Atomistic Modeling of Thermal Transport in Large Unit Cell Crystals

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**Project Description**

***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.

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.

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.

**Approach and Methodology**

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 theforce 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.

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 crystals38–40 or Allen-Feldman

theory41, 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.***

**Silicon Thermal Conductivity Over-Predicted using Classical MD**

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

simulation20 compared to the experimental value of 31 W/m-K39). In fact, no available silicon 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

**Relationship to CIT/ICES Strategic Focus**

Atomistic simulation of PCM materials fits directly into CIT’s nanotechnology initiative and is a focus of the Data Storage Systems Center (DSSC). This project is also aligned with ICES’s Center for Multiscale Modeling for Engineering Materials (CM2EM) and Center for Nano-enabled Device and Energy Technologies (CNXT), both of which McGaughey is affiliated with. The work will provide a compelling example of multi-scale modeling by demonstrating how high-level (quantum) computational techniques can feed into and drive classical-level methods.

**Present and Future Funding**

Preliminary funding for this project was through the PITA grant “Multi-scale modeling of phase change materials,” with Jason Larkin as the supported graduate student. Jason initiated the collaboration with Dr. Juarez Da Silva from the Sao Paulo Institute of Physics, which been fruitful to date. He does not have support in place for the 2010-2011 academic year.

The Dowd fellowship will enable the team to complete the development of interatomic potentials for a wide range of Ge-Sb-Te materials. With these interatomic potentials in hand, the team will be competitive for funding from NSF’s Thermal Transport Processes (ENG-CBET) and Electronics, Photonics & Device Technologies (ENG-ECCS) programs, SRC’s Device Sciences – Modeling and Simulation program (a call will open in Spring 2011), and CMU’s DSSC. The team will collaborate with CMU’s Jim Bain (ECE, DSSC), who does experimental work on PCM materials and devices and Jon Malen (ME), who thermally characterizes micro- and nanoscale materials and devices. Together, they will apply for funding from NSF’s Interdisciplinary Research (IDR) program.

[1] G. Burr, et al., arXiv:1001.1164v2 [cond-mat.mtrl-sci] 29 Mar 2010.

[2] J. L. F. Da Silva, et al., *Phys. Rev. B* **78**, 224111 (2008).

[3] J. L. F. Da Silva, et al., arXiv:0903.2456v1 [cond-mat.mtrl-sci] 13 Mar 2009.

[4] S. Caravati, et al, *Appl. Phys. Lett*. **91**, 171906 (2007).

[5] J. Tominaga, et al., *Jpn. J. Appl. Phys.* **47** (2008) pp. 5763-5766.

[6] T.C. Chong, et al., *Appl. Phys. Lett.* **88**, 122114 (2006).

[7] A.V. Kobolov, et al., *Appl. Phys. Lett.* **91**, 021911 (2007).

[8] M. Hase, et al., *Phys. Rev. B* **79**, 174112 (2009).

[9] J. Akola, et al.,”, *Phys. Rev.* B **76**, 235201 (2007).