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UNIVERSITY OF CALIFORNIA RIVERSIDE

Mixed Topics in Computational Thermal Transport

A Dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

 in

Mechanical Engineering

by

Laura Rita de Sousa Oliveira

June 2017

Dissertation Committee:

Professor P. Alex Greaney, Chairperson Professor Brady Gibbons Professor Chen Li Professor Bryan Wong

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Chairperson

University of California, Riverside

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ABSTRACT OF THE DISSERTATION

Mixed Topics in Computational Thermal Transport

by

Laura Rita de Sousa Oliveira

Doctor of Philosophy, Graduate Program in Mechanical Engineering University of California, Riverside, June 2017 Professor P. Alex Greaney, Chairperson

Heat transfer is ubiquitous in both naturally occurring and engineered materials. As technology progresses, the length- and time-scales of thermal transport decreases, becoming comparable with the mean free paths and relaxation times of the vibrations that drive it. Increasingly, an atomistic-level understanding of thermal transport is pivotal in predicting and controlling heat transport in materials and devices. Modeling approaches that permit an atomistic understanding of heat transport, and the implementation of complex approximations of the phonon Boltzmann transport formalism include classical molecular dynamics and density functional theory (DFT). Results are presented for equilibrium molecular dynamics (EMD) simulations of the thermal conductivity of a series of clustering and non-clustering point defects in graphite using the Green–Kubo method, aimed to advance our knowledge of the evolution of the microstructure of graphite while in service in a graphite-moderated nuclear reactor. The Green–Kubo method — commonly used for predicting transport properties by scientists and engineers across fields — relates the property of interest to the lifetime of fluctuations in its thermodynamic driving potential. The integral of the autocorrelation fluctuations requires a long averaging time to reduce remnant noise and is a principal source of error. A new approach is proposed to quantify — on-the-fly — the uncertainty on transport properties computed using the Green-Kubo formulation, based on recognizing that the integrated noise is a random walk. EMD is also used to explore thermal transport in breathing metal–organic frameworks (MOFs), coveted for numerous applications due to their large surface area and modularity. A simple geometric model of thermal conductivity is proposed as a heuristic for the quick evaluation of transport in flexible MOFs, and a quantum-based approach is undertaken to explore deviations from the heuristic, such as rattler modes and phonon-focusing. Phonon properties calculated with DFT for (1) uranium dioxide and (2) silicon, for fuel and spintronics applications respectively, are also briefly discussed.

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Chapter 1

Introduction and motivation

Heat transfer is ubiquitous in both naturally-occurring and engineered materials, and it is unsurprising that accurately predicting thermal transport is essential in a wide array of engineering applications. Heat sinks and thermal barrier coatings are obvious examples of such applications, where thermal conductivity is directly linked to the materials' performance and lifetime. There are also a large number of materials applications for which thermal transport properties are interrelated with a number of other properties that dictate performance. For instance, phase change materials and the hypothesized memristors depend on thermal transport to set the resistance memory. Thermoelectric materials, i.e. materials allowing a direct conversion between electric power and a temperature difference, are also an excellent example of this indirect relationship — the performance of a thermoelectric material is determined by its thermoelectric figure-of-merit, ZT, which, in turn, is a partial function of thermal conductivity. Thermal transport has also featured heavily in nanofluids research. Nanofluids are a promising new material for numerous engineering applications beyond cooling (e.g. lubrication [31], sheathing [83], or hydraulics [151]), as well as applications in other fields (e.g. medicine [173], geophysics [174]). It is clear from these examples that understanding and controlling heat transport is pivotal to research in both materials and devices within a broad range of scales.

Electronic and phononic transport are the fundamental mechanisms for heat transport in solids. In metals heat is transported primarily by free electrons, whereas in semiconducting and insulating materials heat is primarily carried by phonons (i.e lattice vibrations). That said, the relationship between materials and their thermal properties is substantially more complex than merely determining the dominant heat carriers. The size, composition, structure and composition of a material all play a role in thermal transport. Moreover, thermal treatments, such as annealing, sintering, and irradiation, can affect the structural properties of materials and thus alter their thermophysical properties as well. Defects or imperfections in the crystal structure are among the structural changes that affect the thermal conductivity of solid-state materials.

During the 19th century, and the first half of the 20th century, transport calculations were limited to Fourier's law (proposed in 1811). Fourier's law is an empirical formulation of heat transfer and, despite its vast applicability at the macroscale, it fails to provide an accurate overview of heat transfer at smaller time and length scales. Debye was the first to attribute heat conduction to delocalized lattice waves [35], and Peierls the first to use the Boltzmann transport equation (BTE) towards phonon transport, which accounts for phonon scattering mechanisms [125]. The evolution of computational methods such as classical molecular dynamics and electronic structure methods has since advanced our knowledge of thermal transport at the atomic level. Of the computational tools available to date, molecular dynamics (MD) simulations provide a powerful approach for quickly obtaining atomistic-level insight into the physics of mass, momentum or energy transport processes in materials. For MD calculations of thermal conductivity two approaches are possible: (1) perturb and drive systems out of equilibrium to then measure their response, or (2) simulate systems in equilibrium and measure small local fluctuations with the Green– Kubo formulation. Quantum mechanical methods, such as density functional theory (DFT), provide additional information on phonon properties, such as dispersion relations or even anharmonic scattering matrices [106]. Different methods can often be combined to obtain more accurate and faster predictions.

The first topic addressed in the course of my PhD was to quantify the *thermal re*sistance from irradiation defects in graphite for a collection of different defects and clusters of defects (chapter 4). This work was performed primarily using classical MD simulations of systems in equilibrium (approach (2)), with the choice of defects to investigate being partially informed by DFT calculations. Additional work has continued to rely on these methods, and variants thereof, to study thermal transport. What we learned from using equilibrium MD to study of thermal transport was leveraged to develop a new method to manage integration error in the Green-Kubo method on-the-fly (chapter 5). Uncertainty quantification on-the-fly is particularly useful towards high-throughput computational screening of materials. The work produced on phonon-focusing and rattler-mode interference in thermal conductivity transitions of the breathing metal-organic-framework MIL-53 (chapter 6) was also partially motivated by the recent focus in high-throughput materials research. In it we develop a heuristic to quantify thermal transport changes in *breathing* metal-organic frameworks. In the process of validating the suggested heuristic, we discover and investigate phonon-focusing and rattler-mode phonon-interference phenomena in the MIL-53 framework isomers. DFT calculations similar to the ones performed towards this last project have been put to use to study *thermal transport in fuels, and spintronic materials* (chapter 7) towards collaborative projects developed in conjunction with an experimental team in the Mechanical Engineering department at the University of California, Riverside, and a computational Nuclear Science and Engineering team at Oregon State University. A brief introduction to each of the research projects in chapters 4–7 and what motivated them is provided in the next paragraphs, followed by chapters on the *background and theory* (chapter 2), and the *computational methods* (chapter 3) used towards the research presented. In each of the research chapters (i.e. chapters 4–7), additional background and methodology details are provided. Some details will be repeated, as chapters 4–7 are in full or in part reproduced from accepted (chapters 4, 5, and 7) and submitted (7) manuscripts.

1.1 Thermal resistance from irradiation defects in graphite

In the early 1940s, polycrystalline graphite was the only abundantly produced material with the required purity to be used as a moderator in nuclear reactors [68]. While other reactor materials have since been adopted, graphite continues to be used as a moderator and reflector in older commercial reactors and research reactors. At the present time, graphite is being considered for the development of high-tech fuel elements for next-generation nuclear reactors. The moderating properties of graphite are structure and temperature dependent and accurately predicting the thermal conductivity of graphite and other fuel assembly materials — including how their thermal conductivity evolves under irradiation — is vitally important for the design of accident-tolerant fuels.

The **objective** of this research is to obtain an atomistic-level understanding of scattering processes from collections of irradiation-induced point defects and to establish a systematic understanding of how defect-type, number and different defect-type ensembles affect thermal resistance and phonon mean free path in graphite. We do so, hoping that the insight we garner can be incorporated into approaches for quantitatively predicting the lattice thermal conductivity that are based on solving the Boltzmann transport equation. Such a tool would be useful to nuclear engineers and materials scientists in the process of designing new reactors and fuel systems that are accident tolerant. To this end we performed equilibrium molecular dynamics simulations and computed the change to thermal conductivity due to a series of clustering and non-clustering point defects using the Green-Kubo method.

1.2 Method to manage integration error in the Green-Kubo method

As described above, the ability to reliably predict transport properties is essential in the search for new materials for a wide variety of applications. The Green–Kubo formalism [49, 82] is a well-established approach to compute transport properties, including thermal conductivities, using equilibrium molecular dynamics (EMD) — the underlying principle is that the processes that dissipate small local fluctuations are the same that are responsible for a material's feedback to a stimulus. There are clear advantages to using an equilibrium approach: while both equilibrium and non-equilibrium methods suffer from size artifacts, the use of periodic boundary conditions in EMD allows for a smaller system size; for anisotropic systems, one EMD simulation suffices to compute the full transport tensor; and EMD can be used irregardless of the linearity of the transport regime with system size. There is, however, also one major pitfall. Fully converging the autocorrelation function requires very long simulation times, and often a compromise has to be made between including the contribution of slow processes and introducing a random error, or excluding these processes and introducing a systematic truncation error.

In this project we use the knowledge obtained from the research performed towards expanding our understanding of *Thermal resistance from irradiation defects in graphite*, in which we tested multiple approaches to converge the integral of the heat current autocorrelation function (HACF), to accomplish our **objective** of developing a method that allows researchers to make better informed decisions about where to truncate the autocorrelation function (ACF) and how to optimize computational resources on-the-fly, based on recognizing that the integrated ACF error mimics a random walk. This method was inspired by thermal transport calculations, but is applicable to other transport quantities computed with the Green–Kubo approach.

1.3 Phonon-focusing and rattler-mode interference in thermal conductivity transitions of the breathing metal-organic– framework MIL-53

Metal–organic frameworks (MOFs) are crystalline structures comprised of secondary building units (SBUs), i.e. single nodes or clusters of metal-ions, bridged by organic linkers. MOFs are highly porous and have exceptionally large surface area, which makes them ideal for gas sorption and storage applications, such as carbon sequestration and hydrogen storage. Furthermore, because MOFs are inherently modular with property-correlated building blocks (SBUs and linkers) and topology, they can be tailored to a myriad other applications [36, 76, 60, 150, 84, 170]. Unsurprisingly, there is an increased trend in the use of high-throughput approaches to explore the phasespace of MOFs, for which it would be useful to develop heuristic methods that allow the rapid computing of framework properties.

"Breathing" MOFs, such as MIL-53, are flexible MOFs that undergo a reversible transformation between narrow pore (np) and large pore (lp) structures as a response to external stimuli such as temperature [97] and pressure [95] changes, or host-interaction [95, 96]. Flexible MOFs are desirable for sorption-related applications, but new possibilities, such as shock absorption [171] are also currently being explored. Sorption processes involve exothermic and endothermic reactions [172], and the ability of the framework to transport heat or transfer it to the host is paramount in determining applicability. Mechanical dampening likewise requires heat dissipation. Our **objective** is to determine if thermal transport properties can be estimated from the vibrational modes of lp and np structures and, moreover, if these properties scale continuously with framework geometry, working towards the development of heuristic models for thermal conductivity prediction in MOFs. To this end, a suite of DFT and tight-binding DFT calculations of MIL-53(Al) were performed, including computing the dispersion relations for the first time (to our knowledge), which led to the discovery of rattling modes and phonon focusing effects in this framework.

In this work, I have not been responsible for producing the thermal conductivity calculations, the data for which was provided to me. Additionally, the rattler toy model was also developed by other people.

1.4 Thermal transport in fuels, and spintronic materials

In addition to the research projects above, collaborative projects have been undertaken with research groups at the University of California, Riverside and at Oregon State University. Two of these projects, the results from which have been incorporated into one submitted manuscript and one accepted manuscript of which I am a secondary author, all fall under the umbrella of thermal transport. The first project described herein relates to *predicting variability of thermal conductivity in nuclear fuels*, and the second concerns the *spin Hall effect and spin phonon interactions in p-Si*.An introduction to these collaborations is described in the following subsections.

1.4.1 Predicting variability of thermal conductivity in nuclear fuels

For this project, our group is collaborating with researchers in the Nuclear Science and Engineering department at Oregon State University. Ultimately, the goal is to develop a frequency-dependent phonon transport solver (based on the BTE) to perform engineeringscale thermal transport predictions taking into account atomistic-scale materials properties. The inclusion of thermal boundary resistance within phonon transport calculations has been a first step in reaching the goal. This was accomplished for UO_2 , a material that undergoes fission and experiences a reduction in thermal conductivity due to emerging xenon bubbles and other fission byproducts, and thus greatly benefits the study of heat transfer at a microscopic level. Our **objective** in this project is to perform DFT calculations to produce the atomistic phonon transport properties needed to obtain accurate thermal transport results with the phonon BTE, as implemented by our colleagues.

1.4.2 Spin Hall effect and spin phonon interactions in p-Si

Our collaborators at UCR have observed the coupling of spin, charge and thermal transport (SMTR) behavior in p-Si for the first time [93]. At the origin of SMTR behavior in p-Si are spin-phonon interactions [93]. Kumar and his group further hypothesize that spin relaxation due to phonon absorption or emission may change phononic thermal transport behavior [93], and thus propose monitoring changes in thermal properties to quantify the spin-mediated behavior. We have calculated phonon properties of silicon with various spin concentrations with the **objective** of ascertaining the influence of spin polarization on phonon properties.

Chapter 2

Background and theory

2.1 Phonon thermal transport

Fourier's law was proposed in 1811 based on experimental results and can be written in differential form as

$$\mathbf{J} = -\kappa \nabla T,\tag{2.1}$$

where **J** is the heat flux, κ is the thermal conductivity of a material, and ∇T is the temperature gradient. The heat equation, which governs the temperature distribution in an object, can be written as

$$C_v \rho \frac{\partial T}{\partial t} = -\nabla \phi + Q, \qquad (2.2)$$

where ρ is the mass density, C_v the specific volumetric heat (in $\mathbf{J} \cdot \mathbf{Kg}^{-1}\mathbf{K}^{-1}$), t the time and ψ is the heat flow, or J, through the material, and Q is energy being added or removed from the system [1, 101]. At equilibrium, i.e. when Q is zero, by combining Fourier's law and the heat equation (Eq. 2.2), assuming no mass transfer and constant properties, one obtains the partial differential equation

$$-\kappa \nabla^2 T = \rho C_v \frac{\partial T}{\partial t} \ [101]. \tag{2.3}$$

This equation can be solved to give the temperature distribution in a system of interest, given the appropriate boundary and initial conditions. Fourier's law accurately describes the diffuse nature of heat transfer at the macroscale. However, in the last 30 years, the lengths and time scales that are accessible have greatly decreased and become comparable to mean free paths (MFPs) and relaxation times. Macroscopic theories do not provide an accurate overview of heat transfer at such small scales [106]. An example of this is the several orders of magnitude under-prediction of thermal conductivity at localized hotspots at the junctions of transistors [129]. In another example, the nanostructuring of materials, i.e. the patterning or inclusion of structural features in the nanometer (nm) scale, has resulted in the substantial reduction of thermal conductivity of materials in comparison with their bulk counterpart [94, 43]. Accurately describing and understanding heat transport at small length scales requires an atomistic perspective of transport. Moreover, ballistic transport — which occurs when the mean free path (MFP) and relaxation times of the carrier are comparable to the length and time scales of transport in a material — is not described by Eqs. 2.1 and 2.3, which further require knowledge of materials' properties and that the system behaves classically and can be modeled as a continuum.

A modern approach to thermal transport was first established by the Einstein and Debye models, both based on Planck's quantization and able to account, to some extent, for the temperature dependence of thermal conductivity (at high temperatures). Debye was the first to attribute heat conduction to delocalized lattice waves [35]. Lattice vibrations, or phonons, are responsible for most of the heat transfer that occurs in insulators and semi-conductors. In the case of radiation, photons are the heat carriers, and in the case of convection and conduction heat transfer mechanisms, atom and molecular collisions, phonons, and electrons are responsible for heat transfer. In electrically conducting materials (e.g. most metals and metal-alloys), thermal transport is predominantly carried by electrons, and in effective semi-conducting thermoelectric materials electronic transport is non-negligible. Electronic transport is proportional to the electrons' relaxation time, $\tau(E)$; the electrons' group velocity, $\nu(E)$; the electronic density of states, D(E); the fermi energy, f_0 ; and the temperature, T. The quantities that depended on the energy, E, are generally computed with electronic methods, and must be integrated over the Brillouin Zone to yield electronic thermal conductivity. Electronic transport is not featured in the research on this thesis, and this is the only mention of it, but the calculation of electronic thermal transport in this way is described clearly in Ref. [154].

Resuming the phonon discussion, the Einstein model treats each solid as many individual, non-interacting quantum harmonic oscillators, with a single associated frequency. This is not the case in the Debye model, which assumes multiple allowed frequencies, with an upper bound defined by the distance between atoms in a material. As with the Einstein model, phonons obey Bose–Einstein statistics and the average phonon number is given by the Bose–Einstein distribution:

$$\langle n \rangle_{BE} = \frac{1}{e^{\hbar\omega/k_B T} - 1},\tag{2.4}$$

where h is Planck's constant, ω is the phonon frequency, k_B is the Boltzmann constant, and

T is the temperature. At the core of Debye's model is also the Dulong–Petit law, which accurately approximates the molar specific heat capacity of many elementary solids at high temperatures to 3R, where R is the gas constant $(8.314 \text{ J} \cdot \text{mol}^{-1})$, but which does not take into account anharmonicity, as with the rest of Debye's model. A harmonic interatomic potential would yield an infinite thermal conductivity for an idealized solid, whereas an anharmonic potential accounts for scattering and yields a finite thermal conductivity as a result [154]. If the forces between atoms were purely harmonic, there would be no mechanism for phonon-phonon collision, and scattering would be limited by phonon collisions with lattice imperfections and crystal boundaries. The scattering that occurs due to an anharmonic potential can be classified into normal (i.e. momentum conserving) and Umklapp scattering [154]. Imperfections and boundaries scatter phonons elastically, and the phonon energy is conserved. Changing individual phonons' energy is required to obtain thermal equilibrium, and this occurs only through phonon-phonon scattering, and Umklapp scattering in particular. Umklapp scattering is the reflection or translation of the phonon wave vector to another Brillouin zone. In Umklapp scattering momentum is conserved through the addition of another reciprocal vector G that "flips" the phonon back into the first BZ, as in

$$k_1 + k_2 = k_3 + G, (2.5)$$

where k_1 , and k_2 are the two interacting phonon waves. In Umklapp scattering, the waves are beyond the long wavelength limit and k_3 is the resulting vector, that places the scattering phonon outside the BZ. A more detailed explanation of normal and Umklapp processes can be found in Kittel's *Introduction to Solid State Physics* [72]. These interactions can be incorporated as scattering mechanisms within the phonon Boltzmann transport equation (BTE) formalism suggested by Peierls [125]:

$$\frac{\partial \psi_{\lambda}}{\partial t} + \mathbf{v}_{\lambda} \cdot \nabla_{\mathbf{r}} \psi_{\lambda} = \left(\frac{\partial \psi_{\lambda}}{\partial t}\right)_{collision},\tag{2.6}$$

where ψ_{λ} is the phonon distribution as a function of time, t, and the spatial coordinate, **r**, \mathbf{v}_{λ} is the phonon group velocity, and λ denotes a particular phonon mode of wavevector **q** and a given polarization [106]. The left-hand side of Eq. 2.6 describes the phonon population in a region of phase-space as a result of phonons' ordinary spatial velocities and temporal variations. An external field term has been assumed to be zero in the BTE phonon transport formulation in Eq. 2.6. The collision term on the right-hand side of the equation denotes the change in the phonon distribution function due to (elastic and inelastic) collisions between phonons and interactions with the background medium. The difficulty in solving this equation depends largely on the assumptions made about the collision term. If a single mode relaxation time approximation is made, the collision term can be written as

$$\left(\frac{\partial\psi_{\lambda}}{\partial t}\right)_{collision} = \frac{\psi_{\lambda o} - \psi_{\lambda}}{\tau},\tag{2.7}$$

where the initial distribution function, $\psi_{\lambda o}$, is the Bose–Einstein distribution (Eq. 2.4), $\langle n \rangle_{BE}$, and τ is the relaxation time, i.e. the time between phonon scattering events. The total relaxation time is related to the relaxation times of individual mechanisms (e.g. impurity scattering, normal scattering, Umklapp scattering) by Matthiessen's rule:

$$\frac{1}{\tau_{total}} = \frac{1}{\tau_{impurities}} + \frac{1}{\tau_{Umklapp}} + \frac{1}{\tau_{Normal}} + \dots$$
(2.8)

This, of course, assumes these mechanisms are independent. A more complex form of the BTE includes a *3-phonon* linearized collision integral most often specified under the assumption of a uniform, one-dimensional temperature gradient [106]. The single mode relaxation time approximation and the inelastic-*3-phonon* linearized collision integral terms are a good approximation and the most commonly used methods for solving the BTE in the thermal sciences [106], but do not include 4-phonon and higher order processes.

Expressions for thermal conductivity can be obtained by solving the BTE — a derivation of a thermal conductivity expression from the 3-phonon approach is offered by Minnich *et al.* [106]. The use of relaxation times due to three-phonon scattering was pioneered by Klemens [73], Herring [55], Callaway [19], Holland [58] and Slack [145] in the 1950–60s, but the lack of knowledge of the 3-phonon scattering matrices even for simpler solids meant this method was not fully considered until 2003 [17, 106]. Under the single relaxation time approximation, by enforcing energy conservation, thermal conductivity for an isotropic crystalline material can be expressed using simple kinetic theory as

$$\kappa_p = \frac{1}{3} \int_0^{\omega_{max}} C(\omega) v(\omega) \lambda(\omega) d\omega, \qquad (2.9)$$

where the specific heat is

$$C(\omega) = \hbar \omega D(\omega) \frac{d\langle n \rangle_{BE}}{dT}.$$
(2.10)

In the above equation, $D(\omega)$ is the phonon density of states per unit volume and unit frequency interval; $\langle n \rangle_{BE}$ is again the Bose–Einstein distribution, $v(\omega)$ the phonon group velocity; $\lambda = v\tau$ the phonon mean free path (MFP), and $\tau(\omega)$ the phonon lifetime. Some of the inputs required by this formalism have only become computationally feasible in the last 30 years or so, in parallel with atomistic scale materials research and development. For instance, phonon dispersion relations — which describe the phonon frequency, ω , for different wave vectors \mathbf{q} and polarizations throughout the Brillouin Zone (BZ) — can now be computed from first principles for some materials, and can be measured using inelastic neutron scattering including for some asymmetric materials [106].

2.1.1 Computation

Computational tools that permit the study of thermal transport have been advancing at a fast pace and over different length scales. The use of increasingly complex approximations within the BTE formalism as mentioned in the last paragraph is a good example of these advancements. Figure 2.1 shows some of the state-of-the art approaches used to understand thermal transport at different scales. Green's functions (used at the nano-scale, as shown in Fig. 2.1) are a formalism that can be used to solve for inhomogeneous differential equations with specified initial conditions or boundary conditions. This is the only reference to Green's functions, as they are not relevant for the research reproduced in this document. Further information on the application of Green's functions to thermal transport can be found in Minnich's review of advances in the measurement and computation of thermal phonon transport properties [106]. First principles, or ab initio methods, however, in particular density functional theory (DFT), are crucial to some of the work done in the course of my PhD. In addition to a short description of its application to heat conduction, DFT is discussed in more detail in the Computational Methods section. In addition to DFT, classical molecular dynamics simulations — not included in Fig. 2.1 — also allow for atomistic- to nano-scale thermal transport calculations and will feature heavily in the research discussed in this document.



Figure 2.1: Overview of state-of-the-art tools to study heat conduction and enable a microscopic understanding of thermal conductivity across different scales [106].

The use of the BTE was historically limited due to the unavailability of quantumbased calculations of phonon properties, such as dispersion relations or anharmonic scattering matrices [106]. There is a wide array of density functional theory packages (currently the most commonly used *ab initio* method), such as VASP, Siesta, Quantum Expresso or GAMESS, to mention a few. In addition to their direct use to obtain phonon properties, *ab initio* approaches are used to determine interatomic potentials for various crystal structures without the need to include adjustable parameters. Such potentials can, in turn, be used within the substantially more expedient classical molecular dynamics approach. Interatomic potentials were most often empirically or semi-empirically constructed, but the widespread use of DFT has resulted in an increasingly large number of *ab initio* potentials that are more widely applicable — empirical potentials are often only adequate to describe a limited set of structures, based on the experimental data the potential parameters have been fit to. First principles calculations of both harmonic and anharmonic parameters are increasingly more common. In 2010, Ward and Broido computed harmonic and anharmonic interatomic force constants (IFCs) from density functional perturbation theory (DFPT), i.e.

without introducing any adjustable parameters [166], to properly reflect the physically distinct behaviors of the normal and Umklapp scattering processes and include the scattering of acoustic phonons by optic phonons. Ward and Broido further used their results to assess the validity of the relaxation time approximation for silicon and germanium, which they found to accurately represent the thermal conductivity of both materials [166]. In DFPT, the second order perturbation of the DFT total energy is obtained by expanding the total energy with respect to changes in the Kohn-Sham electron wave functions. A section in DFPT can be found in the *Computational Methods* chapter. In general, *ab initio* calculations have elucidated several heat transfer mechanisms that had escaped researchers for years. One such example is the breadth of the thermal phonon spectrum and the relevance of low frequency, long MFP phonons to heat conduction. We are no longer limited to treat the phonon spectrum using average properties in a grey approximation. For instance, calculations of Silicon based on its average MFP have underestimated the contribution of low frequency phonons to thermal conductivity. In fact, at room temperature MFPs in Si range from a few nanometers to 10 microns, and phonons with a MFP above 1 micron contribute over 40% to thermal conductivity [40, 30]. This illustrates the importance of considering multiple relaxation times when interpreting thermal measurements in bulk and nano-structured materials. While not directly contributing to heat transfer, optical modes provide important scattering channels for acoustic phonons and thus indirectly contribute to heat conduction; the effect of optical mode scattering varies between materials and is also manifest in the temperature dependence of thermal conductivity [166, 153, 152]. Using ab initio methods, Lindsay et al. [91] have recently identified new criteria that affect thermal
conductivity at a microscopic level, including acoustic phonon bunching, which restricts the interactions among acoustic phonon modes, and a large acoustic-optical gap, which similarly inhibits the participation of optical modes in phonon-phonon scattering.

DFT provides the most detailed atomistic information, but is very computationally expensive and is often not feasible for domains larger than a few atoms or long simulation times. A useful approach to bypass some of the difficulties of DFT is classical molecular dynamics (MD). As large-scale computing capabilities continue to grow, parallel simulations are starting to be able to handle systems with tens of millions of atoms [134, 65]. The position and momentum space trajectories of a system of classical particles can be predicted using the Newton laws of motion — in an MD simulation, the only required inputs are an atomic structure and an appropriate interatomic potential. A whole section in classical MD can be found in the *Computational Methods* chapter. Classical MD has the advantage of naturally including anharmonic effects through the form of the interatomic potential. Neglecting electrons removes the ability to model the associated electrical and thermal transport, but phonon transport can often be modeled with classical MD, the potentials for which can, as discussed earlier in this section, be informed by *ab initio* methods. Harmonic theory is only exact at zero temperature [101], making classical MD also suitable for modeling systems at temperatures where the anharmonic effects, which are more difficult to model theoretically, become important.

There are two major approaches for predicting thermal conductivity from MD simulations: equilibrium and non-equilibrium methods. Each has advantages and disadvantages, and the method chosen strongly depends on the problem of interest [101]. Generally

speaking, the equilibrium approach is superior for bulk phase simulations and the direct method is best for finite structures [101]. Non-equilibrium or direct methods rely on disturbing the system of interest and measuring its response, while in equilibrium methods the principle is the same, but the response is ascertained from small, local deviations from equilibrium. The Müller-Plathe method [116] is a simple and popular non-equilibrium approach that consists of creating a temperature differential by exchanging the energy/momentum of the hottest molecule in a region of a slab selected to be the *cool* region, with that of the coolest atom in the *hot* region thus imposing a flux on the system. The thermal conductivity is obtained from the linear parts of the temperature distribution of the fictitious gradient. I briefly dabbled with the Muller-Platte method, but did not use it towards the research reproduced in this document. As such, a greater focus will be place on the Green-Kubo (GK) equilibrium approach instead, which features heavily in this thesis (chapters 4 and 5).

2.1.2 Green–Kubo method

Mathematically, transport properties can be obtained from small, local fluctuations by integrating the current autocorrelation function as

$$\gamma = \alpha \int_0^\infty \langle \mathbf{A}(t)\mathbf{A}(t+\tau) \rangle \ d\tau, \qquad (2.11)$$

where γ is the transport property of interest and **A** the current that drives it. The expression $\langle \mathbf{A}(t)\mathbf{A}(t+\tau)\rangle$ is the autocorrelation function of quantity **A** and α is a temperature dependent coefficient, and this is the Green–Kubo method. For thermal conductivity, κ , the Green–Kubo expression becomes

$$\kappa = \frac{V}{3k_B T^2} \int_0^\infty \langle \mathbf{J}(t) \mathbf{J}(t+\tau) \rangle \ d\tau, \qquad (2.12)$$

where k_B is Boltzmann's constant, T the temperature, and V the volume of the simulated region, \mathbf{J} is the heat-flux, and $\langle \mathbf{J}(t)\mathbf{J}(t+\tau)\rangle$ is the non-normalized heat current autocorrelation function (HCACF). Within classical molecular dynamics \mathbf{J} is computed as

$$\mathbf{J} = \frac{1}{V} \left[\sum_{i} e_i \mathbf{v}_i - \sum_{i} \mathbf{S}_i \mathbf{v}_i \right], \qquad (2.13)$$

where e_i is the total energy per atom *i* at a given time, *t* (i.e., Eq. 2.13 corresponds to a single time step), **v** is the atom velocity vector and **S**_{*i*} is the stress tensor for each atom and has 6 components: xx, yy, zz, xy, xz, yz. The HCACF, $\langle \mathbf{J}(t)\mathbf{J}(t+\tau)\rangle$, can be numerically computed as

$$\langle \mathbf{J}_n \mathbf{J}_{n+m} \rangle \equiv \sum_{n=0}^{N-m} \frac{\mathbf{J}_n \mathbf{J}_{n+m}}{N-m},$$
(2.14)

where \mathbf{J}_n is the value of \mathbf{J} at the n^{th} time step, i.e. $\mathbf{J}_n = \mathbf{J}(t_n)$, for n = 0, 1, 2, ..., N, and \mathbf{J}_{n+m} is \mathbf{J} at the $(n+m)^{th}$ time step, or $\mathbf{J}(t_n + \tau_m)$, for m = 0, 1, 2, ..., M. N and M are, respectively, the maximum number of steps in the simulation and in the HCACF. Analytically, the autocorrelation function is computed as the inverse Fourier transform of the same transform of the current multiplied by its complex conjugate, averaged over N-m. It follows that to obtain good statistical averaging M must be significantly less than N, and that the error associated with the HCACF increases over time for fixed N. The Green– Kubo method is reiterated in chapters 4 and 5. In chapter 4 it is used to compute thermal resistance from irradiation defects in graphite. For a system in equilibrium the average current of any property is zero, and the HACF is expected to decay to zero given sufficient time. Instead, large oscillations with a significant contribution to the integral have been observed [119, 140, 24, 86, 34]. In chapter 5, we devise a new method to quantify the uncertainty from these oscillations on-the-fly and better use resources to compute thermal conductivity with the Green–Kubo formalism.

2.1.3 Imperfections

Crystal structure defects can be of different types and dimensions. Vacancies, interstitials, and impurities are zero-dimensional or point defects. A vacancy, as the name indicates, occurs when an atom is missing from a periodic crystal structure, and can either be formed when the solid is formed, occur naturally as a result of thermal vibrations, or can be induced, for instance in a cascading reaction due to neutron scattering. Interstitials, atoms that occupy a place outside the normal lattice positions, are a type of point defect that can form in the same way as vacancies. In the first project we consider such type of defects and clusters of defects in graphite, which can occur during the processing of the material or while in service due to irradiation. We also consider the Stone–Wales defect, involving a change in connectivity of two π -bonded atoms, which are rotated by 90° with respect to the midpoint of their bond. The details and results of this research can be found in chapter 4.

Imperfections have an important contribution in limiting the MFP. The effect of imperfections becomes more noticeable at low to medium temperatures. In this regime phonon-phonon scattering is weak, and defect scattering plays a more significant role [154]. Fig 2.2 shows the predominance of different types of scattering with temperature. The different regimes have informed the choice of temperature (300 K) of the simulations performed in the first project. While molecular dynamics is only rigorously applied to solids above the Debye temperature, to determine the comparative scattering effect of different types and concentrations of impurities it is to our advantage to consider a regime before phonon-phonon scattering becomes the dominant mechanism.



Figure 2.2: The solid line corresponds to results predicted from a model that considers phonon dispersions and contributions from different phonon branches, and is compared with experimental results (symbols) [25, 154]. The different scattering regimes are also indicated.

Beyond point defects, dislocations (linear defects), stacking faults, twin or grain boundaries (planar defects) have a significant effect on thermal conductivity. The impact of the structure (e.g. through nanostructuring) and defect inclusion to thermal transport is a good example of this effect. Let us consider boundary scattering, which plays a more significant role at low temperatures, a regime where phonon-phonon scattering is weak, and the thermal conductivity is approximately proportional to $\frac{1}{T^3}$ (see Fig 2.2). In the limit that ballistic scattering becomes dominant, and boundaries scatter diffusively versus specularly, boundary phonon scattering is essentially agnostic to the direction of phonons and a "gap" (decrease) in thermal conductivity forms around the boundaries. This effect was discovered by Haas and Biermasz [33] and later explained by Casimir [20] and is thus often designated the Casimir effect. The Boltzmann transport equation is never directly used in this research. However, some of the first principles calculations described in chapter 7 are used to inform the solution of the BTE for phonon transport in Si and UO_2 performed by our collaborators. Ultimately, the aim of this work is to include the whole phonon spectrum and corresponding life times into the BTE, and further correctly describe phonon boundary scattering.

2.2 Random Walk

In a random walk, a trajectory is defined by a succession of random steps. An example of a simple one-dimensional random walk is to flip a fair coin and select to move one step right or one step left for a fixed, heads or tails, outcome. If v_i is the velocity (i.e. step length and direction) at some step i, where i = 1, 2, 3, ..., n, the position of the random walk after n steps, x(n), is the sum of velocity oscillations up to that point:

$$x(n) = \sum_{i=1}^{n} v_i.$$
 (2.15)

For any velocity distribution with mean zero and standard deviation σ_v , the root mean square translation distance after *n* steps or, in other words, the expectation of the absolute value of the displacement of a random walk is

$$E(x(n)) = \sigma_v \sqrt{n}.$$
(2.16)

Consider the random walks in Fig. 5.2 b), with a step size distribution $N \sim (0, \sigma_v)$ as shown in Fig. 5.2 c). The expectation of position as a function of time for the random walk is

$$E(x(t)) = \delta t \sigma_v \sqrt{\frac{t}{\delta t}} = \sigma_v \sqrt{t \delta t}.$$
(2.17)

The Green-Kubo method, introduced in section 2.1, requires large systems, and long simulation times to reduce the error associated with computing the autocorrelation function (Eq. 5.3). In chapter 5, by characterizing the integrated autocorrelation function noise as a random walk, we are able to estimate an expectation envelope for the noise, as that defined in Eq. 2.17 for the random walk.



Figure 2.3: a) corresponds to velocity fluctuations that give rise to a random walk; b) a set of 10 random walks is shown in black and the expected root mean square translation distance at time t is plotted in red; c) is the distribution of the random walks shown in b).

2.3 Metal–organic frameworks

The term metal-organic framework (MOF) was introduced in 1995 [168] to designate extended crystalline structures comprised of secondary building units (SBUs), i.e. single nodes or clusters of metal-ions, bridged by organic linkers. An example of a MOF and its most basic components are shown in Fig. 2.4. The highly porous nature and exceptionally large surface area of MOFs make them ideal for gas sorption and storage applications [133, 164], such as carbon sequestration and hydrogen storage [117, 105]. Beyond their porosity, MOFs are inherently modular. Moreover, the building blocks of MOFs (SBUs and linkers), and the framework topology are often property-correlated, making MOFs suitable for a wide array of applications. Separation [36, 167], chemical sensing [76], drug transport [60], catalysis [150], and charge storage/conduction [84, 170] are some examples of other common applications for which MOFs are heavily researched.



Figure 2.4: MIL-53(Cr), where MIL stands for Matriaux de l'Institut Lavoisier, is a type of MOF. The metal ion and ditopic linker are its constituting elements. While a chromium metal ion is depicted in this figure as the MIL-53 SBU, other studied systems include Al, Ga, In, Fe, and Sc as the metal-ion instead.

For the past 15 years, the discovery, study and synthesis of new MOFs have been increasing rapidly [46]. The increasing amount of not only experimental, but computational research done on MOFs with the intent of predicting novel structures is evidenced by the number of available framework databases. A database of computation-ready MOF structures derived from experimental data, and a method for assembling periodic and non-periodic framework structures *in-silico*, termed Automated Topological Generator for Framework Structures (AuToGraFS), has been implemented by Addicoat *et. al.* [2]. The Cambridge Structural Database (CSD) included about 20, 000 MOFs in 2013 [138]. Yet another useful database of MOFs is the CoRE (computation-ready, experimental) MOF database, with publicly available atomic coordinates for over 4700 porous structures [28].

The challenge of efficiently designing and constructing new crystalline solid-state materials from molecular building blocks has driven a significant portion of the research in MOFs in the last few years. This research has promoted the abstraction of MOFs to simpler geometries. Reticular chemistry offers a way to represent MOFs as elementary building blocks abstracted as shapes such as triangles, squares, tetrahedra and octahedra. Reticular chemistry applied to MOFs first appeared in 2003 in the work of Yaghi *et al.* [169], and a comprehensive description of MOF geometries (see Fig. 2.5 for examples) can be found in the work of Li *et al.* [88]. O'Keeffe and Yaghi *et al.* have also put forth the reticular chemistry structure resource (RCSR) database of, and symbols for, crystal nets [122]. This level of abstraction is useful for the high-throughput discovery of MOFs, which has been the underlying motivation of the research developed on MOFs in the course of my Ph.D. In chapter 6, we propose abstracting linkers and nodes as resistors as an heuristic for the fast screening of framework thermal properties.



Figure 2.5: Figure a) corresponds to MOF-505. The second and third figures in a) illustrate how the structure can be abstracted as shapes. Two possible abstractions are shown. This image was reproduced from [88]. Fig. b), partially reproduced from [88] and [29], corresponds to MOF-5 and its abstraction, showing the $Zn_4(-CO_2)_6$ SBU as an octahedron, and the terephthalate linker as a rod. Fig c) provides a glimpse into the diversity of MOFs. Fig. i) is an HKUST-1 MOF [88]; Fig. ii) is an **nnt-a** type net MOF [88]; Fig. iii) is a MOF with a **ttu** type net, which is a derivative from a net-type designated corundum [88]; and Fig. iv) is a mIm-MOF-14, an example of an interpenetrated MOF [74].

The 2013 review article written by Furukawa *et al.* [46] offers an encompassing overview of the effects of framework chemistry on the functionality and application of MOFs. Furukawa *et al.* discuss design strategies to facilitate the synthesis of families of materials with similar framework topology but varying in pore size and the type of functional groups present in the linkers. The focus of the paper is on how ultrahigh porosity, high thermal and chemical stability, elevated catalytic activity and proton conductivity can be achieved and tuned, not just across families of MOFs, but within a single MOF. Heterogenous functionalities of MOFs can be obtained by flexible, or otherwise isomerizing, frameworks. In 2002, Kitagawa [156] and Férey [142, 10] independently published pioneering works on "breathing" MOFs, the phenomenon by which flexible MOFs undergo a reversible transformation between narrow pore (np) and large pore (lp) structures. The dynamic micropores of breathing MOFs have been shown to open and close as a response to external stimuli such as temperature [97] and pressure [95] changes, or host-interaction [95, 96].

2.3.1 Flexible metal–organic frameworks

Flexible MOFs exhibit structural reversible transformability while maintaining crystalline order. The varying chemical interactions within MOFs, ranging from strong coordination bonds to weaker dispersion forces and hydrogen bonding interactions, may result in significant structural flexibility in response to temperature, hydrostatic pressure, or uniaxial stress [89]. In addition to thermal and mechanical stimuli, host-guest interactions and photochemical stimuli may also induce phase transitions in MOFs. Studies of flexible MOFs have been increasing since the first major conceptual article appeared in 2004 [70, 138], but only less than 100 compounds revealing significant breathing transitions or related stimuli responsive properties were included in the Cambridge Structural Database as of 2014 [138]. The most reported phenomena are breathing and swelling (see Fig. 2.6).

Breathing MOFs, as the MIL-53 in Fig. 2.4, transform between narrow pore (np) and large pore (lp) forms resulting in a major volume change. Researchers have found that lattice-fence or wine-rack motifs, like that of MIL-53, can be designed by adding dangling, flexible side groups pinned to the backbone of the linkers and whose motion is transduced to the framework [138]. Swelling (e.g. in MIL-88) is characterized by an enlargement of

the cell without changes in the unit cell or, generally, the space group [138]. A volumeconserving flexibility mode (e.g. in ZIF-8), as described by Schneemann *et al.* (Fig. 2.6), is linker rotation, where the spatial alignment of the linker changes as it rotates around an axis [138]. Seo *et al.* have developed a 3-D pillared-layer coordination polymer which selectively rotates to allow adsorption for guests that interact with the nodes only [141]. Subnetwork displacement requires that a system have disconnected frameworks that interact only through weak forces. A 2-D example of an interdigitated framework that shows gate opening/closing as a function of pressure from a nitrogen, oxygen and methane mix is reported by Kitaura *et al.* [71]. There are also examples of so called rigid MOFs that show phase transitions due to thermal expansion (e.g. MOF-5, HKUST-1) [138]. MOFs can also undergo reversible amorphization when exposed to mechanical stress, or exhibit drastic pressure-induced phase transitions, associated with striking bond rearrangements. Some MOFs have been reported to exhibit negative linear compressibility (NLC) and massive positive or negative thermal expansion (PTE and NTE) [89].



Figure 2.6: Fig. a) is a paddle-wheel and serves as an inorganic brick for many known flexible MOFs [138], as is the case with the flexible Mil-53 shown in Fig. c). Fig b) is MIL-88A, and exhibits an entirely different form of flexibility [22]. Fig. d) is a classification of different flexibility modes in MOFs [138]. Types A, B and C are non-volume conserving.

In chapter 6, we apply our heuristic approach to a single property — estimating

thermal transport —, and to a single flexible framework, but not only could the same strategy be used to estimate other properties, such as elastic constants by approximating the nodes and linkers as springs instead of resistors, it could be (better) applied to other flexible modes (examples are mentioned above). While to our knowledge, there have been no similar heuristic models proposed for heat transport, Sarkisov *et al* [136] have proposed a simple method to predict framework flexibility based on treating the structures as a system of rigid elements connected by hinges (or 'sticks and balls' as informally referred to in the previous section). This approach has the drawback that MOFs are therefore exclusively classified based on their topology. As Cheetham *et al* [89] points out, the framework topology describes the overall connectivity pattern of the MOF building units and it is vitally important not only for its mechanical properties, but also for its chemistry. Cheetham *et al.* [89] show that SBUs can be analyzed and their rigidity and flexibility estimated based on strong (covalent or coordinative bonds) and weak (hydrogen bonds, dispersion forces) interactions [89]. Both Cheetham *et al.* [89] and Sarkisov *et al* [136] provide complementary ways to systematically guide the search for flexible (or rigid) MOFs.

The motivation for the research produced in chapter 6 further supports the need for more studies of thermal transport in MOFs, which to date have received limited attention [51]. Gas sorption involves exothermic and endothermic processes, and the ability to transport heat into and out of a framework can be a limiting factor in the performance of MOFs for sorption-related applications, such as adsorption chillers or hydrogen storage. The limitation of these devices is not storage capacity, but the efficient removal of latent heat of adsorption [172, 132]. Mechanical dampening, for shock adsorption [171] or energy storage applications, likewise requires heat dissipation. For applications requiring or benefiting from dynamic, or flexible, MOFs, it is not only necessary to compute thermal conductivity, but to understand how it varies with structural transitions between breathing states. Our aim is to determine if thermal transport properties can be estimated from the vibrational modes of lp and np structures and, moreover, if these properties scale continuously with framework geometry.

Chapter 3

Computational methods

Molecular dynamics (MD) encompasses several approaches or models used to simulate (n-body) materials at the atomic and molecular scale. In classical MD, simulations are advanced by numerically solving Newton's equations of motion; in some quantum-based MD approaches (e.g. Hartree-Fock theory) the Schrödinger equation is used, while others resort to different strategies: density functional theory (DFT) is based on an electronic density functional formulation, and there are some hybrid approaches, such as the Car-Parrinello method which combines equations of motion with a density functional approach. While molecular dynamics simulations are often used to infer nano-scale properties, the use of periodic boundaries makes it a useful tool to compute meso- and macro-scale properties as well. In addition to property calculations, MD further allows insight into the physics of atoms and molecules, depending on the methods and approximations used. Classical molecular dynamics, density functional theory, and time-dependent density functional theory are the most relevant methods for the execution of the work done and proposed in this thesis, and an overview of these methods is therefore provided below. A more thorough discussion of these and other molecular dynamics methods can be found in: *Computational Materials Science, Fundamentals to Applications* [85], and *Ab Initio Molecular Dynamics, Basic Theory and Advanced Methods* manual [99]. Other sources are indicated in the text; in order to maintain consistency throughout this discussion the notation used deviates slightly from that of the various sources used.

3.1 Classical molecular dynamics

Classical molecular dynamics (MD) is a computational technique for simulating complex systems at the molecular and atomic scale. The development of computational approaches based on quantum mechanics (QM) has yet to render classical MD obsolete. Predictions and understanding of various systems' kinetic and thermodynamic properties and mechanistic behavior can be made without resorting to QM, and classical MD is significantly less computationally expensive, allowing for simulations of thousands of atoms. Furthermore, quantum behavior can, in some cases, be approximated with an appropriate interatomic potential.

In classical MD the total forces on all atoms are computed and used to solve Newton's equations of motion to determine how the atoms evolve. This is done iteratively, using a numerical scheme. For each atom, i,

$$\mathbf{F}_i = m_i \mathbf{a}_i = m_i \frac{d^2 \mathbf{r}_i}{dt^2},\tag{3.1}$$

where \mathbf{F}_i is the force exerted on atom *i*, *m* its mass and \mathbf{a}_i its acceleration. If the interatomic force is conservative (i.e. it depends on positions, not velocity), then

$$\mathbf{F}_{i} = -\nabla_{i} U(\mathbf{r}_{1}, \mathbf{r}_{2}, \dots \mathbf{r}_{N}) = -\nabla_{i} U(\mathbf{r}^{N}), \qquad (3.2)$$

where U is the potential energy of the system as a function of the position, \mathbf{r} , of all of its Nparticles. There is not a complete analytical solution for systems comprised of more than two bodies, and in order to integrate the equations of motion for many-body systems it is necessary to resort to numerical schemes [16]. For this reason, Eq. 3.2 consists of 3Nsecond-order differential equations, N for each coordinate, which are coupled through the nonlinear potential function. To find the three-dimensional phase-space trajectory of the system at hand, initial conditions (at least position and velocity) need to be specified prior to beginning the calculation. A discrete time step, δt , to advance the simulations needs to be selected, such that the positions and velocities can be found at $t + \delta t$ from the forces evaluated at t. There are several possible self-consistent preserving methods to advance the equations of motion, but the Verlet algorithm [159, 160] is often used due to its simplicity and reasonably low error. While it is not necessarily the case that MD codes will use this algorithm or variation of it shown below, it serves to illustrate how the equations of motion are advanced. The leapfrog [110], or velocity Verlet, includes a mid-step calculation of the velocity,

$$\mathbf{v}\left(t+\frac{1}{2}\,\delta t\right) = \mathbf{v}(t) + \frac{1}{2}\,\mathbf{a}(t)\,\delta t,\tag{3.3}$$

based on the initial velocity, $\mathbf{v}(t)$, and acceleration, $\mathbf{a}(t)$, to be included in the calculation of the new position,

$$\mathbf{x}(t+\delta t) = \mathbf{x}(t) + \mathbf{v}\left(t + \frac{1}{2}\,\delta t\right)\,\delta t.$$
(3.4)

The acceleration at the next time step, $\mathbf{a}(t + \delta t)$, is directly obtained from the interaction potential. The new velocity then becomes

$$\mathbf{v}(t+\delta t) = \mathbf{v}(t) + \frac{1}{2} \left(\mathbf{a}(t) + \mathbf{a}(t+\delta t) \right) \delta t.$$
(3.5)

3.1.1 Interatomic potentials

The interaction between the atoms is defined by \mathbf{F}_i (see Eq. 3.2) and modeled through interatomic potentials, making them paramount in classical MD simulations. Interatomic potentials are generally based on simple functional forms that reflect on the types of bonding they are designed to represent, but can have varying degrees of complexity. Atomic force field models describe the behavior of the atoms in the system through the use of interatomic potential functional forms selected to best describe the system and properties of interest [102]. The problem of finding a potential to accurately mimic true energy surfaces is not trivial. Adjustable parameters are generally chosen such that the empirical potential matches results obtained with first principles calculations or experimental data [102]. Potentials also vary in terms of the number of atoms that interact with each other (pair potentials versus many-body potentials), the nature of the bonding described (covalent, polar covalent, ionic, metallic, hydrogen, van der Waals), and whether short and/or long range interactions are being considered [102, 85]. The Lennard-Jones potential [63],

$$\phi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$
(3.6)

where σ and ε are fitting parameters, is commonly used due to its simplicity and reasonably good performance for neutral atoms [85]. Other potentials include the Born-Meyer, and the Morse potentials [114], both central-force potentials, i.e. a function only of the distances between pairs of atoms [85]. In simple metals there is little to no directionality to the bonds but the interaction between delocalized electrons must be included in the description of the bonding; accurate descriptions of the interatomic potentials must include quantum mechanical effects that arise from when charge distributions overlap and the electrons are forced to occupy a smaller volume [85]. Embedded-atom model (EAM) potentials are used to compute metallic materials' properties — in addition to a pair potential, they includes an electron energy functional dependent on the interatomic distance between atoms [85]. In bond-order potentials, the general expression for each atom's energy is

$$E_i = \frac{1}{2} \sum_{j=1}^{Z_i} \left[q V_R(r) + b V_A(r) \right], \qquad (3.7)$$

where parameter q depends on the local electronic density, V_A and V_R are repulsive and attractive parameters, respectively, Z the number of nearest neighbors and b is the bond order parameter, meaning it controls the strength of the chemical bond (including the number of bonds and sometimes also angles and bond length). The total system energy is the sum of all atomic energies [85]. The Tersoff potential [149], the Brenner potential [14], the charge-optimized many body (COMB) [143, 90], and the reactive force field (ReaxFF) [157] are examples of bond-order potentials.

The adaptive intermolecular reactive empirical bond order (AIREBO) potential [148] is a bond-order potential designed for carbon and hydrogen systems. The AIREBO potential consists of three terms:

$$E = \frac{1}{2} \sum_{i} \sum_{j \neq i} \left[E_{ij}^{REBO} + E_{ij}^{LJ} + \sum_{k \neq i} \sum_{l \neq i, j, k} E_{kijl}^{TORSION} \right].$$
(3.8)

Starting from the end of Eq. 3.8, the TORSION term describes various dihedral angle preferences in hydrocarbon configurations; the Lennard-Jones (LJ) term adds longer-ranged interactions using a form similar to the standard Lennard-Jones potential; and the REBO term shares some of the same terms with Brenner's potential, and confers the model reactive capabilities. Reactive force potentials are variations of bond-order potentials that enable atoms to respond to their local environment and determine their charge: bond formation and breaking, for instance, can be simulated with this type of potential. These offer more resolution to some problems, but are more computationally expensive than simpler potentials; that computational expense is still lower than density functional calculations. Interatomic potential functions are approximations, and thus so are the calculations that are based on them.

3.2 Time-independent density functional theory

The behavior and properties of materials are often a direct result of the atomic bonding type. Knowledge of the electronic distribution of a system is paramount to understanding the nature of bonding and it is not surprising that we should need to rely on electronic structure methods to understand and predict certain materials properties. The time-independent Schrödinger equation, which describes the energy of the electrons and nuclei in a material, is

$$\mathcal{H}\psi = E\psi,\tag{3.9}$$

where E is the system energy, ψ the wave function and \mathcal{H} is the Hamiltonian operator given by

$$\mathcal{H} = \sum_{i=1}^{N} \left(-\frac{1}{2} \nabla_i^2 + V_{ext}(\mathbf{r}_i) \right) + \sum_i \sum_{j>i} \frac{1}{r_{ij}}, \qquad (3.10)$$

for many-body electronic structure calculations, in *atomic units*. The above Hamiltonian assumes the Born-Oppenheimer approximation is used, i.e. the positively charged nuclei of the atoms that integrate the system are considered to be fixed with respect to the electrons, such that a static external potential, $V_{ext}(\mathbf{r}_i)$, describes the interaction between the nuclei and the electron, and the wave function, ψ , a stationary electronic state. For a system with M nuclei, if Z_{α} is the nuclear charge and $r_{i\alpha}$ is the distance between the i^{th} electron and the α^{th} nucleus, the external electrostatic (Coulomb) potential is

$$V_{ext}(\mathbf{r}_i) = -\sum_{\alpha=i}^M \frac{Z_{\alpha}}{r_{i\alpha}}.$$
(3.11)

In Eq. 3.10, the first term in the Hamiltonian corresponds to the kinetic energy of the electrons in the system and N is the total number of electrons; the last (summation) term

is the electron-electron interaction energy, where r_{ij} is the distance between the i^{th} and j^{th} electrons. Even with the Born-Oppenheimer approximation, the Schrödinger equation (Eq. 3.9) can not currently be solved exactly for systems larger than the hydrogen atom, making it necessary to find other methods to solve more complex problems. Of the existing approaches to perform many-body electronic calculations, the most ubiquitously used is based on a *density functional theory* (DFT) formulation of quantum mechanics [85].

At the core of DFT is the relationship between the electron density of a system, ρ , and the system's wave function, ψ :

$$\rho(\mathbf{r}_1) = N \int \dots \int |\psi(\mathbf{r}^N)|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N, \qquad (3.12)$$

where \mathbf{r}_1 corresponds to an arbitrary electron position, and \mathbf{r}^N is the position of all N electrons in the system. The most remarkable aspect of this relationship is that, for any value of N, it bijectively maps a function with 3N variables, ψ , to a function, ρ , that is dependent on only 3 variables as shown by Hohenberg and Kohn [75]. In other words, for each unique wave function there is a unique electronic density function. DFT furthermore relies on the second Hohenberg–Kohn theorem, which states that there exists an energy functional, $E[\rho]$, for which the correct ground state electron density is a global minimum. The energy density functional is not known, nor is it currently known how to find it exactly.

The Thomas-Fermi (TF) and Thomas-Fermi-Dirac (TFD) models are the earliest formulations of DFT and precede the Hohenberg–Khon theorems by nearly four decades. The Kohn–Sham method was published shortly after Hohenberg and Khon's theorems and it addresses several inadequacies of the TF/TFD models. It is also the basis of most DFT calculations done today. Following from the Hamiltonian described by Eq. 3.10, a density functional could be written as

$$E[\rho] = T[\rho] + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + V_{ee}[\rho], \qquad (3.13)$$

where $T[\rho]$ is the kinetic energy of the system's electrons, $V_{ee}[\rho]$ is the electron-electron interaction and the middle term is the nuclear-electron interaction. If the classical Coulomb integral (or Hartree energy),

$$E_H[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_2 - \mathbf{r}_1|} d\mathbf{r}_1 d\mathbf{r}_2$$
(3.14)

is used to describe the electrostatic energy of the charge distribution, $V_{ee}[\rho]$, then

$$V_{ee}[\rho] = E_H[\rho] + (V_{ee}[\rho] - E_H[\rho]), \qquad (3.15)$$

where $V_{ee}[\rho] - E_H[\rho]$ is a correction factor. As aforementioned, a major innovation in Kohn and Sham's approach is the assumption that a many-electron system can be written as the sum of one-electron orbitals, ψ_i , as

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2, \qquad (3.16)$$

the discrete equivalent of Eq. 3.12. This simplifies how to find solutions to the Schrödinger equation, and it includes shell discontinuities as a natural part of the solution — the discreteness of the shell structure of electrons was a major source of error in the earlier, TF/TFD models. According to the Kohn–Sham approach the kinetic energy can be obtained as

$$T_{KS}[\rho] = \sum_{i=1}^{N} \left\langle \psi_i \left| -\frac{1}{2} \nabla_i^2 \right| \psi_i \right\rangle.$$
(3.17)

We can therefore rewrite $E[\rho]$:

$$E[\rho] = T_{KS}[\rho] + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_H[\rho] + E_{XC}[\rho]$$
(3.18)

where $E_{XC}[\rho]$ is a correction term that includes all the corrections between the sum of the kinetic and Coulomb energies and the correct answer. This term is called the exchangecorrelation energy because it includes the exchange interaction that occurs in electrons, and other fermions, due to the Pauli's exclusion principle, and the electron-electron correlation [5]. The minimum for the Kohn–Sham functional (Eq. 3.18) can be obtained by varying the functional for a fixed number of electrons with respect to the density (Eq. 3.16) [99]. Summarily, the Kohn–Sham equation is equivalent to the Schrödinger equation of a fictitious system of non-interacting particles, usually electrons, with the same density as a system of interacting particles. Furthermore, expressing the Kohn–Sham in terms of $\rho(\mathbf{r})$ allows mapping a many-body problem onto a single-body problem with the same internal energy.

The optimization procedure is generally started with an initial wave function, ψ_i^0 guess, from which an initial electron density, ρ_0 is constructed, according to see Eq. 3.16. The Kohn–Sham potential, found by taking the derivative of the Kohn–Sham functional (Eq. 3.18), is

$$V_{KS}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_1|} d\mathbf{r_1} + \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})}.$$
(3.19)

The Hamiltonian (which includes the kinetic energy term excluded in the potential above) is therefore:

$$\mathcal{H}_{KS} = -\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r}). \tag{3.20}$$

Solving the Schrödinger equation,

$$\mathcal{H}_{KS}\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}),\tag{3.21}$$

yields a new set of N orbital wave functions ψ . From these a new ρ is computed and used

in Eq. 3.19, the process is repeated until a ρ does not vary by more than the specified tolerance [85].

The exchange-correlation energy term is the unknown in the Kohn–Sham expression, and how it is approximated is thus key to DFT. The most widely used approximation are the generalized gradient approximation (GGA), and the local density approximation (LDA), but several others exist [99]. While the LDA depends exclusively on the value of the electronic density at each point in space, and are of the form

$$E_{xc} = \int \rho(\mathbf{r}) \varepsilon_{xc}(\rho) d\mathbf{r}, \qquad (3.22)$$

GGA methods are also based on its local gradient, and is of the form

$$E_{xc} = \int \rho(\mathbf{r}) \varepsilon_{xc}(\rho, \nabla \rho) d\mathbf{r}, \qquad (3.23)$$

where $\nabla \rho(\mathbf{r})$ is the gradient of $\rho(\mathbf{r})$. Often times the correlation-exchange energy will be represented as the sum of a correlation and an exchange terms [85].

The initial wave function with which the calculation is generally started is the sum over a set of functions designated the basis set. Different structures benefit from varying basis sets. For instance, for solids, the basis set should satisfy Bloch's theorem:

$$\phi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\phi_{\mathbf{k}}(\mathbf{r}). \tag{3.24}$$

In Eq. 3.24, **R** is a direct lattice vector, **r** is the position, and **k** the wave vector; ϕ is a repeating wave function with the same periodicity as the crystal it is intended to describe. According to the theorem the energy eigenstates for an electron in a crystal can be written as the periodic wave described in Eq. 3.24, i.e. as a Bloch wave [85]. Plane waves,

$$\phi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{G} c_{G} e^{i\mathbf{G}\cdot\mathbf{r}}, \qquad (3.25)$$

where \mathbf{G} is a reciprocal lattice vector, satisfy that condition, and are therefore often used to model solids [85]. Plane waves are also relatively easy to code and evaluate, and including a large number of plane waves often suffices to obtain the desired accuracy; the convergence properties are often governed by a single energy cut-off parameter, which corresponds to the basis set with the highest energy [85]. For strong directional bonds, atomic orbitals are preferable for the basis set and generally fewer gaussian functions are needed to describe the electronic distribution so they can be computationally less expensive; non-plane-wave basis sets also facilitate calculations of non-periodic structures [85]. Overall there needs to be a balance between accuracy and computational expense, though convenience (e.g. the software available) also comes into play.

Finally, the topic of pseudopotentials should be addressed. Pseudopotentials are used to model the inner shell of the atoms, including the nucleus and inner electrons. Inner core electrons contribute less significantly to bonding than valence electrons, and in order to speed calculations these electrons and the nucleus are sometimes treated as nonresponsive by means of a pseudopotential [85]. Use of pseudopotentials is normally first validated against calculations performed including all electrons. While empirical methods can be used to derive pseudopotentials, they are more likely to be computed with first principles [85].

3.3 Density functional perturbation theory and the frozenphonon method

As briefly discussed in the section on *phonon thermal transport*, density functional perturbation theory (DFPT) has been used in the literature to obtain harmonic and anharmonic interatomic force constants (IFCs) to compute the phonon spectra and vibrational and elastic properties of materials. Within the scope of the research described in this document, DFPT has been and will be used in addition to non-DFPT methods to perform calculations to obtain both phonon density of states and dispersion relations, and elastic constants. As such, a summary of DFPT and some of its the underlying approximations are discussed in this section. A more detailed review and discussion of the formalism and its applications can be found in Refs. [9, 99].

The Born-Oppenheimer approximation, introduced in the previous section on DFT, is a necessary condition to DFPT. Because the electrons respond instantaneously to changes in the ionic positions, the forces acting on the ions in equilibrium can be calculated from the energy obtained with DFT as

$$\mathbf{F}_{I} \equiv \frac{\partial E(\mathbf{R})}{\partial \mathbf{R}_{I}} = 0, \qquad (3.26)$$

where \mathbf{R}_{I} is the position of the I^{th} ion, and \mathbf{F}_{I} the force acting on it [9]. Similarly, several other experimental observables can be obtained from taking various order derivatives of DFT energy or charge density calculations. Marx and Hutter [99] offer a table with some examples. In the harmonic approximation, the second-order derivative of the ground state energy with respect to the atomic positions is used to calculate the dynamical matrix,

$$D_{I\alpha,I\beta} = \frac{1}{\sqrt{M_I M_J}} \frac{\partial^2 E_{KS}}{\partial R_{I\alpha} \partial R_{I\beta}},\tag{3.27}$$

where the different ions are labeled I, J = 1, 2, ..., N and the cartesian coordinates with α, β = 1, 2, 3, and from which the vibrational properties of materials can be computed (e.g. the frequencies are the eigenvalues of the matrix). In the course of this research, we resort to the frozen-phonon method more often than DFPT. In the frozen-phonon method, the force constant matrix is calculated by explicitly displacing each atoms in all directions computing the energy with DFT. One drawback of the frozen-phonon method is that large supercells are needed to accurately calculate the force constant matrix — the cells need to be large enough not to feel the forces due to atomic displacement across the boundaries. Another approach is using the Linear Response method.

In addition to the Born-Oppenheimer approximation, the Hellman-Feynman theorem [54, 42] is also fundamental to DFPT; it states that the first derivative of the eigenvalues of a Hamiltonian, H_{λ} , that depends on a parameter λ (**R** in the case of lattice dynamics) is given by the expectation value of the Hamiltonian derivative. Eq. 3.26, for instance, would thus become

$$\mathbf{F}_{I} \equiv \frac{\partial E(\mathbf{R})}{\partial \mathbf{R}_{I}} = -\left\langle \psi(\mathbf{R}) \left| \frac{\partial H_{BO}(\mathbf{R})}{\partial \mathbf{R}_{I}} \right| \psi(\mathbf{R}) \right\rangle, \tag{3.28}$$

where $\psi(\mathbf{R})$ is the electronic ground-state wave function of the Born-Oppenheimer Hamiltonian. For a generalized potential and the more general perturbed parameter λ , it follows from the Hellmann-Feynman theorem that:

$$\frac{\partial E}{\partial \lambda_i} = \int \frac{\partial V_\lambda(\mathbf{r})}{\partial \lambda_i} \rho_\lambda(\mathbf{r}) d\mathbf{r}, \qquad (3.29)$$

and

$$\frac{\partial^2 E}{\partial \lambda_i \partial \lambda_i} = \int \frac{\partial^2 V_\lambda(\mathbf{r})}{\partial \lambda_i \partial \lambda_i} \rho_\lambda(\mathbf{r}) d\mathbf{r} + \int \frac{\partial \rho_\lambda(\mathbf{r})}{\partial \lambda_i} \frac{\partial V_\lambda(\mathbf{r})}{\partial \lambda_i}, \qquad (3.30)$$

where $\frac{\partial \rho_{\lambda}(\mathbf{r})}{\partial \lambda_{i}}$ is the electron density response and can be evaluated by linearizing Eqs. 3.16 and 3.17, leading to

$$\Delta \rho(\mathbf{r}) = 2 \sum_{i=1}^{N} \psi_i^*(\mathbf{r}) \Delta \psi_i(\mathbf{r}), \qquad (3.31)$$

where in density functional perturbation formalism the Δ operator,

$$\Delta = \sum_{i} \frac{\partial}{\partial \lambda_i} \Delta \lambda_i, \qquad (3.32)$$

applied to the Konh-Sham orbitals, i.e. $\Delta \psi_i(\mathbf{r})$, indicates the orbitals' variation which can be obtained by standard first-order perturbation theory [103, 9]:

$$\left(\mathcal{H}_{KS} - \epsilon_i | \Delta \psi_i \right) = -\left(\Delta V_{KS} - \Delta \epsilon_i\right) | \psi_i \rangle, \qquad (3.33)$$

where \mathcal{H}_{KS} is the unperturbed Kohn-Sham Hamiltonian (see Eq. 3.20),

$$\Delta V_{KS} = \Delta V_{ext}(\mathbf{r}) + \int \frac{\Delta \rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_1|} d\mathbf{r_1} + \frac{d}{d\rho} \left(\frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} \right) \Big|_{\rho = \rho(\mathbf{r})} \Delta \rho(\mathbf{r})$$
(3.34)

(i.e. the variation of the Kohn-Sham potential (Eq. 3.19)), and $\Delta_{\epsilon_n} = \langle \psi_i | \Delta V_{KS} | \psi_i \rangle$. Including the variations to the Kohn-Sham potential does not alter the self-consistent nature of the approach. There are different perturbation formalisms, but this section provides an overview of the method.

3.4 Density functional tight-binding method

The density functional tight-binding (DFTB) method is a semi-empirical approach rooted in DFT, as the name suggests. DFTB offers a significant improvement in efficiency without a significant compromise on accuracy, given it is based on first principles, for a wide array of molecules, and solid state materials [48]. DFT is perhaps the most popular first principles approach for materials properties calculations, but its computational cost makes it difficult to use with larger systems, longer time scales, multiple system simulations (e.g. for high-throughput calculations), etc.. The trade off between speed and accuracy makes DFTB optimal in such cases. The "tight-binding" aspect of the method refers to the tight binding of the electrons to the atom to which they belong. It implies a limited interaction with the potentials and states of the surrounding atoms and that the wave function of the electrons should therefore be similar to the atomic orbital of the corresponding atom. Expressing every one-electron wavefunction as the linear combination of atomic orbitals,

$$\psi_i(\mathbf{r}) = \sum_{\mu} c_{i\mu} \phi_{\mu}(\mathbf{r}), \qquad (3.35)$$

where the summation of the Greek letters runs over all basis functions [6], is the key idea behind DFTB, introduced by Slater and Koster [146]. Slater and Koster call it the tight binding or Bloch method and their historic paper — which includes the Slater–Koster table used to build a tight binding hamiltonian — provides the systematic procedure for formulating a tight binding model [124]. For DFTB, the eigenproblem is set up as follows:

$$\sum_{\nu} \mathcal{H}^{\sigma}_{\mu\nu} c^{\sigma}_{\nu} = \epsilon^{\sigma}_{\mu} \sum_{\nu} S_{\mu\nu} c^{\sigma}_{\nu}, \qquad (3.36)$$

where the Hamiltonian is

$$\mathcal{H}^{\sigma}_{\mu\nu} = \left\langle \phi_{\mu} | \hat{\mathcal{H}}^{\sigma} | \phi_{\nu} \right\rangle \tag{3.37}$$

and the overlap matrices are

$$S_{\mu\nu} = \langle \phi_{\mu} | \phi_{\nu} \rangle \,. \tag{3.38}$$

In the above equations, ϕ_{μ} and ϕ_{ν} are located on atoms A and B, respectively, and the index σ indicates the spin state [6]. Henceforth, however, I will neglect the spin index for simplicity. Most often, only valence electrons are considered and Eq. 3.35 includes only one radial function for each momentum state: one for s-states, three for p-states, etc. [85]. Eq. 3.36 can be arrived at in a couple of different, but equivalent ways [85, 44]. Matthew *et al.* state that semi-empirical tight binding calculations start from the assumption that the total electronic energy of a solid can be written as

$$E = \sum_{i=1}^{N} \epsilon_i + \frac{1}{2} \sum_{\mu} \sum_{\nu(\neq\mu)} U(|\mathbf{R}_{\mu} - \mathbf{R}_{\nu}|), \qquad (3.39)$$

where $U(|\mathbf{R}_{\mu} - \mathbf{R}_{\nu}|)$ is a short-range pairwise repulsion between atoms A and B and the ϵ_i 's are the eigenvalues of a Schrödinger-like equation that is not self-consistent:

$$\hat{\mathcal{H}}\psi_i(\mathbf{r}) = \left(-\frac{1}{2}\nabla_i^2 + V(\mathbf{r})\right)\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}) \ [44].$$
(3.40)

Eq. 3.40 is solved variationally within the basis of localized atomiclike functions (Eq. 3.35), leading to the secular Eq. 3.36 [44]. At this point I will again remark that the notation in this document has been modified from the original sources to maintain consistecy. An important distinction between DFT and tight binding DFT, is that the basis functions do not need to be evaluated in the tight binding approach, the only information required to compute the electronic structure of the system are the Hamiltonian and S matrix elements, which are written in parameterized form [130].

Let us return to Eq. 3.17 from the previous section. It can be shown that Eq. 3.17 can also be written as

$$T_{KS}[\rho] = \sum_{i=1}^{N} \epsilon_i - \int V(\mathbf{r})\rho(\mathbf{r})d\mathbf{r},$$
(3.41)

where $V(\mathbf{r})$ is the one-electron potential, unique up to a constant. A careless comparison between this result (i.e. Eq. 3.17/3.41) and the total DFTB electronic energy (Eq. 3.39) suggests that this a very simplistic form of the energy, as it appears to neglect all the other terms in the Kohn–Sham functional (Eq. 3.18) and further assumes that all terms are now pairwise and short-range [44]. Moreover, it seems self-consistency is no longer being enforced. This is, of course, not the case. Instead, the one-electron potential $V(\mathbf{r})$ can be estimated by substituting it for the Kohn-Sham potential, $V_{KS}(\mathbf{r})$ (Eq. 3.19). This would yield a potential much like the Kohn-Sham potential with an additional term. In this approach to solving Eq. 3.40, DFBT becomes more efficient that DFT by substituting a superposition of atomic densities into the Kohn-Sham form (Eq. 3.19).

Yet another approach — the most common — relies on treating the matrix elements as disposable parameters and to fit them to experiments and other calculations and to assume the basis functions are orthogonal so that the S can be taken to be a unit matrix [44]. To reiterate, Slater and Koster proposed a parameterization that includes at least four functions ($ss\sigma$, $sp\sigma$, $pp\sigma$ and $pp\pi$) of interatomic distance to fit for a solid with spbonding [146]. In the same way, a solid with s, p, and d orbitals would have at least 10 functions. Other approaches and a detailed explanation of the variational principle used to solve the DFTB equations is offered by Refs. [124]. As Paxton [124] points out, tight binding is the cheapest and simplest model that can capture the quantum mechanical subtleties in bonding. This makes it ideal for calculations of phonon properties using the frozen phonon method (introduced in the previous section) on large, highly anisotropic systems, such as the metal–organic framework MIL-53.

Chapter 4

Thermal resistance from irradiation defects in graphite

4.1 Introduction

In the early 1940s, polycrystalline graphite was the only abundantly produced material with the required purity to be used as a moderator in nuclear reactors [68]. While other reactor materials have since been adopted, at the present time, graphite is still in high demand for the development of high-tech fuel elements for next-generation nuclear reactors. Graphite or pyrolytic carbon is included in many nuclear fuel assemblies to encapsulate the fissile material. In these applications, in addition to utilizing its high temperature strength the graphite acts as a neutron moderator and reflector. In some fuels graphite encapsulates the fissile materials in which case all the heat produced by fission in a fuel pin must be conducted out through the graphite. As the moderating properties of graphite are temperature dependent, accurately predicting the thermal conductivity of graphite and other fuel assembly materials — including how their thermal conductivity evolves under irradiation — is vitally important for the design of accident tolerant fuels.

The thermal conductivity (κ) of graphite is experimentally found to change with synthesis conditions and while in service as a direct result of radiation [69]. This indicates that κ is not an intrinsic property and is instead governed by the defect morphology of the graphite. Simulations typically measure intrinsic properties, but we aim to determine an atomistic level understanding of scattering processes from collections of irradiation induced point defects and to establish a systematic understanding of how defect type, number and different defect-type ensembles affect thermal resistance and phonon mean free path in graphite. We do so with the goal that the insight that we gain can be incorporated into approaches for quantitatively predicting the lattice thermal conductivity that are based on solving the Boltzmann transport equation. Such a tool would be useful to nuclear engineers and materials scientists in the process of designing new reactors and fuel systems that are accident tolerant. As the first step along this path, we have computed the energy and structure of a zoo of point defects and determined their separate effects on thermal conductivity along and across the basal plane.

In section 4.2 we establish and validate our method for computing thermal conductivity of defect-free graphite. More specifically, we discuss advantages and challenges associated with the Green-Kubo formalism: in section 4.2.1 we discuss different approaches to converge the heat current autocorrelation function (HCACF) and propose a solution based on our findings; the issue of size convergence is explained and addressed in section
4.2.2. After establishing an adequate system size, we introduce defects and compute their formation energies in Section 4.3. Values are obtained using classical molecular dynamics and compared with density functional theory (DFT) calculations. Interstitial defects are also annealed to find the most energetically favorable configuration. In section 4.4 we compare the perfect crystalline system, where transport is limited by crystal lattice anharmonicity and the acoustic phonons carrying the bulk of heat are only scattered by other phonons, with systems with point defects, where defect scattering is expected to play a crucial role in thermal transport. Concluding remarks are presented in section 4.4.1.

4.2 Computational method and validation

Molecular dynamics modeling captures the anharmonic interactions of atomic vibrations that carry heat and both equilibrium and non-equilibrium simulations can be used to predict thermal conductivity [137]. The Green-Kubo formalism [49, 82] is a well established equilibrium molecular dynamics approach that has been used successfully to compute thermal conductivity in a wide range of materials from silicon [161] to metal-organic-frameworks [52]. This method is derived from the fluctuation-dissipation theorem and computes the thermal conductivity, κ , from the equilibrium fluctuations in the heat current vector, **J**, by:

$$\kappa_{xx} = \frac{V}{k_B T^2} \int_0^\infty C_{\mathbf{J}xx}(\tau) \, d\tau, \qquad (4.1)$$

where k_B , T and V are the Boltzmann's constant, temperature and volume of the simulated region respectively. The term $C_{\mathbf{J}}(\tau) = \langle \mathbf{J}(t)\mathbf{J}(t+\tau) \rangle$, and is the non-normalized heat current autocorrelation function (HCACF). The net flow of heat fluctuates about zero at equilibrium and the thermal conductivity is related to how long it takes for the fluctuations to dissipate. Both equilibrium and non-equilibrium molecular dynamics (NEMD) simulations suffer from size artifacts that must be mitigated. In NEMD, the simulated system size must be larger than the intrinsic mean-free path of the phonons in order to eliminate ballistic transport between the heat source and sink [137]. Equilibrium MD affords one a smaller system size as phonons may move through periodic boundaries unhindered.

Simulations were performed with the large-scale equilibrium classical molecular dynamics software LAMMPS [128] in the microcanonical ensemble (NVE) at 300 K for 0.6 ns with a 0.2 fs time step and periodic boundary conditions. Note that this is well below the Debye temperature for graphite (approximately 2500 K in the basal plane and 950 K along the *c*-axis [69]). However, our goal is a comparative analysis of phonon scattering from and around the defect. As scattering from classically occupied high frequency modes is present with and without the defect this has little contribution to the *change* in κ . The adaptive intermolecular reactive empirical bond-order (AIREBO) potential function formulated by Stuart *et al.* [147] was used for all simulations. The AIREBO potential includes anharmonic terms in the carbon bonds, an adaptive treatment of the non-bonded and dihedral angle interactions and has the capability to model the interaction between layers in graphite [147]. Two main challenges result from using the Green-Kubo: (1) determining an appropriate system size and (2) converging the HCACF. We shall first address the later challenge and propose a solution based on the work of Chen *et al.* [26].

4.2.1 HCACF convergence

There is no average net heat flux, $\langle \mathbf{J} \rangle$, for a system in equilibrium, and the HCACF, *i.e.* the term inside the integral in Eqn. (6.1), is therefore expected to decay to zero given suffi-

cient time. Instead, long lived oscillations with a significant contribution to the computed thermal conductivity have been observed [120, 140, 24, 86]; this behavior is illustrated in Fig. 4.1. The HCACF is crucial in computing κ using the Green-Kubo method and yet there is little consensus among researchers on whether these oscillations are significant to thermal transport or a result of noise, and on what approach to take. A discussion of this behavior and of possible approaches is essential in understanding the limitations of the Green-Kubo and validating thermal transport calculations.

Figure 4.1(a) shows the accumulation of the averaged HCACF along a basal direction over a typical simulation. It can be seen that the tail of the HCACF contains many fluctuations, but rather than these decaying smoothly as more data is averaged there occur sporadic events that can overwhelm the average to add new fluctuations to $C_J(\tau)$ and significantly change the initial value $C_J(0)$. These large events show up in the majority of simulations and for all simulated system sizes. Long lasting oscillations are prevalent along the basal plane and different in character to oscillations along the c-axis (see Fig. 4.1). Fluctuations along the c-axis exhibit a much higher frequency and oscillate around zero with the HCACF converging to zero with only minor instabilities affecting its integral. Fluctuations along the basal plane, on the other hand, do not fade away during computation time and significantly affect κ . In graphite, κ calculations in the c-direction are not affected by HCACF fluctuations as much as basal plane calculations are. This makes results perpendicular to the basal plane easier to compute and more reliable.

Along the basal plane the HCACF exhibits a two-stage decay: a rapid decay associated with high frequency phonons and a slower decay associated with lower frequency



Figure 4.1: In Fig. 4.1(a), the HCACF is computed as the simulation progresses along x for the perfectly crystalline 11x11x11 super cell. At first only a few values contribute to the ensemble average and the initial HCACFs are noisy. As the averaging time progresses the HCACF becomes smoother with the exception of well defined crests and troughs, most of which do not fade away during the total simulation time. Figures 4.1(b), 4.1(c) and 4.1(d) correspond to the HCACF noise (computed as F(t)), the final HCACF, and the integral of the HCACF, respectively, for all simulations of the perfect 11x11x11 super cell system along y and z (or c).

phonons. Similar two-stage decay (or three-stage decay) is observed in many single element materials and different authors have modeled κ by fitting the HCACF to the sum of two or more exponentials [24, 86, 100]. This is a more physically meaningful approach than a single exponential fit in that it captures multiple relaxation processes, but it appears to neglect the contribution of the HCACF tail and to play a part in the systematic underestimate of κ [137, 86]. When addressing the issue of convergence in the HCACF we have examined a wide variety of strategies. These strategies included direct integration of the HCACF truncated to various cutoffs, fits of varying sums of exponentials to the truncated HCACF, and fits in the frequency domain. Here we present only a few of the best or otherwise insightful findings and a brief discussion of our approach.

- (i-iv) Direct numerical integration of the truncated HCACF up to (i) 50 ps, (ii) 5 ps, (iii-iv) and a noise dependent cut off time, t_c, proposed by Chen *et al.* and described below [26]. For (iv) individual cut-offs were computed for each HCACF as shown in Figs. 4.1(b)-4.1(d), and for (iii) an average t_c was used for each simulation set.
 - (v) Single exponential fits to the first 5ps of the HCACF.
 - (vi) The fitting procedure proposed by Chen *et al.*, which includes a fixed offset term in the fitting function:

$$\frac{C_{\mathbf{J}}(\tau)}{C_{\mathbf{J}}(0)} = A_1 e^{-\tau/t_1} + A_2 e^{-\tau/t_2} + Y_0, \qquad (4.2)$$

such that κ is computed as

$$\kappa_{xx} = \frac{VC_{\mathbf{J}xx}(0)}{k_B T^2} (A_1 t_1 + A_2 t_2 + Y_0 t_c), \qquad (4.3)$$

where A_1 , A_2 , Y_0 , t_1 and t_2 are fitting parameters. Chen *et al.* argue that including the offset Y_0 reduces the computational error. In our implementation of this we used the simplex method to optimize the fit variables. It is physically meaningless to have negative Y_0 and this term was weighed with a Heaviside function to prohibit negative Y_0 terms. We also imposed the condition that $A_1 + A_2 + Y_0 = 1$.

(vii) Double exponential of the form in (vi) with Y_o set to zero.

(viii) Triple exponential of the form:

$$\frac{C_{\mathbf{J}}(\tau)}{C_{\mathbf{J}}(0)} = A_1 e^{-\tau/t_1} + A_2 e^{-\tau/t_2} + (1 - A_1 - A_2) e^{-\tau/t_3},$$
(4.4)

fit to each HCACF.

The issue of the cut-off time should now be discussed, before analyzing the results in Fig. 4.2. The necessity to truncate the HCACF is illustrated in Fig. 4.1 in which it can be seen that after roughly 2–5 ps the integrals of the autocorrelations diverge even though the HCACF is almost zero. This divergence arises from the integration of random fluctuations in $C_{\mathbf{J}}(\tau)$ effectively adding a random walk to the integral of $C_{\mathbf{J}}(\tau)$. The error from this random walk grows over time, while the systematic error from omitting the long tail of slow decay processes in the HCACF diminishes over time. There exists an optimal truncation point that minimizes the error in the integral of $C_{\mathbf{J}}(\tau)$, but there is little consensus in the literature on how to determine it [140, 137]. While selecting a consistent cut-off may often suffice to obtain a comparative analysis, it introduces a systematic error in the estimation of the HCACF, potentially neglecting the contribution to k of lower phonon modes. Chen et al. [26] propose obtaining a quantitative description of the numerical noise in the relative fluctuation of the HCACF, F(t), defined as

$$F(t) = \left| \frac{\sigma(C_{\mathbf{J}})}{E(C_{\mathbf{J}})} \right|,\tag{4.5}$$

where σ is the standard deviation and E the expected value of the HACF in an interval $(t, t + \delta t)$. The cut-off point is determined to be above an F(t) of 1 (see Figs. 4.1(b)-4.1(d)), *i.e.* when the fluctuations become the same scale as the mean. Chen suggests that F(t) is

insensitive to the choice of δ . We find this is the case for only small variations and between a δ of 1, 3, and 5 ps the best results correspond to the 1 ps interval. Both 3 and 5 ps intervals resulted in outliers with a significant effect on κ . The variability we observed with the choice of δ suggests that to obtain a good fit using this method requires a balance between having sufficient data points to compute the local averages while maintaining enough temporal resolution to reasonably determine when in time the noise exceeds F(t) = 1. A cut-off point was computed for each run and the average cut-off point for a given system was then obtained. Each system was simulated 10 times. We compared κ for the cases when δ was 1, 3 and 5 ps with κ being computed using both each independent simulation's cut-off (as in Chen et al.) and using the average cut-off for all simulations. We found that using the average cut-off yielded similar results with error bars significantly smaller than using the corresponding systems' individual run cut-offs to compute κ for each simulation within a cell size. In theory, if we could consider the average local fluctuations in the heat flux over an infinite amount of time, we should be able to find a "true" thermal conductivity of a given system. It is then reasonable to assume that each HCACF is an approximation to an HCACF obtained over infinite time and that there is a "true" cut-off point, thus providing an argument for using the average cut-off on each individual run to compute κ . When only the first two terms of the HCACF were computed, as in (vii), Y_0 contributed up to nearly 100 W/(mK) in the most extreme case. This illustrates the insufficiency of the two exponential fits to estimate κ . The sum of three exponential fits yields results very similar to the strategy adopted by Chen *et al.* with the added modification of using the average cut-off instead of each individual simulation's cut-off. However, as the number of



Figure 4.2: These figures correspond to κ measured for different super cells along x (4.2(a)) and y (4.2(b)) in the basal plane and along the c-axis (4.2(c)). In addition to establishing size convergence, the figures illustrate a set of different approaches (labeled in the legend) considered to converge the HCACF and the corresponding standard error. Method (iii) was selected.

fitting variables increases, results are expected to mimic those of a full integration and the fit loses its physical significance. This correspondence nevertheless suggests Eqn. (4.4) to be an adequate fit and substantiates the cut-off method. More strikingly, simply using the average cut-off as the HCACF integration limit yields similar results with error bars comparable to the fit. The correct behavior of the HCACF along the basal plane is thus more accurately explained by the fit type suggested by Chen at al. than merely the sum of exponentials, but in order to compute actual κ values, the fit introduces an unnecessary hassle to no gain. Furthermore, the nature of the HCACF along the c-axis is very different than that of the basal plane, as can be seen by looking at Figs. 4.1 and 4.2 and this fit type is not adequate to explain the HCACF perpendicular to the basal plane. That said, the error bars are noticeably smaller when the HCACF is integrated only up to t_c than when they are integrated over the total HCACF time. The simplest, most effective approach is to select the cut-off for each simulation by setting F(t) = 1, but to use the average cut-off of all simulations when computing each simulation's individual κ . This method is adequate to compute κ along any direction for highly oriented graphite. In light of this analysis, a similar simulation time with a lower HCACF is likely to yield more accurate κ results, as it would allow more time for convergence and not necessarily lower the cut-off.

While there is no consensus on the best method to reduce noise and capture the nature of the HCACF of graphite and other materials, the approach selected in this paper yields κ estimates higher than a sum of exponentials, with moderately small error bars and without the need of a complicated fit. This method was used for all defect calculations along the basal plane and along c, taking into account that the cut-off along c must neglect the first values of F(t) = 1 which take place in the initial decay stages (see Fig. 4.1). Being consistent with the choice of method is often sufficient for a significant comparative analysis and this method allows us to do that.

4.2.2 Size convergence

Periodic boundary conditions allow simulations of a small number of particles to mimic the behavior of an infinite solid; however, they limit the number and wavelength of the vibrational modes available to carry heat. Thus, when using the Green-Kubo method it is first necessary to establish size convergence. Thermal conductivity values were computed for perfectly crystalline systems of varying size, as can be observed in Fig. 4.2. An 8 atom unit cell was defined and 7 systems ranging between $3x_3x_3$ and $15x_{15x_{15}}$ super cells were simulated (again 10 times each). Along the basal plane the systems' size was asymmetric in the x and y dimensions with x smaller than y — this was done to better gauge potential size artifacts. While there was a large variability in the thermal conductivity, the values are scattered between 300 and 400 W/(mK) along the x direction and 350 and 450 W/(mK) along the y. This suggests a size artifact not evident just looking at the system size increase within each direction and that only comes into play within each system. For this reason different x and y values were maintained when computing thermal conductivity in defective systems as well. For computations performed with defects, the 11x11x11 super cell was selected to allow for a big enough compute cell with a feasible computational expense associated. The 11x11x11 super cell corresponds to a 10648 atom system in the perfect graphite, with a 270.5 \times 468.6 \times 737.9 nm^3 volume in the x, y, and z directions, respectively.

4.3 Identifying defect structures

In irradiated graphite carbon atoms are displaced due to cascade reactions giving rise to many point defects. We categorize these into defects that have a strong driving force for clustering, such as vacancies and interstitials, and defects that are less driven to cluster such as bond rotation defects, and isotopic defects. The following clustering defects were considered: a single interstitial (Fig. 4.3(b)), a single vacancy (Fig. 4.3(j)), clusters of 2–8 interstitials (Figs. 4.3(c)-4.3(i)) and clusters of 2–3 vacancies (Figs. 4.3(k) and 4.3(l)). For a single interstitial, three interstitial locations were considered, as depicted in Fig. 4.4(a). Similarly, four configurations were simulated for 2-interstitial clusters, as shown in Fig. 4.4(b). The single vacancy site is between the centers of hexagonal voids on the planes adjacent to the plane of the vacancy, *i.e.* where the type A single interstitial is positioned in Fig. 4.4(a), but in the lower, less visible layer. The added vacancies lie directly between atom sites on the adjacent layers. The non-clustering defects considered were a Stone-Wales defect (Fig. 4.3(a)) and an isotope. The C^{14} isotope was selected for having a higher mass than C^{13} , another common carbon isotope, and thus being expected to have a higher contribution to changes in κ . The defects were introduced to the center of the selected 11x11x11 perfect system; the interstitial defects were placed between the 11th and 12th layer of the 22 layer cell, and the remaining defects within the 11th layer, as shown in Fig. 4.5.

Formation energies were computed using classical MD for all defects. These calculations were used to estimate the likelihood of formation of each defect, where the energy per defect is given by

$$E_d = E_D - \frac{E_O}{N_O} * N_D.$$
 (4.6)

 N_D and N_O are the number of atoms in the defective system and the corresponding nondefective system, in that order. E_D corresponds to the total energy of the system and E_O to the total energy of the perfect system of the same size.

The optimization process for the classical calculations is described in the flowchart



Figure 4.3: Illustration of the defects examined in this study: Stone-Wales defect (4.3(a)); single interstitial (4.3(b)); 2-8 interstitials (4.3(c) - 4.3(i)); single vacancy (4.3(j)), di-vacancy (4.3(k)), and 3 vacancies (4.3(l)). The interstitial defects are shown in their annealed configurations.



Figure 4.4: Possible defect types for single (Fig. 4.4(a)) and two-interstitial defects (Fig. 4.4(b)).

in Fig. 4.6 as was performed using the FIRE scheme [11] as implemented in LAMMPS. As part of the process to optimize the geometry of the interstitial defects, low energy interstitials (type A in Fig. 4.4(a) and type C in Fig. 4.4(b) for one and two-interstitial defects respectively) were also annealed and subsequently cooled. The defects were annealed to 1500 K for 500 ps and cooled to 300 K for 1 ns, in the canonical (NVT) ensemble. By



Figure 4.5: Slice of a graphite system with an hexagonal platelet, indicating the location of the defect. There are 22 total layers in the system.

Defect Type	Single: A	Single: B	Single: C	Two: A	Two: B	Two: C	Two: D
LAMMPS	$3.57 \ \mathrm{eV}$	$4.73 \mathrm{~eV}$	4.46 eV	4.99 eV	3.27 eV	$2.95 \ \mathrm{eV}$	2.98 eV
Literature (DFT, LDA) [87]	$6.7~{ m eV}$	$7.7~{ m eV}$	$7.4 \mathrm{~eV}$	-	-	-	-

Table 4.1: Classical MD energy calculations for single and double interstitial defect types based on location. The values obtained for a single interstitial are compared with available density functional theory (DFT) calculations using the local density approximation (LDA) from Ref.[87].

doing this we allowed the already low energy interstitial defects to migrate and rearrange

themselves into potentially lower energy configurations.

Energy values for the different defect types and numbers are depicted in Fig. 4.7 and in



Figure 4.6: Schematic of the optimization procedure applied to classically simulated defects before computing formation energies.

Table 4.1. Classical interstitial defect energies were computed for the optimized structures before and after annealing. It is notable in Fig. 4.7, that the annealing process often yielded defect structures with considerably lower energy than those reached by direct relaxation using the FIRE algorithm — even for very simple defects such as a lone interstitial. There is, however, good agreement in the overall trend of defect energies as modeled with the AIREBO empirical potential and those from Li *et al.*, computed using density functional theory (DFT) with the local density approximation (LDA) [87]. Furthermore, the type Asingle interstitial when annealed becomes structurally similar to Li *et al.*'s 5.5 eV formation energy "free" interstitial, computed with DFT. Stone-Wales defects have the lowest formation energy of all intrinsic defects in graphenic systems [108], calculated with DFT at 5.2 eV [87].



Figure 4.7: These energies correspond to the defects depicted in Fig. 4.3. In the case of the interstitial defect-types, values were computed both for annealed and non-annealed systems.



Figure 4.8: Anisotropy ratio (κ_a/κ_c) computed for both x and y for different defect types, including defects found to be most energetically favorable (Fig. 4.8(a)); κ obtained for different defect types along x and y (Fig. 4.8(b)) and in the basal plane (Fig. 4.8(c))

4.4 Thermal resistance from defects

While the thermal conductivity of near-perfect graphite has been reported to be as high as 4180 W/(mK) along the basal plane [113], the experimentally measured anisotropy ratio (κ_a/κ_c) of near-ideal graphite has been found to be just below 210 at 300 K [59]. This suggests the Green-Kubo calculations to be an order of magnitude below experimental values in the basal plane, but within the expected order of magnitude for κ along the c-axis. Finally, κ for nine defects including the more energetically favorable ones was computed using the Green-Kubo method as with the perfect crystal. Thermal conductivity for the hexagonal platelet was also computed using different super cell sizes (Fig. 4.10). While κ is within the error bars along the basal plane for all defects, the overall trend suggests a decrease in thermal conductivity with the presence of defects, as would be expected. More distinctly, the systems with interstitial clusters exhibit a clear decrease in the thermal conductivity along c (see Fig. 4.8(c)). Note that these defects correspond to low configuration energies as well and are therefore more likely to occur. Frenkel pairs is one type of defect that is expected to emerge from exposure to radiation due to knock-out reactions; the added effect of vacancy and interstitial clusters would significantly reduce κ perpendicular to the basal plane.

Performing a discrete cosine transform (DCT) of the HCACF reveals the presence of localized modes exclusively associated with the lower thermal conductivity defect types (see Fig. 4.9). We performed DCTs for the defect systems both along x, y and z, and found two notable differences between systems in the DCT of the c-axis HCACF. Systems containing interstitial platelets develop a series of peaks at ~ 1.3 , 2.5 and 3 THz. We attribute these to rattling of the platelets in the *c*-direction and the defects being large enough to have relatively low frequency vibrational modes. More interestingly, there is a dramatic reduction in the intensity of low frequency modes in the HCACF of the systems with diminished thermal conductivity.



Figure 4.9: Discrete cosine transform applied to the c-axis HCACF for different defect types.

There is little difference in terms of how the number of interstitials (between 5 and 8) in a cluster affect the overall thermal conductivity in the system, but there is a noticeable

change as the system size increases — the systems containing an hexagonal platelet increase in κ with system size (see Fig. 4.10). This seems to suggest that the defect concentration has an effect on the total thermal conductivity as well. The last system corresponds to an 11x11x11 super cell with two hexagonal defects equally spaced and, as expected, it shows a lower thermal conductivity than the same system size with a single defect.



Figure 4.10: Hexagonal platelet κ and corresponding standard error computed along x and y in the basal plane (Fig. 4.10(a)) and along the c-axis (Fig. 4.10(b)) for 4 different super cell sizes including the 10648 base atom system, and for two hexagonal platelets in the same base system.

If instead of considering κ we assume that defects make an additive contribution to the systems' thermal resistance, r, then we might expect $r_{\text{defect}} = r_{\text{defective}} - r_{\text{perfect}}$, and that thus the thermal resistance for a system containing two defects would be $r_{2\text{defects}} =$ $r_{\text{perfect}} + 2 \cdot r_{\text{defect}}$, or $r_{2\text{defects}} = 2.32 \pm 0.32 W/(mK)$ for the hexagonal platelet. It appears from Fig. 4.10(b) that adding a defect does not double its thermal resistance, but reducing the size to half does; a fit through a system with varying defect numbers may shed light into how κ scales with defect concentration for each defect type.

4.4.1 Conclusions

In this work we have reported calculations of the reduction in thermal conductivity of graphite due to a series of point defects typical under irradiation. The calculations reveal three important conclusions:

- Clustered interstitial defects are stable (with respect to lone interstitials) and strongly detrimental to the thermal transport in both the in-plane and *c*-axis directions.
- In addition to lowering the thermal conductivity they also increase the thermal conductivity anisotropy.
- Although the noise in the calculations of κ is large, it is clear that the platelets create larger thermal resistance than the constituent number of lone interstitials.

In pebble bed reactors graphite is used to encapsulate the fissile materials and thus the graphite experiences an extremely large neutron dose. The average fuel temperatures in such a reactor is 1200 K (with peak temperatures expected to stay below 1500 K) [62]. At these temperatures interstitials are highly mobile and readily condensing to interstitial platelets. These platelets are responsible for *c*-axis swelling under irradiation [69]. Our work indicates that this has a doubly negative effect on thermal conductivity; elongating grains along their thermally resistive directions while also increasing the thermal resistance in these directions.

In addition to computing the reduction in thermal conductivity due to defects we have performed a systematic comparison of various numerical strategies for reducing uncertainty in the integration of the HCACF. Our simulations reveal infrequent large heat current fluctuations that are large enough to overwhelm the averaged HCACF. The origin of these fluctuations is unclear to us at this stage and we speculate two possible causes. It is possible that the fluctuations are a manifestation of Fermi-Pasta-Ulam recurrence [41] or some related breakdown of ergodicity over the time period accessible to simulation. An alternative explanation is that the fluctuations are physically realistic processes similar to rogue ocean waves and caused by amplitude dependence of the phonon dispersion in graphite. It has been proposed that carbon nanotubes possess soliton-like heat carriers [23] and it is possible that similar conditions may arise in graphite. These two potential explanations are incompatible and would require one to treat the fluctuations differently: in the first case removing their effect from computed thermal conductivity, and in the latter case performing enough simulations to obtain a statistically significant sampling of these infrequent fluctuations.

Chapter 5

Method to manage integration error in the Green-Kubo method

5.1 Introduction

Transport properties are ubiquitous in materials science and engineering. Heat sinks and thermal barrier coatings are two obvious examples where thermal conductivity is paramount for materials' performance, but there are also a huge number of materials applications in which transport properties are folded in with a number of other properties to dictate performance. Nanofluids are a promising new material for numerous applications [21, 66, 107] that include heat dissipation [66, 107] for which, in addition to thermal transport, viscosity calculations are necessary to better our understanding of heat transfer mechanisms. Moreover, the rheological characterization of fluid materials has numerous engineering applications beyond cooling (e.g. lubrication [31], sheathing [83], or hydraulics [151]), as well as applications in other fields (e.g. medicine [173], geophysics [174]). Viscous ionic electrolytes in batteries are an example where viscosity, diffusion and ionic conductivity [64] all play an important role in the materials' eventual performance. In short, the ability to reliably predict transport properties is essential in the search for new materials for a wide variety of applications. Molecular dynamics (MD) simulations provide a powerful approach for quickly obtaining atomistic level insight into the physics of mass, momentum or energy transport processes in materials. Two approaches are possible: MD can be used to (1) simulate systems in equilibrium or (2) perturb and drive systems out of equilibrium to then measure their response.

Equilibrium molecular dynamics (EMD) calculations are performed using the well established Green–Kubo formalism [49, 82], which relates transport quantities to the duration of fluctuations in a microscopic state of the system — the underlying principle is that the processes that dissipate small local fluctuations are the same that are responsible for a material's feedback to a stimulus. Mathematically this is achieved by integrating the current autocorrelation function as is shown in the general expression for the Green–Kubo method:

$$\gamma = \alpha \int_0^\infty \langle \mathbf{A}(t)\mathbf{A}(t+\tau) \rangle \ d\tau, \tag{5.1}$$

where γ is the transport property of interest and **A** the current that drives it. The expression $\langle \mathbf{A}(t)\mathbf{A}(t+\tau)\rangle$ is the autocorrelation function of quantity **A** and α is a temperature dependent coefficient. For instance, for thermal conductivity, κ , the Green–Kubo expression becomes

$$\kappa = \frac{V}{3k_B T^2} \int_0^\infty \langle \mathbf{J}(t) \mathbf{J}(t+\tau) \rangle \ d\tau, \qquad (5.2)$$

where k_B is Boltzmann's constant, T the temperature, and V the volume of the simulated region, \mathbf{J} is the heat-flux, and $\langle \mathbf{J}(t)\mathbf{J}(t+\tau)\rangle$ is the non-normalized heat current autocorrelation function (HCACF). This method is widely used by materials scientists, chemists and physicists. In addition to thermal conductivity calculations [52, 161, 59, 140], it has been used to calculate viscosity [31, 13, 174], diffusivity [67, 118] and ionic conductivity [64] for a wide range of materials, by integrating the pressure tensor, velocity and ionic flux autocorrelation functions (ACFs), in that order.

There are clear advantages to using an equilibrium approach: while both equilibrium and non-equilibrium methods suffer from size artifacts, the use of periodic boundary conditions in EMD allows for a smaller system size; for anisotropic systems, one EMD simulation suffices to compute the full transport tensor; and EMD can be used irregardless of the linearity of the transport regime with system size. There is, however, also one major pitfall. Fully converging the autocorrelation function requires very long simulation times, and often a compromise has to be made between including the contribution of slow processes and introducing a random error, or excluding these processes and introducing a systematic truncation error. In this paper, by recognizing that the integrated ACF error mimics a random walk, we propose a method that allows researchers to evaluate this trade off on-the-fly and make better informed decisions about where to truncate the ACF and how to optimize computational resources. In the remainder of the paper, we will focus exclusively on thermal transport. It is left for the reader to draw the obvious parallels with other transport properties. The next paragraphs concern the origin of the oscillations, existing approaches to integrate the autocorrelation function, and the introduction of the concept of a random walk in the HCACF. Our proposed method and its implementation to an example data set are described next, followed by the discussion and conclusion remarks.

5.1.1 The oscillatory behavior of the autocorrelation function

The HCACF, $\langle \mathbf{J}(t)\mathbf{J}(t+\tau)\rangle$, can be numerically computed as

$$\langle \mathbf{J}_n \mathbf{J}_{n+m} \rangle \equiv \sum_{n=0}^{N-m} \frac{\mathbf{J}_n \mathbf{J}_{n+m}}{N-m},\tag{5.3}$$

where \mathbf{J}_n is the value of \mathbf{J} at the n^{th} time step, i.e. $\mathbf{J}_n = \mathbf{J}(t_n)$, for n = 0, 1, 2, ..., N, and \mathbf{J}_{n+m} is \mathbf{J} at the $(n+m)^{th}$ time step, or $\mathbf{J}(t_n + \tau_m)$, for m = 0, 1, 2, ..., M. N and M are, respectively, the maximum number of steps in the simulation and in the HCACF. Analytically, the autocorrelation function is computed as the inverse Fourier transform of the same transform of the current multiplied by its complex conjugate, averaged over N - m. It follows that to obtain good statistical averaging M must be significantly less than N, and that the error associated with the HCACF increases over time for fixed N. This is applicable to other transport properties. For a system in equilibrium the average current of any property is zero, and the ACF is expected to decay to zero given sufficient time. Instead, large oscillations with a significant contribution to the integral have been observed [119, 140, 24, 86, 34]. Fig. 5.1 a) depicts an example of fluctuating HCACFs and the growing error in the corresponding integrals, and Fig. 5.1 b) the longevity of the fluctuations.

If we were able to sample an infinite system for infinite time, we should find the system's *true* ACF and thus a fixed true transport quantity. It follows that, for the thermal transport example we have been using, κ , computed with Eqn. 6.1, is

$$\kappa = \kappa_{true} \pm \Delta \kappa =$$

$$\alpha \lim_{t \to \infty} \int_0^\infty \langle \mathbf{J}(t) \mathbf{J}(t+\tau) \rangle \ d\tau \pm \alpha \int_0^{\tau_{max}} \eta(\tau) \ d\tau,$$
(5.4)

where τ_{max} is the maximum time for which the HCACF is computed, and $\alpha = \frac{V}{3k_BT^2}$. The first term in the equation is the *true* integrated HCACF, and the second term the integral of the HCACF noise that comes about due to insufficient averaging. As shall be discussed more thoroughly in due course, at least two sets of different frequency oscillations can be distinguished that mirror the fast and slow fluctuations in the heat current.

Accurately predicting the ACF is critical for transport predictions using the Green– Kubo method. Notwithstanding, there is little consensus in the literature as to what approach to take to mitigate the noise and the cumulative quality of the integrated noise has seldom been used to inform the choice of ACF integration approach. The next paragraphs reference some of the most common ACF integration approaches and a few less common strategies found in the literature. While it has been shown that the Green–Kubo approach can be successfully used with quantum-based calculations [4, 98], simulation size and length present a major difficulty in using EMD approaches within *ab initio*, and other methods [162, 18] continue to offer greater advantages. However, as computers become faster, DFT MD transport calculations could become more common, and error estimation more important. Within classical MD, the evolution of computing means averaging large enough systems for longer will become less of an issue, thus reducing or even eliminating the error from these calculations. However, there is an increasing trend to develop highthroughput approaches for the rapid screening of materials, which in turn require quick, on-the-fly approaches for uncertainty quantification. The method introduced herein meets these requirements.

5.1.2 Common autocorrelation function integration approaches

A common strategy to reduce the noise in the ACF is to fit an exponential to the first few picoseconds ($\tau < 10$) [24, 86]. The system depicted in Fig. 5.1 exhibits a rapid decay associated with high frequency phonons and a slower decay associated with lower frequency phonons; similar two- or three-stage decay is observed in many single element materials and different authors have modeled κ by fitting the HCACF to the sum of two or more exponentials [24, 86, 100]. This approach captures multiple relaxation processes and is therefore more physically meaningful than a single exponential fit, but it is ineffective when the HCACF can not be represented by an exponential fit [135, 52, 34] and it forces a behavior description of the HCACF that might not be accurate. The same is true of shear relaxation times in viscosity calculations. For ionic liquids' calculations, authors have also fit the pressure tensor autocorrelation function to Kohlrausch's law [50, 104] and/or applied weighing factors to their fits [175, 56]. Fits to the frequency domain are also a solution, depending on the resulting ACF for given data [135, 52]. Some strategies include direct integration of the ACF truncated to various cutoffs. Whether direct integration is performed or a fit is applied, the cutoffs are oftentimes arbitrarily selected [61, 115, 111]. They can also be more systematically determined, for instance by taking the running mean of the integrated autocorrelation at its plateauing region [27, 32]. Recently, Chen et al. have proposed a noise sensitive mathematical approach: to truncate the HCACF when the scale of the fluctuations becomes the same as the mean, i.e. when $\left|\frac{\sigma}{E}\right| > 1$, where σ is the standard deviation and E the expected value of the HCACF in an interval $(\tau, \tau + \delta \tau)$ [26]. Chen et al. further suggest including a fixed offset term, Y_0 , to the exponential fitting approach (e.g. $A_1 e^{-\tau/t_1} + A_2 e^{-\tau/t_2} + Y_0$) to the normalized HCACF. In a study concerning thermal transport in irradiated graphite, we implemented and compared this and other methods [34]. The method of Chen et al. is a useful, systematic approach, but it neglects the growing nature of the uncertainty that results from integrating over the noise. Other approaches that acknowledge the incremental error of the HCACF integral have been proposed [175, 3]. For instance, Zhang et al. [175] use a time decomposition method to compute a growing standard deviation to which they suggest fitting a power law, and from which a cutoff can be selected based on a desired % error. With the insight gained from the graphitic systems studied, we develop here a new approach to quantify and mitigate the noise introduced with the Green–Kubo. This approach is based on recognizing that the ACF fluctuations around zero integrate into Brownian noise, i.e. for each simulation a random walk is effectively added to the integral of the true ACF. Before proceeding, it is perhaps useful to briefly introduce the notion of a random walk and how it relates to the noise in the HCACF.

5.1.3 Random walk

A random walk is a succession of Markovian (uncorrelated) random steps. This has the property that the expected root mean square (RMS) displacement after N steps is $\langle x_N \rangle = \sigma_d \sqrt{N}$, where σ_d is the standard deviation of the magnitude of the steps (i.e. the displacement). Here we argue that the noise in the HCACF has the statistical properties of a stream of uncorrelated fluctuations or excursions from zero. Although these fluctuations have a characteristic duration the time integral of a fluctuation equates to one jump in a random walk. If one determines the timescale over which the HCACF noise is uncorrelated (the jump frequency δt) and the typical integrated excursion (jump magnitude, d) then one can equate the accumulation of noise integration error to the RMS displacement of the equivalent random walk. The equivalence of the HCACF to a stream of uncorrelated fluctuations that when integrated yield a random walk is demonstrated in Figs. 5.2 a)-c). In these simulations the average step size is $\sigma_v \delta t$, where σ_v is the standard deviation of the noise velocity $(d/\delta t)$, i.e. the velocity at which the random walk occurs through time. The standard deviation of the velocity (σ_v) is effectively that of the steps. The total number of Markovian steps over time t is $N = t/\delta t$, and so the expected uncertainty U(t) after integrating to time t is given by:

$$U(t) = \delta t \sigma_v \sqrt{\frac{t}{\delta t}} = \sigma_v \sqrt{t \delta t}$$
(5.5)

In this relationship computing σ_v is straight forward, and so the remaining challenge is to determine the uncorrelated fluctuation time δt .

By characterizing the integrated HCACF noise as a random walk, or as a sum of random walks, in terms of δt and σ_v , we propose that one can use Eqn. 5.5 to compute an *uncertainty envelope* that informs on how quickly the integrated noise error in a single simulation grows. From the uncertainty envelope of a *single* simulation one can compute the expected uncertainty in the average of any number of simulations. The crucial point is that information about the distribution of error in many simulations can be obtained from a first, short (a few hundred picoseconds) simulation, and thus after the first simulation has been performed, one can decide on an optimal computational strategy for minimizing uncertainty.

Upon quick inspection, the HCACFs shown in Fig. 5.1 appear to be converged by 20 ps. Fig. 5.2 e) shows the result of integrating random fluctuations in the 20–50 ps interval of the HCACF tail. To parallel Figs. 5.2 a) and b), which depict an example of fluctuations (in a)) that give rise to a random walk (in b)), a single HCACF tail is depicted in Fig. 5.2 d), but the integrals of 18 HCACFs' tails are plotted in Fig. 5.2 e). The noise in this data (Fig. 5.2 b)) is *not* uncorrelated from point to point along the data stream but instead has some memory of itself. To predict the uncertainty from this noise we must compute the lifetime for this memory to find the timescale at which the noise becomes uncorrelated.

Instead of a jump (or walk) at every interval in the autocorrelation, jumps are better described by (some of) its peaks (see the line in magenta in Fig. 5.2 d)). The distribution in Fig. 5.2 f) corresponds to the compound HCACF tails for the 18 simulations. Fig. 5.2 g) was obtained from the peaks as exemplified in Fig. 5.2 d). A normal distribution with the standard deviation for each case and mean zero is shown in red, and the distributions with the correct mean in black and magenta for the whole set of tails and peaks, respectively, in Figs. 5.2 f) and g). The distributions will again be addressed in the Results section.

The method developed to quantify the uncertainty that results from the Green– Kubo approach by treating the noise in the autocorrelation function as a random walk is introduced in the Methods section, but not before a more detailed explanation of the dataset used for Figs. 5.1 and 5.2 is offered.

5.2 Methods

All simulations used to perform error analysis were obtained with the large-scale equilibrium classical molecular dynamics software LAMMPS [127], using the adaptive intermolecular reactive empirical bond-order (AIREBO) potential function formulated by Stuart et al. [147]. The simulations correspond to a size-converged $11 \times 11 \times 11$ perfectly crystalline graphite supercell with 10648 atoms and a $27.05 \times 46.86 \times 73.79$ Å³ volume in the x, y, and z directions, respectively. Previous work has shown that this system is large enough to be size converged for thermal conductivity [34]. We use data from nine simulations that were relaxed and equilibrated in the microcanonical ensemble (NVE), using a standard Velocity-Verlet quadrature scheme, for 50 ps after being given a thermal energy equivalent to 300 K before starting to record the HCACF. Each of the nine runs was simulated for an additional 0.6 ns with a 0.2 fs time step and periodic boundary conditions. Because κ can be computed in all lattice directions from a single simulation using the Green–Kubo formalism, there are 18 HCACFs along the basal plane of the graphite supercell with which to perform data analysis (nine each along x, and y, that is $[2\overline{1}\overline{1}0]$, and $[01\overline{1}0]$). This data was obtained for a previous publication on the thermal conductivity of irradiated graphite [34]. A longer 8.0 ns simulation with a 0.4 fs time step was also performed, under the same conditions. Based on the premise that the noise of the integrated HCACF is akin to a random walk, we can use Eqn. 5.5 to compute the root mean squared of the noise integrated up to time τ_{max} . This is the expected deviation (or error) from the mean for each random walk, and we can thus compute the standard deviation of said error at time τ_{max} in an average of N random walks, with the same characteristic δt and σ_v , as $S_N = \sigma_v \sqrt{\frac{\tau_{max} \delta t}{N}}$.

Decomposing the noise into uncorrelated fluctuations is the first step, required to discern between a single random walk or the sum of varying frequency random walks. Then, to characterize the random walks one must determine the standard deviation of these fluctuations and the average interval between them. If the random fluctuations occurred at the same interval that the HCACF is recorded, the expected noise uncertainty envelope would be as indicated in Fig. 5.3 c), in the dashed red line. This largely underestimates the integrated noise. A moving average low pass filter with a 0.4 ps window applied to the noise reveals that at least two distinct sets of noise frequencies are present (see Fig. 5.3 a)). This indicates that instead of a single random walk with the same time step as that of the HCACF, the noise is best described by the sum of different frequency random walks. Finding the contribution of each random walk to the expected error can be difficult, but a series of frequency passes (see Fig. 5.4) can help examine the contribution of varying frequencies in the noise to the expected error. The subsequent analysis is performed with the separate sets of noise identified as having the largest contribution to the expected error and shown in Fig. 5.3 a). While the noise behaves similarly to a random walk, the system has a memory of itself and the fluctuations should be correlated with each other. The correlation time obtained from the autocorrelation function of the noise gives the average time interval, δt , at which the fluctuations are Markovian. This method is applied to a single simulation as detailed in the following steps, with the aid of Fig. 5.3:

i The first step is to isolate the noise from the data. This is easily done by selecting a portion of the tail, if it is clear the HCACF is converged after some time. Otherwise, a fit could be used to extract the noise. Using the tail of the HCACF to analyze

the noise is generally preferable to using a fit, as it removes the uncertainty that arises from guessing the behavior of the HCACF. The choice of interval $(30-50 \ ps)$ to characterize the noise is explained in the Results.

- ii The second step is to filter the noise for different frequencies. This step is exemplified in Fig. 5.3 a). A low pass filter allows us to distinguish two main sets of oscillations, in red and in blue. While only one pass, separating frequencies below and above 2.5 THz, is illustrated in Fig. 5.3 a), more could be applied (see Fig. 5.4) to gain a better understanding of the noise. This is discussed more throughly in the Results. The contribution of each set of data is considered as described next.
- iii The third step consists in computing the autocorrelation of the different frequency noise components. For the low and high frequency noise found in step *ii* and depicted in Fig. 5.3 a), the ACFs are shown in red and blue, respectively, in Fig. 5.3 b).
- iv The fourth step is to fit a single exponential $a_i e^{-\frac{t}{\tau}}$ to each of the above autocorrelations. The fits are shown in magenta and cyan, for the low and high frequency cases, in that order. The fitting parameter τ provides an estimate of the interval of our near-random walk noise. The autocorrelation of the low frequency noise (in red) is comparable to that of the whole system (in black). It is already clear that the contribution of the low frequency HCACF noise explains most of the random walk uncertainty.
- v The fifth step is to compute the standard deviation, σ , of each of the noise contributions.

vi The sixth and final step is to compute the uncertainty envelope by using the calculated τ and σ in Eqn. 5.5. In Fig. 5.3 c), the magenta uncertainty envelope corresponds to the low frequency oscillations, and the cyan envelope to the contribution of the high frequency noise. As anticipated, the high frequency noise envelope is not much greater than the envelope calculated with the HCACF interval (in dashed red). The combined error of high and low frequency noise (in dashed black) is barely distinguishable from that of the low frequency noise (in magenta). As expected, the contribution of low frequency oscillations largely explains the noise.

 τ and σ are all that is necessary to characterize the random walk. This means a simulation could be undergoing and its data used to evolve the uncertainty envelope on-the-fly. An example of this is shown in the results. For the present data set, the low frequency oscillations explain nearly all of the noise, and it would suffice to consider the autocorrelation of the whole, unfiltered noise, to obtain an estimate for the integrated noise envelope. A more thorough discussion of the filtering is offered in the Results. Also in the Results, this approach is applied to the 18 HCACFs, thus allowing us to obtain an error estimate of the *uncertainty envelope*. We also show that a frequency decomposition analysis similar to that applied to the HCACF can be used directly on the heat-flux to determine a suitable simulation time-step to optimize HCACF convergence.

5.3 Results

We applied steps i-vi to all HCACFs. The second step involves identifying different noise frequencies. It is worthwhile to remark on the difficulty of extricating individual random walks from a sum of random walks. For instance, applying a filter (as in Fig. 5.4) can syphon out data that belongs to a lower frequency random walk. In Fig. 5.4, frequency filters are applied with windows ranging between 0.04 and 0.56 ps at a 0.04 ps interval. Each time, the data filtered is removed from the overall noise. One might be tempted to say, from evaluation of Fig. 5.4, that there are multiple high frequency random walks, with time fluctuations $\tau = 0.04, 0.08, \text{ and } 0.12 \text{ ps}$, for instance, and that might be correct or the sets of filtered data might belong to a single random walk. If the former is true, the contribution of the independent sets of high frequency data were calculated to be negligible compared to the low frequency data, in the same way the high frequency data obtained with a single $(0.4 \ ps)$ filter, as shown in Fig. 5.3 a), does not significantly contribute to the overall noise (see Fig. 5.3 c)). Similarly, the low frequency noise could be resumed to the sum of its parts, but this would remove the underlaying characteristics of the noise. For this reason, having identified distinct frequency ranges in the noise, and having determined that their contribution is remarkably unequal we proceed with the analysis performed as described in steps i-vi.

For all simulations, τ was computed as to minimize the standard deviation, with the caveat that the maximum allowed value for τ was limited by the lowest intercept with zero between all noise autocorrelation functions. This is because we fit to the natural logarithm of the noise autocorrelation. This does convene us, however, in that we aim

to calculate the effect of the fast rate of decay of the systems' memory reflected in the noise. Moreover, a similar argument to there being a true autocorrelation function for the heat-flux can be made with regards to the noise. If the frequency of the noise is the same across samples, there is one true autocorrelation function that describes the interval for which the noise is correlated, i.e., before it becomes random. For the high frequency noise, $\tau_H = 0.27 \pm 0.02$ ps and is one order of magnitude greater than the interval of the HCACF $(\delta t = 0.02 \text{ ps})$, but, as depicted in Fig. 5.3 c) for the calculated uncertainty envelope of a single HCACF tail, it has a low impact in the overall uncertainty envelope. For the low frequency noise, τ_L is 4.6 ± 0.78 ps. The standard deviation for the high frequency noise, σ_H , is $8.06 \pm .11 \times 10^{-8} \ eV^2/\AA^4 ps^2$ and for the low frequency noise σ_L is $2.89 \pm 16 \times 10^{-7}$ eV^2/\mathring{A}^4ps^2 . Figure 5.5 a) shows how the noise integrals compare to the envelope (in cyan) computed from the mean τ_L and σ_L obtained from the 18 HCACF tails, using Eqn. 5.5, including the error (in blue) obtained by propagating the standard error of each quantity; the above stated uncertainties for τ_H , τ_L , σ_H and σ_L are the standard error. In Fig. 5.5 b) in the inset the envelope is compared with the full HCACF integrals. The standard error computed over of the 18 HCACF integrals is also depicted in Fig. 5.5 b) (in solid green), including in the inset, as is the standard error computed over the set of 216 sets of 50 ps HCACF integrals to which the 18 sets can be reduced (in dashed green) by splitting each 600 ps set of **J** values in 12 sets of 50 ps. This method of splitting the heat current data into many small parcels and computing the HCACF independently for each parcel means that the individual HCACF's are more noisy, but there are more data sets from which to infer the standard error in the integral. This method predicts an uncertainty slightly smaller that the random walk method. The approach is appealing because it is simple and it appears to provide a narrow estimate of uncertainty. Unfortunately, the tails of HCACFs computed from neighboring data windows is found to be correlated and so the approach underestimates the error providing a false degree of certainty. It can be seen in Fig. 5.5 b) that nearing 30 ps the error defined as the standard error of the HCACF integrals becomes more ill defined. Again, this is because over time each of the HCACFs has less data to average over. The possibility that **J** is still correlated after the length of the HCACF implies that, unlike the method proposed herein, a correct noise estimate with the standard error approach requires multiple simulations with differing starting points. As seen in Fig 5.10, with the *random walk* approach a few hundred picoseconds suffice to characterize the error and obtain an *uncertainty envelope*.

In Figs. 5.2 f) and g) it can be observed that for the 20–50 ps interval selected the HCACF tails have a non-zero mean. This suggests that the HCACFs might not have been fully relaxed by 20 ps. In Fig. 5.6 we consider the distributions of \mathbf{J} (Fig. 5.6 a)), the noise in the 30–50 ps interval for the entire data (Fig. 5.6 b)), and for the case where the peaks are computed from a moving average with a 1 ps interval (Fig. 5.6 c)) as shown in Fig. 5.2 d). Figures 5.6 b) and c) correspond to Figs. 5.2 e) and f) for the smaller interval. Figure 5.6 reassures us that over all simulations the system is close to relaxed by 30 ps. However, not all individual simulations seem to have converged by 30 ps. While the distribution of \mathbf{J} for each simulation reveals a consistently normal distribution with mean zero, the mean of the distribution of individual HCACF tails fluctuates around but is not consistently at zero. This is not an issue because the random walk approach to estimate the uncertainty of the

Green-Kubo method is largely insensitive to prevailing steady deviations from zero and it considers these variations as real slow decay processes.

Figure 5.7 evidences that the random walk method is robust to slow decay processes affecting the characterization of the noise. Upon first impression the integral in purple, in Figs. 5.5 b) and 5.7 a), stands out as having a large noise — it is well above the mean of all integrals (shown in red in the inset in Fig. 5.5 b)). Yet, since its value is large, the error is a smaller fraction of the total integral value. There are possibly three factors at play here. (1) A random walk is, well, random, and the uncertainty envelope is merely an estimate of the expected value of any random walk for a given σ and τ . (2) Figure 5.7 a) includes the individual uncertainty envelopes computed with the random walk approach for each simulation. In both cases $\sigma_L \approx 2.9 \times 10^{-7} \text{ eV}^2$.Å⁻⁴.ps². However, τ_L is 1.24 ps for the simulation (in brown), and 6.32 ps for the simulation in purple, so some of the error does seems to be due to a lower noise frequency and it is accounted for in the envelope. (3) A closer look at this HCACF reveals that it is not yet converged (see Fig. 5.7 b)). In this particular case, the noise due to the random walk is not the main cause for the discrepancy between this HCACF integral and the remainder. This is in agreement with the above discussion of the individual simulations' distribution. The uncertainty envelope for this simulation being below the integrated HCACF is thus consistent with the random walk method being broadly agnostic to slow decay processes. To reinforce this idea, we computed τ_L after displacing the HCACF tail by the mean so it oscillates around zero and it equals 6.28 ps, not noticeably different from $\tau_L = 6.32$ ps as calculated above. In other words, because we're interested in the rapid decay process of the HCACFs, slow rate
processes in the HCACF are not mistaken for noise.

The random walk uncertainty quantification approach could be a valuable tool for guiding researchers on how the noise varies over time or across simulations. To test this, a simulation of the same system was performed along x and y for 8.0 ns. For the 8.0 ns simulation data was collected at 0.04 ps intervals. The set of 18 simulations of 600 ps each adds to 10.8 ns, or 5.4 ns if we consider the x and y independently, with data collected every 0.02 ps. A total of 200,000 data points are available for averaging over the single simulation, and 270,000 for a 9 simulations set. As expected, the final HCACF for the 8.0 ns simulation is much smoother than any of the HCACFs from the 600 ps simulations, but as shown in Fig. 5.8 it continues to retain some of its oscillatory features. In Fig. 5.8, the integrated mean HCACFs for x and y for each of the two sets of 9 simulations are compared to the x and y HCACF integrals obtained from the 8.0 ns simulation and their corresponding uncertainty envelopes. Fig. 5.8 a) also shows the impact of a single outlier on the integrated HCACF average. Strikingly, the noise obtained from a single large simulation with fewer data points is lower than that obtained by averaging multiple simulations over a greater number of data points.

Recall that each simulation was performed from scratch by replicating a unit cell and conferring each system a temperature using individual seeds for each simulation. To determine if the discrepancy between the cross-autocorrelation averaging and the singlesimulation autocorrelation averaging was maintained over a similar simulation length for the same seed, we subdivided the 8 ns simulation into a set of 10 800 ps simulations and averaged over them (see Fig. 5.9). Cross-simulation averaging with the same amount of data actually seems to reduce the error slightly. Most importantly, the smaller interval selected for a larger simulation is a worthwhile tradeoff.

An example of an on-the-fly application of the suggested approach is given in Fig. 5.10 a), which shows the running mean of the evolving random walk uncertainty envelope as the simulation progresses. The correlation (R) between τ and the evolving envelope is 0.52, and that between σ and the envelope is 0.56, both with a zero P value. This indicates a strong dependence of the envelope variance on both variables. The % error is computed throughout the simulation as the ratio between the envelope and the integral of the HCACF (see Fig. 5.10 b)). It is interesting to notice that around 4 ns there is a steep decrease in the expected HCACF integrated noise, after which point the variation in the uncertainty diminishes.

To determine if there was an apparent direct correspondence between the system's Lyapunov memory and the system's energy fluctuation memory, we computed the Lyapunov instability, λ , which was found to be around 0.55 *THz*. Several simulation intervals for the system size were considered, including the 0.2 *fs* interval used for our simulations. The systems lose coherence between 15–20 *ps*. The distance, d(t), between systems was computed as $|(X)_A - (X)_B|$, where $(X)_A$ are the coordinates of system A, started an approximate 10^{-5} Å distance away from system B.

To evaluate the hypothesis that the origin of the noise in the tails results from larger peaks in **J** that have not been averaged out due to insufficient data, we performed an autocorrelation through **J** with both a gradual and a rough cut-off of these peaks (see Fig. 5.11 a)). The results obtained (see Fig. 5.11 b)–e)) indicate otherwise. A cut, soft — *i.e.*, such that the value of **J** is reduced by a higher fraction the further away from zero **J** it is — or abrupt — *i.e.*, removing peaks above and below a cut-off — through **J** reveals the importance of the peaks to set the shape of the HCACF (see Fig. 5.11 b)), but it provides evidence contrary to our hypothesis that the correlation between a few wider peaks were at the origin of the random walk type noise. If we consider a moving average (in red) through **J**, we find that it perfectly captures the trend of the HCACF (see Fig. 5.11 b)). The normalized HCACF obviates that the trend of the data is more acutely captured by the moving average. The normalized HCACF discrepancy between the moving average and the actual data could be omitted by normalizing the moving average autocorrelation function by the first element of the true HCACF.

If we, conversely, only consider the data from the highest peaks, setting all other data to zero (in blue in Fig. 5.12), some of the noise fades away, but so does the overall trend of the HCACF. A cut through the data increases the noise as expected (in yellow in Fig. 5.12), by reducing the amount of data to average over. In as far as we can ascertain, the noise is coupled to the overall fluctuations of **J**.

5.4 Conclusion

In this paper we propose a method for quantifying the uncertainty of the autocorrelation function and thus that of transport properties computed using the Green-Kubo approach. This method is based on the premise that the noise of the autocorrelation function is akin to discrete white noise and it integrates into a random walk. The value of

this method goes beyond estimating the error of a single simulation and it can be used to determine the minimum duration of a simulation to achieve a desired error threshold, as evidenced in Fig. 5.10. Most valuably, for a stipulated error, this method can be used to determine the optimal simulation time on-the-fly. While we have not found conclusive evidence for the origin of the noise, we have determined it is coupled to the overall trend of the measured flux, and that the error is largely the result of fluctuations at frequencies below terahertz. Moreover, our results indicate that it is preferable to trade off a smaller time step for a longer total simulation time with a wider time step, to smooth the long-term oscillatory behavior of the HCACF, provided the time step is large enough to account for the relevant physics of the simulated system. Transport properties computed with equilibrium MD can be optimized by combining (1) performing a single simulation to determine the minimum required simulation time to reach a desired Markovian error with (2) performing multiple independent simulations with which to obtain a robust average autocorrelation function and standard error. The suggested approach can also be used to determine if slow decay processes are present in the autocorrelation by comparing the noise distribution to a normal with the mean and standard deviation found to characterize the noise. The method herein is suitable for high-throughput approaches for which expeditious simulations and uncertainty quantification are paramount.



Figure 5.1: Panel a) shows the HCACFs (the decaying functions) plotted along side their integrals (the curves that rise to a plateau) computed from 9 separate simulations of a 10648 atom perfectly crystalline and periodically contiguous block of graphite. The data was taken from a study to determine the influence of Wigner defects on thermal transport in graphite [34]. The dashed lines correspond to the heat flux along the $[2\bar{1}\bar{1}0]$ direction and the solid lines to the heat flux along $[01\bar{1}0]$. The system was found to be converged for size, and κ is expected to be the same in both directions along the basal plane. This plot illustrates the increasingly diverging noise of the HCACF integrals, present even after 50 ps. To the eye, the ACFs look nicely converged after 10–15 ps. Plot b) shows the gradual convergence of the HCACF with increasing averaging time during a single simulation. The amplitude of the fluctuations in the tail of the HCACF decays over time, but it is notable that continued averaging does not remove the pattern of the fluctuations.



Figure 5.2: a) corresponds to the step or velocity fluctuations that give rise to a random walk; b) a set of 10 random walks is shown in black and the expected root mean square translation distance at time t is plotted in red; c) is the distribution of the random walks shown in b). d) corresponds to the tail of a HCACF, depicting the noise fluctuations that integrate to a large error akin to a random walk, shown in e) for all HCACF tails. The black lines correspond to heat-flux measurements along the x-direction ($[2\bar{1}\bar{1}0]$), and the blue ones along the y-direction ($[01\bar{1}0]$). Both values were measured along the basal plane, and this distinction should not matter. The data set is explained in the Methods section. For the selected 20–50 ps interval, the distribution of all data points across the multiple simulation tails is shown in f). A 1 ps moving average was used along with a peak find algorithm to plot major peaks in the HCACF tails, as shown in d), in magenta. The peak distribution for all data is offered in g). The dashed red lines in f) and g) correspond to a normal distribution with the standard deviation of each of the distributions and mean zero. A normal distribution with the mean for each of the data sets is shown in the solid lines for each case.



Figure 5.3: The noise of a HCACF tail in the 30–50 ps interval is shown in a) decomposed into high frequency (in blue) and low frequency (in red) noise. The autocorrelations of the noise (in black), the high frequency (in blue) and low frequency (in red) components of the noise are shown in b), along with fits through the high frequency (in cyan) and the low frequency (in magenta) autocorrelations. In c) the integrated tail appears in black, the uncertainty envelope for δt equal to the interval of the HCACFs is shown in dashed red; the uncertainty envelopes corresponding to the high frequency and low frequency noise are in cyan and magenta, respectively. The dashed black line that follows along the magenta is the combined uncertainty envelope of the high and low frequency noises, i.e. the square root of the sum of their squares.



Figure 5.4: This graph shows the application of multiple pass filters to isolate existing frequencies in the HCACF noise. The first filter applied selects out data below a 0.04 ps interval (the blue high frequency line at the bottom of the graph) and leaves the remaining frequencies. The next filter has a 0.08 ps window and is used to filter the low frequency data remnant from the first pass. This procedure is performed for 0.04 ps intervals up to a filter with a 0.56 ps window.



Figure 5.5: In a) the tail of the HCACFs, their integral, the uncertainty envelope (cyan) calculated as described in the text and its error (in blue) are all plotted. On the inset in b), instead of only considering the noisy tails of the HCACFs, the whole HCACFs are represented. In both a) and the inset in b) the solid black lines correspond to results along the y-direction, and the dashed black lines to results along the x-direction. The bold red line in the inset in b) is the integral of the average of the HCACFs; the solid green line is the standard error computed for the 18 HCACF integrals; and the dashed green line is the standard error of the 216 50 ps HCACF integrals that can be obtained from the 18 sets of data with 600 ps each. These lines are shown in the inset in b) for perspective, but also in the larger plot in b) for a clearer distinction between them and the cyan line, which shows the uncertainty calculated as described in the text, using the random walk approach.



Figure 5.6: Figure a) is the normal distribution over all **J**. Figure b) is the distribution of the noise from the tails in the 30–50 ps interval. Figure c) is the distribution of the peaks fit to the noise from the tails in the 30–50 ps interval, as shown in Fig. 5.2 d).



Figure 5.7: Figure a) shows two extremes both in terms of their total integrated value, and the interval, τ_L , of their low frequency oscillations. The uncertainty envelope for the integrated HCACF in purple is slightly above the maximum standard error (in blue), whereas that of the HCACF integral in brown is below. The corresponding noise, and noise integrals for these extrema are shown in Fig. b).



Figure 5.8: Figure a) shows the averaged HCACFs for all simulations along x (in cyan) and y (in magenta), the HCAFCs for x (in blue) and y (in red) for the large, 8 ns, simulation and the corresponding integrals in the same color. To observe the effect of a single outlier, all HCACFs except the *purple* one (see Fig. 5.7) are averaged. The resulting HCACF and integral are plotted in dashed yellow. Figure b) shows the integrals (using the same color scheme as in Fig. a)) with the corresponding uncertainty envelope around them.



Figure 5.9: This Fig. shows the integrated HCACF average for all simulations along x (in cyan) and y (in magenta) for the subset of 800 ps simulations resulting from the 8 ns simulation, the integrated HCAFCs for x (in blue) and y (in red) for the large, 8 ns, simulation and the corresponding uncertainty envelope around them.



Figure 5.10: In a), in addition to the HCACF, the moving average of the uncertainty envelope computed using the random walk approach is also propagated through the simulation time. In b) the % error is computed as the uncertainty envelope over the total integral.



Figure 5.11: The heat-flux (in black), \mathbf{J} , a 0.4 ps moving average of \mathbf{J} (in red), and a gradual cut-off of the higher peaks of \mathbf{J} (in green) are shown in Fig. a). The HCACF and integral for each of the above cases is shown in Fig. b) as is, and is normalized in Fig. c). Figures d) and e) are a zoom in on Figs. b) and c) in that order. The color coding is maintained throughout the figures.



Figure 5.12: Figure a) shows \mathbf{J} (in black), a transform on \mathbf{J} that keeps its higher peaks and replaces data between the peaks with a zero value (in blue), and a line at 550 *ps* representing a cut-off of the \mathbf{J} data above it. Figure b) shows the normalized HCACF for the above cases, and including those depicted in Fig. 5.11 a). The HCACF as is shown in Fig. c). The color code is kept constant between Figs. 5.11 and 5.12.

Chapter 6

Phonon-focusing and rattler-mode interference in thermal conductivity transitions of the breathing metal-organic-framework MIL-53

6.1 Introduction

The term metal-organic framework (MOF) was introduced in 1995 [168] to designate extended crystalline structures comprised of secondary building units (SBUs), i.e. single nodes or clusters of metal-ions, bridged by organic linkers. The highly porous nature and exceptionally large surface area of MOFs make them ideal for gas sorption and storage applications [133, 164], such as carbon sequestration and hydrogen storage. Yet, that is only the tip of the iceberg. Because MOFs are inherently modular with property-correlated building blocks (SBUs and linkers) and topology, they can be tailored to a myriad other applications. Separation [36, 167], chemical sensing [76], drug transport [60], catalysis [150], and charge storage/conduction [84, 170] are some examples of other common applications for which MOFs are heavily researched. It is unsurprising that there is an increased trend in the use of high-throughput approaches to explore the vast phasespace of MOFs, for which it becomes necessary to develop heuristic methods that allow the rapid computing of framework properties.

In 2002, Kitagawa [156] and Férey [142, 10] independently published pioneer works on "breathing" MOFs, the phenomenon by which flexible MOFs undergo a reversible transformation between narrow pore (np) and large pore (lp) structures. The dynamic micropores of breathing MOFs have been shown to open and close as a response to external stimuli such as temperature [97] and pressure [95] changes, or host-interaction [95, 96]. Photoresponsive frameworks, while still very scarce, are beginning to emerge in the literature [109, 15, 38], and electrical and magnetic interactions are predicted as possible mechanisms for tuning pore size [138], making MOFs ideal candidates as smart materials. Flexible MOFs are desirable for sorption-related applications, but new possibilities, such as shock absorption [171] are also currently being explored. Sorption processes involve exothermic and endothermic reactions [172], and the ability of the framework to transport heat or transfer it to the host is paramount in determining applicability. The US Department of Energy is currently developing hydrogen storage devices with powder compacts of MOF-5 as the adsorption bed as part of the Hydrogen Fuel Cell Program. The limitation of these devices is not storage capacity, but the efficient removal of latent heat of adsorption [172, 132]. Mechanical dampening likewise requires heat dissipation. For applications requiring or benefiting from dynamic MOFs, it is not only necessary to compute thermal conductivity, but to understand how it varies with structural transitions between breathing states. Our aim is to determine if thermal transport properties can be estimated from the vibrational modes of lp and np structures and, moreover, if these properties scale continuously with framework geometry. To this end, the dispersion relations of MIL-53(Al) were computed, in *ab initio*, for the first time, and equilibrium molecular dynamics (MD) simulations were performed to investigate phonon thermal transport in lp and np states of MIL-53(Al). We further derived a model for the thermal conductivity tensor in terms of linker and node resistances to evaluate its scalability between breathing phases, as illustrated in Fig. 6.1. Heuristic methods have the benefit of being exceptionally useful towards high-throughput MOF design. The work presented herein begins to probe the extent to which heuristic models can be of use for thermal conductivity prediction in MOFs.

6.2 Methods

6.2.1 Thermal Conductivity

The MIL-53(Al) thermal conductivities, κ , were computed using the well-established Green-Kubo formalism [49, 82]:

$$\kappa = \frac{V}{3k_B T^2} \int_0^\infty \langle \mathbf{J}(t) \mathbf{J}(t+\tau) \rangle \ d\tau, \tag{6.1}$$

where k_B , T and V are the Boltzmann's constant, the temperature, and the volume of the simulated region respectively. **J** is the heat-flux, and $\langle \mathbf{J}(t)\mathbf{J}(t+\tau)\rangle$ is the non-normalized heat current autocorrelation function (HCACF). The Green-Kubo expression (Eqn. 6.1), based on the fluctuation-dissipation theorem, relates instantaneous fluctuations in the system heat-flux to thermal transport, and it allows thermal conductivity calculations from equilibrium classical molecular dynamics simulations. Classical molecular dynamics simulations were performed with the large-scale atomic/molecular massively parallel simulator (LAMMPS) software [127]. All simulations were performed on a $3 \times 3 \times 3$ supercell with 2,052 atoms and periodic boundary conditions. This supercell size is shown to converge κ , in agreement with thermal conductivity studies of MOF-5 that have independently shown a $2 \times 2 \times 2$ supercell size to yield converged κ values [52, 61]. Molecular dynamics simulations require the specification of an appropriate set of interatomic potentials. In this paper we use the intramolecular and non-bonded force field parameters adjusted by Vanduyfhuys et. al. along with the atomic partial charges resultant from Vanduyfhuys et al.'s DFT Mulliken population analysis [158] to explore the host-independent pressure behavior of the MIL-53(Al) framework.

To compute the lattice parameter of the MIL-53 at 300 K, the $3 \times 3 \times 3$ MIL-53 supercell was optimized at 0 K. In the isothermal–isobaric ensemble (NPT) with the cell free to change volume, the temperature was increased slowly to 1,000 K and cooled down back to 0 K. The negative expansion coefficient was obtained by fitting to the simulation. The $3 \times 3 \times 3$ MIL-53 supercell was scaled to its mean volume at 300 K. In addition to a SCHEME minimization, to find the most energetically favorable configuration, the $3 \times 3 \times 3$ MIL-53 supercell was annealed to 300 K for 5 ns from 0 MPa to 300 MPa and back to 0 MPa for another 5 ns in NPT, relaxing the atomic structure as well as supercell shape and size. After relaxing the atomic structure, along with the size of the compute cell, all systems were given a thermal energy equivalent to 300 K and equilibrated in the microcanonical ensemble (NVE) for 50 ps before starting to record the HCACF. The simulations were then performed for an additional 5 ns with 1 fs time step and periodic boundary conditions. Throughout the period in NVE the average temperature remained at approximately 300 K, the HCACF was computed out to 50 ps, and 40 simulations with different starting configurations were averaged to obtain each datum.

6.2.2 Phonon properties

Phonon properties for both lp and np MIL-53(Al) were computed with a selfconsistent-charge density functional tight binding (SCC-DFTB) approach [39], using the DFTB+ software package [7]. The parameter sets, or Slater Koster files, used for the calculations are provided by the developers [45] and can be downloaded from the DFTB+ website (under "matsci"). A comprehensive review of DFTB can be found in the literature [131, 139, 39]. Relaxation calculations were performed with a 76 atom unit cell obtained from a database of computation-ready MOF structures derived from experimental data, the CoRE (computation-ready, experimental) MOF database [28]. The atomic positions were optimized using the conjugate-gradient algorithm to near 5×10^{-7} eV/Å and the electronic optimization was within 3×10^{-7} eV. The Brillouin zone was sampled by a converged $2 \times 2 \times 2$ Monkhorst-pack scheme k-point mesh [112, 123]. The hessian was computed using a double-sided finite difference approach implemented through Phonopy [155] from the force constants obtained for a $2 \times 2 \times 1$ supercell and a displacement amplitude of 0.01 Å for each one-sided atomic displacement. Periodic boundary conditions were enforced in all directions.

Group velocities, \mathbf{v}_g , were calculated for the acoustic bands, i.e. $\nu = 1, 2, 3$, along the reciprocal wave vectors, \mathbf{k} , corresponding to the *a*, *b*, *c*, and linker directions, using the Phonopy software package [155], as

$$\mathbf{v}_{g}(\mathbf{k}\nu) = \frac{1}{2\omega(\mathbf{k}\nu)} \left\langle \mathbf{e}(\mathbf{k}\nu) \left| \frac{\partial D(\mathbf{k})}{\partial \mathbf{k}} \right| \mathbf{e}(\mathbf{k}\nu) \right\rangle, \tag{6.2}$$

where **e** and D are the eigenvectors and density of states, respectively. The values in Table 6.3 are the Γ point velocities, and were approximated by calculating the average of a plateauing region of group velocities along the modes near the Γ point, where the velocities are stable.

The number of phonon states at a given frequency, ω , wave vector, \mathbf{k} , and temperature, T, can be approximated by the Bose–Einstein distribution, $f(\omega, T)$. We define phonon flux at a given wave vector, \mathbf{k} , frequency and temperature, $\phi(\mathbf{k}, \omega, T)$, as

$$\phi(\mathbf{k},\omega,T) = \mathbf{v}_g(\mathbf{k},\omega)\hbar\omega(\mathbf{k})D(\mathbf{k},\omega)f(\omega,T),$$
(6.3)

where $2\pi\hbar$ is Planck's constant, such that $E(\omega) = \hbar\omega$. In the approximation that MIL-

53(Al) is orthogonal, which holds true for both DFT and DFTB calculations (see Table 6.2), the volume of the Brillouin Zone is given by $V_{BZ} = |\mathbf{k}_{a^*} \cdot \mathbf{k}_{b^*} \cdot \mathbf{k}_{c^*}|$, where a^* , b^* , and c^* are the reciprocal lattice vectors. The density of states $D(\mathbf{k}, \omega)$ is the number of phonons at \mathbf{k} of frequency ω , per volume, such that $D(\mathbf{k}, \omega) = \int_0^{V_{BZ}} \omega(\mathbf{k}) dV_{BZ} = \int_0^{V_{BZ}} \omega |d\mathbf{k}_{a^*}| |d\mathbf{k}_{b^*}| |d\mathbf{k}_{c^*}|$. The flux here is arbitrarily defined over a surface that is $|d\mathbf{k}|^2$.

Sorting the phonon branches can be a daunting task and we have, therefore, opted to consider the sum of the phonon flux over multiple frequencies. Over all frequencies at a given \mathbf{k} , the sum is given by:

$$\phi_{\mathbf{k}}(T) = \sum_{\nu}^{3N} \phi_m(\mathbf{k}, T), \qquad (6.4)$$

where N is the number of atoms in a unit cell, and 3N the total number of phonon branches.

Validation of DFTB+

Albeit less accurate than the more common density functional theory (DFT) approach, DFTB has been shown to perform well on various systems from molecules to periodic materials [7], and offers a significant reduction in computational costs. In addition to the DFTB calculations, we relaxed the lp and np MIL-53(Al) with DFT to compare the relaxed geometries obtained with both methods. For the DFT calculation, a unit cell was relaxed with the plane-wave Vienna *Ab-initio* Simulation Package (VASP) [80, 77, 78, 79], using the project-augmented wave (PAW) method [12, 81] in the local density approximation (LDA)[126]. Energy convergence to 0.1 eV was attained with a Γ -centered 4×4×4 irreducible Monkhorst-Pack k-point sampling of the Brillouin zone and a 800 eV kinetic energy cut-off. The structure, cell size and shape were relaxed with a Gaussian smearing approach,

Bond	DFTB $(Å)$	DFT (A)	Potential [158] (\mathring{A})
O_l - C_1	1.309	1.264	1.27
C_1 - C_2	1.489	1.476	1.50
C_2-C_3	1.401	1.390	1.40
C_3-C_3	1.388	1.379	1.39
C_3 - H_l	1.101	1.095	1.08
O ₁ -Al	1.921	1.886	1.95
O_n -Al	1.908	1.830	1.85
O_n - H_n	0.960	0.972	0.91

until ionic and electronic tolerances reached 0.05 eV/Å and 0.01 meV, respectively.

Table 6.1: Table of bond lengths obtained for MIL-53(Al) using DFTB, DFT, and Vanduyfhuys *et al.* [158] classical potential. The subscripts n and l indicate a node and a linker atom, respectively. C_1 is the carbon linked to the linker oxygens, the C_2 atom bonds to C_1 , and C_3 refers to the hydrogenated carbon atoms in the benzene rings.

All bond lengths are within 0.1 \mathring{A} of each other, as can be seen in Table 6.1. The lattice parameters, volume and angles are shown in Table 6.2 for the lp and np MIL-53(Al) structures. The DFTB calculations consistently overestimate b and c and underestimate a. Experimental measurements of thermally-actuated MIL-53(Al) [92] result in a monoclinic structure, not observed in either DFT or DFTB calculations. The np MIL-53 structure appears to be barely triclinic for both DFT and classical potential calculations.

6.3 Thermal conductivity model

A simple heat propagation model for MOFs can be derived from the thermal resistivities in the nodes and linkers, R_N and R_L . Fig. 6.1 illustrates this idea. Notice that each unit cell has four nodes and R_N corresponds to a two-node cluster and includes the bridges between the cluster and the linker on each side of it. The MIL-53 structure is approximately orthorhombic, and we shall use this approximation to describe the suggested

MIL-53 (Al)	Method	a (Å)	b (Å)	c (Å)	volume (\mathring{A}^3)	$\alpha \deg$	β deg	$\gamma \deg$
lp	DFTB	16.306	6.858	13.836	1,547.2	90.000	90.000	90.000
	DFT	16.466	6.602	13.007	1,414.3	90.000	90.003	90.000
	Experiment (77 K) [92]	16.913	6.624	12.671	1,419.6	90.000	90.000	90.000
	Potential [158]	16.410	6.541	13.757	1,476.6	90.062	90.000	90.007
np	DFTB	19.240	8.436	7.383	1,198.3	90.000	90.031	90.000
	DFT	19.067	7.191	6.579	902.383	90.003	89.988	90.001
	Experiment (77 K) [92]	20.824	6.871	6.607	863.9	90.000	113.949	90.000
	Potential [158] (at 300 K, 300 MPa)	19.417	6.374	6.319	782.1	89.996	90.001	89.934

Table 6.2: Table of lattice parameters for MIL-53(Al). The lattice parameters and angles described herein follow the orientation indicated in Fig. 6.1

thermal transport model. For heat to travel across one unit cell in either the [100] or [001] directions it must travel along an alternating sequence of linkers and nodes (crossing exactly two of each per unit cell). The heat flow along any chain can be written as $\dot{Q} = -2C_{\text{linker}}\Delta T$, where ΔT is the temperature change along the chain, and the thermal conductance of the chain, C_{linker} , is obtained from the thermal resistance across a node and a linker

$$C_{\text{linker}} = \frac{1}{2(R_N + R_L)}.$$
 (6.5)

Armed with the heat current along a single chain we can now determine the heat flux in any direction. For the heat flux J_{xx} along [100] it would thus follow that

$$J_{xx} = -\frac{2C_{\text{linker}}\Delta T}{L_y L_z} = -2C_{\text{linker}}\frac{L_x}{L_y L_z}\frac{\partial T}{\partial x} = -\kappa_{xx}\frac{\partial T}{\partial x}$$
(6.6)

where L_x , L_y and L_z are the length of the unit cell along the x-, y- and z-directions, and κ_{xx} is the thermal conductivity along x. Using the same approach, and assuming a thermal conductance C_{chain} along the alternating chain of metal and oxygen atoms in the z direction, we can write the thermal conductivity tensor:

$$\kappa = 2C_{\text{linker}} \begin{pmatrix} \frac{L_x}{L_y L_z} & 0 & 0\\ 0 & \frac{L_z}{L_x L_y} & 0\\ 0 & 0 & \frac{C_{\text{chain}}}{C_{\text{linker}}} \frac{L_y}{L_x L_z} \end{pmatrix}$$
(6.7)



Figure 6.1: Illustration of the scalability of the the thermal conductivity tensor between breathing states in MIL-53.

6.4 Computational Results and Discussion

6.4.1 Thermal conductivity simulations and model results

The values for C_{linker} and C_{chain} were obtained from a zero pressure thermal conductivity calculation, and used with the also classically obtained thermal expansion results to determine the model predicted thermal conductivities. The solid lines in Fig. 6.2 correspond to the expected thermal conductivity based on the model, plotted against the actual thermal conductivity values obtained. The error bars correspond to the standard error for the thermal conductivity. Although heat is conducted along the linkers for both axes, from Fig. 6.2 we can observe that the thermal conductivity of lp MIL-53(Al) is over twice as large along *a* than *c*. This anisotropy is in good agreement with the elastic constants in those directions, as computed by Ortiz *et al.* [121] — 90.85 GPa along *a*, and 33.33 GPa along *c*, not taking into account sheer stresses — which indicate that the softer modes correspond to the deformation direction.

It is clear from Fig. 6.2 that the trend predicted by the geometric framework model



Figure 6.2: MIL-53(Al) thermal conductivity classical potential calculations at different pressures and corresponding standard error, and expected change in thermal conductivity as predicted by the geometric model (solid lines). The inset shows the actual thermal expansion/contraction of the framework as a function of temperature, in a classical potential.

is followed at least to some extent, but does not accurately match the computational results. The linkers are not interconnected along the channels and, in the vacuum, heat would be solely conducted through the chains of aluminum nodes. As the pores of the MIL-53 close, the density of chains in the plane perpendicular to the *b*-axis (as indicated in Fig 6.1) increases and so does the thermal conductivity. Albeit overestimated, the geometric model correctly predicts this behavior (the green line in Fig. 6.2). A similar argument for κ along *a* and the increase in linker density. In this case, the model response is grossly overestimated (see blue line in Fig. 6.2). Contrary to the change along *a*, the plane perpendicular to *b* expands and the density of linkers is reduced, thus the model predicted decrease in thermal conductivity (the orange line in Fig. 6.2). This trend is not matched by our calculations, which predict a nearly steady response to the geometric change in this direction. The geometric model does not fully capture the thermal conductivity behavior during the geometric transition. To elucidate the discrepancy between the simulation and the model results, we have computed phonon properties semi-empirically for the lp and np MIL-53(Al).

6.4.2 Features of the open- and closed-pore MIL-53(Al) dispersion relations

The phonon dispersion relations along a, b, c, and in the linker direction for both the lp (Fig. 6.3) and np (Fig. 6.4) MIL-53(Al) have been calculated with tight-binding DFT. The group velocities along the same directions near the Γ point are shown in Table 6.3.



Figure 6.3: Fig. a) is the dispersion relation computed along the linker and aluminum chain, and the density of states for MIL-53(Al) for the open-pore structure. A zoom-in on the lower phonon modes of the dispersion relation in the same region given in b). Figure c) shows a zoom in of the dispersion relation along a and c.

If we contrast Figs. 6.3 a) and 6.4 a), we observe only a small variation in the density of states for the lp and np frameworks: there is a small fractional increase in the



Figure 6.4: Figure a) is the dispersion relation computed along the linker and aluminum chain, and the density of states for MIL-53(Al) for the closed-pore structure. A zoom-in on the lower phonon modes of the dispersion relation in the same region given in b). Figure c) shows a zoom in of the dispersion relation along a and c.

number of states in the acoustic region in the np structure; lower frequency optical modes are also slightly more abundant in the np structure, and higher modes in the lp MIL-53(Al). For the most part, the optical modes are mostly flat in both frameworks and therefore do not carry heat. However, a small number of curved optical modes can be found in the lp MIL-53(Al) that are suppressed in the np structure. In non-bulk materials, where the length of the material is comparable to phonon mean free paths, the flattening of dispersion branches noticeably reduces the average group velocity of the phonon population [8]. This induces a *phonon confinement effect*, whereby both defect and Umklapp scattering increase as a

Direction	Chain (or b)		Linker			a			С			
Mode	1	2	3	1	2	3	1	2	3	1	2	3
lp	1,767	3,438	10,082	8,611	3,517	12,025	4,018	8,777	10,785	3,443	6,761	8,664
np	6,801	4,062	4,366	4,816	4,591	13,721	8,246	4,376	14,001	6,450	6,489	9,449

Table 6.3: Group velocities for the lp and np MIL-53(Al) acoustic modes in units of m/s. The modes (1, 2, and 3) for each direction are listed in increasing order of frequency.

result of the reduction in phonon group velocity [8]. Thin film materials of MIL-53 would be expected to incur a noticeable decrease in thermal conductivity due this mechanism.

In Figs. 6.3 b), 6.3 c), 6.4 b), and 6.4 c) we consider the more revealing acoustic modes. The deformation of MIL-53 is accompanied by changes in phonon group velocities along the chain and linker directions. This suggests that the lattice mode contributions to the linker resistance R_L changes as the network is deformed, and so the central premise that the linkers are independent thermal resistors does not hold. The average group velocities along the chain is barely altered in the "breathing" of the MIL-53. The average linker group velocity is smaller along the chain for the closed pore structure, yet it decreases for both aand c. This increase in the group velocity along c, albeit small, could contribute to increase thermal conductivity in this direction, opposing model expectations.

Rattler modes

To help interpret the phonon dispersion we have developed a simple chain and spring model for an idealized framework. The model is as depicted in Fig. 6.5 b), a 2-D network comprised of a 1-D chain of masses connected to each other by springs, and an additional spring and mass to model a rattler. The dispersion of these toy models reveals rattler behavior in which the acoustic band flattens into a *rattler mode* with zero group velocity and the trajectory of the acoustic band is picked up by an optical mode. This crossover behavior produces a band gap in the dispersion, and flattens the acoustic mode. As the framework transitions between the open- and closed-pore structures, it tenses up both along the linker and chain (see Table 6.2). As indicated in Fig. 6.3, the same feature of the dispersion shows up along the linker, and channel (b) directions in the lp structure, but not in the np one. Fig 6.6 reveals this feature as a kink that shows up along the projection of the linker in a and c.



Figure 6.5: Model of a 1-d chain with a rattler, as portrayed in b), and an example, Fig. a), where its acoustic mode is dampened by the optical mode of the rattler.



Figure 6.6: 2-dimensional dispersion relation of a cross-section through Γ along the plane defined by the reciprocal vectors a^* and b^* .

Phonon focusing

Yet another interesting phenomenon we have observed is phonon focusing. Evidence of phonon focusing is suggested by the apparent inconsistency in the group velocities (in Table 6.3) and the 1-D dispersions, as in Figs. 6.3 and 6.4. A zoom in on the acoustic modes near the gamma point, shown in Fig. 6.7 a), and the corresponding group velocities in Fig. 6.7 b), help illustrate that the 1-D dispersion is insufficient to portray the behavior of the acoustic modes in the open and closed-pore frameworks. The phonon flux (see Eq. 6.4) of the open-pore structure is depicted in Fig. 6.8 for the whole Brillouin zone. In it, we can, for instance, observe that modes existing along the linker direction, beyond the gamma point, *focus* along the chain.



Figure 6.7: A zoom in on the acoustic modes near the gamma point for the closed and open-pore structures along the chain and the linker is shown in a). The corresponding group velocities at each point are shown in b). The red arrows point to two modes with seemingly the same slope (and thus group velocity) in the 1-D region represented in a), and their very divergent group velocities, in b).



Figure 6.8: Phonon flux of the open-pore structure depicted for the whole Brillouin zone.

Conclusion

In addition to suggesting a heuristic for determining the effect of topological changes on thermal transport in metal–organic frameworks, we have also proposed a toy model for understanding the dispersion behavior of the frameworks. To our knowledge, the phonon properties of MIL-53 had not been before been calculated. In performing these calculations we further found evidence of rattler modes, in agreement with the toy model developed, and phonon focusing effects. This research is not yet in publication form, and is expected to suffer some small transformations before being submitted to a journal. A reader is therefore advised to look for the published version of this work.

Chapter 7

Thermal transport in fuels and spintronic materials

7.1 Predicting variability of thermal conductivity in nuclear fuels

7.1.1 Introduction

The calculations described in this section are part of a larger effort to accurately simulate thermal properties in nuclear fuels and structural materials. For this project, our group is collaborating with researchers in the Nuclear Science and Engineering department at Oregon State University. Ultimately, we aim to develop a frequency-dependent phonon transport solver to perform engineering-scale thermal transport predictions capable of taking into account atomistic-scale materials properties. By bridging the gap between atomic-scale and meso- and macro-scale simulations, we expect to expand on the capabilities of existing approaches to model more complicated transport phenomena, including anharmonic (three- and four-phonon) scattering contributions from normal and Umklapp processes and materials defects (e.g. point defects, clusters of point defects, grain boundaries). To achieve this, our collaborators have already adapted the neutron transport solver RattleSnake [165] to accept input from variables consistent with phonon transport simulations [53]. Rattlesnake was developed using the Multi-physics Object Oriented Simulation Environment (MOOSE) [47] framework, and solves a second-order form of the Boltzmann transport equation (BTE) using the Self-Adjoint Angular Flux formulation in a finite element spatial discretization.

A first application of the aforementioned code adaptation has been the simulation of phonon transport in uranium dioxide with xenon impurities, including the role of thermal boundary resistance (TBR). The uranium dioxide (UO₂) fuel in nuclear reactors experiences a significant reduction in thermal conductivity during its operation cycles. Daughter products from fission, including emerging xenon bubbles, build up and cause disruption to thermal transport. The build up of xenon drastically reduces thermal conductivity in the fuel. Towards this project, phonon properties of UO₂ have been calculated and used within the single mode relaxation time approximation of the BTE. These results have been incorporated into a manuscript currently accepted by the *Journal of Heat Transfer* [53]. The phonon DFT calculations performed for this project are detailed in the next section. In addition to the UO₂ calculations, preliminary calculations have been performed with Si. Si has been exhaustively studied (see *phonon thermal transport* section of this report) and thus is an ideal material to perform verifiable frequency-dependent deterministic transport simulations. Moreover Si has a diamond-like crystal structure (i.e. two interpenetrating face-centered cubic cells) and thus relatively small unit and primitive cells, which allow it to be modeled with DFT quickly and with relative ease. The dispersion relations, frequency and MFP spectrum over the frequency domain, temperature, and mode dependent specific heat capacity can be used to inform BTE deterministic transport calculations. In the future, the code being developed by our collaborators will likely include frequency coupling (i.e. phonon-phonon scattering), for which different higher-force constants would need to be obtained. Two- and three-order force constants can be computed with Phono3py [?], which interfaces with VASP, and is a later version of the Phonopy [] code, frequently used throughout my PhD.

7.1.2 Results

For the first-principles calculations, we employed the plane-wave basis projector augmented wave method within the framework of density functional theory as implemented by VASP [77, 78, 79]. The local density approximation (LDA) [126] was used for the exchange correlation potential. A plane-wave energy cutoff of 600 eV was employed. Calculations were performed with a $2 \times 2 \times 2$ super-cell of the UO₂ unit cell (with 4 O and 8 U atoms). This includes the interatomic force constants (the hessian matrix), computed with atomic displacements implemented by Phonopy [155] based on the structure symmetry of UO₂ (Fd-3m). The perfect super-cell was found to be relaxed beyond $1 \times 10^{-3} eV/Å$ ionic tolerance and a $1 \times 10^{-5} eV$ electronic tolerance. The phonon dispersion (see Fig. 7.2) and phonon group velocities were computed using Phonopy. A large $6 \times 6 \times 6$ Monkhorst-Pack k-point grid was used for all calculations (Fig. 7.1). Such a large grid is unnecessary for phonon calculations. However, UO_2 is anti-ferromagnetic and there exist ferromagnetic solutions to the Kohn Sham equation nearby the anti-ferromagnetic one, and VASP can get trapped into a ferromagnetic state. To guaranteed calculations have been correctly performed, it is convenient to plot the electronic density of states for which a higher number of k-points than is otherwise needed is usually advisable. On the account of the proximity of the existing solutions, the calculations performed for UO_2 proved more complex than initially anticipated. The MAGMOM tag was selected to ensure that alternating uranium atoms in the structure had opposing spins, and the spin of the oxygen atoms was set to zero. We further used a Hubbard parameter, U, of 4.50 eV, and a Hund's exchange parameter, J, of 0.50 eV. The results agree with those obtained by Wang *et al.* [163]. Similarly, the phonon dispersion, shown in Fig. 7.2 relation is in good agreement with that obtained in the same reference [163]



Figure 7.1: Total and partial (for the orbitals listed in the legend) electronic density of states for UO_2 with U correction for a) our calculations and b) Wang *et al.*'s calculation [163].

Similar calculations have been successfully performed with Si. The Si calculations



Figure 7.2: Phonon dispersion relations for UO_2 .

are much more straightforward and can be computed with a primitive, 3 atom, unit cell, instead of the full unit cell (needed for UO_2 to force opposing spins on its uranium atoms such that the total magnetic moment was zero).

For a frequency dependent phonon distribution in steady state, the first order form of the Boltzmann transport equation (BTE) can be written in terms of an equilibrium radiance, $\phi_{g,p}(\mathbf{r})$, within the single mode relaxation time approximation, as

$$\Lambda_{g,p}\hat{\mathbf{\Omega}}\cdot\nabla\psi_{g,p}(\mathbf{r},\hat{\mathbf{\Omega}}) = \phi_{g,p}(\mathbf{r},\hat{\vec{\Omega}}) - \psi_{g,p}(\mathbf{r},\hat{\vec{\Omega}})$$
[53]. (7.1)

In Eq. 7.1, $\hat{\Omega}$ is a direction vector in polar and azimuthal coordinates, defined such that $\phi_0 = \int_{4\pi} \psi(\mathbf{r}, \mathbf{\Omega})$; $\Lambda_{g,p}$ is the mean free path; and $\psi_{g,p}$ is the angular radiance and solution of the BTE, all defined in terms of G equally spaced discrete frequency intervals, or groups $[\omega_{g-1}, \omega_g]$, where g = 2, ..., G, and polarization, p. For an isotropic material, assuming an equal distribution of states in k-space, the equilibrium radiance can be approximated as

$$\phi_{g,p}(\mathbf{r}) = \frac{\hbar}{8\pi^3} \int_{k_g-1}^{k_g} d|\mathbf{k}||\mathbf{v}_{g,p}|\omega_{g,p}\delta_p|\mathbf{k}_g|^2 \langle n \rangle_{BE}$$
[53] (7.2)

where δ_p is the degeneracy in the phonon branches, and $\langle n \rangle_{BE}$ the Bose–Einstein distri-

bution (Eq. 2.4). Figure 7.3 b) shows the radiance for the dispersion relation of UO₂ at a cross section of the Brillouin Zone through the Γ point, depicted in 7.3 a).



Figure 7.3: a) 2-dimensional dispersion relation of UO_2 at a cross section of the Brillouin Zone, passing through Γ . b) Radiance in the same region as a), computed for each dispersion surface. Each surface does not necessarily correspond to a single phonon branch.

In addition to the calculations performed to date, future work will require obtaining the second- and third-order interatomic force constants (IFCs). As mentioned earlier, this can be done using Phono3py. The calculation details for Si are the same as are shown in the next section, and have not been repeated here.

7.2 Spin Hall effect and spin phonon interactions in p-Si

7.2.1 Introduction

Spintronics is a relatively new field of solid state physics pertaining to the study of the intrinsic spin of the electron and its associated magnetic moment aimed at using spin — rather than charge — as a way of encoding, transferring and processing information. Spin injection from a ferromagnetic source and the Spin Hall Effect (SHE) are two methods by which spin can be injected into a material [93]. The SHE was first predicted in 1971 by Dyakonov and Perel [37], and again in 1999 by Hirsch [57]. Spin and charge currents are coupled through the spin-orbit interaction, in that an electric current induces a spin current that is transverse to it resulting in an accumulation of spins of opposite signs on opposing boundaries, much like in the magnetic Hall effect. Unlike with the magnetic Hall effect, however, the presence of a magnetic field is not necessary to induce spin separation.

Silicon is considered an ideal material for spintronics due to its relatively long spin diffusion length [93], and it has been suggested that p-Si exhibits the spin Hal effect, though to date no evidence had been obtained. Sandeep Kumar's group at the UCR, however, have observed the coupling of spin, charge and thermal transport behavior in p-Si — specifically, magneto-thermal transport behavior, which is analogous to spin Hall magnetoresistance and is called as spin Hall magneto thermal resistance (SMTR) [93]. At the origin of SMTR behavior in p-Si are spin-phonon interactions [93]. Kumar and his group further hypothesize that spin relaxation due to phonon absorption or emission may change phononic thermal transport behavior. The experimental set up designed to test this approach is described in detail in the manuscript [93]. To ascertain the influence of spin polarization on phonon properties, we have calculated phonon properties of silicon with various spin concentrations. The results obtained are reproduced in the next section, close to the form they are in the manuscript [93] to be published in which this research is included.

7.2.2 Results and discussion

The spin-phonon interaction may remove or scatter a band of phonons from the heat current [93, 144] leading to a reduction in thermal conductivity. This behavior is observed in the experiments. To ascertain the influence of spin polarization on phonon properties, a suite of density functional theory (DFT) calculations were performed to compute Si's phonon dispersion and group velocities with increasing spin concentration. The phonon dispersion of silicon containing a net spin concentration was computed for spin concentrations from zero to 4.6×10^{-3} per valence electron using the plane-wave DFT Vienna Ab-initio Simulation Package (VASP) [79, 78, 79]. All calculations were performed in the local density approximation (LDA) [126] using the project-augmented wave (PAW) method [12, 81], with a Monkhorst-Pack grid of $3 \times 3 \times 3$ irreducible k-points and a plane wave energy cutoff of 1200 eV. The interatomic force constants (the hessian matrix) were computed from a single $3 \times 3 \times 3$ super-cell constructed from the Si primitive cell with atomic displacements implemented by Phonopy [155] based on the structure symmetry of Si (Fd-3m). The equivalent perfect super-cell was found to be relaxed to within 1×10^{-3} eV/Å ionic tolerance and a $1 \times 10^{-6} eV$ electronic tolerance. The phonon dispersion and phonon group velocities were also computed using Phonopy. The net estimate of the mean
variation in acoustic mode group velocity as a function of temperature and spin concentration was determined by integrating velocities computed on a $101 \times 101 \times 101$ k-point grid over the Brillouin zone. The results are summarized in Fig. 7.4 (a)-(f), and show a monotonically increasing red shift in the frequency of optical gamma point phonons with increasing spin polarization. This prediction is in agreement with the Raman spectroscopy measurements performed by Kumar's group at UCR.

Accompanying the red shift of Γ -optical phonons is a reduction in the group velocity of the transverse acoustic phonons (plotted explicitly in Fig. 7.4 (d)). This retardation of acoustic phonons can by itself yield a reduction in thermal conductivity before additional thermal resistance due to the acoustic phonon scattering in spin relaxation processes. Figures 7.4 (e) and (f) show the fractional reduction in thermal conductivity (computed from Boltzmann transport theory using the single relaxation time approximation) as a function of sweeping temperature and sweeping through spin concentration. The overall trends show a marked similarity with the experimentally measured magneto-thermal transport results presented in this work indicating that phonon softening can contribute to the measured results but that there are probably also additional phonon scattering contributions due to phonon participation in spin relaxation processes.



Figure 7.4: Plots showing DFT predicted phonon properties as a function of spin concentration. In plots (a)–(e) results are plotted for spin concentrations of 0, 0.046, 0.23, 0.46, 1.39, 2.3, 3.2, and 4.6 per 10^3 valence electrons, with the plot color from blue through green to yellow going in order of increasing spin concentration. Plot (a) shows the phonon dispersion, plot (c) the phonon density of states with inset (c) the showing the reduction in the gamma point optical phonon frequency as a function of spin. Plot (d) shows the group velocity of acoustic phonons along the $\{100\}$ direction for different spins from which it can be seen that there is a marked softening of the transverse acoustic modes. Plot (e) shows the resulting predicted variation in thermal conductivity due to spin $(\kappa(T, H)/\kappa(T, 0) - 1)$ as a function of temperature. This was obtained from Boltzmann transport theory assuming the single relaxation approximation. Plot (f) shows the predicted variation in thermal conductivity when sweeping the spin concentration at temperatures of 300, 250, 200, 150, 100, and 50 K (colored from dark red to orange with increasing temperature. It is clear from this data that spin induced phonon softening can account for some of the observed reduction in thermal conductivity, but not all of it indicating that is probably increases phonon scattering due to phonos participating in spin relaxation processes.

Chapter 8

Future work

In this final chapter, a few suggestions are offered for the direction the work presented in this document could take.

An approach to quantify the uncertainty in the Green–Kubo method with a single simulation, on-the-fly, is proposed in chapter 5. We further investigate the nature of the noise, and determine it to be coupled with the overall trend of the measured flux. This deviation from ergodicity could be further investigated by characterizing the noise according to the method proposed for a variety of systems. Introducing systematic changes in atomic mass, crystal structure and atomic inhomogeneity, i.e. considering more complex, multielement systems, and determining how that affects the size and frequency of oscillations, and their attenuation through time, might help shed some light on the origin of the noise. Our calculations seem to indicate that the system size has no influence in the frequency at which oscillations in the flux autocorrelation become random; however, the effect of system size could be investigated more thoroughly. Additionally, flux autocorrelations have varying shapes. It would be worthwhile to determine what adaptations of the method developed in chapter 5 would be necessary to quantify uncertainty for the most common forms of flux autocorrelation functions, so the method can be universally applied.

In chapter 6, we offer a heuristic to quantify the switching behavior in thermal conductivity in metal-organic frameworks with *breathing* modes. It would be worthwhile exploring deviations from this heuristic for other flexibility modes (e.g. swelling, sliding of interdigitated frameworks, linker rotation). Moreover, this could be done by collecting data for multiple structures with the same flexibility mode and determining if structure conformations for each mode tend to obey similar behavior. It is important to note that the heuristic suggested here for *breathing* MOFs is not adequate at its current stage to be used independently to estimate thermal transport variations in flexible frameworks. In addition to this heuristic for predictions in the variation of thermal transport, a similar model can be investigated for transformations in the elastic properties of the material, by modeling nodes and linkers as springs. Importantly, because of the coupling between transport and elastic properties, it is possible these models can be combined for a more accurate description of the variations in thermal transport, or alternatively that these models deviate from the predicted results in the same way. More complex versions of the geometric thermal transport model, with variational resistances, for instance, could be explored, but it is unclear at this point if there would be an added benefit to doing this.

The aim of this work is to guide our understanding of thermal transport in MOFs, such that it can be used in the design of tunable transport properties. Towards this goal, the toy spring model developed to illustrate the effect of rattling modes as those present in the MIL-53, could further be probed to investigate other dispersion properties, such as the observed phonon-focusing. Beyond the development of phenomenological approaches to predict thermal transport, the use of phonon intensity to investigate phonon focusing effects in computational studies of materials is something that seems to be generally missing in the literature. Therefore, developing a consistent methodology for investigating this phenomenon would also be worth pursuing.

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