I. INTRODUCTION

From its discovery in 1821, thermoelectricity has seen constant attention by the scientific community. Its source lies deep in the fundamental nature of solid state materials. Through understanding thermoelectricity we meld all the concepts underpinning ; a well defined thermoelectric theory is the pinnacle of solid-state physics (SSP).

Thermoelectricity is not only a central area of research for SSP, but also has enormous practical significance. Current bulk thermoelectrics achieve thermoelectric figure of merit ZT up to one, which results in a practical thermal efficiency (heat to work) of just 4%, six times less than modern internal combustion engines.

Despite this low figure, thermoelectrics still see niche use in refrigeration and space exploration due primarily to their exceptional reliability. By increasing ZT up to three, new applications in heat recovery systems and solar thermal generators emerge, improving the thermal efficiency of current power generation methods. Theoretically, there is no upper limit to ZT, and as it approaches infinity, efficiencies at the Carnot limit can be obtained. If we achieve $ZT \rightarrow \infty$, all heat gradients will be maximally exploitable for high value electrical energy; once where there were water wheels, there became hydroelectric dams, now where there is heat, there will be thermoelectricity.

II. BACKGROUND THEORY

A. Thermoelectricity

In 1821, Thomas Seebeck discovered that a circuit made from two dissimilar metals, with junctions at different temperatures would deflect a compass magnet (Fig. 1), he had discovered thermoelectricity. The temperature gradient $\vec{\nabla}T$ between the junctions generates an electromotive force:

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

where S is the Seebeck coefficient, defined as the induced voltage per unit temperature difference, mathematically $\Delta S = \frac{\Delta V}{\Delta T}$ [3]. 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 [6]:

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

where $\vec{J}$ and σ are the current density $\frac{I}{A}$ and electrical conductivity at a given location in the material and $\vec{\nabla}T$ and $\vec{\nabla}V$ are the temperature and resultant voltage gradients across the material. If we were to repeat the experiment conducted by Seebeck (Fig. 1), 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 $\vec{J} = 0$, the metals Seebeck coefficient can be determined.

Thermoelectricity, its uses and current nanocomposite research are well summarised by J. W. Bos [4] and A. J. Minnich et al. [5].
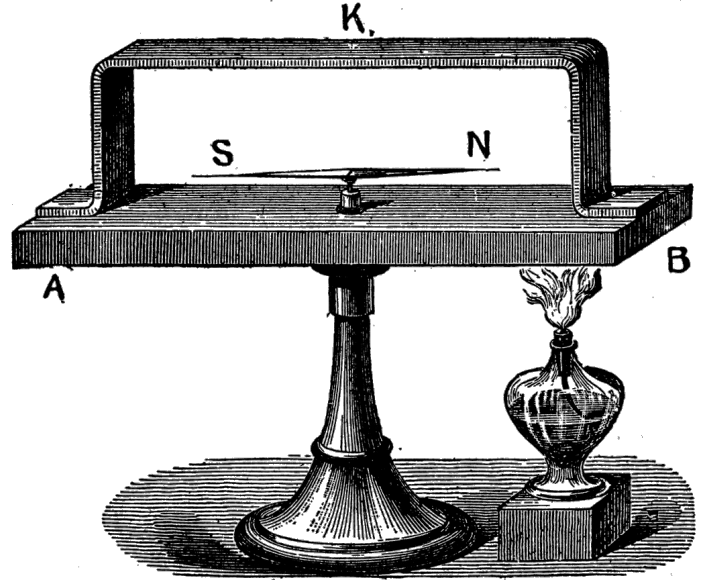

Fig. 1. Thomas Seebeck's original thermoelectricity experiment diagram [2]. A compass needle lies on top of one metal, underneath a bridge of a different metal (K), connected by two junctions and heated at one of these junctions.

B. Statistical Mechanics

Using the kinetic theory, with relevant assumptions, charge density $\vec{J}$ of an arbitrary charge carrier can be described microscopically [7]:

$$\vec{J} = \frac{nq^2\vec{E}\tau}{m} \tag{3}$$

where n is free charge carrier density, q is the charge of the carrier, $\vec{E}$ 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 [6]:

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

where m^* is the electron effective mass, spin refers to electron spin and $\vec{k}$ is the electron wavevector over the Brillouin zone. These new concepts are all derived from the **NFE!** (**NFE!**) model, as described in Kittel [7].

The Boltzmann transport equation "describes the statistical behaviour of a thermodynamic system not in thermodynamic equilibrium" [8] and its general definition is:

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

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 quasiparticles, free to move around the lattice and

they are distributed according to the Bose-Einstein distribution [7]:

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

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 [7]:

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

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 [6]:

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

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

C. Nanocomposites

Composite materials "are materials made from two or more constituent materials with significantly different physical or chemical properties, that when combined, produce a material with characteristics different from the individual components" [9]. Nanocomposites are identical in concept to traditional composites, except the constituent materials are at that 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 Fig. **??**. 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.

2D -¿ 1D -¿ 0D

III. PROJECT THEORY DISCUSSION

A. Assumptions

For our project we will be using the phonon and **NFE!** models, which bring with them a multitude of assumptions. For the phonon model, our main assumption is that our system is at least 50 atomic oscillators [7]; this means we are limited to a $50\text{Å} = 5\text{nm}$ fabrication size. Current fabrication methods are at best 25nm [**?**], so our 50 oscillator assumption is well met. For both the phonon and the **NFE!** model, we assume an ideal gas, i.e., particles do not interact with each other and can move freely around the lattice, effected only by lattice perturbations. This is known to be a good assumption for the low temperatures in SSP [7].
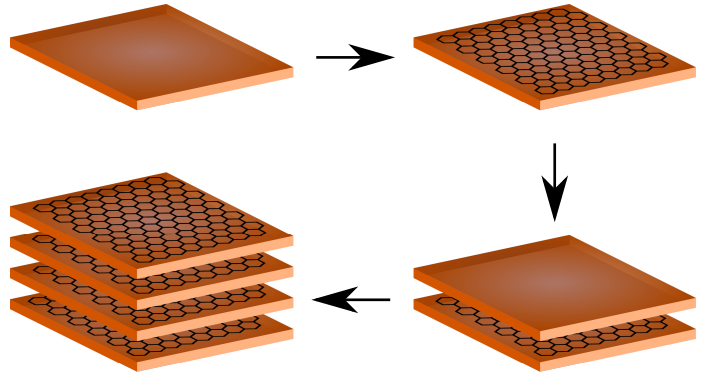

Fig. 2. Superlattice of graphene and copper. Alternate layers of nanoscale copper and graphene are sandwiched together.

Based on this limited initial analysis, we believe these assumptions should be valid with an accurate final model possible. If it transpires that these assumptions cannot be valid, we will seek alternative models.

B. Thermoelectric Efficiency

The thermoelectric efficiency is best expressed in the dimensionless parameter ZT with thermal efficiency $\eta = \eta(Z\bar{T}, T_h, T_c)$, where Z is the figure of merit, $\bar{T} = \frac{1}{2}(T_h + T_c)$, T_h is the temperature at the hot junction and T_c is the temperature at the cold junction. Note that the T in the commonly cited ZT really refers to $Z\bar{T}$. This is omitted due to the temperature appearing of both sides of the expression for ZT:

$$Z\bar{T} = \frac{S^2 \sigma \bar{T}}{\kappa_e + \kappa_{ph}} \tag{9}$$

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. This is derived in D. M. Rowe's Modern Thermoelectrics [10].

Current thermoelectric materials ZT values against temperature are plotted in figure Fig. **??**

The mean time between collisions τ from (3) is of vital importance for our project.

C. PGEC! (PGEC!)

A core research topic for our project is the idea of **PGEC!**. How can we achieve this? What are the constraints?

IV. CONCLUSIONS & PROJECT AIMS

Thermoelectric theory provides a good basis from which we can understand SSP. Using phonon and **NFE!** models together with the Boltzmann transport equation (5) we aim to develop a **PGEC!** inspired mechanism through which ZT can be improved and test this mechanism computationally. In pursuit of this aim, it is likely that we utilise nanocomposite material design for the introduction of multiple boundary defects.
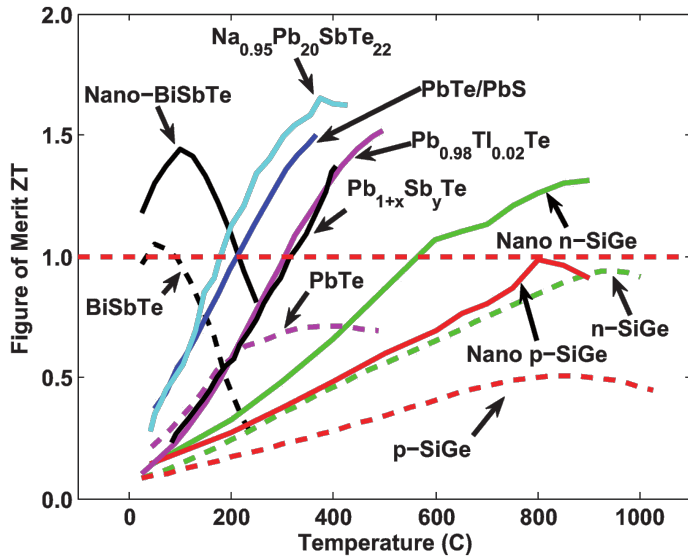
Fig. 3. Plot of thermoelectric figure of merit ZT against temperature. Note ZT is proportional to the thermal efficiency $ZT \propto \eta$ [5].

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