PHAS0097 Project

Literature Review

Minimising Thermal Conduction in Model Materials With Disorder on Different Length Scales

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1 Introduction

Today, one of the biggest crises facing humanity is climate change. From researchers to diplomats, influential voices have called for urgent action to build a sustainable future [1], with countries, such as the United Kingdom, setting net-zero targets by 2050. [2] [3]

From carbon capture to clean energy, net-zero can be achieved in many ways. However, rising energy demands makes energy efficiency improvement necessary; the energy losses must be minimised.

Energy is primarily dissipated as heat, with some additional acoustic losses. This is commonplace in metals, which are good thermal conductors. Conversely, thermal insulators retain their heat; this makes them important for thermoelectrics [4] and the building sector. Currently, thermal insulation techniques in buildings predominantly use fiberglass, which traps air within glass fibers [5]. Foamy materials, which leverage air to maintain heat, are also used [6]. However, these materials are bulky, hence unsustainable to produce. A reduction of the thermal conductivity from the current ultralow value of $\kappa \sim 10^{-1}\,\mathrm{W\,m^{-1}\,K^{-1}}$ to $\kappa \sim 10^{-3}\,\mathrm{W\,m^{-1}\,K^{-1}}$ would decrease building insulation coatings from $10\,\mathrm{cm}$ to $1\,\mathrm{mm}$. Such a material would be much more sustainable to produce, carrying significant implications for a net-zero future.

The thermal conductivity κ relates the steady-state heat flux J to the temperature gradient ∇T, over a material, through Fourier's law [7]. It is given in arbitrary dimension as

$$J = -\kappa \nabla T. \tag{1}$$

Minimising κ is an incredibly challenging task due to the underlying physics regarding Heisenberg's Uncertainty Principle. Additionally, modelling many-body interactions between carriers remains a difficult endeavour.

2 Calculating and achieving minimal thermal conductivity

This section will go over the method which will be used to compute κ in this project. This is covered in the first subsection. The remaining subsections discuss theoretical strategies to minimise κ, with their underlying physics.

2.1 Calculating thermal conductivity: Green-Kubo method

Multiple formalisms can describe the thermal conductivity of materials. For crystals, the phonon gas and Debye-Peierls' model capture phonon scattering mechanisms [8]. For disordered materials, the Allen-Feldman theory focuses on diffusons and propagons as heat carrying modes [9]. Whilst these models are excellent for detailing the physics behind thermal conductivity, they are too specialised. For this project, we need a model which can describe thermal conductivity regardless of the material.

The Green-Kubo relations achieve this due to their mechanical derivation. They are a relationship between a macroscopic transport coefficient γ and a microscopic time-dependent variable A, taking the following form [10]

$$\gamma = \int_0^\infty \left\langle \dot{A}(t)\dot{A}(0) \right\rangle \mathrm{d}t. \tag{2}$$

It follows that the thermal conductivity κ is given by [11]

$$\kappa = \frac{1}{3Vk_\mathrm{B}T^2} \int_0^\infty \langle \mathbf{J}(0)\cdot\mathbf{J}(t)\rangle \,\mathrm{d}t\,, \tag{3}$$

where V is the volume and t is the time. The factor of 3 reflects the three spatial dimensions. This integral measures the correlation of the time-evolving heat flux $\mathbf{J}(t)$ between two different times automatically for all times. It is therefore referred to as an auto-correlation function, which is a computational technique widely used in molecular dynamics.

The beauty of Green-Kubo is that it is an approximate derivation purely from the Hamiltonian formalism with an applied external field, with no locality assumptions. The derivation assumes the response to the applied field is linear, hence it is also referred to as a "linear response theory" [11]. This foundation makes the Green-Kubo method robust for describing the thermal conductivity of any material, which is a clear improvement on the previous models mentioned.

However, Green-Kubo does not consider phonons inherently [12], which are fundamental to the theory of thermal transport. As such, unlike the specific models mentioned, it is difficult to gain an insight into the underlying physics behind the material's heat transport just from using Green-Kubo relations.

2.2 Lowering thermal conductivity: Rattling mechanisms

One way to lower κ is to exploit "rattling mechanisms". Materials behaving this way, such as $CsAg_5Te_3$, have been very promising for thermoelectrics [13]. An illustration of the caging mechanism for $CsSnI_3$ is shown in Figure 1.

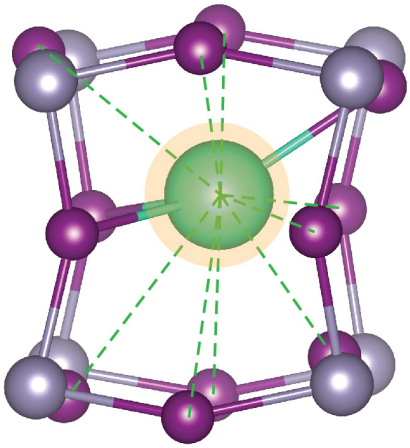

Fig. 1: Schematic demonstrating the rattling mechanism of cesium tin iodide, $CsSnI_3$. The heavy cesium ions ($132.9\,\mathrm{g\,mol^{-1}}$, green) are caged by the ligher tin ($118.7\,\mathrm{g\,mol^{-1}}$, dark purple) and iodine ($126.9\,\mathrm{g\,mol^{-1}}$, light purple) atoms, and as such rattle. Diagram taken from Berkeley Lab News Center [14], atomic masses from U.S. National Library of Medicine [15].

In these materials, the weakly bonded heavy ions are 'caged' by the strongly bonded lighter ions. Inside these cages, the heavy ions are said to strongly vibrate (rattle) and emit phonons, hence the mechanism's name. Due to caging and the heavy ions' weak bonds, these phonons are unable to propagate far and are mostly scattered, thus localised within the cage [16] [17]. Localised phonons are known to occur in disordered crystals, manifesting in a phenomenon called Anderson localisation [18] [19]. This theory is the main driver of the low thermal conductivity of disordered materials in comparison to crystals, and is additionally promising for quantum computing [20] [21].

2.3 Lowering thermal conductivity: Modular layered superlattices

A more complicated framework to lower κ is to look at the problem from a 'modularised layer' perspective. In 2021, researchers found that the material which exhibits the lowest thermal conductivity is the bulk superlattice $Bi_4O_4SeCl_2$, recording the ultra-low value of $\kappa = 0.1\,\mathrm{W\,m^{-1}\,K^{-1}}$ at room temperature [22]. Here, two types of bonding between stacked layers were investigated to lower the directional thermal conductivity; they were then combined into a 'superlattice' to synthesise a material with very low transverse and longitudinal phonon velocities. This is illustrated in Figure 2.

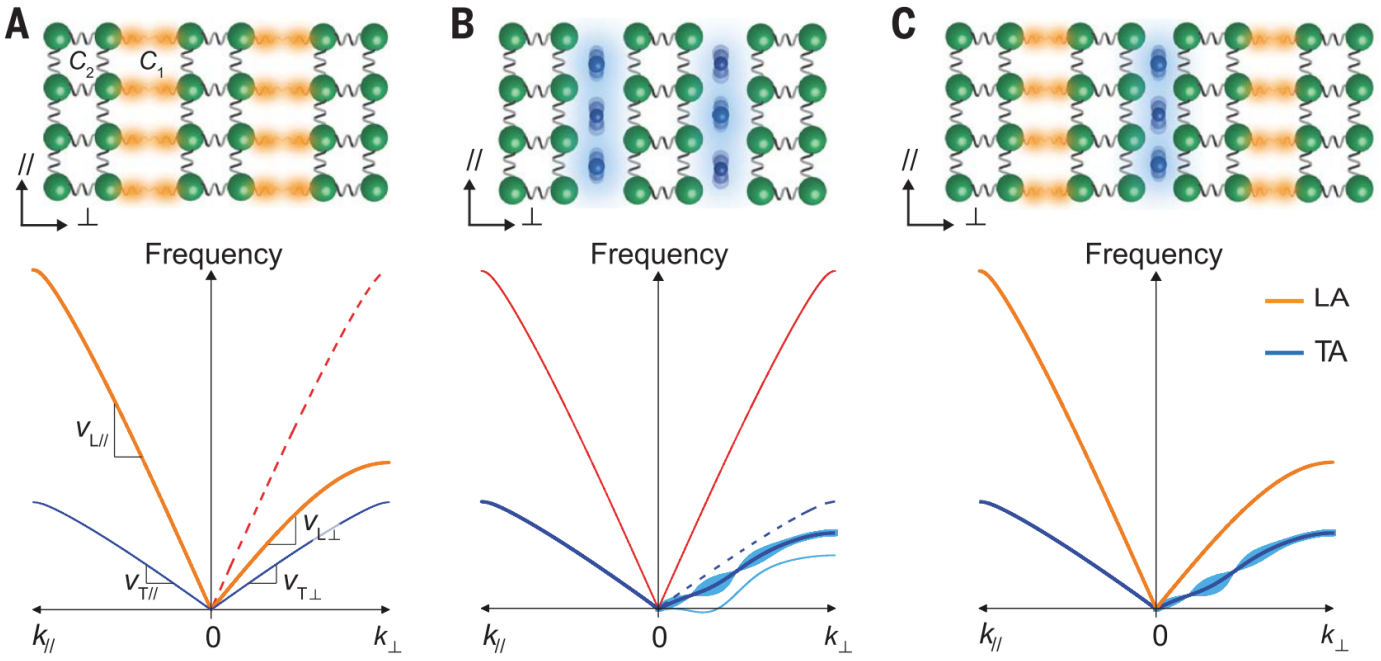

Fig. 2: Diagram showing three types of layer-stacking in the research carried out by the University of Liverpool [22]. (**A**) Schematic of a material suppressing longitudinal phonon modes. (**B**) Schematic of a material suppressing transverse phonon modes. (**C**) Schematic of a material combining the techniques of (**A**) and (**B**), suppressing both longitudinal and transverse phonon modes, as shown in the dispersion relation.

To suppress longitudinal modes, weak bonds between layers of $Bi_2O_2Cl_2$ were introduced, with a spring constant much lower than that of the intra-layer bonds. This suppression is illustrated by the flatter dispersion relation for the longitudinal modes in Figure 2A, implying that longitudinal phonon modes propagate much slower. As phonons can be thought of as quasiparticles carrying heat, it makes sense that slower phonons correspond to decreased thermal conductivity.

To suppress transverse modes, $(Bi_2O_2)^{2+}$ layers were bridged together by layers of intermediary undersized Se^{2-} ions. These ions electrostatically attracted neighbouring layers, causing shear in-plane distortions. This caused transverse phonons to propagate slower, reducing the material's thermal conductivity.

Finally, the two techniques of layering were combined to form a $Bi_4O_4SeCl_2$ superlattice, alternating between varying bonding strengths and undersized ion layers. This suppressed both longitudinal and transverse modes of phonons, considerably lowering the overall phonon velocity and subsequently the overall thermal conductivity.

3 Project Aims and Objectives

The main aim of this project is to drive κ as low as possible, by introducing disorder on different length scales, therefore localising vibrations. Previous projects have investigated random mixtures of masses and perturbation to Lennard-Jones parameters (bonding strengths), introducing controlled disorder whilst retaining the anharmonicity of phonons. This project will build on previous work by investigating more complicated structures, such as the rattling mechanisms and superlattices previously described. To this end, a mesoscale model will be developed in Python, with its thermal conductivities being calculated via molecular dynamics.

3.1 Calculating thermal conductivities in LAMMPS

As the thermal conductivity is well described by grouped atomic vibrations, it can be computed using molecular dynamics. This project will be using LAMMPS (**L**arge-scale **A**tomic/**M**olecular **M**assively **P**arallel **S**imulator). LAMMPS is a classical molecular dynamics simulation software which is accessible and easy to use [23]. It is also simple to facilitate the creation of simple cubic crystals in LAMMPS.

LAMMPS supports four techniques to calculate the thermal conductivity, three of which rely on non-equilibrium molecular dynamics (NEMD). These are the Langevin, Muller-Plathe and energy alteration methods.

The final method is the previously discussed Green-Kubo formalism. As it is an ensemble-average, this technique is superior to its NEMD equivalents. However, the system must be adequately equilibrated prior to usage, so it is likely be computationally expensive. Despite this drawback, its increased accuracy makes it the preferred candidate for thermal conductivity computation.

3.2 Developing the mesoscale model in Python

Although LAMMPS supports simple structure creation, complicated structures are difficult to construct within its input configuration. However, LAMMPS has the ability to read datafiles which describe intricate structures. To this end, Python can be used to create these files, defining the structure within.

To achieve this, just two Python functions can be written. The first will define basis points within a region of space in a given lattice arrangement, and the second will (arbitrarily) assign atoms to these basis points. The Lennard-Jones parameters are easily configurable from LAMMPS, so these will not be necessary to implement in Python.

Initially, the mesoscale model will be used to construct simple structures. Throughout time, the model's capabilities will be extended to describe more complicated structures, eventually reaching a point where sophisticated crystals, such as the $Bi_4O_4SeCl_2$ superlattice, can be constructed within Python.

3.3 Analytical work: which parts contribute to thermal conductivity?

4 Conclusion and next steps

This literature review discussed the vital role of thermal insulators for a sustainable future. A reduction to the minimum thermal conductivity available for building insulation can reduce the amount of material produced for this purpose, having significant implications for net-zero targets [5] [6].

The review presented two structures which exhibit ultralow thermal conductivity: rattling crystals and superlattices. These structures will be developed using a mesoscale model built in Python, and their thermal conductivities calculated via the molecular dynamics software LAMMPS. Afterwards, we will attempt to minimise these values by identifying and eliminating the vibrations contributing the most to the conductivity.

Concurrently to writing this literature review, LAMMPS has been initialised and understood, whilst the mesoscale model has been developed to a point where simple layering is possible. With the literature review finished, much more time can be spent developing the mesoscale model to the level which is needed.

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