UNIVERSITY OF LEEDS

DOCTORAL THESIS

Simulating the thermal conductivity of lower mantle minerals

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School of Earth and Environment

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Declaration of Authorship

I, Ben TODD, declare that this thesis titled, "Simulating the thermal conductivity of lower mantle minerals" and the work presented in it are my own. I confirm that:

- This work was done wholly or mainly while in candidature for a research degree at this University.
- Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated.
- Where I have consulted the published work of others, this is always clearly attributed.
- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.
- I have acknowledged all main sources of help.
- Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself.

Signed:

Date:

Do it!
Just do it!

Don't let your dreams be dreams.
Yesterday you said tomorrow, so just do it!
Make your dreams come true!
Just do it!

Some people dream of success,
while you're gonna wake up,
and work hard at it!
Nothing is impossible!

You should get to the point,
where anyone else would quit,
and you're not going to stop there.
No, what are you waiting for?

Do it!
Just do it!
Yes you can!
Just do it!

If you're tired of starting over,
stop giving up.

Shia LeBeouf

UNIVERSITY OF LEEDS

Abstract

Faculty of Environment
School of Earth and Environment

Doctor of Philosophy

Simulating the thermal conductivity of lower mantle minerals

by Ben TODD

The Thesis Abstract is written here (and usually kept to just this page). The page is kept centered vertically so can expand into the blank space above the title too...

Acknowledgements

The acknowledgments and the people to thank go here, don't forget to include your project advisor…
Everyone is smart, set yourself apart by being kind.

Contents

List of Figures

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List of Abbreviations

CMB	**C**ore-**m**antle **b**oundary
LLSVP	**L**arge, **l**ow-**s**hear-**v**elocity **p**rovince
ULVZ	**U**ltra **l**ow **v**elocity **z**one
DAC	**D**iamond **a**nvil **c**ell
$MgSiO_3$	Magnesium Silicate
$FeSiO_3$	Iron Silicate
bdg	**b**ri**dg**manite
pv	**p**ero**v**skite
ppv	**p**ost-**p**ero**v**skite
LAMMPS	**L**arge-scale **A**tomic/**M**olecular **M**assively **P**arallel **S**imulator
DFT	**D**ensity **F**unctional **T**heory
MD	**M**olecular **D**ynamics
EMD	**E**quilibrium **M**olecular **D**ynamics
NEMD	**N**on-**e**quilibrium **M**olecular **D**ynamics
DM	**D**irect **M**ethod
GK	**G**reen-**K**ubo
ACF	**A**uto-**c**orrelation **f**unction
MFP	**M**ean **f**ree **p**ath
FSE	**F**inite-**s**ize **e**ffects
BPT	**B**allistic **p**honon **t**ransport

Physical Constants

Boltzmann constant	$k_B = 1.380\,648\,528 \times 10^{-23}\,\mathrm{J\,K^{-1}}$
Boltzmann constant	$k_B = 8.617\,330\,350 \times 10^{-5}\,\mathrm{eV/K}$

List of Symbols

a	distance	m
P	power	W (J s^{-1})
ω	angular frequency	rad

For/Dedicated to/To my…

Chapter 1

Introduction

1.1 Why is thermal conductivity important?

Knowledge of the thermal conductivity of solids is key in a wide range of technological applications and for our understanding of natural systems.

1.1.1 Man-made applications

Low thermal conductivities are required in thermoelectric materials, to maximise the efficiency of heat-electricity conversion (Snyder and Toberer, 2008).

1.1.2 In the context of the Earth

For example, in the Earth's lower mantle thermal conductivity controls the nature of planetary convection (Tosi et al., 2013), and the heat flux out of the core which powers the geotherm.

The lower mantle encompasses the region between the mantle transition zone (660 km deep, ~1900 K, ~25 GPa) and the CMB (2891 km deep, ~4000 K, ~136 GPa). The composition of this region can be approximated as 80% $MgSiO_3$/magnesium silicate perovskite (bridgmanite) and 20% MgO/magnesium oxide (periclase), both of which are insulators and past their Debye temperatures at lower mantle conditions.

1.2 What is thermal conductivity?

Thermal conductivity determines whether a material is a conductor or insulator of heat, both of which have many technological applications.

1.2.1 What affects it?

pressure, temperature, and composition

1.2.2 Mechanisms of heat transport

RADIATIVE AND ELECTRONIC TOO

Heat is transported as lattice virbrations, or phonons. The further phonons travel before scattering (mean free path, MFP) the more efficient the heat transport and thus higher the thermal condutivity. A number of effects (MENTION MATTHIESSEN'S RULE) cause phonons to scatter: (1) collisions with other phonons in the lattice, (2) boundaries or defects in the material, and (3) impurities in the atomic structure.

1.3 Previous work - geophysics

INSERT GEOPHYSICS INTRO HERE ASWELL

A range of atomic scale simulation methods are available to determine the lattice thermal conductivity of materials. These are invaluable for calculating thermal conductivity at conditions of which experiments are difficult, e.g. the extreme conditions found in the Earth's lower mantle (pressures and temperatures up to 136 GPa and 4000 K at the core-mantle boundary).

1.3.1 Mantle/core dynamics

Thermal conductivity in the deep Earth influences dynamic processes such as mantle convection and heat loss from the core (Lay, Hernlund, and Buffett, 2008).

1.3.2 Thermal conductivity of the lower mantle

Many studies assume lowermost mantle thermal conductivity to be 10 $Wm^{-1}K^{-1}$ (e.g. Lay, Hernlund, and Buffett, 2008), but uncertainty in the extrapolation of results made at low pressures and temperatures gives a range of 4 - 16 $Wm^{-1}K^{-1}$ (Brown and McQueen, 1986; Osako and Ito, 1991; Hofmeister, 1999; Goncharov et al., 2009; Manthilake et al., 2011; Ohta et al., 2012).

There have been several computational studies to calculate the lattice thermal conductivity of bridgmanite at CMB conditions. Osako and Ito (1991) measured the lattice thermal conductivity of $MgSiO_3$ perovskite, using a modified Ångstrom method. They investigated a temperature range of 160 - 340 K at ambient pressure. At 300 K, a conductivity of 5.1 $Wm^{-1}K^{-1}$was obtained. This value is similar to that reported for chemical and structural analogues, $MgSiO_3$ enstatite (5.0 $Wm^{-1}K^{-1}$REF) and $CaTiO_3$ perovskite (4 $Wm^{-1}K^{-1}$REF). The authors extrapolated the value to mantle conditions, neglecting radiative thermal conductivity. They predicted a value of 3.0 $Wm^{-1}K^{-1}$just beneath the mantle transition zone at 1900 K, and 12.0 $Wm^{-1}K^{-1}$at the top of the D'' layer at 2500 K, a four-fold increase. Thermal conductivity is highlighted as an important indictor of lowermost mantle structure, whether or not the D'' layer can behave as a thermal boundary between core and mantle.

Manthilake et al. (2011) measured $MgSiO_3$ perovskite at 26 GPa and 473 - 1073 K, and periclase at 8 and 14 GPa between 373 - 1273 K. In order to estimate values of thermal conductivity at the top and bottom of D'' for a lower mantle compositional model of 4 perovskite : 1 periclase, the authors extrapolated their measurements to high temperature and pressure. For an iron-free mantle, thermal conductivities of 18.9 ± 1.6 $Wm^{-1}K^{-1}$and 15.4 ± 1.4 $Wm^{-1}K^{-1}$are estimated for the top of D'' and CMB respectively. Similarly, for a mantle composition with Fe, thermal conductivities of 9.1 ± 1.2 $Wm^{-1}K^{-1}$and 8.4 ± 1.2 $Wm^{-1}K^{-1}$are calculated. This highlights the importance of impurities in controlling thermal conductivity in the lower mantle.

Ohta et al. (2012) measured the lattice thermal diffusivity of $MgSiO_3$ perovskite and post-perovskite at room temperature and pressures up to 144 GPa (using a diamond-anvil cell (DAC) and light heating thermoreflectance). These results suggest a perovskite-dominant lowermost mantle would have conducitivity of around 11 $Wm^{-1}K^{-1}$, and that parts of the lowermost mantle where post-perovskite is stable will have a conductivity approximately 60% higher. The authors suggest that these differences in conductivity between phases will not have a large effect on CMB heat flux, assuming the double-crossing perovskite phase model. The lattice conductivity of $MgSiO_3$ perovskite is shown to increase with pressure and decrease with temperature as expected. The inclusion of impurities is expected to decrease lattice thermal conductivity.

MANTHILAKE'S HIGH T RESULTS? CAN'T FIND REFERENCE?

My approach is similar to that of Ammann et al. (2014), who use the direct method and interatomic potentials reporting a value of $\sim$8.5 $Wm^{-1}K^{-1}$. Stackhouse, Stixrude, and Karki (2015) again use the direct method but with density functional theory, yielding conductivity of 6.8 ± 0.9 $Wm^{-1}K^{-1}$. Using Green-Kubo, Haigis (2013) report a value of 12.4 ± 2.0 $Wm^{-1}K^{-1}$ for conditions of 3000 K, 139 GPa. Tang et al. (2014) and Dekura, Tsuchiya, and Tsuchiya (2013) employed first principles, anharmonic lattice dynamics techniques, obtaining values of $\sim$1 $Wm^{-1}K^{-1}$ (CMB conditions) and 2.3 $Wm^{-1}K^{-1}$ (for 4000 K and 100 GPa) respectively. These results are much lower than other studies, and could be because of LD TRUNCATION OF CONDUCTIVITY [CRITICAL ANALYSIS].

1.4 Thesis outline

In Chapter 2 we provide an overview of the methods and expand on issues. I outline my computational approaches, for the non-equilibrium molecular dynamics direct method and equilibrium molecular dynamics Green-Kubo method. I show convergence of computed conductivity with respect to simulation cell size and shape

In Chapter 3, PRESSURE/TEMPERATURE EFFECTS. DISCUSS [P/T] SCALING LAW / THEORETICAL MODEL

1.4.1 Aims

1.4.2 Objectives

Chapter 2

Intro/Background/Theory 2

2.1 Atomic-scale modelling

Knowledge of thermal conductivity is important for modelling the deep earth, but can not be measured experimentally at core mantle boundary conditions. Atomic scale simulations sidestep experimental limitations, but system size must be chosen carefully in order to determine accurate conductivity values. Classical molecular dynamics approaches are utilised, with the intention of constraining appropriate system parameters.

A range of atomic scale simulation methods are available to determine the lattice thermal conductivity of materials. These are invaluable for calculating thermal conductivity at conditions of which experiments are difficult, e.g. the extreme conditions found in the Earth's lower mantle (pressures and temperatures up to 136 GPa and 4000 K at the core-mantle boundary).

2.1.1 Molecular dynamics

Parameter drift/convergence

We ensure all calculations are run for a sufficient length of time for the conductivity value to converge. When conductivity fails to converge it means either the simulations needs to be run for longer (unlikely with our nanosecond-scale classical calculations), or the system temperature has drifted. When NVE simulations are run for a long time there is noticable drift in the average system temperature (due to numerical approximations in the equation of motion), which in turn causes drift in the computed conductivity.

2.1.2 Interatomic potentials / Atomic interactions?

With the interatomic potential of Oganov, Brodholt, and Price (2000) we simulate bridgmanite ($MgSiO_3$ perovskite). To assess finite-size effects we use larger simulation cells than those employed in previous studies. The atom counts associated with these cells (the largest cell considered having over 100,000 atoms) means an ab initio study would be impractical, necessitating the use of interatomic potentials. We expect the potentials to represent the finite size effects well, even if computed conductivities may inaccurate compared to first-principles calculations.

WHY OGANOV?

WHAT CUTOFFS?

2.1.3 LAMMPS

LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) is a classical molecular dynamics code (Plimpton, 1995).

2.1.4 DFT/other

Required? Subsubsection somewhere?

2.2 Computing thermal conductivity

Stackhouse and Stixrude (2010) review different methods to compute thermal conductivity, in the present work we focus on two of these: (1) Equilibrium molecular dynamics based on the Green-Kubo relations to determine the thermal conductivity from heat flux fluctuations and their time-dependence (Green, 1954; Kubo, 1957; Kubo, 1966; Schelling, Phillpot, and Keblinski, 2002). (2) The non-equilbrium molecular dynamics-based "direct method", where thermal conductivity is calculated from an imposed heat flux and corresponding temperature gradient via Fourier's Law (Müller-Plathe, 1997; Nieto-Draghi and Avalos, 2013).

2.2.1 Direct method

The direct method is the computational implementation of a typical experiment to measure thermal conductivity, using Fourier's law to relate heat flux (q) and temperature gradient (∇T) to thermal conductivity (k),

$$q = -k\nabla T. \tag{2.1}$$

In the direct method energy is transferred from one group of atoms to another, creating hot and cold regions between which heat flows. The resultant temperature gradient is measured by calculating the temperature of individual groups of atoms along the direction of the heat flux. Simulation cells tend to be long relative to their cross-sectional area, defined as height by width (see Figure 2.1). Cell boundaries are periodic and the hot and cold sections are half the cell length apart, meaning heat flows in both directions from hot to cold (one of which is across the length-end periodic boundary). This results in two similar temperature gradients which can be averaged.

From kinetic theory [[[REF?]]], conductivities computed by the direct method (k_L) are dependent on length of simulation cell,

$$k_L = \frac{1}{3} C_V v l_L, \tag{2.2}$$

where C_v is the volumetric heat capacity, v is the average phonon drift velocity, and l_L is the phonon mean free path. The finite size of the simulation cell truncates the mean free path, underestimating conductivity compared to that of the bulk material (k_∞). Using results from simulations of varying cell length (L), conductivity is extrapolated to a length-independent value (where b is a material dependent parameter),

$$k_L{}^{-1} = bL^{-1} + k_\infty{}^{-1}. \tag{2.3}$$

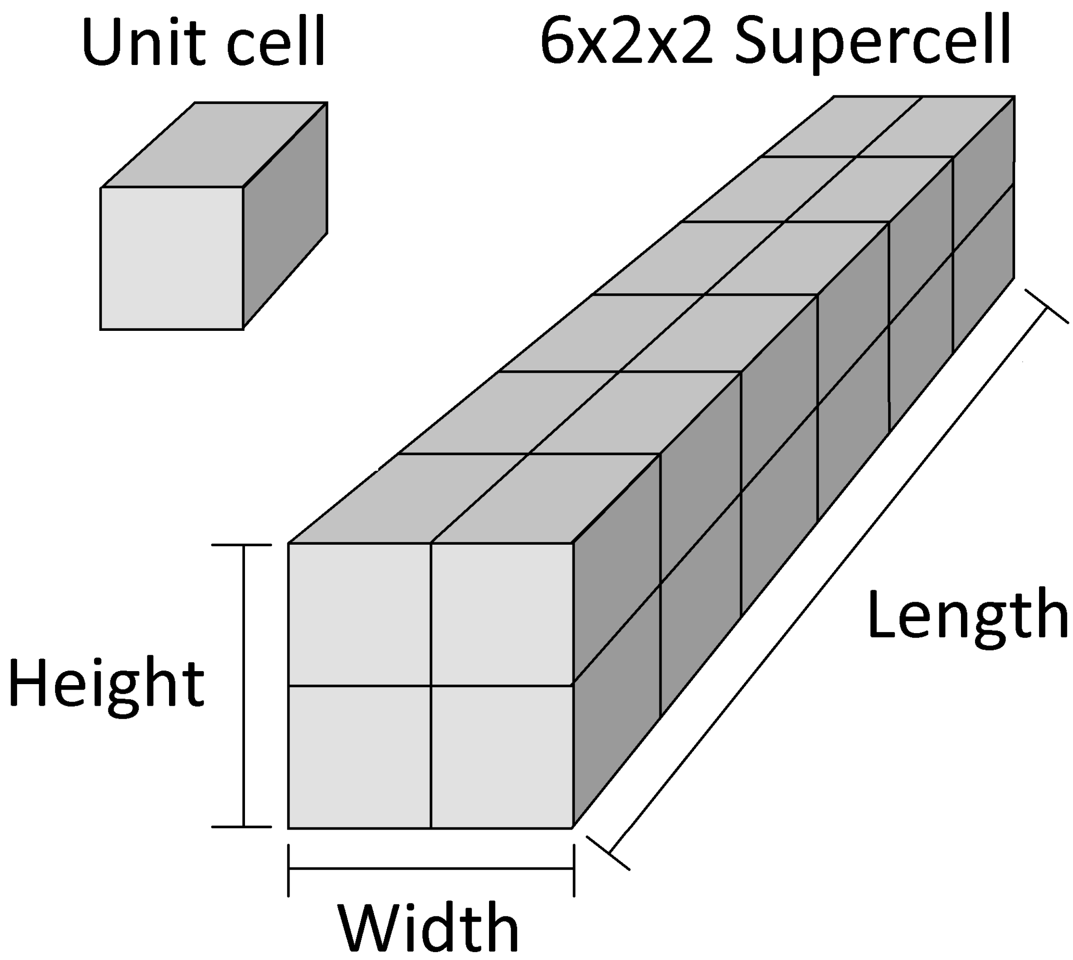

FIGURE 2.1: The unit cell represents the smallest box of atoms that can be replicated to produce a crystal structure. A supercell is an arrangement of unit cells.

Inverse conductivities from direct method simulations are plotted against corresponding inverse cell lengths. A straight line is fit to the data and extrapolated to the y-axis (at which the inverse cell length equals zero and real length equals infinity), where the intercept gives the inverse of the bulk material conductivity (Schelling, Phillpot, and Keblinski, 2002).

Problems arise when the data do not support a linear trend. There are two effects of finite system size that can cause an individual direct method simulation to diverge away from an inferred/expected linear trend, both of which result in overestimation of the length-dependent conductivity data point. First, when the distance between hot and cold sections (controlled by cell length) is shorter than the MFP, phonons travel ballistically (i.e. without any scattering events) from heat source to sink (Sellan et al., 2010). Conductivites in shorter length cells are overestimated when this occurs, reducing the gradient of the linear fit and thus underestimating the extrapolated conductivity.

For a given length, conductivity is dependent on the CSA, or aspect ratio of the simulation cell. Conductivity is overestimated due to an underestimation of phonon-phonon scattering, from sparse phonon phase sampling in cells where cross-section is small compared to length. Phonons that aren't resolved cannot contribute to phonon-phonon scattering effects. Reduced scattering means heat transport is

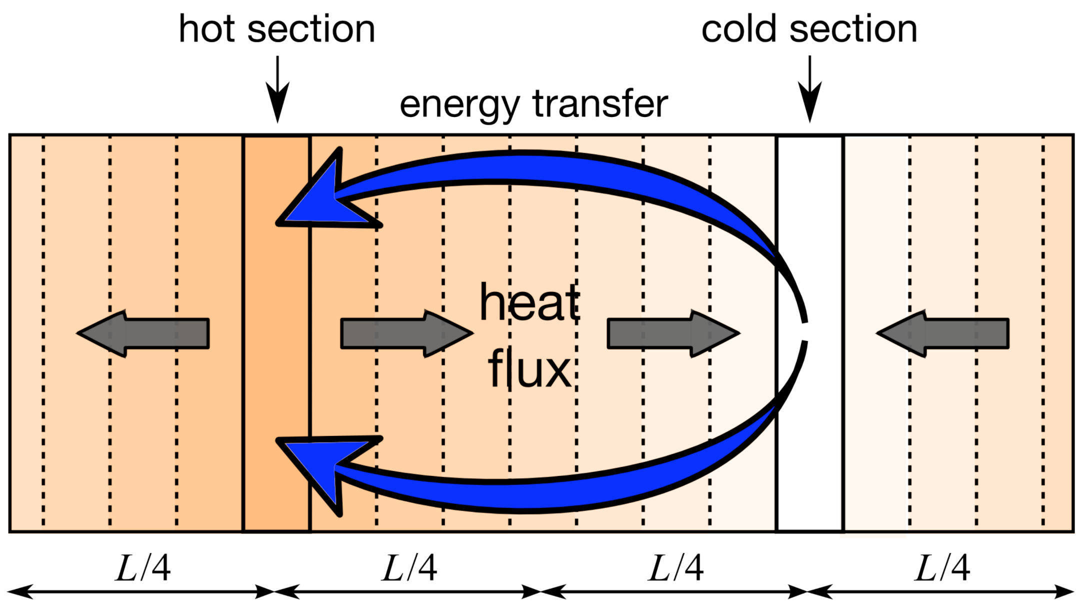

FIGURE 2.2: Movement and distribution of heat in the direct method. Orange to white scale represents temperature (modified from Stackhouse, Stixrude, and Karki, 2015).

artificially more efficient than expected from the bulk material.

[[[SPECIFIC ALERT, REFERENCING THINGS I FOUND]]] However, the required CSA to abate this FSE is length-dependent. When the CSA is smaller than required for all cell lengths (e.g. 1x1 [FIGURE]), all conductivities are overestimated (Thomas, Iutzi, and McGaughey, 2010, albeit for nanotube diameter?). As the CSA is increased, the data points (and thus also the extrapolated result) shift to lower conductivities (higher inverse conductivities). It is at this point that the short cells with lengths of similar order, will report conductivities converged with respect to CSA. Assuming these cells are sufficiently long to avoid the ballistic phonon transport (BPT), a linear fit can be extrapolated to obtain conductivity (for CSA around 2x2, the case at 4000 K).

The convergence is not necessarily observed concurrently for longer cells however, where they might show overestimated conductivities compared to the fit through the short cells (Hu, Evans, and Keblinski, 2011). This would cause the fit to all data to be steeper than it should, increasing the extrapolated result. [[[HOPEFULLY THIS IS TRUE]]] I can show that increasing CSA does not change the computed conductivity at short lengths, but does reduce values from longer cells and bring them into alignment with the expected fit.

2.2.2 Green-Kubo

The Green-Kubo method uses auto-correlation functions (ACFs) to quantify time-dependence of heat fluxes (shown in Figure 2.4, and Equation 2.4), in a simulation cell of roughly cubic dimensions (WHY??) and spatially-consistent average temperature. Instantaneous heat fluxes can be used to determine how energy is dissipated within a system, where brief flux events mean heat is transferred quickly indicating high thermal conductivity [[[and vice versa, BUT IS THIS TRUE?]]].

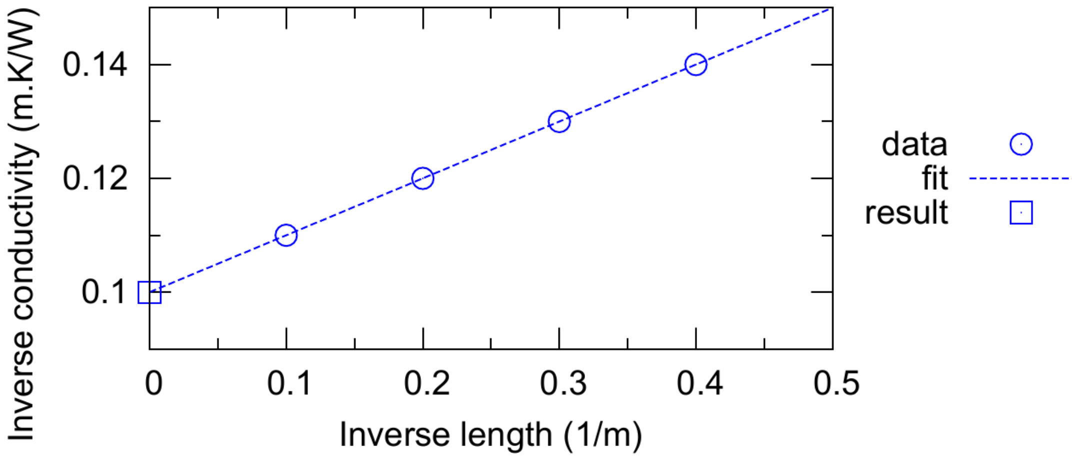

FIGURE 2.3: Idealised example of linear extrapolation procedure. Inverse computed conductivities are plotted against inverse simulation lengths. Extrapolation to y-axis gives conductivity of an infinite system length, i.e. the bulk material.

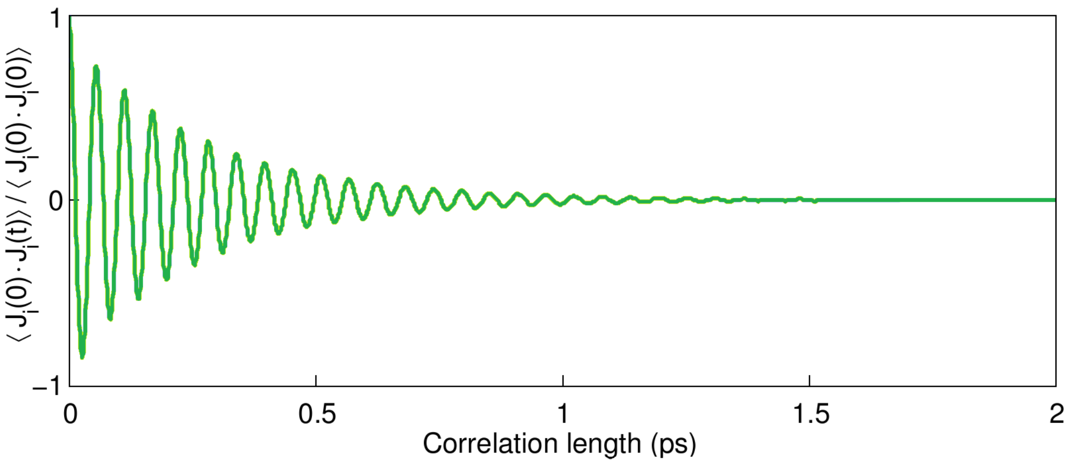

FIGURE 2.4: Normalised ACF. Correlation is taken over a longer length than shown on this plot (100 ps), however the function decays to less than 1% of its initial value at 2 ps. It continues to oscillate about zero, with a positive average value.

The auto-correlation is obtained over the net heat flux series in each crystallographic direction, for a timescale up to a chosen correlation length.

$$ACF_i = \langle J_i(0) \cdot J_i(t) \rangle \,, \tag{2.4}$$

where i specifies direction, J is heat flux, and t is the correlation length. The integral of heat flux ACF is proportional to thermal conductivity via the Green-Kubo equation (see Figure 2.5 and Equation 2.5),

$$\kappa_i = \frac{V}{k_B T^2} \int_0^\infty \langle J_i(0) \cdot J_i(t) \rangle \, dt, \tag{2.5}$$

[[[I am using "k"s and "kappa"s to represent thermal conductivity, kappa here and k earlier?]]] where V is the simulation cell volume, k_B is the Boltzmann constant, and T is the average temperature of the system. In this study we use Green-Kubo results as an independent check on the direct method, as they do not have the same finite size-effects. Obtaining a converged conductivity result simply depends on using a large enough cell volume / number of atoms.

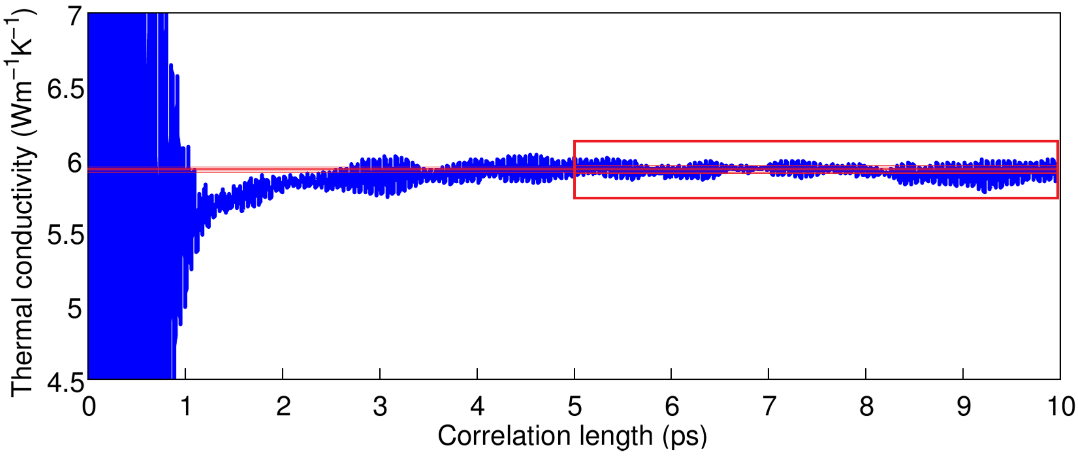

FIGURE 2.5: Integrated ACF, multiplied by constants to get thermal conductivity. Large variation in the first 1 ps corresponds to the correlation time where the ACF is unconverged (still decaying / large oscillations). Thermal conductivity is averaged from correlation time of 5 ps - 10 ps (region in red box).

The individual integrals obtained from the Green-Kubo show variation from the average combined integral on the order of the mean. Many simulations from different intital temperature conditions are required in order to ensure good sampling of conductivity, as well as ensuring the computation time for each is long enough for convergence. This makes Green-Kubo a computationally expensive method, especially for large systems.

The ACF should decay to zero as correlation time tends to infinity, however noise in the ACF prevents this. This will ultimately cause the integral to diverge/drift on long timescales. Howell (2012) fits a series of exponential decays to their ACF, forcing the expected decay to zero and subsequent (constant) integral convergence. This is represents a significant improvement on the conductivity estimate at long correlation lengths, but is mostly similar with the un-fit integrals early in the correlation. (INTEGRAL DRIFT FIGURE, JUST THE ONE INTEGRAL FOR 100PS)

(STACKHOUSE 2010 REFERENCES Volz and Chen 2000; Sun and Murthy 2006)

2.2.3 Other

(3) Anharmonic lattice dynamics (Tang and Dong, 2009). (4) Combined quasiharmonic lattice dynamics and molecular dynamics method [Koker (2009)].

2.2.4 Finite-size effects

[[[Give its own section, or as subsection in each method?]]]
Computational techniques are not limited by the reproduction of physical conditions like experiments, however they are affected by the size and shape of the simulation cell. The effects of the finite system size available for computation must be checked, as systems with too few atoms are sometimes unable to reproduce the behaviour of the bulk material. If the wavelength of a phonon is too long to fit into a cell, it is not able to transport heat like it should. In the case of the direct method, the length to cross sectional area (CSA) aspect ratio can also matter.

Considering systems of varying size, length-dependent conductivities are obtained from the direct method and extrapolated to the bulk material (Schelling, Phillpot, and Keblinski (2002)). The validity of this extrapolation procedure have been called into question (e.g. Sellan et al. (2010)), when a linear trend cannot be fit through the length-dependent conductivities. We describe finite-size effects (FSE) which cause the conductivity result of a simulation to diverge from the value expected by a linear trend, and offer a comparison with results obtained from the Green-Kubo method. The two methods have previously been compared (e.g. Schelling, Phillpot, and Keblinski (2002) [[[REFERENCED EARLIER IN THIS PARAGRAPH, THIS OKAY?]]]), and have been found to give results in good agreement.

The finite-size effects (FSE) I describe are associated with phonon-phonon scattering, or the lack thereof, and boundary-scattering or truncation of phonon mean free path due to limited system sizes. These phenomena combine to misrepresent the phonon behaviour of the bulk material.

The FSE observed for a material change with thermal conductivity/phonon MFP, and thus are pressure, temperature, and composition sensitive. Higher conductivity(or is it MFP?) materials/conditions require larger systems to eliminate FSE (and vice versa) [[[BUT IS THIS TRUE?]]].

2.3 Previous work

2.3.1 Method comparison

2.3.2 Finite-size effects

Should this section be interspersed into when FSE are mentioned in methods?

STUFF THAT MIGHT BE WRONG BECAUSE FSE?

Chapter 3

Constraining the finite-size effects of molecular dynamics methods to compute thermal coductivity

3.1 Introduction

3.1.1 Intro Intro (remove this subsection header later)

Knowledge of the thermal conductivity of solids is key in a wide range of technological applications and for our understanding of natural systems. For example, in the Earth's lower mantle thermal conductivity controls the nature of planetary convection (Tosi et al. (2013)), and the heat flux out of the core which powers the geotherm. Low thermal conductivities are required in thermoelectric materials, to maximise the efficiency of heat-electricity conversion (Snyder and Toberer (2008)).

A range of atomic scale simulation methods are available to determine the lattice thermal conductivity of materials. These are invaluable for calculating thermal conductivity at conditions of which experiments are difficult, e.g. the extreme conditions found in the Earth's lower mantle (pressures and temperatures up to 136 GPa and 4000 K at the core-mantle boundary).

(MOVE - to where though?) Many studies assume lowermost mantle thermal conductivity to be 10 $Wm^{-1}K^{-1}$ (e.g. Lay, Hernlund, and Buffett (2008)), but uncertainty in the extrapolation of results made at low pressures and temperatures gives a range of 4 - 16 $Wm^{-1}K^{-1}$ (Brown and McQueen (1986), Osako and Ito (1991), Hofmeister (1999), Goncharov et al. (2009), Manthilake et al. (2011), and Ohta et al. (2012)).

Chapter 4

Modelling the thermal conductivity of lower mantle minerals

4.1 Adding iron

insert text here...

4.2 Making the model

Due to uncertainty in the lower mantle's compositional distrubution, properties like thermal conductivity are averaged considering the relative abundance of each mineral component. There are also endmember relations to consider within each mineral, the concentration of impurities, and mineral phase transitions.

A simple weighted average can be taken to combine the contributions of individual minerals, whereas mixing between endmembers is not as linear. Ohta et al. (2017) provide an equation for interpolating conductivity between compositional endmembers, specifically (Mg,Fe)O (ferro)periclase. I apply it to (Mg,Fe)SiO_3 perovskite [[[PRESUMABLY ALSO WORKS FOR bdg<->p-Pv?]]].

Okuda et al. (2017) present a temperature scaling relation for bridgmanite, which I additionally apply to the Fe-endmember. By having temperature-dependent values I am able to obtain an equation that gives thermal conductivity as a function of both temperature and composition, for a given (studied/fit?) endmember pair.

4.2.1 Fitting the data

[Equations from Ohta et al., 2017 (eq. 7,8,9), and Okuda et al., 2017 (eq. 5)]

I want to determine lattice thermal conductivity as a function of temperature and composition, using calculated and fit constants. For the method I will use I need to know how the conductivity of endmember minerals changes with physical conditions. In order to keep temperature the only dependent variable, I will scale volume linerarly with temperature [FIGURE]. At this point I can scale the conductivity of an endmember with temperature within the fitted range (Okuda et al., 2017).

Considering Ohta et al. (2017) the linear interpolation between the conductivities two endmembers can be perturbed, forming the trough characteristic of varying composition. While $FeSiO_3$ generally has a lower thermal conductivity than $MgSiO_3$, the minimum is located at an intermediate composition. The effect of impurity scattering is larger than inherent changes due to chemistry.

Compositional dependence

Ohta et al., 2017
* = already cited somewhere above

Ohta eq. 7

$$\kappa_{latt} = \kappa_i \left(\frac{\omega_0}{\omega_M}\right) arctan \left(\frac{\omega_M}{\omega_0}\right) \tag{4.1}$$

κ_{latt} - output conductivity as function of t & x (Wm^{-1}K^{-1}), considering mineral specific parameters
κ_i - the composition-dependent conducitivity, if it were linearly interpolated between endmembers (Wm^{-1}K^{-1})
ω_0/ω_M - temperature-dependent parameter to perturb κ_i, to create the "trough" trend in composition-dependent conductivity
ω_0 - *"the phonon frequency where the intrinsic mean free path is equal to that due to solute atoms"*
ω_M - *"the phonon frequency corresponding to the maximum of the acoustic branch of the phonon spectrum"*

Ultimately this is the equation we are trying to solve. The two components κ_i and ω_0/ω_M, are both temperature and composition-dependent. κ_i gives the compositionally-weighted average conductivity, a linear interpolation between endmembers at a certain temperature. ω_0/ω_M controls the conductivity decrease due to the impurity effect, the magnitude of which depends on the temperature and composition of interest.

Ohta eq. 8

$$\left(\frac{\omega_0}{\omega_M}\right)^2 = \frac{\chi^T}{C\,(1-C)} \tag{4.2}$$

*ω_0/ω_M - temperature-dependent parameter to perturb κ_i, to create the "trough" trend in composition-dependent conductivity
*ω_0 - *"the phonon frequency where the intrinsic mean free path is equal to that due to solute atoms"*
*ω_M - *"the phonon frequency corresponding to the maximum of the acoustic branch of the phonon spectrum"*
χ^T -temperature-dependent parameter to . . . ???
χ - *"a constant"*. . .
T - temperature of interest (K, default data fit between 1000 - 5000 K, but extrapolation should be reasonable)
C - composition mix of interest (dimensionless, values between 0 and 1)

The equation that splits ω_0/ω_M into its temperature and composition-dependent components, where χ is a temperature-dependent variable. $C\,(1-C)$ is largest when $C = 0.5$ *or* 50%, relating to the shape of the trough formed by this fit.

χ^T scaling

$$\chi^T = A\, e^{BT} \tag{4.3}$$

*χ^T -temperature-dependent parameter to . . . ???

*χ - *"a constant"*...*
*T - temperature of interest (K, default data fit between 1000 - 5000 K, but extrapolation should be reasonable)
A - coefficient in χ^T variation with temperature
B - exponent in χ^T variation with temperature

χ is a temperature-dependent variable, but a plot of χ against T has no obvious trend. A simple exponential can be fit to χ^T against T however, with a coefficient A and exponent B.

Ohta eq. 9

$$\kappa_i = (1 - C)\,\kappa_{MgSiO_3} + C\,\kappa_{FeSiO_3} \tag{4.4}$$

*κ_i - the composition-dependent conducitivity, if it were linearly interpolated between endmembers ($Wm^{-1}K^{-1}$)
*C - composition mix of interest (dimensionless, values between 0 and 1)
κ_{MgSiO_3} - temperature and volume-dependent conductivity for Mg endmember ($Wm^{-1}K^{-1}$)
κ_{FeSiO_3} - temperature and volume-dependent conductivity for Fe endmember ($Wm^{-1}K^{-1}$)

An equation that describes the conductivity of an endmember mix, assuming the relation is a simple weighted mean. C, in this case specifically, is the proportion of Fe atoms swapped into the system for Mg. The actually dependence of conductivity with composition is more complicated on the atomic scale, this intermediate average value adjusted in Eq. 4.1 (Ohta et al., 2017, Eq. 7).

Temperature dependence

Okuda et al., 2017

Okuda eq. 5

$$\kappa_{adj} = \kappa_{ref} \left(\frac{T_{ref}}{T}\right)^a \left(\frac{V_{ref}}{V}\right)^g \tag{4.5}$$

κ_{adj} - temperature and volume-dependent conductivity of an endmember ($Wm^{-1}K^{-1}$)
κ_{ref} - reference conducitivty of an endmember ($Wm^{-1}K^{-1}$)
T_{ref} - reference temperature at which above conductivities are calculated (K)
*T - temperature of interest (K, default data fit between 1000 - 5000 K, but extrapolation should be reasonable)
a - exponent controlling temperature-dependent conducitvity of an endmember
V_{ref} - reference volume of an endmember (E-30 m^3)
V - temperature-dependent volume of an endmember (E-30 m^3)
g - exponent controlling volume | density-dependent conducitvity of an endmember

Okuda et al. (2017) present a model for density and temperature-dependent conductivity (actually from Manthilake 2011, REF???), which utilises exponents obtained from fitted data. A reference value is scaled to infer conductivity at the conditions of interest.

Volume scaling ($y = mx + c$)

$$V = \frac{\partial V}{\partial T} T + V_{T_0} \tag{4.6}$$

*V - temperature-dependent volume of an endmember (E-30 m^3)
$\partial V / \partial T$ - fit gradient, change of volume with temperature (E-30 m^3/K)
*T - temperature of interest (K, default data fit between 1000 - 5000 K, but extrapolation should be reasonable)
V_{T_0} - intercept volume for T=0 K (E-30 m^3)

I take Eq. 4.5 (Okuda et al., 2017, Eq. 5) a step further, by obtaining V in terms of T. This dependence is effectively linear over the temperatures considered, meaning Eq. 4.1 (Ohta et al., 2017, Eq. 7) is dependent solely on temperature, composition, and fit or calculated constants.

Chapter 5

Modelling the lower mantle with variable thermal conductivity

5.1 Main Section 1

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5.1.1 Subsection 1

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Chapter 6

Summary/Discussion/Conclusion

6.1 Main Section 1

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6.1.1 Subsection 1

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Appendix A

Frequently Asked Questions

A.1 How do I change the colors of links?

The color of links can be changed to your liking using:
`\hypersetup{urlcolor=red}`, or
`\hypersetup{citecolor=green}`, or
`\hypersetup{allcolor=blue}`.
If you want to completely hide the links, you can use:
`\hypersetup{allcolors=.}`, or even better:
`\hypersetup{hidelinks}`.
If you want to have obvious links in the PDF but not the printed text, use:
`\hypersetup{colorlinks=false}`.

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