

5 Thrust B: Lattice Dynamics and Thermal Transport

5.1 Thermal Conductivity and Specific Heat

Thermal conductivity, \mathbf{k} , is a second-order tensor defined by the Fourier Law,

$$\mathbf{q} = -\mathbf{k}\nabla T, \quad (8)$$

an empirical relation that relates the heat flux vector in a material, \mathbf{q} , to the temperature gradient, ∇T . Because thermal transport is a carrier-level process (phonons and other vibrational entities in the materials of interest here), techniques for predicting thermal conductivity from first-principles must be rooted at the atomic-level. The relationship between thermal conductivity and phonon properties can be seen in an equation derived from the phonon Boltzmann transport equation under the relaxation time approximation,^{38,39}

$$\mathbf{k} = \sum_i c_{v,i} \mathbf{v}_{g,i} \mathbf{v}_{g,i} \tau_i. \quad (9)$$

The summation is over all phonon modes in the system, and $c_{v,i}$, $\mathbf{v}_{g,i}$, and τ_i are the phonon specific heat, group velocity vector, and relaxation time.[§] The total specific heat, c_v , is given by

$$c_v = \sum_i c_{v,i} = \sum_i \frac{k_B x_i^2 e^{x_i}}{(e^{x_i} - 1)^2}, \quad (10)$$

where $x_i = \hbar\omega_i/k_B T$, \hbar is the Planck constants divided by 2π and k_B is the Boltzmann constant. Equation (10) is derived from the Bose-Einstein statistics that describe phonons.

The challenge in applying Eqs. (9) and (10) is to specify the phonon properties. Typically, assumptions are made (e.g., the phonon dispersion is described by a Debye model, a single relaxation time is assumed for the entire system), and/or models for the relaxation times are fit to experimental data.^{38,39,99} In such cases, the true nature of the phonon physics, which requires detailed consideration of the full spectrum, may be lost.¹⁰⁰ As discussed in Section 3, the required phonon properties can be obtained from lattice dynamics calculations. The thermal transport community has not embraced this approach, however, due to the complexity of the underlying anharmonic theory.

In Thrust B, we propose to explore the nature of thermal transport in large unit cell crystals. As discussed in Section 2.1, *we hypothesize that the thermal transport is a combination of sub-unit cell effects, similar to what exists in a disordered material, combined with phonon-like transport between unit cells.* To carry out this investigation, we will first develop tools to study thermal transport at the sub unit cell level using methods developed for disordered materials. These tools and the lattice dynamics calculations described in Section 3 will then be applied together to study gas hydrates, zeolites, and Zintl compounds. We will also investigate ways to improve the speed and efficiency of anharmonic lattice dynamics calculations. The initial development work will be done using force constants obtained from empirical force fields: Stillinger-Weber for silicon,¹⁰¹ SPC/E and Lennard-Jones for gas hydrates,¹⁰² and BKS for zeolites.^{103,104} Force fields are not available for Zintl compounds. As the DFT work in Thrust A proceeds, we will transition to using force constants obtained from first principles.

[§]Sparavigna and co-workers,^{40,89–93} Broido and co-workers,^{30,37,43,94–97} and Chernatynskiy and Phillpot⁹⁸ predicted the thermal conductivity of crystals without making the relaxation time approximation using an iterative solution technique. Their approach is less intuitive, more complex, and more computationally-demanding than the anharmonic lattice dynamics-based technique proposed here. Based on the results of Turney et al.,^{32–34} we believe that the relaxation time approximation is strongly justified for predicting the thermal conductivity of an equilibrium system and has notable advantages over the iterative technique, particularly with regards to the speed of the calculation.

5.2 Task B1: Disordered Solids

As discussed in Section 2.1, we hypothesize that some of the mechanisms of thermal transport in large unit cell crystals may be like those in a disordered material. In Task B1, we will develop lattice-dynamics based tools for predicting the thermal transport properties of non-metallic disordered solids. The work will focus on amorphous silicon. In addition to being a good test system, amorphous silicon is used in photovoltaic solar cells and thin film transistors, two applications where thermal issues are important. The McGaughey group has performed MD simulations using empirical force fields on amorphous silicon¹⁰⁵ and experimental data are available for validating the predictions.^{106,107} The tools developed will be suitable for modeling other disordered solids.

Two major challenges exist for performing lattice dynamics calculations on disordered solids:

- The systems are not periodic.
- Not all vibrational modes propagate (i.e., they are not phonon-like and cannot be represented as plane waves). Non-propagating modes cannot be included in the sum in Eq. (9). The contribution of non-propagating vibrational modes to scattering and thermal conductivity must be handled in a different way, as discussed below.

Previous efforts in this area^{41,42,108} have (i) used empirical force-fields to obtain the force constants, and (ii) not simultaneously considered propagating and non-propagating thermal energy transport mechanisms.[¶] *As such, thermal transport in amorphous materials at room temperature is still poorly understood.*

Non-Periodicity

The length scales associated with thermal transport in disordered materials are small. A kinetic theory calculation indicates that the average phonon mean free path in an amorphous solid will be a few atomic bond lengths. We therefore hypothesize that it will be possible to use periodic boundary conditions with finite-sized unit cells to represent the bulk material.

To determine the required system size for amorphous silicon, we will build a series of simulation cells with an increasing number of atoms. The challenge associated with an amorphous solid is that the atomic positions are not regular and the atoms will thus not naturally fit into an orthorhombic unit cell. Test structures will be obtained from MD simulation by melting a crystal structure and then rapidly quenching it. We have found that the structure of amorphous silicon is well represented by cells with as few as 200 atoms.¹⁰⁵ We will then use harmonic lattice dynamics calculations to predict the phonon density of states for each test structure and identify the minimum simulation cell that does not show size effects.

Non-Propagating Modes

The vibrational modes in a disordered material can be classified as propagons, diffusons, and locons,¹⁰⁸ all of which may contribute to scattering and thermal conductivity. The classification is done by calculating mode participation ratios, which quantify the fraction of the atoms that participate in a given mode. The participation ratio is calculated using the normalized polarization vectors of the vibrational modes [i.e., the eigenvectors from Eq. (5)]. The cutoff between propagons, diffusons, and locons is typically set on a system-by-system basis. Throughout this part of the proposed work, we will endeavor to establish more rigorous classification guidelines. We will also explore how the different types of vibrational entities couple.

Modes with a high participation ratio are propagons and behave like phonons. They have a well-defined group velocity and their contribution to the thermal conductivity can be predicted

[¶]An exception is recent work by Donadio and Galli,¹⁰⁹ who studied thermal transport in silicon nanowires with amorphous surfaces described by the Tersoff force field.

from Eq. (9). The propagon contribution to the thermal conductivity decreases with increasing temperature as a result of increased anharmonicity, which leads to more frequent scattering events. Diffusons, which have a lower participation ratio than propagons, are non-localized but do not propagate (i.e., they do not have a well-defined group velocity). Their contribution to thermal conductivity can be predicted from a model proposed by Allen and Feldman,^{41,110}

$$k_D = \frac{1}{V} \sum_i c_{v,i} D_i. \quad (11)$$

Here, V is the system volume, the sum is over all diffusive modes, and D_i is the mode diffusivity, which can be obtained to first-order from a harmonic lattice dynamics calculation. The diffuson contribution to the thermal conductivity increases with increasing temperature as a result of the temperature-dependence of the specific heat [Eq. (10)]. Previous studies have examined the role of diffusons in amorphous solids, raising important questions about the relative roles of anharmonicity and quantum effects.⁴² Locons are localized, non-propagating modes, identifiable by a small participation ratio and negligible diffusivity. While important in low-dimensional systems, the locon contribution to thermal conductivity is not significant in 3-D systems.¹¹¹ Locons may still scatter with propagons and diffusons, however, so their existence cannot be ignored.

No study to date has examined all the vibrational entities in the same system. Diffusons are typically assumed to dominate in amorphous materials, in large part because they can be easily modeled under the harmonic approximation. It has been found, however, that diffusions alone cannot account for all the thermal transport in amorphous materials.⁴² Our lattice dynamics calculation framework presents an ideal framework for studying the combined and coupled roles of propagons, diffusons, and locons.

We will first examine the relative contributions of propagons, diffusons, and locons to the thermal conductivity of amorphous silicon. Initial work will be done using the Stillinger Weber empirical force field. We will transition to a first-principles analysis as force constants become available from Thrust A. The calculations will be performed on isotopically pure samples. To compare to experimental measurements, the effects of scattering by isotopes, boundaries, and point defects will be included by calculating an effective relaxation time using the Matthiessen rule.^{38,39,99,100}

Our scientific objective in studying amorphous silicon will be to explain the temperature dependence of its thermal conductivity (it increases with increasing temperature). While some argue that the increase is due to quantum effects associated with the specific heat,¹⁹ others suggest that it is also due to increased anharmonicity with increasing temperature.^{17,18} Our ability to calculate and decompose the thermal conductivity in a first principles, quantum framework will allow us to separate the effects of these two potential mechanisms.

5.3 Task B2: Large Unit Cell Crystals

We hypothesize that not all the vibrational modes in a large unit cell crystal are effective at propagating [i.e., Eq. (9) is not appropriate for some modes] and that energy transport mechanisms at length scales smaller than the lattice constant are important. This hypothesis is consistent with the experimental data shown in Fig. 2(b) and MD-predicted thermal conductivities of zeolites,⁹ methane hydrate,⁵² and metal-organic frameworks,¹¹² which show weak temperature-dependence. Thermal transport within the unit cell may be affected by local distortions of the unit cell or the presence of non-framework species (e.g., caged gas molecules in a hydrate, the cations required to maintain charge neutrality in aluminum-silicon zeolites, and adsorbed gas molecules in a zeolite or metal organic framework). Also of interest is the role played by optical phonons. Large unit cell crystals have many optical phonon branches that can: (i) scatter

the acoustic phonons that are generally assumed to dominate thermal transport, but (ii) carry a significant amount of thermal energy due to their shear numbers.⁶⁰

Using the analysis tools for ordered and disordered materials discussed in Sections 3 and 5.2, we will analyze thermal transport in gas hydrates, zeolites, and Zintl compounds. These material systems, in addition to covering a range of energy-related applications, are also distinct in their structures. Gas hydrates are built from weakly-bonded, closed cages. Zeolites are rigidly-bonded structures containing Angstrom-sized pores and channels. Zintl compounds are not porous.

Gas Hydrates

A gas hydrate is a crystal built from water cages that are stabilized by the presence of trapped gas molecules (e.g., methane, CO_2).³ The two cages in the type I structure are shown in Fig. 7(a). Natural deposits of methane hydrate in seafloor sediment and permafrost contain an estimated 10^{16} kg of methane, making them the largest terrestrial hydrocarbon source. Methane hydrate is also a potentially purer source for methane than what is currently available from oil fields, natural gas fields, and coal beds. There is also interest in using hydrates to store CO_2 . In all of these cases, it is important to know the thermal properties (both specific heat and thermal conductivity) to allow for the accurate modeling of reservoirs and deposits, and how they will respond to temperature changes that may cycle on a daily or yearly basis.

Methane hydrate is only stable at high pressures (above 20 bar at a temperature of 275 K),³ making field and laboratory experiments challenging. Molecular simulation is emerging as a powerful tool to study gas hydrates, as it can model extreme environments and offers the ability to make atomic-level observations not possible in experiments. Previous modeling efforts have focused on identifying suitable interatomic potentials^{113–115} and studying isothermal processes such as crystal nucleation, growth, and dissolution.^{116–120} Limited experimental or theoretical work has characterized the thermal properties of gas hydrates and their behavior under conditions of non-thermal equilibrium.^{25,52,102,114,121,122} *No work to date has identified the underlying atomistic mechanisms of thermal transport in gas hydrates. Understanding these mechanisms is needed to predict how gas hydrates will respond to environmental changes.*

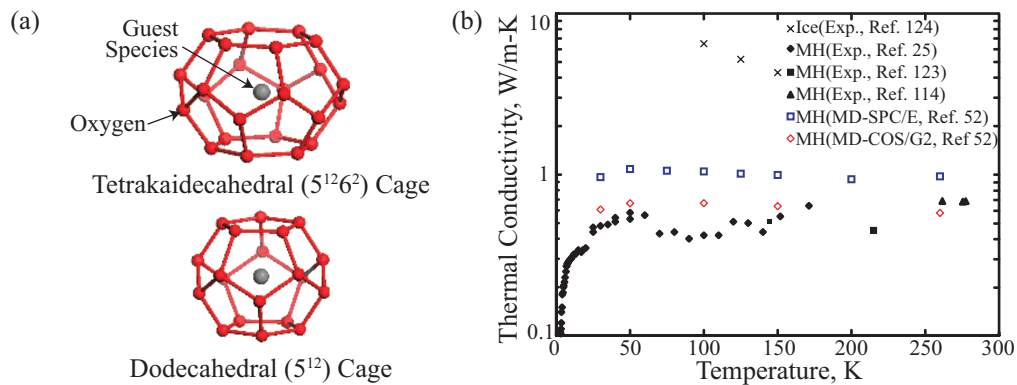


Figure 7: (a) Structures of tetrakaidecahedral ($5^{12}6^2$) and dodecahedral (5^{12}) cages that form gas hydrates. Water molecules and guest species are red and gray balls. Hydrogen bonds between water molecules are red sticks. (b) Thermal conductivity of methane hydrate (MH)^{25,52,114,123} and ice¹²⁴ measured in experiments and predicted from MD simulations using the SPC/E and COS/G2 potentials.