First Principles Modeling of Thermal Transport in Large Unit Cell Crystals

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1   Project Objectives

The objective of this project is to build a robust, accurate, and efficient computational framework for predicting the thermal conductivity and specific heat of large unit cell non-metallic crystalline solids using electronic structure calculations and lattice dynamics calculations.

We will apply the framework to gas hydrates, zeolites, and Zintl compounds, all large unit cell crystals of interest to energy-related challenges and opportunities. Previous experimental and computational results suggest that thermal transport in such large unit cell crystals is more like that in disordered materials than in crystals with only a few atoms in their unit cell. We seek to uncover the underlying physical mechanisms and to suggest strategies for the design of materials with tailored thermal properties.

Our approach first uses dispersion-corrected density functional theory (DFT) calculations to determine atomic force constants. The force constants are then used in harmonic and anharmonic lattice dynamics calculations to predict the properties (e.g., specific heats, velocities, relaxation times) of the full spectrum of phonons and other vibrational entities. The vibrational properties are then used in thermal transport frameworks (e.g., the phonon Boltzmann transport equation) to predict specific heat and thermal conductivity. The use of lattice dynamics calculations instead of molecular dynamics (MD) simulations allows for the natural inclusion of quantum effects. The accuracy of the underlying DFT calculations, as opposed to using empirical force fields to obtain the force constants, will make the predictions directly comparable to experimental measurements. This undertaking is possible due to our team's expertise in atomistic thermal transport, electronic structure calculations, and high-performance computing.

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2 Introduction

2.1 Motivation

A crystal is defined by a repeating set of lattice points, each of which has the same basis of atoms (the unit cell) attached to it.[1] Large unit cell crystals, examples of which are shown in Fig. 1, are relevant to a diverse collection of energy-related challenges and opportunities. In many of these cases, thermal transport plays a critical role. For example:

- Natural deposits of methane hydrate,[2,3] Fig. 1(a), in the sea floor and permafrost contain an estimated 10^{16} kg of methane, making them the largest terrestrial hydrocarbon source. Significant international and DOE-led domestic efforts are directed at identifying deposits and efficiently extracting and transporting the methane.[4–6] There is concern about how the release of large amounts of methane from hydrates (due to natural or human effects) will influence climate change, the carbon cycle, and seafloor stability. There also is growing interest in using hydrates to store CO_2.[7] Methane hydrate is only stable at high pressures (above 20 bar at a temperature of 275 K),[3] making field and laboratory experiments challenging. *Our modeling framework will allow for prediction of how gas hydrate deposits respond to temperature changes, critical in predicting their environmental behavior and stability.*

- Zeolites,[8,9] Fig. 1(b), contain Angstrom-sized pores and channels. They are relevant to catalysis, molecular separation, and gas storage applications. Synthesis of zeolite samples at the length scales required to make thermal measurements ($\sim$cm) is challenging, so that little data about their thermal properties is available. It is important to understand how zeolites will respond to ambient temperature changes. For example, the propagation of a thermal wave through a gas storage material could lead to rapid cooling, desorption, and gas release. *Phonon-level analysis of zeolites will elucidate the mechanisms by which they store and transport thermal energy.*

- In thermoelectric energy generation, waste heat (e.g., from engine exhaust) is used to generate electricity.[10–12] To maximize the thermoelectric figure a merit, thermal conductivity should be minimized, while electrical conductivity and the Seebeck coefficient should be maximized. Large, complex unit cell crystals such as clathrates, skutterudites, and Zintl compounds, Fig. 1(c), can have thermal conductivities lower than 1 W/m-K.[11] *Using theory to identify the underlying thermal transport mechanisms will accelerate the design of new thermoelectric materials with even lower thermal conductivities.*

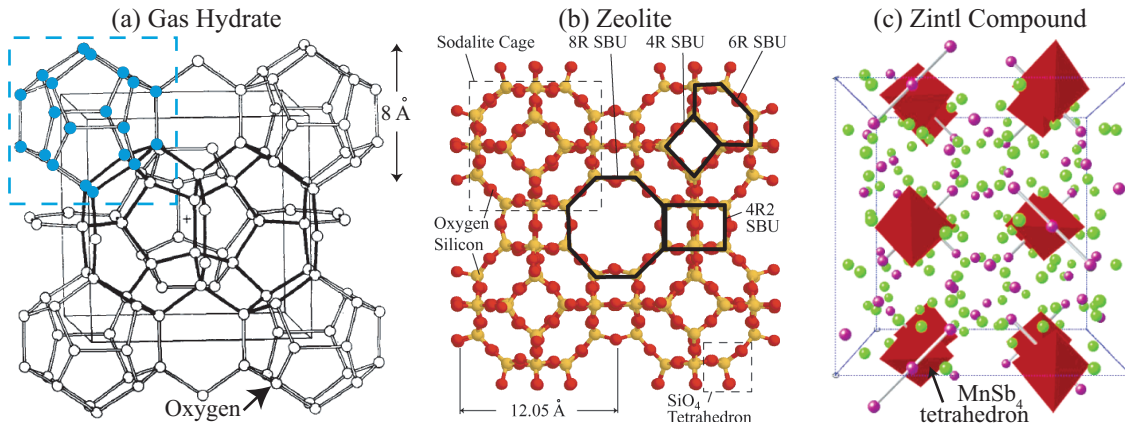(a) Gas Hydrate   (b) Zeolite   (c) Zintl Compound

Figure 1: Large unit cell crystals, for which the application of phonon-based thermal transport models is questionable. (a) Type-I gas hydrate (water molecule cages that house gas molecules). Only oxygen atoms are shown.[2] (b) Zeolite-A.[9] SBU = secondary building unit. (c) Zintl compound $Yb_{14}MnSb_{11}$.[13] The unit cell contains $[Sb_3]^{7-}$ trimers, $[MnSb_4]^{9-}$ tetrahedra, and Sb^{3-} anions in a Yb^{2+} sublattice.

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At steady state, the bulk thermophysical properties of interest are specific heat, c_v, which describes a material's ability to store thermal energy, and thermal conductivity, k, which describes a material's ability to transport thermal energy. The thermal diffusivity, $\alpha = k/\rho c_v$, where ρ is density, is relevant to transient conditions. For example, in periodic heating/cooling at frequency ω, the thermal penetration depth is $(\alpha/\omega)^{1/2}$. At the carrier-level, thermal storage and transport in non-metallic crystals is dominated by phonons, quanta of energy associated with atomic vibrations.[1,14–16] One can think of a phonon as an energy wave that propagates through a periodic system. Finite thermal conductivity exists because phonons scatter with other phonons, defects, and system boundaries. The specific heats and thermal conductivities measured in an experiment are a collective effect of the full spectrum of phonon modes in a material.

Experimental thermal conductivity data for diamond, silicon, quartz, amorphous carbon, amorphous silica, and amorphous selenium are plotted in Fig. 2(a). Experimental data for five large unit cell non-metallic crystals are plotted in Fig. 2(b). As temperature increases, the diamond, silicon, and quartz data show the behavior typical of a crystal: an initially increasing thermal conductivity (related to the temperature dependence of the specific heat) followed by a $1/T$ decay (related to phonon-phonon scattering). The amorphous phases show the typical monotonic increase of thermal conductivity with increasing temperature, which has been attributed to the specific heat and how anharmonicity couples with disorder.[17–19] The large unit cell crystals all have thermal conductivities less than 2 W/m-K that generally increase with increasing temperature, similar to the amorphous phases. One of the central themes of the proposed work is the explanation of this behavior, which *we hypothesize to be related to sub-unit cell level effects that cannot be captured by standard phonon transport theory.* We imagine a combination of sub-unit cell level transport typical of a disorder phase, where thermal energy moves between atoms, coupled with phonon-like transport between unit cells.

The current paradigm for predicting specific heat and thermal conductivity is to use empirical force fields in classical molecular dynamics (MD) simulations.[20–23] This approach is limited by: (i) a lack of force fields for many material systems, (ii) errors introduced by the inability of the
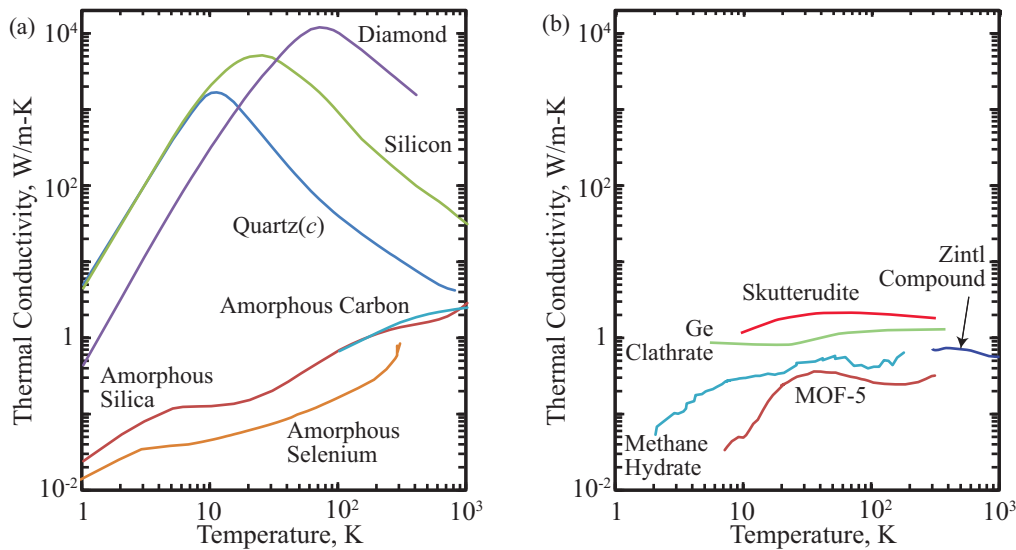

Figure 2: Experimentally measured thermal conductivity for (a) amorphous and small unit cell crystalline materials,[24] and (b) large unit cell crystals: methane hydrate,[25] MOF-5,[26] the clathrate $Sr_8Ga_{16}Ge_{30}$,[27] the skutterudite $La_{0.31}Co_4Sn_{1.48}Sb_{11.2}$,[28] and the Zintl compound $Yb_{14}MnSb_{11}$.[13] The large unit cell crystals all have thermal conductivity magnitudes and trends comparable to the amorphous phases.

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force fields to accurately describe atomic interactions, (iii) the large computation time needed to perform MD simulations, and (iv) the neglect of quantum effects. Our proposed first-principles approach uses quantum mechanics-based electronic structure (specifically dispersion-corrected DFT) calculations and lattice dynamics calculations to directly predict phonon properties, and from these, specific heat and thermal conductivity.[29–34] All materials of interest can be modeled within the same framework. In general, DFT provides a better description of phonons than do force-field approaches, which translates to more accurate thermal property predictions. Although DFT calculations are computationally demanding, the time can be considerably reduced by using efficiently-parallelized codes.

2.2 Integrating Electronic Structure Theory and Thermal Transport

The procedure for making a lattice dynamics-based thermal conductivity prediction is shown in Fig. 3. Harmonic, cubic, and quartic atomic force constants are first calculated from an empirical force field or using DFT.[29,31] Ignoring the higher-order force constants is expected to be valid up to half of the melting temperature.[32] The force constants are then used in lattice dynamics calculations to predict the properties of the vibrational modes (phonons in crystals, other entities such as diffusons in disordered materials).[16,30,32,35–37] These properties are then used in a thermal transport framework (e.g., the phonon Boltzmann transport equation for crystals[38–40] or Allen-Feldman theory[41,42] for disordered solids) to predict thermal conductivity. The majority of previous efforts have focused on one part of this procedure. *We will build an integrated computational framework that starts from DFT and ends with a true first-principles thermal conductivity.*

Atomic force constants, the derivatives of the system energy with respect to the atomic positions, are typically obtained analytically or numerically from an empirical force field.[23,32,43] Force fields are algebraic expressions with parameters fit to experimental data (e.g., lattice constants, elastic constants, defect energies) or to potential energy surfaces from electronic structure calculations on related, but simpler systems. Force fields are rarely fit to phonon or thermal properties. As a result, force fields that accurately predict mechanical behavior often do a poor job of predicting thermal behavior. For example, silicon phonon dispersion curves in the [100] direction predicted by the Stillinger-Weber (SW) force field are shown in Fig. 4 along with experimental data.[44] The SW force field does not reproduce key features of the experimental curves. Notably, the frequencies of the transverse acoustic branch near the edge of the Brillouin zone are too high, which leads to an over-prediction of the phonon group velocities, needed to predict thermal conductivity. Comparable differences exist for other force fields for silicon.[45] Based on these results, we should not expect the silicon thermal conductivity calculated using the SW force field to agree with the experimental value, which it does not (62 W/m-K at a temperature of 1000 K from MD simulation[20] compared to the experimental value of 31 W/m-K[39]). In fact, no available silicon
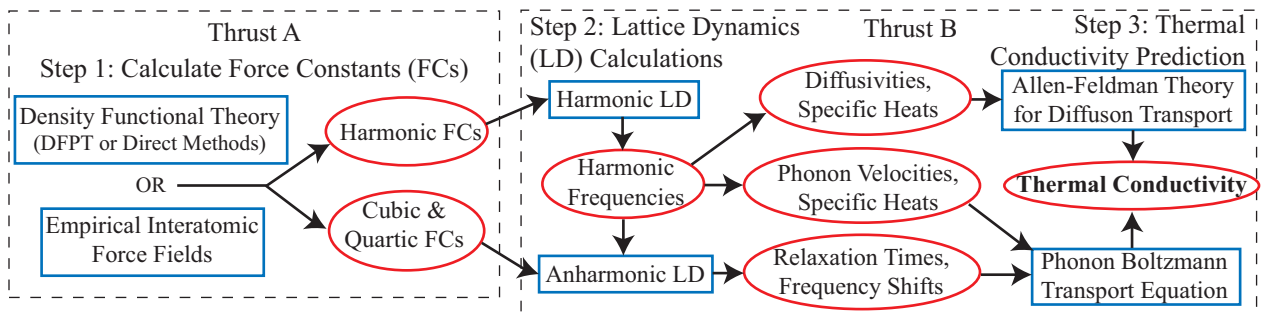

Figure 3: Procedure for lattice dynamics-based thermal conductivity prediction. The modeling tools are in blue boxes and their outputs are in red ovals. Thrusts A and B are described in Sections 4 and 5.

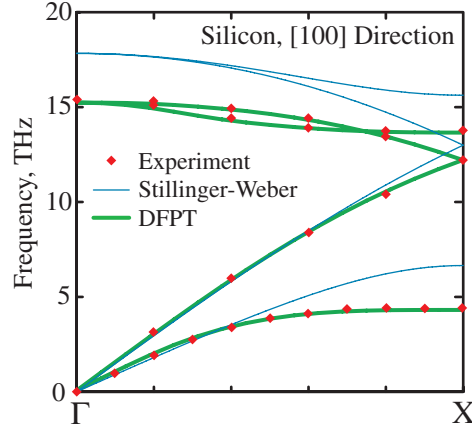Alan McGaughey, Wissam Al-Saidi, and Kenneth Jordan

Figure 4: Silicon [100] dispersion curves from experiment, the SW force field, and DFPT calculations.

force field, used in either MD simulation or lattice-dynamics based methods, successfully predicts its thermal conductivity.[43]

With advances in electronic structure methodologies [e.g., density functional perturbation theory (DFPT)] and increases in computational power, force constants of periodic systems can now be obtained from electronic structure calculations.[29,31,46,47] In Fig. 4, dispersion curves for silicon, calculated using harmonic DFPT force constants, are compared to experimental measurements and the SW predictions. The agreement of the DFPT results to experiment is excellent, particularly in contrast to the results obtained using the SW force field.

Cubic force constants, which describe three-phonon interactions and are needed to predict thermal conductivity, can also be obtained from DFT. Broido and co-workers have used DFT and DFPT to provide the input to an iterative solution of the phonon Boltzmann transport equation for predicting thermal conductivity.[30,37] They found excellent agreement between their predictions for diamond, silicon, and germanium and experimental measurements (within 10% between temperatures of 100 and 300 K). To our knowledge, this report is one of only a few examples in the literature of a truly first-principles thermal conductivity prediction.[48,49] The application of this approach to large unit cell crystals and disordered solids has not been explored.

2.3 Overview of Research Program

Work in first-principles thermal transport modeling has been limited by the complexity of: (i) The underlying thermal transport theory, where including phonon interactions requires anharmonic lattice dynamics calculations, and (ii) The electronic structure calculations for determining cubic and quartic atomic force constants, the inputs to anharmonic lattice dynamics calculations.

Building a framework for performing first-principles thermal transport modeling on large unit cell crystals is a challenging endeavor because:

- Significant computational resources are required to (i) calculate force constants, and (ii) perform anharmonic lattice dynamics calculations on large unit cells.

- A comparison of the accuracy and computational demands of DFPT (where the electronic charge density is perturbed) to the more intuitive displacement-force method (where the atomic positions are perturbed to find the force constants), has not been performed.

- The application of DFPT to predict cubic force constants in existing software packages is limited to (i) small unit cells if information about all phonon modes is required,[30,37] and (ii) gamma-point (i.e., zone-center) phonons otherwise.[50,51]

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- The applicability of phonon transport theories to large unit cell crystals is questionable. Using a simple kinetic theory calculation, the average phonon mean free path is typically estimated to be less than the unit cell size, a non-physical result.[52]

We propose to address the above four points through two integrated research thrusts.

In Thrust A, described in Section 4, we will develop the ability to use dispersion-corrected DFT and the displacement-force method to calculate the cubic and quartic force constants for the complete Brillouin zone for any unit cell. This ability will enable the first-principles study of thermal transport in any solid system. We will compare the displacement-force method to DFPT and explore how force constant calculations can be sped up with minimal loss of accuracy.

In Thrust B, described in Section 5, we will apply lattice dynamics calculations to predict the properties of the full vibrational spectrum (phonons and other vibrational entities) of gas hydrates, zeolites, and Zintl compounds. We will also apply lattice dynamics calculations to predict the vibrational properties of amorphous silicon, as we believe that some of the thermal transport mechanisms in large unit cell crystals are similar to those in disordered materials [see Figs. 2(a) and 2(b)]. These vibrational properties will then be used to predict thermal conductivity and specific heat. We will also explore ways to speed up anharmonic lattice dynamics calculations, of critical importance for studying large unit cell systems.

The computational work will be performed on dedicated clusters at Carnegie Mellon University and the University of Pittsburgh and on the TeraGrid (which includes the Pittsburgh Supercomputing Center).[53] The computational tools will be integrated into BigDFT,[54] an open-source massively-parallel DFT code that is part of the widely-used ABINIT software release.[50] We have strong support from the ABINIT/BigDFT developers in this endeavor (see attached support letter from Xavier Gonze).

The remainder of the proposal is organized as follows. In Section 3, lattice dynamics calculations are briefly reviewed. Thrust A, the DFT-based calculation of force constants, is described in Section 4. Thrust B, related to the calculation of phonon properties and thermal conductivity of large unit cell crystals, is described in Section 5. Sections 6 and 7 describe our long-term vision and team coordination mechanisms.

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3 Force Constants and Lattice Dynamics Calculations

In this section, we review the concept of a phonon, the lattice dynamics method, and the definitions of the atomic force constants.[16,36,55,56] A phonon is a vibrational entity in a crystalline solid. Every phonon mode has a wave vector $\boldsymbol{\kappa}$, frequency ω, and polarization vector $\mathbf{e}$. The time-dependent amplitude of a phonon mode k perturbed from equilibrium can be written as[57]

$$S_k(t) = S_1 e^{i(\omega_k + \Delta_k)t} + S_2 e^{-i(\omega_k + \Delta_k)t} + \{S_3 e^{i(\omega_k + \Delta_k)t} + S_4 e^{-i(\omega_k + \Delta_k)t}\} e^{-\Gamma_k t}, \tag{1}$$

where S_n are constants, ω_k is the harmonic frequency, Δ_k is the anharmonic correction to the frequency, Γ_k is the mode linewidth (related to interactions between modes), and t is time. The mode relaxation time is $\tau_k = 1/(2\Gamma_k)$. Values of ω, Δ, and Γ for all phonons in a crystal are needed to predict its thermal conductivity and can be obtained from lattice dynamics calculations.[*]

Suppose that the equilibrium potential energy of a system with N atoms is E_0. If each atom i is moved by an amount $\mathbf{u}_i$, the resulting energy of the system, E, can be found by expanding around the equilibrium energy in a Taylor series as

$$
\begin{aligned}
E = {} & E_0 + \sum_i \sum_\alpha \left. \frac{\partial E}{\partial u_{i,\alpha}} \right|_0 u_{i,\alpha} + \frac{1}{2} \sum_{i,j} \sum_{\alpha,\beta} \left. \frac{\partial^2 E}{\partial u_{i,\alpha} \partial u_{j,\beta}} \right|_0 u_{i,\alpha} u_{j,\beta} + \\
& \frac{1}{6} \sum_{i,j,k} \sum_{\alpha,\beta,\gamma} \left. \frac{\partial^3 E}{\partial u_{i,\alpha} \partial u_{j,\beta} \partial u_{k,\gamma}} \right|_0 u_{i,\alpha} u_{j,\beta} u_{k,\gamma} + ...
\end{aligned}
\tag{2}
$$

Here, the i, j, and k sums are over the atoms in the system and the α, β, and γ sums are over the x, y, and z directions. The first derivatives of the potential energy with respect to each of the atomic positions (the linear force constants) are the negatives of the net force acting on each atom. Evaluated at equilibrium, these terms are zero. The first non-negligible term in the expansion, other than the constant E_0, is the second-order term. The second derivative in this term is the harmonic force constant. The higher-order terms contain the cubic, quartic, etc. force constants. *The force constants can be found from empirical force fields or DFT calculations. The origin of the force constants does not affect how lattice dynamics calculations are carried out.*

In the harmonic approximation, the energy expansion is truncated after the second-order term. One of the challenges in working with Eq. (2) is the coupling of the atomic coordinates in the force constants. A transformation from Cartesian to phonon coordinates, S_k, gives

$$(E - E_0)_{harm} = \frac{1}{2} \sum_{i,j} \sum_{\alpha,\beta} \left. \frac{\partial^2 E}{\partial u_{i,\alpha} \partial u_{j,\beta}} \right|_0 u_{i,\alpha} u_{j,\beta} = \frac{1}{2} \sum_k \left. \frac{\partial^2 E}{\partial S_k^2} \right|_0 S_k^* S_k, \tag{3}$$

where the phonon-mode amplitude, Eq. (1), can be obtained from the atomic coordinates as

$$S_k(t) = N^{-1/2} \sum_j m_j^{1/2} \exp(-i\boldsymbol{\kappa} \cdot \mathbf{r}_{j,o}) \mathbf{e}_k^* \cdot \mathbf{u}_j. \tag{4}$$

Here, $i^2 = -1$, m_j is the mass of atom j, $\mathbf{r}_{j,o}$ is its equilibrium position, and the time dependence is contained in $\mathbf{u}_j$. The wave vectors, which span the Brillouin zone, can be determined from the crystal structure. The harmonic frequencies and polarization vectors are obtained from the eigenvalue problem

$$\omega_k^2(\boldsymbol{\kappa}, \nu) \mathbf{e}_k(\boldsymbol{\kappa}, \nu) = \mathbf{D}(\boldsymbol{\kappa}) \mathbf{e}_k(\boldsymbol{\kappa}, \nu), \tag{5}$$

which is derived from the harmonic equations of motion for the atoms. In Eq. (5), ν denotes the dispersion branch and $\mathbf{D}(\boldsymbol{\kappa})$ is the dynamical matrix, constructed using the harmonic force constants.[36] Phonon dispersion curves, density of states, specific heats, and velocities can be obtained

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[*]The relaxation times obtained from a lattice dynamics calculation are related to phonon-phonon scattering. Effects of other scattering mechanisms (e.g., isotopes, boundaries, point defects) can be included using the Matthiessen rule.[15]

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from the frequencies. The phonons modes in the harmonic approximation are non-interacting, though, so that no information about their scattering (i.e., relaxation times) is obtained from a harmonic lattice dynamics calculation.

In an anharmonic lattice dynamics calculation, the third- and diagonal fourth-order terms in the energy expansion are introduced as perturbations to the harmonic solution. Truncating the energy expansion after the fourth-order terms is expected to generate accurate results up to half the melting temperature.[32] † The perturbation accounts for three- and four-phonon processes (with conservation of energy and crystal momentum strictly enforced), and naturally incorporates quantum effects. The outputs of the calculation are Δ, the anharmonic frequency correction (related to the cubic and quartic force constants) and Γ, the phonon linewidth (only dependent on the cubic force constants) for all the phonon modes in the system [see Eq. (1)]. The full expressions for Δ and Γ are too long for reproduction here, but are available.[32,55,65] The anharmonic lattice dynamics approach builds up Δ and Γ on an interaction-by-interaction level, allowing for insight to be gained into the origin of the phonon properties (e.g., which three-phonon processes dominate in the scattering of a specific mode). While many quantum-chemistry computation packages can perform these calculations on molecules, the implementation of anharmonic lattice dynamics calculations for a periodic system is challenging. The McGaughey group has completed this implementation and applied it with force constants calculated from empirical force fields.[23,32–34] Their implementation will also work with force constants obtained from DFT calculations.

As an example of what that can be learned from lattice dynamics-based phonon property prediction, consider Figs. 5(a) and 5(b), taken from a study on silicon thin films by Turney et al.[34] In Fig. 5(a), the frequency-dependent contribution to the in-plane thermal conductivity is plotted. Having access to the full spectrum of phonon properties allows for a quantitative understanding of how lower-frequency modes contribute relatively less as the film thickness is decreased. In Fig. 5(b), the predicted in-plane thermal conductivity (assuming diffuse boundary scattering) is compared to experimental measurements, and provides a lower bound to the available data.
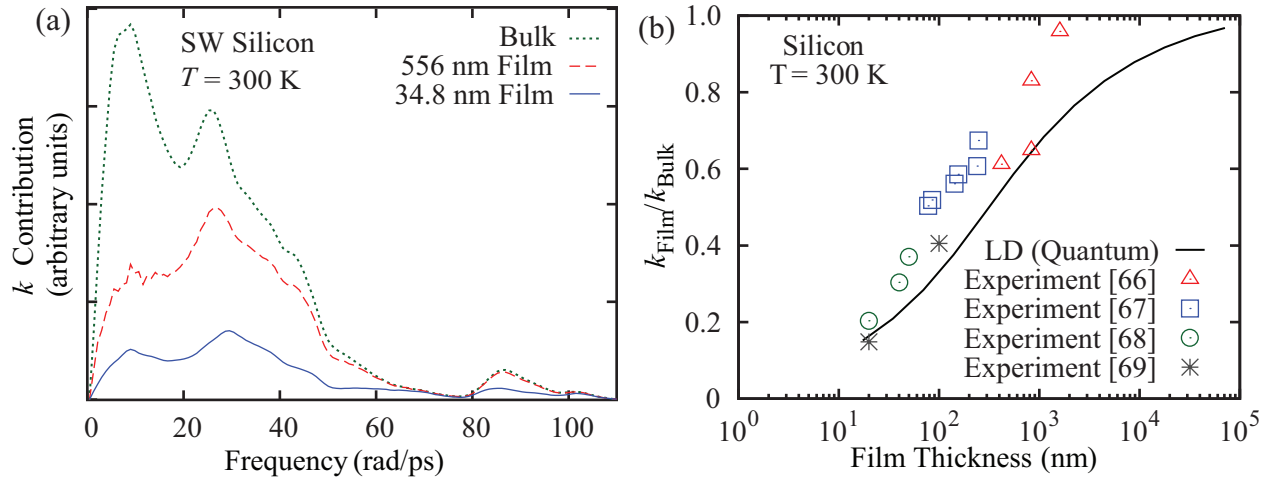

Figure 5: (a) Frequency-dependent contribution to silicon thin film thermal conductivity obtained from lattice dynamics calculations.[34] (b) Comparison of model predictions to experimental thermal conductivity data.[66–69]

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† At higher temperatures, methods for predicting fully-anharmonic phonon properties using MD-generated atomic trajectories have been proposed.[49,58–60] These techniques are limited however, by the classical trajectories predicted from Car-Parrinello DFT-driven MD.[61] Generating truly quantum atomic trajectories remains a very challenging problem, both in terms of computational expense and theoretical complexity.[62–64]

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4 Thrust A: Force Constants from Density Functional Theory

4.1 Electronic Structure Calculations

In an electronic structure calculation, the Schrodinger equation is solved to predict the energy of a system of atoms.[70,71] Because ions are much more massive than electrons, the ionic and electronic degrees of freedom can be decoupled (i.e., the adiabatic approximation). The calculation then amounts to solving for the electronic wave functions for a given set of ionic positions. In the Kohn-Sham DFT approach, the many-electron problem is reduced to solving for the one-electron wave functions.[72–75] The Kohn-Sham equation is similar to the Hartree-Fock equation, except that the effective potential experienced by the electron is expressed as a functional of the electron density of the original many-electron system. The effective one-electron potential includes contributions from the electron-ion interaction, the Hartree potential, and the exchange-correlation potential. We propose to investigate the computational demands and accuracy of two distinct methods for calculating force constants using DFT calculations: (i) the displacement-force method, where the force constants are evaluated by differentiating forces calculated from a set of prescribed atoms displacements, and (ii) DFPT, a linear response theory within the framework of DFT.

4.2 Dispersion-Corrected Density Functional Theory

It is well know that standard DFT methods fail to properly account for long-range van der Waals dispersion interactions, particularly relevant to the gas hydrate structures to be studied here. Different methods have been proposed to remedy this problem. In one of the early schemes, DFT-D2, damped van der Waals atom-atom C_6/R^6 correction terms are added to standard DFT energies.[76,77] The C_6 coefficients, along with the parameters in the damping function, are determined by fitting the DFT-D2 interaction energies to high-level wave function-based calculations on selected dimers. The major drawback of this approach is that the C_6 coefficients are "fixed" and cannot account for changes in the chemical environment of the targeted systems.

Recently, Tkatchenko and Scheffler[78] introduced a modified version of DFT-D2 where the C_6 coefficients are determined using the Hirshfeld charges[79] calculated using an atom-in-a-molecule decomposition approach. Specifically, the effective C_6^{eff} coefficient for the ith atom in the solid is defined relative to its "free atom" value C_6^{free} as

$$C_6^{\text{eff}} = \left(\frac{V_A^{\text{eff}}}{V_A^{\text{free}}} \right)^2 C_6^{\text{free}}, \tag{6}$$

where C_6^{free} is determined using time-dependent DFT, and V_A^{eff} and V_A^{free} are the Hirshfeld volumes of the atom-in-a-molecule and of the free atoms. In this method, the van der Waals dispersion is sensitive to the chemical environment of each atom through the Hirshfeld charges.

In our work, we will the vdW-TS approach to include van der Waals dispersion in the standard DFT energies. This procedure adds a negligible amount of computational time compared to DFT calculations and is thus suitable for our large-scale calculations. We have recently implemented this method in VASP, ABINIT, and BigDFT.[80]

4.3 Displacement-Force Method

Force constants can be calculated directly from their definitions given in Eq. (2).[31,46,81,82] First, a series of small displacements are applied to selected atoms in a supercell containing many unit cells. The resulting forces are calculated via the Hellmann-Feynman theorem. The force constants are then calculated by numerically differentiating the forces. ***Through careful consideration of crystal symmetry and appropriate selection of the atomic displacements, accurate force constants through the quartic terms can be efficiently obtained.***[31,83,84] We call this approach the
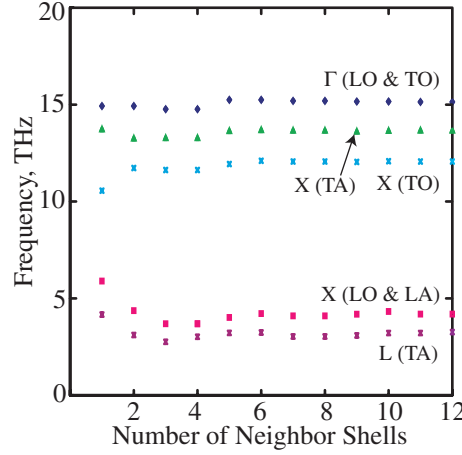
Figure 6: Convergence of DFPT frequencies for bulk silicon at selected points in the Brillouin zone. All values are in excellent agreement with experimental data (see Fig. 4).

displacement-force method, part of a broader class of so-called direct methods.[‡]

The displacement-force method has the following advantages:

- The implementation is straightforward as DFT calculations are only used to obtain the forces. The method can work with any code.

- The quartic force constants do not require additional formalism, as is the case for DFPT.

- It is ideally suited for a two-level parallelization. The DFT force calculations for each set of displacements can be performed in parallel and calculations for different sets of displacements can be performed simultaneously.

The challenge in using the displacement-force method is that large supercells are required to sample a fine resolution of phonon modes. The DFT codes we plan to use, ABINIT and BigDFT, are both efficiently parallelized, allowing us to run jobs over hundreds of cores. Additionally, because some of the materials of interest are non-polar (zeolites, Zintl compounds), the atomic interactions are short-range and many of the force constants will be zero. As an example, consider bulk silicon. To identify the range of the atomic interactions, we took the output from a Quantum Espresso DFPT calculation and set all the harmonic force constants beyond a certain cutoff radius to zero. We then solved the eigenvalue problem needed to get the phonon frequencies. The results for selected points in the Brillouin zone are shown in Fig. 6. When interactions up to the sixth neighbor shell (0.7 nm) are included, all frequencies are within 1% of their converged values. We will perform a similar analysis for the large unit cell crystals.

[‡]The displacement-force method is distinct from the frozen phonon method, where the energy changes that result from atomic displacements corresponding to guessed eigenvectors are used to directly predict the harmonic frequencies.[85] The frozen-phonon method does not provide information regarding the force constants, is limited to phonons whose wavelength is comparable to the unit cell size, and is only easily performed for high-symmetry directions.

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4.4 Density Functional Perturbation Theory

Under the adiabatic approximation, the harmonic force constants are given by[29]

$$\frac{\partial^2 E}{\partial u_{i,\alpha} \partial u_{j,\beta}} = \frac{\partial^2 E_{ion-ion}}{\partial u_{i,\alpha} \partial u_{j,\beta}} + \int \frac{\partial n(\mathbf{r})}{\partial u_{j,\beta}} \frac{\partial E_R}{\partial u_{i,\alpha}} d\mathbf{r} + \int n(\mathbf{r}) \frac{\partial^2 E_R}{\partial u_{i,\alpha} \partial u_{j,\beta}} d\mathbf{r}, \tag{7}$$

where $n(\mathbf{r})$ is the ground-state electronic charge density. The first term on the right side corresponds to electrostatic interactions between the ions and is straightforward to evaluate. The second and third terms are related to the electronic degrees of freedom. The energy derivatives can be evaluated directly. The ground state electronic charge density can be obtained from a DFT calculation. To evaluate the derivatives of the charge density, DFPT is required.[29] In DFPT, linear response theory is applied to the Kohn-Sham equations used to solve for the electronic charge density to determine how the solutions are affected by small perturbations. While DFPT has been widely used for characterizing electronic contributions to thermodynamic properties, its application to modeling anharmonic lattice effects remains computationally challenging.

Using the $2n + 1$ theorem, the first derivative of the electron density can be used to obtain the cubic force constants needed to predict phonon relaxation times in anharmonic lattice dynamics calculations. Calculating the quartic force constants, needed to predict anharmonic frequency shifts, requires a second-order perturbation to the electronic charge density and is significantly more challenging than calculating the harmonic and cubic force constants. Efficient methods are being developed,[86,87] which we will explore as they mature.

The advantage of DFPT is that calculations are performed at the unit cell level. Large supercells are not required to finely resolve the Brillouin zone. The disadvantages of DFPT are that:

- Due to the complexity of the required calculations (DFPT leads to a problem requiring a self-consistent solution), the ability to analyze arbitrary three-phonon interactions has only been developed for diamond and zinc-blend structure,[30,37,88] and is not a feature of available DFT/DFPT codes. The functionality of these codes is typically restricted to studying three-phonon interactions where one phonon is at the center of the Brillouin zone.
- The theory underlying the quartic force constants is complex.

4.5 Proposed Tasks

Important questions remain regarding the computational demands, implementation complexity, and accuracy of the displacement-force and DFPT approaches for calculating force constants. To address these questions, we propose the following research plan. Our initial emphasis will be on the displacement-force method. Because it is more computationally straightforward than DFPT, this approach will allow us to generate quantum mechanics-based force constants for input to the thermal transport modeling in the first year of the program. The existing DFPT functionality in ABINIT will allow us to make detailed comparisons between the two approaches.

We will first develop an implementation of the displacement-force method compatible with BigDFT, starting from the harmonic force constants, then considering the cubic and quartic terms. Our displacement-force implementation will be based on the freely available program PHON,[82] which can generate input and analyze output from any DFT package. PHON currently can only predict the harmonic force constants. We will extend its capabilities to include cubic and quartuc force constants, taking advantage of symmetry as described by Esfarjani.[31] We will carefully examine the size of the displacement step. Too large a step will lead to incorrect results, while too small a step may introduce numerical errors in the higher-order force constants. The initial development will be done using silicon as a test material. Large silicon supercells can easily be created to simulate the calculation conditions for the disordered materials and large unit cell crystals to be studied in Thrust B. We will test our implementation and the accuracy of the displacement-force

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method by comparing to DFPT calculations performed using ABINIT. Of particular interest will be to determine how accurate the force calculations need to be to ensure accurate cubic and quartic force constants.

As the work in Thrust B proceeds, unit cells for amorphous systems will become available and will be analyzed. For these and the large unit cell crystals, the massively-parallel nature of BigDFT is crucial, allowing us to perform force constant calculations for systems containing up to thousands of atoms, which have not previously been attempted. TeraGrid resources (e.g., the Pittsburgh Supercomputing Center) will be used to full advantage in these calculations. BigDFT also runs over multiple graphical processing units (GPUs) and we will have access to a GPU cluster at the University of Pittsburgh for performing such calculations.

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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,

$$\mathbf{q} = -\mathbf{k}\nabla T, \tag{8}$$

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]

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

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

$$c_v = \sum_i c_{v,i} = \sum_i \frac{k_{\mathrm{B}}x_i^2 e^{x_i}}{(e^{x_i}-1)^2}, \tag{10}$$

where $x_i = \hbar\omega_i/k_{\mathrm{B}}T$, $\hbar$ 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 Phillpot[98] 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.

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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 silicon[105] 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 empircal 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

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[¶]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]

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

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-dependance 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 that 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

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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.*
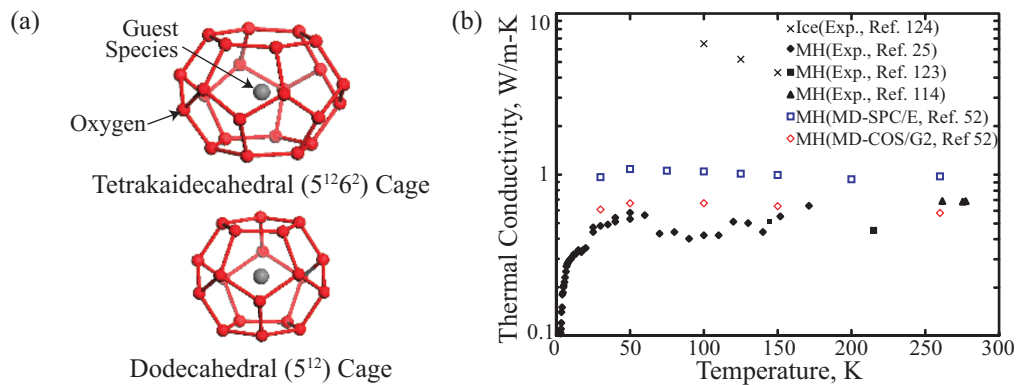

Figure 7: (a) Structures of tetrakaidecahedral ($5^{12}6^2$) and dodecahedral (5^{12}) cages that form gas hydrates. Water molecules and guest species are red and gray balls. Hydrogen bonds between water molecules are red sticks. (b) Thermal conductivity of methane hydrate (MH)[25,52,114,123] and ice[124] measured in experiments and predicted from MD simulations using the SPC/E and COS/G2 potentials.

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The thermal conductivities of methane hydrate [see Fig. 7(b)] and other gas hydrates are anomalous in that their values are low and weakly temperature-dependent, features typical of amorphous materials. Multiple mechanisms have been proposed for this behavior, notably phonon scattering caused by host-guest coupling.[125,126] Jordan and co-workers recently showed, using classical MD simulation, that the presence of the methane guest molecules significantly impacts the calculated thermal conductivity only at temperatures below 50 K.[52] This result indicates that the complicated lattice structure, rather than host-guest coupling, is the main factor establishing the anomalous thermal conductivities.

The systems to be studied are methane and CO_2 hydrates, which have the type I hydrate structure comprised of dodecahedral (5^{12}) and tetrakaidecahedral ($5^{12}6^2$) cages [see Fig. 7(a)]. The empty unit cell contains 46 water molecules (i.e., 138 atoms). Methane and CO_2 molecules are small enough that they can occupy both the large and small cages. The calculations will be carried out assuming occupation of all the cages as well as fractional occupations that correspond to those in experimental samples. We will be particularly interested in the potential localization of vibrational modes and the relative contribution of different vibrational entities to the thermal conductivity.

Gas hydrates, like Ice Ih, display proton disorder resulting from the fact that each proton has two possible locations. Consequently, we will carry out lattice dynamics calculations of the thermal conductivity of methane and CO_2 hydrates for the twelve lowest-energy proton arrangements found from force field calculations. We will then Boltzmann average these results, which will account in a rough manner for the fact that numerous structures, differing in the proton positions, are sampled experimentally.

Also of interest is that the measured thermal conductivities of methane hydrate displays structure in the 70-120 K range, which is not reproduced by classical MD simulation. We speculate that this behavior is due to quantum effects, which we will be able to check due to the fully-quantum nature of our calculation framework.

Zeolites

Zeolites are a subset of the silica structures, materials built from SiO_4 tetrahedra.[8] One length scale up from the SiO_4 tetrahedron, zeolites can be described by secondary building units (SBUs), which are named based on their geometry. For example, a 6R SBU is a ring structure made from six oxygen atoms and six silicon atoms. The unit cell typically contains many SBUs and can be a cage [e.g., in sodalite (SOD), zeolite-A (LTA), or faujasite (FAU), see Fig. 8] or contain large pores that run through the structure (e.g., zeolite MFI).[127] Zeolite frameworks typically contain aluminum atoms in place of some of the silicon atoms and the structures are filled with non-framework cations and diffusing/adsorbed gas species. Zeolites are of interest to gas storage and separation application, and can be used as catalysts.

While there has been a considerable amount of experimental and theoretical work done to investigate the structure of zeolites and the transport of molecules through them,[128–130] there has been limited work done to describe the nature of the thermal transport in these materials.[21,131–135] Zeolites are generally synthesized as powders of micron-sized crystals (to minimize the length of diffusion paths in transport applications), from which it is difficult to extract bulk phase properties. Even then, it is often only possible to make single crystals with sub-millimeter dimensions, making direct property measurements difficult.

The thermal conductivities of quartz and a set of all-silica zeolites, predicted by McGaughey and Kaviany using classical MD simulation, are shown in Fig. 8.[9] As one moves from quartz to SOD to FAU to LTA, the magnitude of the thermal conductivity and the strength of the temperature dependence decrease. ***These intriguing results suggest a transition from thermal transport***
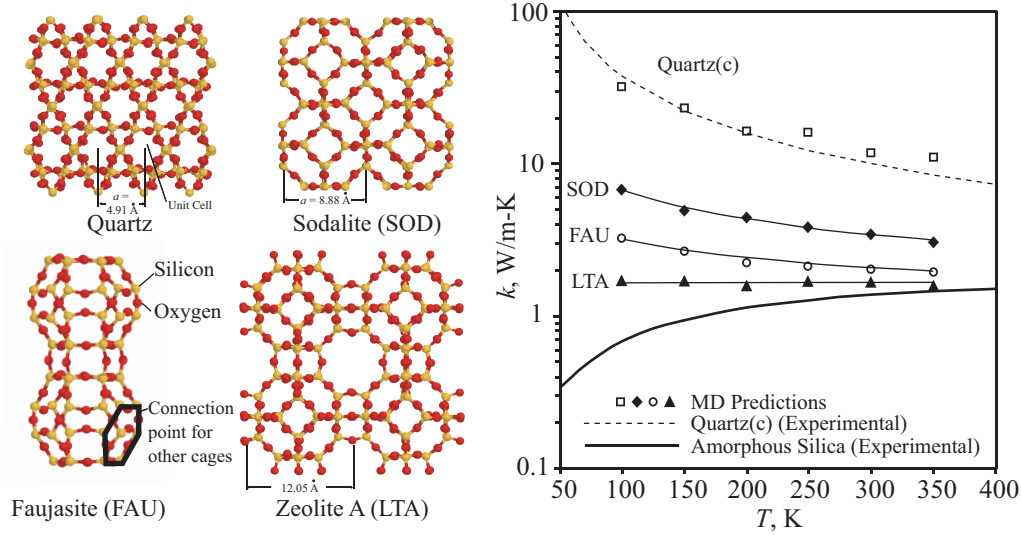
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Figure 8: MD-predicted thermal conductivities of quartz (*c*-direction) and three all-silica zeolites.[9] The lines through the zeolite data are to help guide the eye.

dominated by phonons to diffuson-dominated transport and the possible existence of localized vibrations. This latter hypothesis is supported by McGaughey and Kaviany, who found that the relative thermal conductivities of these silica structures can be qualitatively understood by considering sub-unit cell effects.

Greenstein and co-workers recently synthesized micron-thick LTA and MFI films and measured their thermal conductivities.[133–135] The found that the films had thermal conductivities of order 1 W/m-K between temperatures of 150 and 450 K, with a temperature dependence similar to amorphous materials (i.e., thermal conductivity increased slowly with increasing temperature). They used harmonic lattice dynamics calculations and simple phonon scattering models to study the effects of the aluminum composition and non-framework metal cations on thermal conductivity. They did not explicitly consider phonon interactions in their calculations, however, so that it is difficult to elucidate the mechanisms of thermal transport from their results.

In the proposed work, we will focus our attention on the zeolites LTA (576 atoms in a unit cell that contains well-defined cages connected by oxygen bridges) and MFI (which is not cage-based, but contains a pore network built from 288-atom unit cells). Consideration of these structures, with different aluminum contents, will allow us to compare our predictions to the experimental results of Greenstein and co-workers.[133–135] As with the hydrate, our objective will be to identify thermal transport mechanisms between unit cells and within unit cells. We will also study how the presence of adsorbed gas molecules affects the thermal transport.

Zintl Compounds

The ideal thermoelectric material is a phonon-glass, electron-crystal (PGEC).[11] In a PGEC, electrons have high mobility, while phonons are quickly scattered, leading to a large thermoelectric figure of merit. Recent efforts in thermoelectric material development have focused on lowering thermal conductivity. Significant work has been done related to nanostructuring (e.g., semiconductor superlattices,[136–138] dispersing nanoparticles in a bulk material,[139] or ball-milled alloys[140,141]). An alternative approach is to use complex unit cells.[11] In clathrates and skutterudites, rattler atoms in the unit cell cages can scatter phonons. In Zintl compounds, which we will study here, sub unit cell structures allow for the decoupling of the phonon and electron transport.

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A Zintl compound (e.g., $Ca_xYb_{1-x}Zn_2Sb_2$, $Yb_{14}Al_xMn_{1-x}Sb_{11}$) is a small bandgap semiconductor whose elements have a large different in electronegativity. The unit cell typically consists of a few hundred atoms and contains distinct structural features. In $Yb_{14}MnSb_{11}$, see Fig. 1(c), the 208 atom unit cell contains $[MnSb_4]^{9-}$ tetraherdra, polyatomic $[Sb_3]^{7-}$ cations, and isolated Sb^{3-} and Yb^{2+} cations.[13] The larger structures are covalently bonded, leading to a continuous region of high electron mobility. Doping the ionic substructure leads to high rates of phonon scattering without disrupting the electronic transport. Zintl compounds have been found to have thermal conductivity as low as 0.4 W/m-K (about half of which is related to phonons), making them candidates to replace the SiGe alloys that have dominated high-temperature thermoelectrics for many decades.[11,13,142,143]

We are not aware of any atomic-level modeling work on thermal transport in Zintl compounds. Our objective in this part of the proposed work is to predict their phonon properties, so that the specific reasons why these materials have such low thermal conductivities can be elucidated. From theses results, we will be able to suggest design strategies for further reduction and establish a lower limit to thermal conductivity. We will focus the initial attention on $Yb_{14}MnSb_{11}$, for which experimental thermal conductivity measurements are available between temperatures of 300 and 1200 K.[13,143] Once we have uncovered the mechanisms of thermal transport, we will consider this structure but with Al in place of some of the Mn atoms (i.e.,$Yb_{14}Al_xMn_{1-x}Sb_{11}$), to determine how the phonon properties and thermal conductivity are affected by small perturbations in the unit cell. The analysis will be performed in a similar manner to the proton-disorder studies in the gas hydrates, whereby multiple configurations will be considered and then Boltzmann-averaged to give a result typical of a bulk experimental system.

5.4 Task B3: Speed and Accuracy of Thermal Conductivity Prediction

Reducing the computation time of anharmonic lattice dynamics calculations, which scale with the fourth-power of the number of atoms in the unit cell, is of particular importance for the large unit cells to be studied in Tasks B1 and B2. Using silicon as a test material, in Task B3 we will explore a series of approximations in the lattice dynamics and thermal transport calculations to assess the balance between computation time and accuracy. Specifically, we will:

- Perform the anharmonic lattice dynamics calculations on a coarse Brillouin zone and interpolate to the desired frequency shifts and relaxation times. The interpolated results can be compared to predictions from a finer resolution Brillouin zone to assess their accuracy.

- Ignore the frequency shifts. This approximation may be suitable for materials with low coefficients of thermal expansion.

We will also examine the sensitivity of the lattice dynamics calculations to inaccuracies in the force constants, which may be a result of calculation approximations or precision issues. In doing so, we may be able to reduce the computational cost of the required DFT calculations.

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6   Vision

We are committed to building a research partnership that will last beyond the extent of the proposed program. Potential future projects include:

- Extending first-principles thermal transport modeling to include:
  - Interfaces, prevalent in nanostructured materials. The identification and classification of vibrational modes in disordered materials is important in determining how they couple to phonons at crystal/amorphous interfaces.
  - Anharmonic effects in the calculation of mode diffusivities.
  - Electron-phonon interactions.
- Thermal transport in low-dimensional solids (e.g., carbon nanotubes, silicon nanowires, graphene), where available models cannot explain measured thermal conductivities.[144–150]
- Exploring DFT-MD based approaches for predicting phonon properties and thermal conductivity.[49,60]
- Investigating how emerging computer hardware [e.g., multi-core processors and graphical processing units (GPUs)] can be used in our computational framework.

The ability to accurately predict force constants and phonon properties will also have an impact beyond thermal transport. For example: (i) The large data sets of force constant we generate could be used to develop high-fidelity force fields for use in MD simulations. (ii) Phonon frequencies and relaxation times are needed to interpret Raman and infrared scattering experiments. (iii) Phonon properties are needed to understand phase transitions in solids (e.g., the amorphous-crystalline phase change in $Ge_2Sb_2Te_5$[151]).

7   Coordination

7.1   Work Plan

The work plan is shown in Fig. 9. The research results will be presented at ACS, APS, ASME, and MRS symposia and conferences, and published in chemistry, physics, and engineering journals.
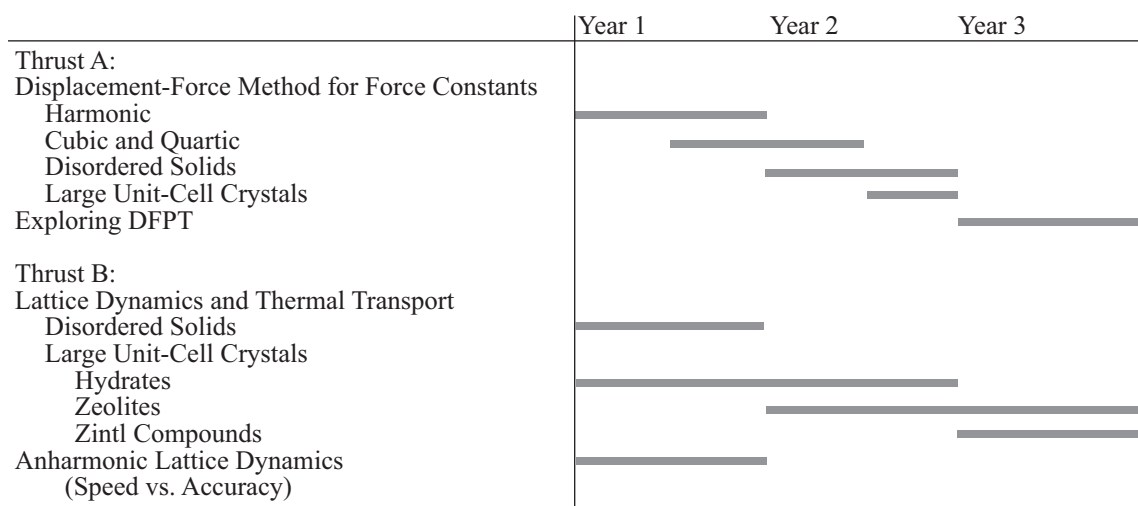

Figure 9: Research task time line

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7.2 Team Members

McGaughey models nanoscale transport phenomena with a focus on thermal transport and fluid structure and flow.[9, 21–23, 32–34, 34, 36, 42, 56, 60, 112, 152–162] He has developed techniques for studying phonon transport in solids using MD simulations and lattice dynamics calculations and has applied them to understand how atomic structure and thermal transport are related in complex crystals and in superlattices. McGaughey will manage the overall project coordination and lead the research efforts in Thrust B.

Jordan is an expert in electronic structure theory and in the computer modeling of hydrogen-bonded systems.[163–184] Recently, he has worked on the thermal conductivity and decomposition mechanisms of hydrates.[52, 102, 115, 185] Jordan will lead the research efforts in Thrust A and be involved with the hydrate work in Thrust B.

Al-Saidi is an expert in advanced electronic structure techniques (e.g., ab initio quantum Monte Carlo methods).[186–194] He has extensive experience on large-scale calculations on the Tera-Grid. He is currently collaborating with Jordan on developing models for describing dispersion in density functional methods. Al-Saidi will oversee the implementation of the force-displacement technique into BigDFT.

The University of Pittsburgh recently established a Center for Simulation and Modeling, with Jordan as co-director. The Center has a staff of four Ph.D.-level consultants who are available to assist with optimization and parallelization of computer codes.

The research tasks will be primarily performed by a post-doctoral fellow at the University of Pittsburgh (advised by Jordan and Al-Saidi) and a Ph.D student at Carnegie Mellon University (advised by McGaughey). Additional graduate student effort (at no cost) will be provided through the Carnegie Mellon University Mechanical Engineering Masters in Science - Project program, where students are required to carry out a research project under the supervision of a faculty member.

7.3 Coordination Mechanisms

Carnegie Mellon University and the University of Pittsburgh are within a fifteen minute walk of each other. This close proximity will allow the entire research team to meet on a bi-weekly basis. The graduate and undergraduate students in the McGaughey and Jordan groups will work closely with one another, as well as with Al-Saidi.

Internet-based computer file repositories will provide instant and synchronized access to all the code-development and research documentation information, and will be used to coordinate paper writing between the collaborators. The computational tools will be made available through BigDFT, Nanohub,[195] ThermalHub,[196] and the McGaughey group wiki.[197]

7.4 Computational Facilities

For smaller calculations, computational time will be available on dedicated clusters in the McGaughey and Jordan groups (see facilities section). For larger calculations, we will apply for time on TeraGrid, where the PIs all have experience in proposal preparation and facilities use.

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[173] T. Sommerfeld and K. D. Jordan, "Electron binding motifs of $(H_2O)_n$-clusters." *Journal of the American Chemical Society* **128** (2006) 5828–5833.

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Alan McGaughey, Wissam Al-Saidi, and Kenneth Jordan

Alan J. H. McGaughey

Education and Training:

McMaster University, Dept. of Mechanical Engineering, Bachelor of Engineering, 1998.
University of Toronto, Dept. of Mechanical and Industrial. Eng, Master of Applied Science, 2000.
University of Michigan, Dept. of Mechanical Engineering, Doctor of Philosophy, 2004.
University of Florida, Dept. of Materials Science and Eng., Postdoctoral Fellow, 2004–2005.

Research and Professional Experience:

Associate Professor, Carnegie Mellon University, Dept. of Mechanical Engineering, 2010-
Courtesy appointment, Dept. of Materials Science and Engineering, 2010-
Assistant Professor, Carnegie Mellon University, Dept. of Mechanical Engineering, 2005-2010
Struminger Junior Faculty Fellow, 2009

Publications:

1. J. E. Turney, E. S. Landry, A. J. H. McGaughey, and C. H. Amon, "Predicting phonon properties and thermal conductivity from anharmonic lattice dynamics calculations and molecular dynamics simulations." *Physical Review B* **79**, 064301 (2009).

2. J. E. Turney, A. J. H. McGaughey, and C. H. Amon, "Assessing the applicability of quantum corrections to classical thermal conductivity predictions." *Physical Review B* **79**, 224305 (2009).

3. S. Shenogin, A. Bodapati, P. Keblinski, and A. J. H. McGaughey, "Predicting the thermal conductivity of inorganic and polymeric glasses: The role of anharmonicity." *Journal of Applied Physics* **105** (2009) 034906.

4. A. J. H. McGaughey and M. Kaviany, "Thermal conductivity decomposition and analysis using molecular dynamics simulations. Part II. Complex silica crystals." *International Journal of Heat and Mass Transfer* **47**, 1799-1816 (2004).

5. A. J. H. McGaughey and M. Kaviany, ``Observation and description of phonon interactions in molecular dynamics simulations." *Physical Review B* **71**, 184305 (2005).

6. D. P. Sellan, E. S. Landry, J. E. Turney, A. J. H. McGaughey, and C. H. Amon, "Size effects in molecular dynamics thermal conductivity predictions." *Physical Review B* **81**, 214305 (2010).

7. J. A. Thomas, J. E. Turney, R. M. Iutzi, C. H. Amon, and A. J. H. McGaughey, "Predicting phonon dispersion relations and lifetimes from the spectral energy density." *Physical Review B* **81**, 081411(R) (2010).

8. J. E. Turney, A. J. H. McGaughey, and C. H. Amon, "In-plane phonon transport in thin films." *Journal of Applied Physics* **107**, 024317 (2010).

9. E. S. Landry and A. J. H. McGaughey, "Thermal boundary resistance predictions from molecular dynamics simulations and theoretical calculations." *Physical Review B* **80**, 165304 (2009)

10. E. S. Landry, M. I. Hussein, and A. J. H. McGaughey, "Complex superlattice unit cell designs for reduced thermal conductivity." *Physical Review B* **77**, 184302 (2008).

Synergistic Activities:

- Developed and taught "Molecular Simulation of Materials," a graduate course offered in the Spring 2006, Spring 2007, and Spring 2010 semesters.
- Host of annual Multidisciplinary Simulator's Meeting at CMU.
- Topic Organizer, 2008 and 2009 Summer Heat Transfer Conferences.
- Organizer, Telluride Science Research Center workshop "Thermal Transport at the Nanoscale," June 2010.
- Organizer, 2011 MRS Spring Meeting Symposium BB: "Nanoscale Heat Transport: From Fundamentals to Devices"

Collaborators and Co-Editors:

Anderson, Willian (Advanced Cooling Technologies), Amon, Cristina (University of Toronto); Anna, Shelley (Carnegie Mellon University); Bain, James (Carnegie Mellon University); Davis, Robert (Carnegie Mellon University; Fedder, Gary (Carnegie Mellon University), Hulbert, Greg (University of Michigan); Hussein, Mahmoud (University of Colorado, Boulder); Islam, Mohammad (Carnegie Mellon University); Jordan, Ken (University of Pittsburgh); Li, Ju (University of Pennsylvania); Kaviany, Massoud (University of Michigan); Keblinski, Pawel (Rensellaer Polytechnic Institute); Moran, Matthew (Isotherm Technologies); Phillpot, Simon (University of Florida); Pipe, Kevin (University of Michigan); Sinnott, Susan (University of Florida); Sholl, David (Georgia Institute of Technology); Wang, Yang (Pittsburgh Supercomputing Center); Yang, Judy (University of Pittsburgh), Yao, Shi-Chune (Carnegie Mellon University)

Graduate and Postdoctoral Advisors and Advisees:

Advisors: Charles Ward, University of Toronto (M. A. Sc), Massoud Kaviany, University of Michigan (Ph.D.) Simon Phillpot, Susan Sinnott, University of Florida, Judith Yang, University of Pittsburgh (Postdoctoral).

Advisees: Eric Landry (M.S, 2007, Ph.D, 2009, Lytron, Inc.), Joe Turney (Ph.D., 2009, post-doc, 2010, United Technologies Research Center), John Thomas (Ph.D, 2010, Johns Hopkins University Applied Physics Laboratory), Minyoung Lee (Ph.D., expected 2010), Jason Larkin (Ph.D., expected 2013), Haibin Chen (post-doc, 2009-). Sang eun Jee (post-doc, 2010-), Alex Massicotte (Ph.D., expected 2014), Wee-Liat Ong (Ph.D., expected 2014).

KENNETH D. JORDAN
Distinguished Professor of Computational Chemistry, University of Pittsburgh (www.pitt.edu/~jordan)

(a) Education and Training

Northeastern University	Chemistry	B.A., 1970
Massachusetts Institute of Technology	Physical Chemistry	Ph.D, 1974

(b) Research and professional Experience

President, Telluride Science Research Center	2009 - present
Co-director, Center for Simulation and Modeling, Univ. of Pittsburgh	2008 - present
Univ. of Pittsburgh, Distinguished Professor of Computational Chemistry	2007 - present
President-Elect, Telluride Science Research Center	2007 - 2008
Faculty Fellow, Institute for Advanced Energy Systems, NETL	2007 - present
Senior Editor, Journal of Physical Chemistry	2004 - present
Telluride Science Research Center Board	2004 - present
ORISE Fellow, National Energy Technology Laboratory, DOE	2003 - 2007
Member, Keck Molecular Electronics Laboratory, Univ. of Pittsburgh	2003 - 2007
Member, Institute of Nanoscience & Engineering, Univ. of Pittsburgh	2003 - present
Associate Faculty, Dept. of Comp. Biology, Univ. of Pittsburgh	2002 - present
University of Pittsburgh, Chair, Dept. of Chemistry	2002 - 2005
Advisory Board, Petroleum Research Fund, ACS	2002 - 2005
Chair, American Conference on Theoretical Chemistry	2002
Editorial Board, Journal of Chemical Physics	2001 - 2003
Secretary/Treasurer, Physical Chemistry Division, ACS	2001 - 2006
Visiting Professor, University of Cambridge	2001
Chair, Vice Chair, Theoretical Chem. Subdivision, Phys. Chem. Div., ACS	1998 - 2000
Director, Center for Molecular and Materials Simulations, Univ. Pittsburgh	1999 - present
Editorial Board, Theoretical Chemistry Accounts	1997 - 2007
Visiting Fellow, JILA, Univ. of Colorado	1997
Promotion of Chemistry, Visiting Professor, Taiwan	1995
Affiliate Staff Scientist, Pacific Northwest Laboratories	1994 - 1997
Visiting Professor, University of Utah	1994 - 1995
Visiting Fellow, Australian National University	1992
Chair, Vice Chair, Theoretical Chem. Subdivision, Phys. Chem. Div., ACS	1988 - 1990
Member, Joint NCSA/PSC Peer Review Board	1986 - 1988
University of Pittsburgh, Professor of Chemistry	1985 - 2007
Program Director for Theoretical Chemical Physics, NSF	1984 - 1985
University of Pittsburgh, Associate Professor of Chemistry	1980 - 1985
University of Pittsburgh, Assistant Professor of Chemistry	1978 - 1980
Yale University, Assistant Professor of Engineering and Applied Science	1976 - 1978
Yale University, J. W. Gibbs Instructor of Engineering and Applied Science	1974 - 1976

(c) Publications

1. H. Jiang and K. D. Jordan, "Comparison of the Properties of Xenon, Methane, and Carbon Dioxide Hydrates from Equilibrium and Non-equilibrium Molecular Dynamics Simulations", J. Phys. Chem. C, **114**, 5555-5564 (20010).
2. E. Myshakin, H. Jiang, R. Warzinski, and K. D. Jordan, "Molecular Dynamics Simulations of Methane Hydrate Decomposition," J. Phys. Chem. A, **113**, 1913-1921 (2009).
3. H. Jiang, E. Myshakin, K. D. Jordan, and R. Warzinski, "Molecular Dynamics Simulations of the Thermal Conductivity of Methane Hydrate", J. Phys. Chem. B, **112**, 10207-10216 (2008).
4. H. Jiang, C. Taylor, and K. D. Jordan "Molecular Dynamics Simulations of Methane Hydrate using Polarizable Force Fields", J. Phys. Chem. B, **111**, 6486-6492 (2007).

5. A. DeFusco, D. Schofield and K. D. Jordan, "Comparison of Models with Distributed Polarizable Sites for Describing Water Clusters," Mol. Phys., **105**, 2681-2696 (2007).
6. R. Kumar, F. F. Wang, G. Jenness, and K. D. Jordan, "A Second Generation Distributed Point Polarizable Water Model", J. Chem. Phys., **132**, 014309:1-12 (2010).
7. G. R. Jenness, O. Karalti, K. D. Jordan, "Benchmark Calculations of Water–Acene Interaction Energies: Extrapolation to the Water–Graphene Limit and Assessment of Various Dispersion–Corrected DFT Methods", Phys. Chem. Chem. Phys., **12**, 6375-6381 (2010).
8. D. P. Schofield and K. D. Jordan, "Molecular Dynamics Simulations of Bromine Clathrate Hydrates", J. Phys. Chem. B, **113**, 7431-7438 (2009).
9. D. P. Schofield and K. D. Jordan, "Theoretical Investigation of the Electronically Excited States of Chlorine Hydrate", J. Phys. Chem. B, **111**, 7690-7694 (2007).
10. T. Sommerfeld, A. DeFusco, and K. D. Jordan, "Model Potential Approaches for Describing the Interactions of Excess Electrons with Water Clusters: Incorporation of Long-range Correlation Effects", J. Phys. Chem. A, **112**, 11021-11035 (2008) (feature article, cover art).

(d) Synergistic Activities
1. President, President-Elect, Telluride Science Research Center (2007- present).
2. Co-chair, Molecular and Ionic Clusters Conference, Niigata, Japan (2010).
3. Senior Editor, Journal of Physical Chemistry (2004-present).
4. Led the effort to establish the University's Center for Simulation and Modeling (2008).
5. Co-organizer, TSRC Workshop on Polarizable Force Fields (2010).

(e) Collaborators and Co-editors
1. Collaborators: Wissam Al-Saidi (Univ. of Pittsburgh), Joel Bowman (Emory Univ.), Kay Brummond (Univ. Pittsburgh), Stuart Carter (Univ. Reading), Richard Christie (Univ. of Pittsburgh), Ted Cohen (Univ. Pittsburgh), Bob Compton (Univ. Tennessee), Mike Duncan (Univ. Georgia), Robert Hinde (Univ. Tennessee), Mark Johnson (Yale Univ.), David Leitner (UNLV), Anne McCoy (Ohio State Univ.), Alex Kaledin (Emory Univ.), Martina Kaledin (Kennesaw State Univ.), Eugene Myshakin (NETL), Hrvoje Petek (Univ. of Pittsburgh), Thomas Sommerfeld (Southeastern Louisiana State Univ.), Dan Sorescu (NETL), Jan Steckel (NETL), Charles Taylor (NETL), Al Viggiano (Air Force Research Lab), Bob Warsinski (NETL), John Yates (Univ. Virginia), Server Yilmaz (Univ. of Pittsburgh), Timothy Zwier (Purdue Univ.)
2. Ph.D. advisor: Professor Robert Silbey (MIT); **Postdoctoral advisor:** None
3. Thesis Advisor and Postgraduate Scholar Sponsor:
 Postdoctoral fellows during past five years and their present locations: Hao Jiang (Univ. Michigan), Revati Kumar (Boston Univ.), Haitao Liu (Inst. Appl. Phys. and Comp. Math. Beijing, China), Daniel Schofield (Seattle Pacific Univ.), Fangfang Wang (Univ. of Pittsburgh)
 Present graduate students: Jing Ding, Li Feng, Glen Jenness, Ozan Karalti, Wendy Lampart, Xiaoge Su, Vamsee Voora, Jiawei Xu, Guozhen Zhang
 Former Ph.D. students during past five years and current locations: Alex Bayden (Virginia Commonwealth Univ.), TaeHoon Choi (Univ. of Chicago), Jun Cui (Infinite Campus, Inc.), Albert DeFusco (Iowa State Univ.), Kadir Diri (Univ. Southern California), Hanbin Liu (Sandia National Lab), Valerie McCarthy (BASF), Brad Tsai (National Taiwan Normal Univ.)

WISSAM A. AL-SAIDI

(a) Education and Training:

Lebanese University	Physics	B.S., 1996.
Ohio University	Physics	M.S., 1999.
Ohio State University	Physics	Ph.D, 2003.
College of William and Mary	Physics	Postdoctoral Fellow, 2003–2006.
College of William and Mary	Physics	Research Scientist, 2006.
Cornell University	Physics	Postdoctoral Fellow, 2006-2008.
University of Pennsylvania	Chemistry	Postdoctoral Fellow, 2008-2009.

(b) Research and professional Experience

University of Pittsburgh, Visiting Research Assistant Professor in department of Chemical and Petroleum Engineering, 2009-present

(c) Publications:

1. De-Li Chen, W. A. Al-Saidi and J. Karl Johnson, "Adsorption of Ar, Kr, and Xe on Metal Surfaces: van der Waals Density Functional Investigations", submitted to Phys. Rev. B. (2010).

2. W. A. Al-Saidi and Andrew M. Rappe, "Density functional study of $PbTiO_3$ nano-capacitors with Pt and Au electrodes", Phys. Rev. B. **82**, 155304 (2010).

3. F.-F. Wang, G. Jenness, W. A. Al-Saidi, and K. D. Jordan, "Assessment of the Performance of Common Density Functional Methods for Describing the Interaction Energies of $(H_2O)_6$ Clusters", Journal of Chemical Physics **132**, 134303 (2010).

4. W. A. Al-Saidi, Eric J. Walter and Andrew M. Rappe, "Optimized norm-conserving Hartree-Fock pseudopotentials for planewave calculations", Physical Review B **77,** 075112 (2008).

5. W. A. Al-Saidi, Shiwei Zhang and Henry Krakauer, "Bond breaking with auxiliary-field quantum Monte Carlo", Journal of Chemical Physics **127**, 144101 (2007).

6. W. A. Al-Saidi, Shiwei Zhang and Henry Krakauer, "Auxiliary-field quantum Monte Carlo of molecular systems with a Gaussian basis", Journal of Chemical Physics **124**, 224101 (2006).

7. Shiwei Zhang, Henry Krakauer, W. A. Al-Saidi, and Malliga Suewattana, "Quantum simulations of realistic systems by auxiliary fields", Comp. Phys.

Comm. **169**, 394 (2005).

8. W. A. Al-Saidi and D. Stroud, "Langevin vortex dynamics for a layered superconductor in the lowest Landau level approximation", Physical Review B **68**, 144511 (2003).

9. W. A. Al-Saidi and D. Stroud, "Phase Phonon Spectrum and Melting in a Quantum Rotor Model with Diagonal Disorder", Phys. Rev. B **67**, 024511 (2002).

10. W. A. Al-Saidi and D. Stroud, "Eigenstates of a small Josephson junction coupled to a resonant cavity", Physical Review B **65**, 014512 (2002).

(d) Synergistic Activities:

- Developed and taught "Electronic Structure: Theory, Simulations and Modeling", a graduate course for physics, chemistry, and engineering students at the University of Pittsburgh (Spring 2010 semester).
- Member, American Physical Society.
- Reviewer for Physical Review Letters, Physical Review B, The Journal of Physical Chemistry, Journal of Chemical Physics, Journal of Physics: Condensed Matter, Journal of Physics A: Mathematical and Theoretical, Modeling and Simulation in Materials Science and Engineering.

(e) Collaborators & Other Affiliations:

1. Collaborators:

Petek, Hrvoje (University of Pittsburgh), Johnson, Karl (University of Pittsburgh), Jordan, Kenneth (University of Pittsburgh), Krakauer, Henry (College of William and Mary), Purwanto, Wirawan (College of William and Mary), Rappe, Andrew (University of Pennsylvania), Stroud, David (Ohio State University), Umrigar, Cyrus (Cornell University), Walter, Eric (College of William and Mary), Zhang, Shiwei (College of William and Mary), Zhao, Jin (University of Pittsburgh).

2. Graduate and Postdoctoral Advisors:

David Stroud, Ohio State University (Ph.D.), Henry Krakauer and Shiwei Zhang, College of William and Mary (postdoctoral), Cyrus Umrigar , Cornell University (postdoctoral), Andrew Rappe, University of Pennsylvania (postdoctoral).

Current and Pending Support

Investigator: Alan McGaughey	

Support: ⊠ Current   ☐ Pending   ☐ Submission Planned in Near Future   ☐ *Transfer of Support

Project/Proposal Title: Multiscale Atomistic Simulation of Metal-Oxygen Surface Interactions: Methodological Development, Theoretical Investigation and Correlation with Experiment (co-PI, PI: Judith Yang, other co-PIs: Simon Phillpot and Susan Sinnott)

Source of Support: Department of Energy

Total Award Amount: $ 641,301   Total Award Period Covered 10/01/2007-08/31/2011

Location of Project: University of Pittsburgh

Person-Months Per Year Committed to the Project.   Cal: Acad: Sumr: 0.5

Support: ⊠ Current   ☐ Pending   ☐ Submission Planned in Near Future   ☐ *Transfer of Support

Project/Proposal Title: IDR - Carbon Nanotube Aerogel Networks for Next-Generation Thermal Management (PI, co-PIs: Shelley Anna, Mohammad Islam, and Kevin Pipe)

Source of Support: National Science Foundation

Total Award Amount: $ 965,874   Total Award Period Covered: 09/01/09-08/31/12

Location of Project: Carnegie Mellon University

Person-Months Per Year Committed to the Project.   Cal: Acad: Sumr: 0.5

Support: ⊠ Current   ☐ Pending   ☐ Submission Planned in Near Future   ☐ *Transfer of Support

Project/Proposal Title: Quantum Mechanics Driven Prediction of Nanostructure Thermal Conductivity

Source of Support: Air Force Office of Scientific Research

Total Award Amount: $ 358,846   Total Award Period Covered 05/01/2010-04/30/2013

Location of Project: Carnegie Mellon University

Person-Months Per Year Committed to the Project.   Cal: Acad: Sumr: 1.0

Support: ⊠ Current   ☐ Pending   ☐ Submission Planned in Near Future   ☐ *Transfer of Support

Project/Proposal Title: Stirling MicroCooler Array with Elemental In-Plane Flow (co-PI, PI: Gary Fedder, other co-PIs: William Anderson, Matthew Moran, Shi-Chune Yao)

Source of Support: DARPA

Total Award Amount: $ 2,600,000   Total Award Period Covered 06/01/2010-05/31/2013

Location of Project: Carnegie Mellon University

Person-Months Per Year Committed to the Project.   Cal: Acad: Sumr: 1.0

Support: ⊠ Current   ☐ Pending   ☐ Submission Planned in Near Future   ☐ *Transfer of Support

Project/Proposal Title: Phonon transport near and across semiconductor interfaces (PI, co-PI: Yang Wang, Pittsburgh Supercomputing Center)

Source of Support: NSF

Total Award Amount: $300,000   Total Award Period Covered 10/01/2010-09/30/2013

Location of Project: Carnegie Mellon University

Person-Months Per Year Committed to the Project.   Cal: Acad: Sumr: 0.25

Kenneth D. Jordan

Current Support
Project Title: Theoretical Studies of Water Clusters with Excess Protons and Electrons and of Biomolecule Energy Landscapes
Source of Support: National Science Foundation
Total Award Amount: $445,000
Summer Support: 0.5 months
Total Award Period Covered: 8/1/2008 – 7/31/2011

Project/Proposal Title: Coordinating Experiment and Theory to Understand how Excess Electrons are Accommodated by Water Networks through Model Studies in the Cluster Regime
Source of Support: DOE
Total Award Amount: $337,465
Summer Support: 0.5 months
Total Award Period Covered: 07/01/2009 – 06/30/2012

Project/Proposal Title: Catalysis with Metal-Decorated Carbon Nanotubes
Source of Support: NETL IAES
Total Award Amount: $41,242
Summer Support: 0.25 months
Total Award Period Covered: 1/15/2010 – 11/30/2010

Project/Proposal Title: Accurate Simulations of CO_2 and Methane Hydrates
Source of Support:: NETL IAES
Total Award Amount: $62,474
Summer Support: 0.25 months
Total Award Period Covered: 1/15/2010 – 11/30/2010

Project/Proposal Title: Photocatalytic Reduction of Carbon Dioxide on TiO_2 Interfaces
Source of Support: NETL IAES
Total Award Amount: $83,300
Summer Support: 0.25 months
Total Award Period Covered: 1/15/2010 – 11/30/2010

Pending
Project/Proposal Title: Investigation of CO_2 Capture Mechanisms by Clay Phases
Source of Support: NETL
Total Award Amount: $115,048
Summer Support: 0.25 months
Total Award Period Covered: 11/15/2010 – 11/14/2010

Project/Proposal Title: Accurate Force Fields for Modeling CO_2 Capture by Ionic Liquids
Source of Support: NETL
Total Award Amount: $91,469
Summer Support: 0.25 months
Total Award Period Covered: 11/15/2010 – 11/14/2011

Project Proposal Title: Photocatalytic Reduction of CO_2
Source of Support: NETL
Total Award Amount: $91,469
Summer Support: 0.25 months
Total Award Period Covered: 11/15/2010 – 11/14/2011

Current Support
  None

Pending

  Project/Proposal Title: Structure of wet-electron states on ferroelectric surfaces
  Source of Support: NSF/SSMC
  Total Award Amount: $333,715
  Total Award Period Covered: 5/1/2011 – 4/30/2014

Facilities and Other Resources for Alan McGaughey

One faculty office and two graduate student/postdoctoral fellow offices. Shared secretarial support (1/6 time). McGaughey and his research group have developed lattice dynamics computer codes suitable for the proposed tasks.

Parts of McGaughey's computational work will be carried out on a 96-core Beowulf Linux cluster installed in September 2006 and expanded in July 2008 and July 2010. The system is housed in Carnegie Mellon Computer Facilities space, with suitable power and cooling capabilities, and uninterrupted power supplies. The system contains one head node and sixteen slave nodes, and can be accessed from anywhere in the world. Eight nodes have two AMD Opteron 275 Dual Core Processors (i.e., four processors per node), 2 GB of RAM, and an 80 GB hard drive. Four nodes have two AMD Opteron 2218 Dual Core Processors, 4 GB of RAM, and an 80 GB hard drive. Four nodes have two AMD Opteron 2427 Six Core Processors, 24 GB of RAM, and a 250 GB hard drives. The system runs on the CBeST v3.0 Beowulf cluster software, custom installed on the system for high performance computing.

Facilities, Equipment, and Other Resources for Ken Jordan and Wissam Al-Saidi

Two faculty offices and 1600 square feet of office space for graduate students and postdoctoral fellows. Shared secretarial support (1/4 time).

Jordan is co-director of The University of Pittsburgh's Center for Simulation and Modeling (SAM), which houses several computer clusters (with a total of about 3000 cores) with high-speed Infiniband networking, which have been designed for parallel applications requiring up to 192 cores. 7% of this resource (i.e., an average of 210 cores) will be made available at no charge for this project. The SAM cluster also has 16 Nvidia Fermi GPUs which can also be used for the proposed research.

Université Catholique de Louvain
Faculté des Sciences Appliquées

UNITE DE PHYSICO-CHIMIE ET DE PHYSIQUE DES MATERIAUX

Louvain-la-Neuve, le 20 janvier 2010

Dear Prof. Kenneth Jordan,

The present letter concerns your project on the computation of thermal conductivities using lattice dynamics and the Boltzman equation, using anharmonic force constants from Density Functional Theory. I estimate that this research project will deliver very important outcomes to the scientific community, especially in the form of added functionalities to the ABINIT software, that is used worldwide (currently more than 1300 mailing addresses on the announce mailing list). I think your group has the adequate know-how to perform this research, and I am confident you will succeed in this project. Moreover, should you meet any problem with the ABINIT implementation, it will be possible to collaborate with us for adequate support and advices.

I wish you a good success,

Prof. X. Gonze

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