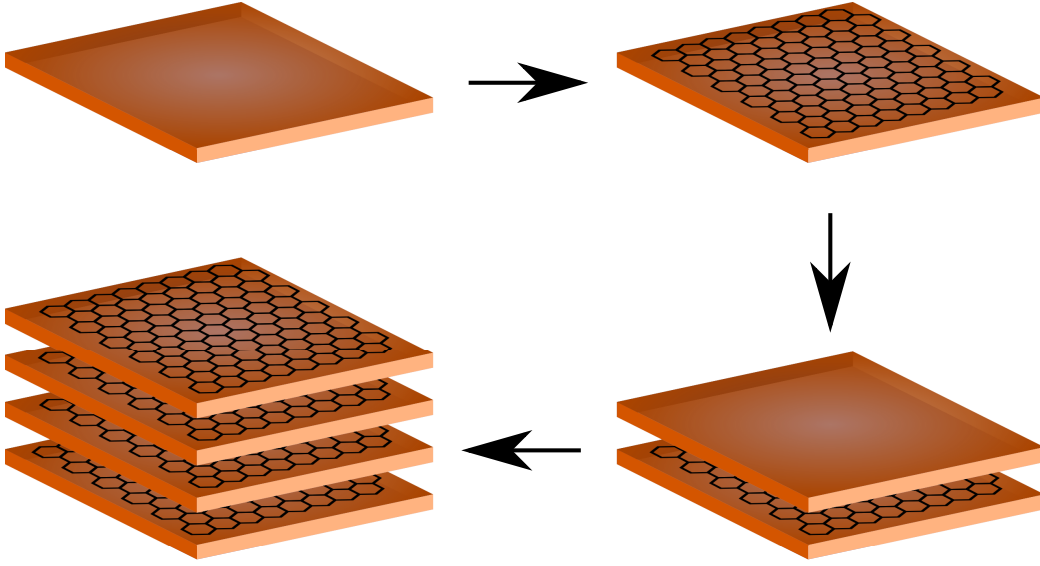


Figure 4: Superlattice of graphene and copper. Alternate layers of nanoscale copper and graphene are sandwiched together.

tions between two or more materials, where each transition forms a new interface. Therefore a thorough understanding of how interfaces affect the propagation of phonons and electrons is required.

The EMA considers a homogeneous host material with a phonon thermal conductivity k_h , that is regularly perturbed by an interface resistance R and separate phonon thermal conductivity k_p , which is then averaged over a relevant length scale d .

Some key questions for our project are; How can we achieve **PGEC!** (**PGEC!**)? What are its constraints? How effective is it at increasing ZT ?

3.1 Thermoelectric Theory

Assumptions

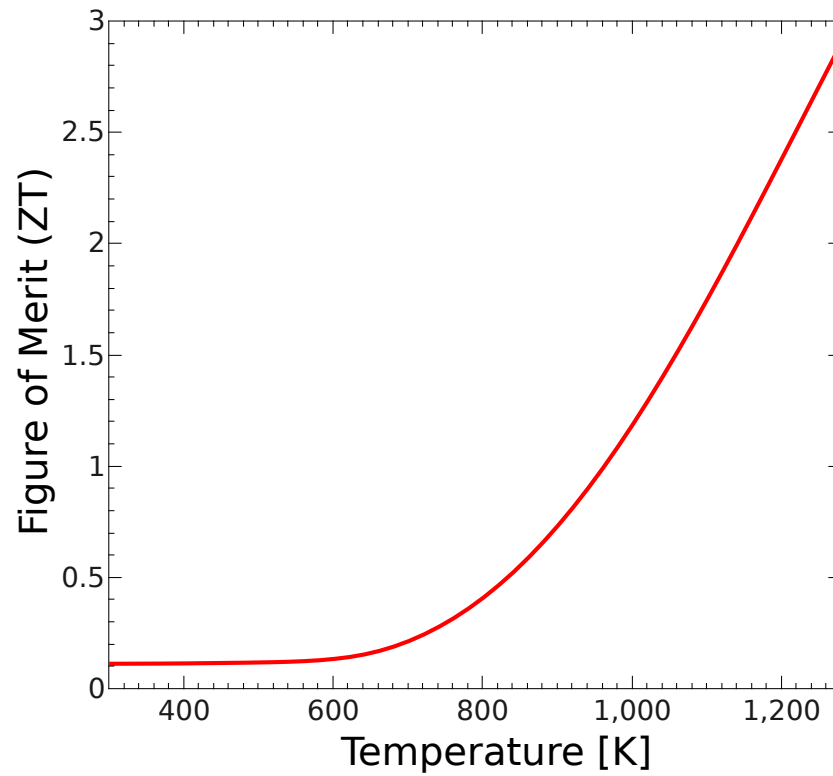


Figure 5: Zero-dimensional nanocomposite structure. Nanoscale spheres are densely packed with a homogeneous host material filling the voids. A temperature gradient is shown, to illustrate use as a thermoelectric.

IV Results and Analysis

V Conclusion and Potential Development

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

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Appendix

- A Further Questions and Thoughts
- B List of Assumptions
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- D Tools and Software
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