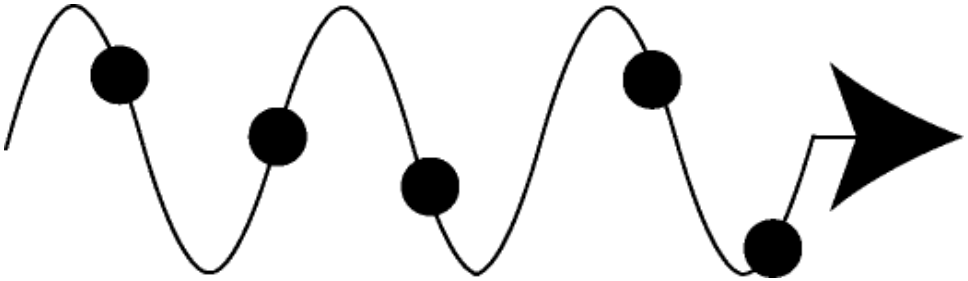

Molecular-Level Modeling of Phonon Transport: Formulation, Implementation, and Applications

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Department of Mechanical Engineering
Purdue University, West Lafayette, IN

IMECE 2016
November 14, 2016

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Carnegie Mellon

Outline

Session I (1:30 PM – 3:15 PM)

1. **Introduction** (McGaughey)
2. Harmonic lattice dynamics, MD simulation (Ruan)
3. Green Kubo, direct method, spectral methods (Ruan)

Session II (3:45 PM – 5:30 PM)

4. Anharmonic lattice dynamics, first principles (McGaughey)
5. Phonon-boundary and phonon-defect scattering (McGaughey)
6. Phonon-electron coupling and non-equilibrium (Ruan)

Acknowledgements

Students & Post-Docs

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- Dr. Wee Liat Ong
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- Harrington Fellowship at UT Austin
- National Science Foundation

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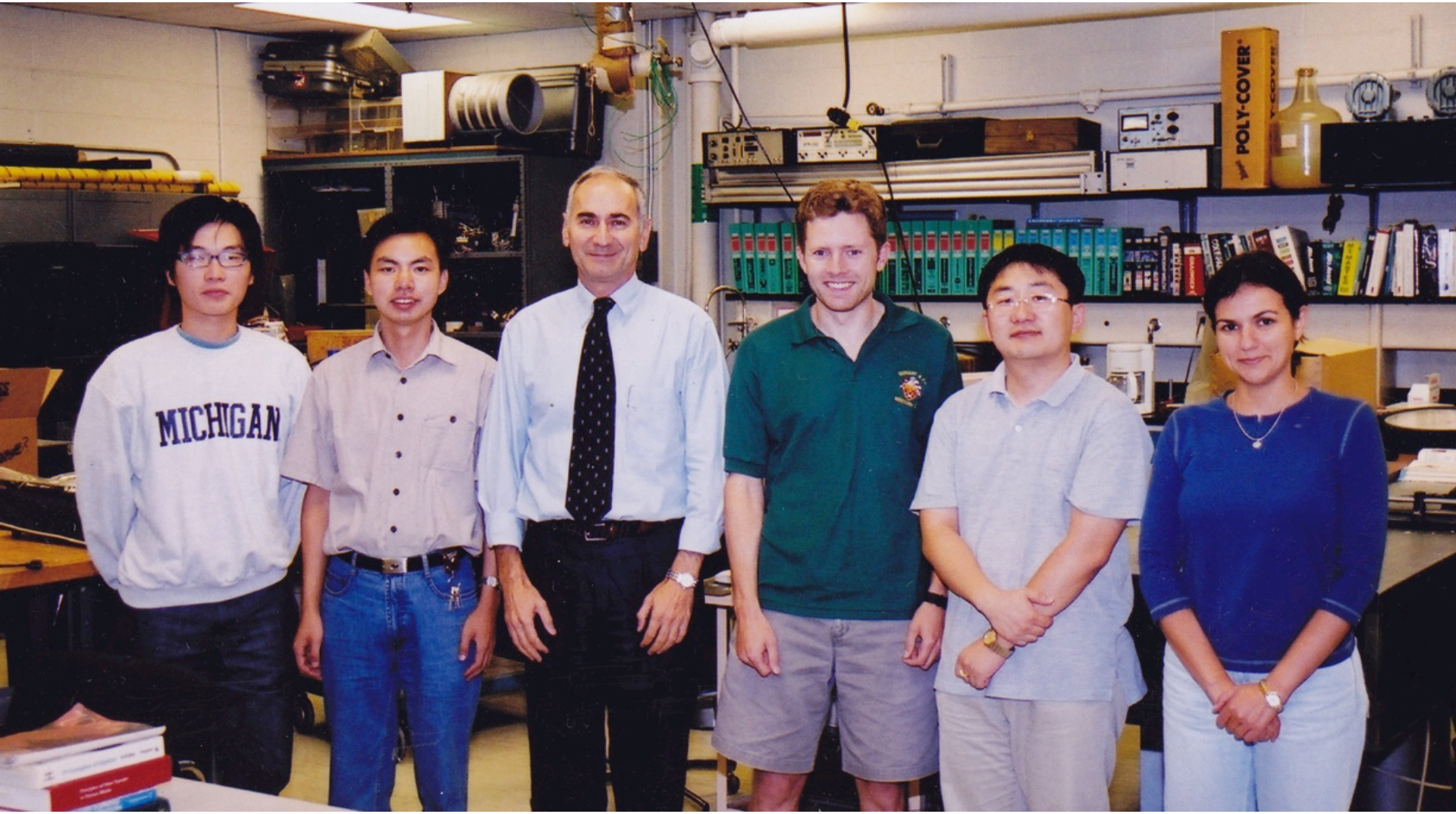
Some History … 2002



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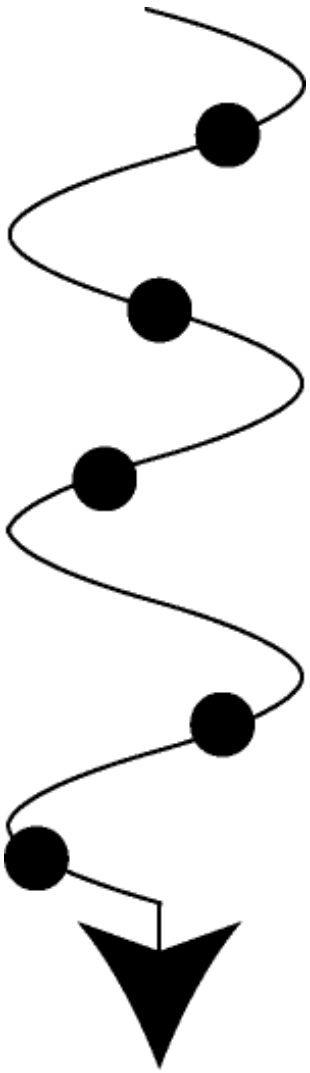
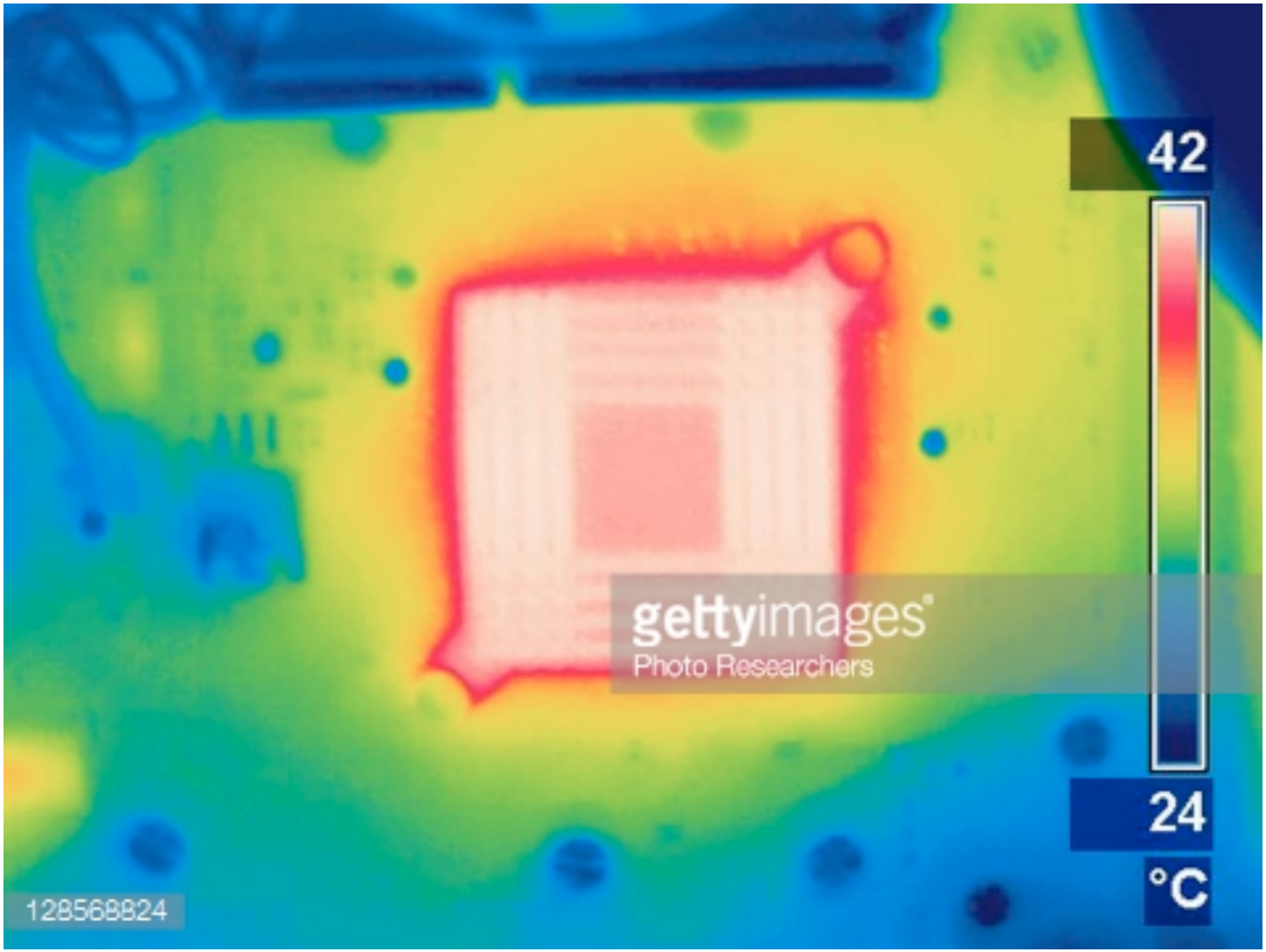
Outline

1. Thermal Conductivity
2. Phonons
3. Computational Tools
4. Impactful Research



Stuff Gets Hot



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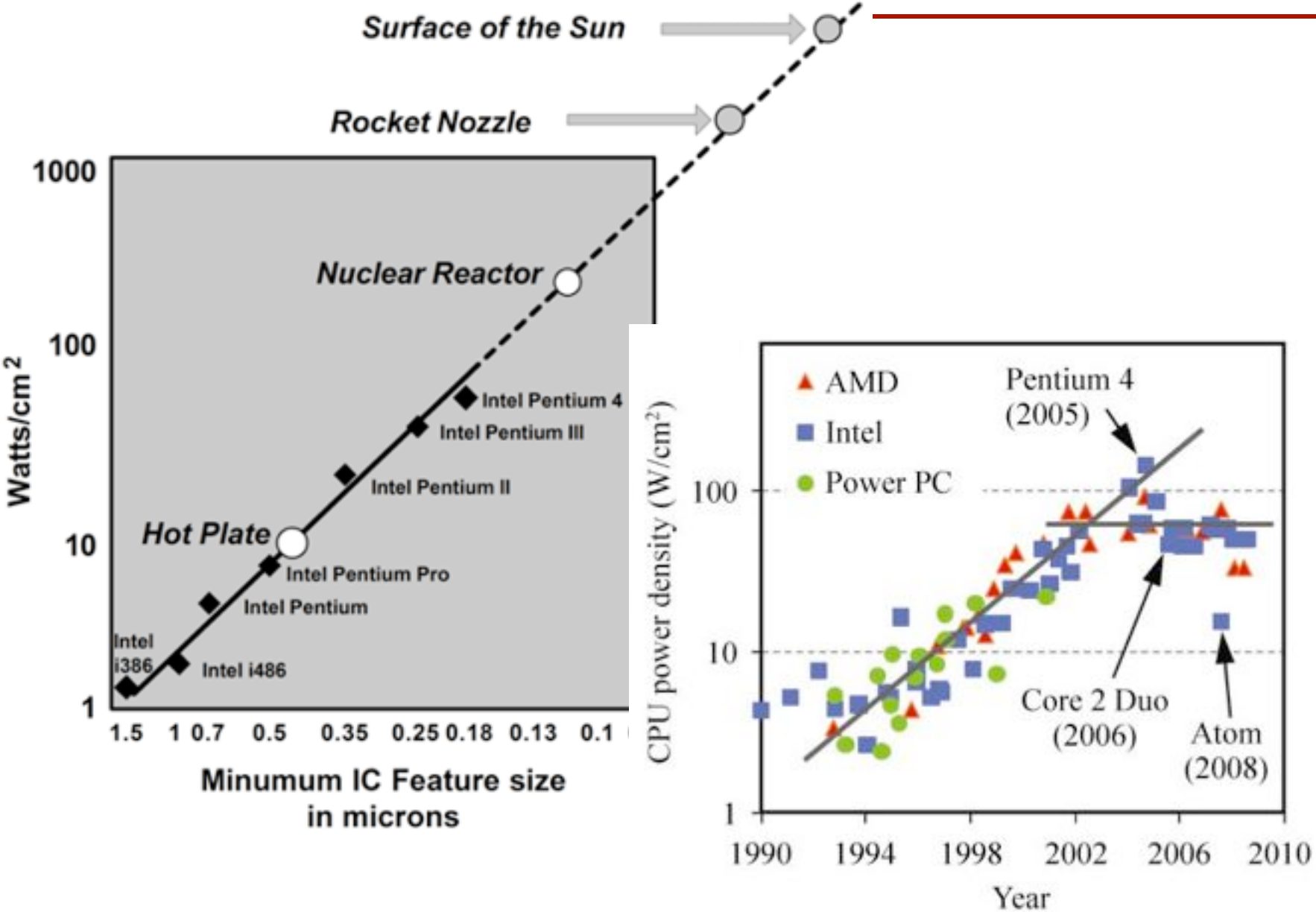

http://www.makeuseof.com
http://www.soccentral.com

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What is Thermal Conductivity?

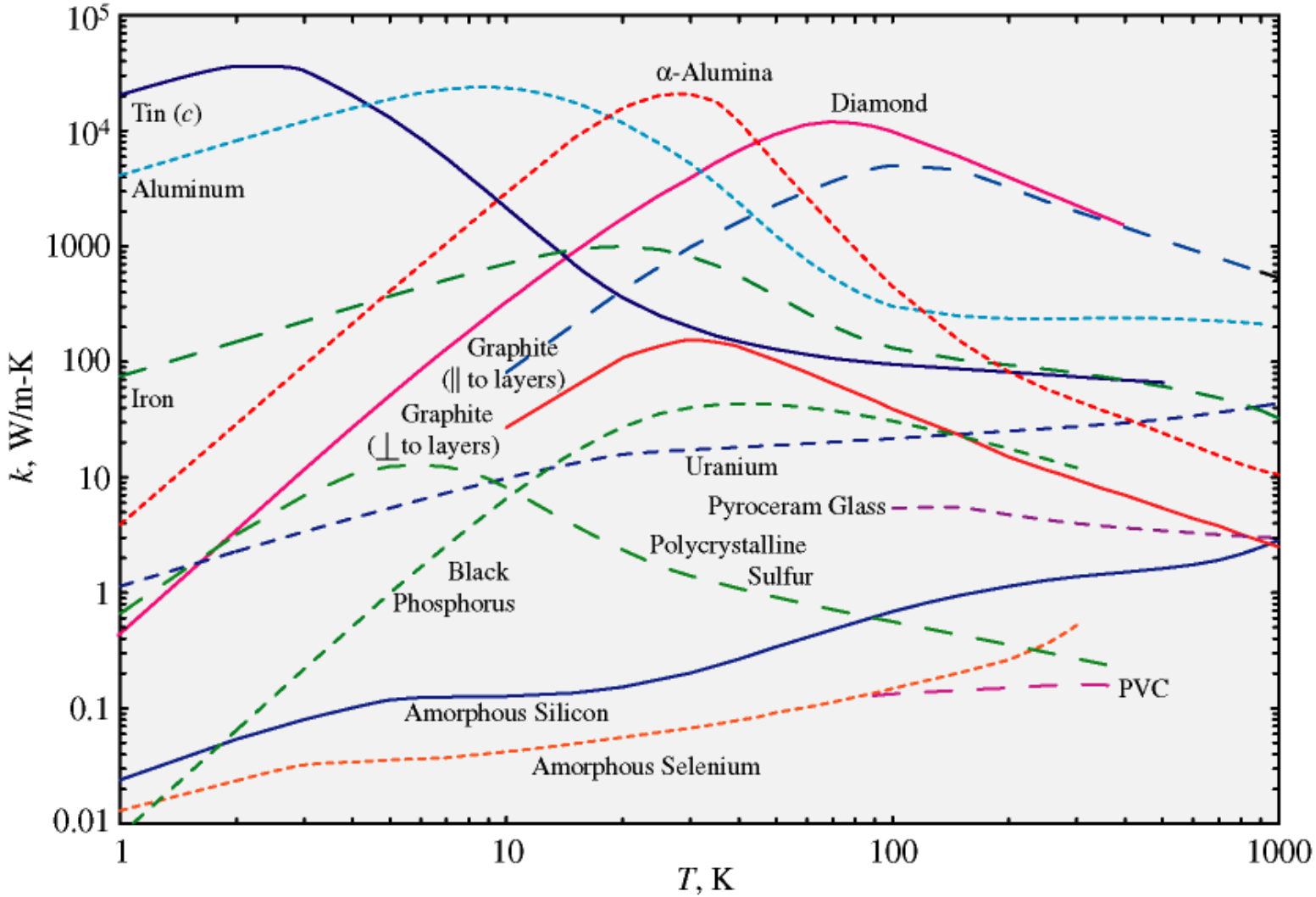
$$\text{Fourier law}: \mathbf{q} = -\mathbf{k}\nabla T$$

heat flux = – thermal conductivity × temperature gradient

- Defined empirically
- Any thermal conductivity prediction invokes the Fourier law

- Combines the effects of all energy carriers
- Provides no information about carrier-level transport

Experimental Thermal Conductivity Data



Phillpot and McGaughey, *Materials Today*, June 2005, 18-20.

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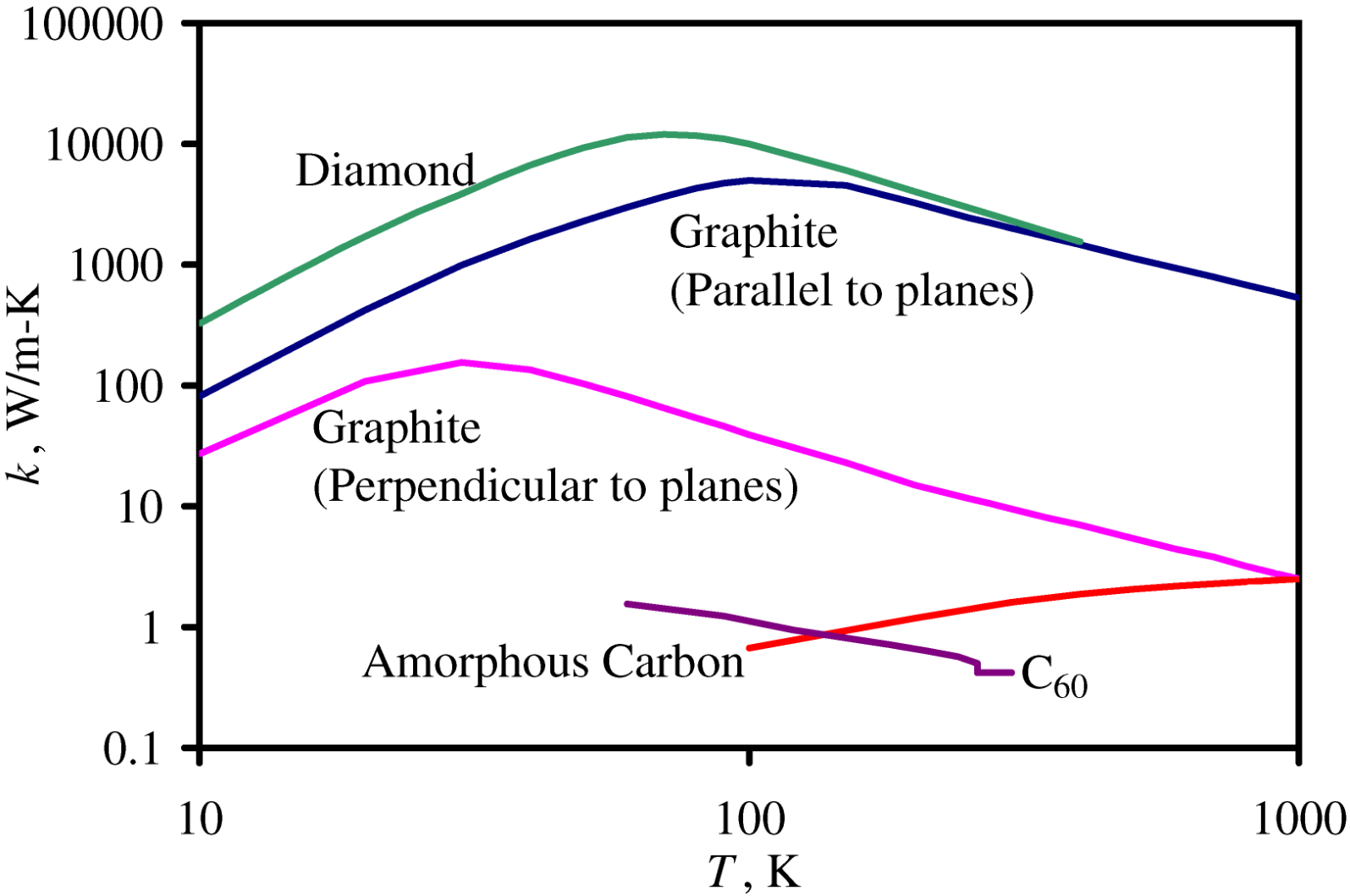
Atomic-Level Consideration



McGaughey, Ph.D. thesis, U. Michigan (2004).

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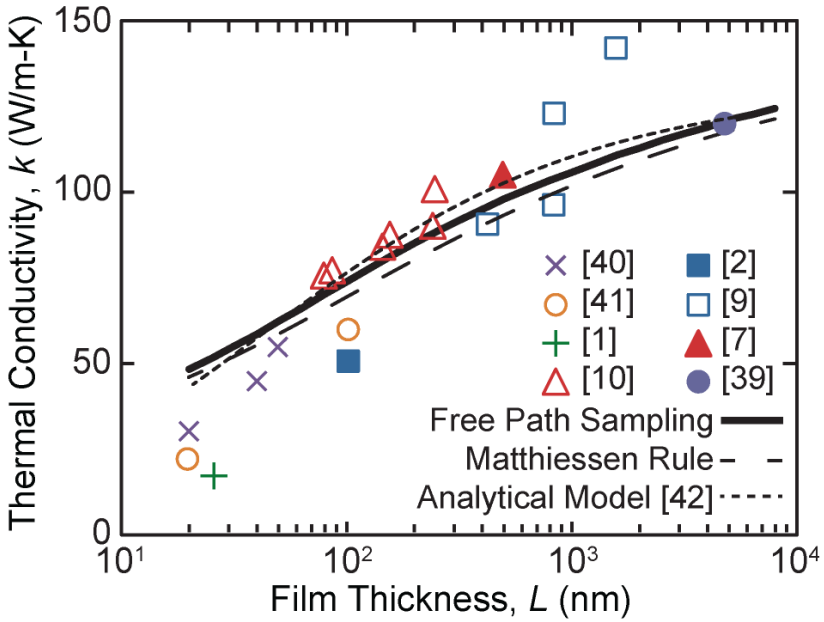
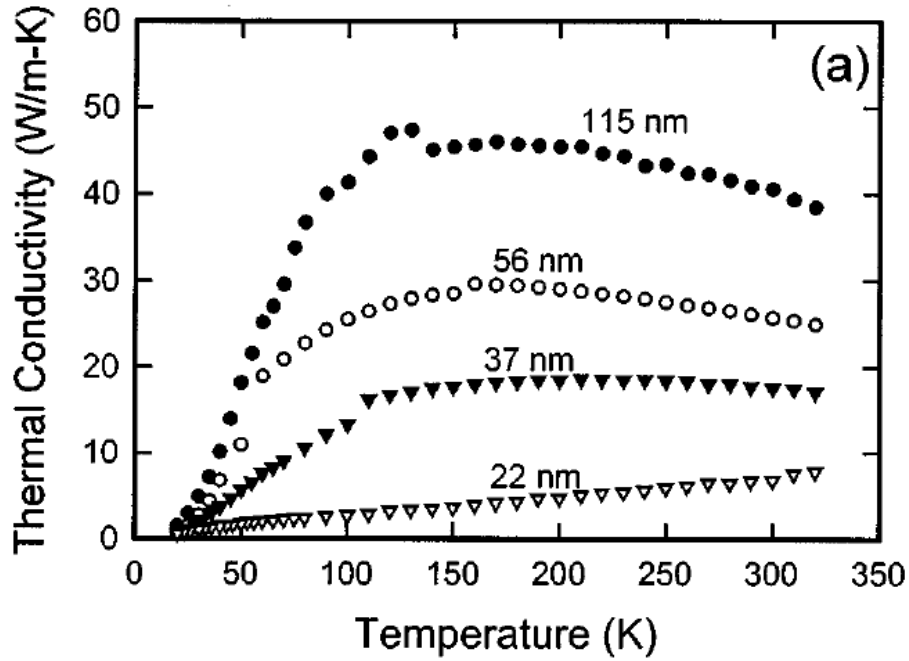
Size-Dependence in Nanostructures

Silicon thin films, in-plane direction



Jain et al., *PRB* **87** (2013) 195301.

Silicon nanowires



Li et al., *APL* **83** (2003) 2934.

Superlattices, carbon nanotubes, graphene, nanostructured alloys, …

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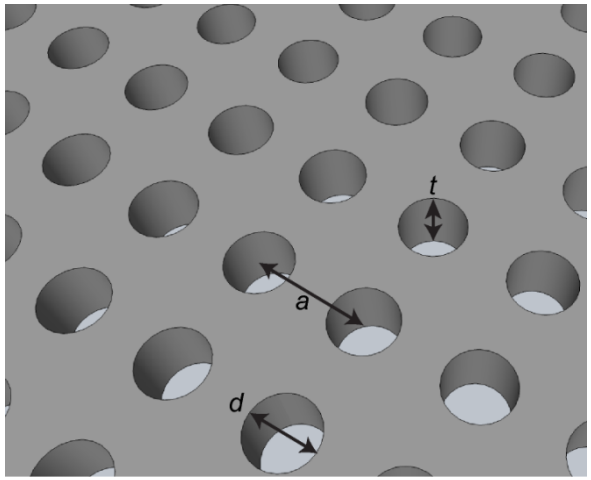
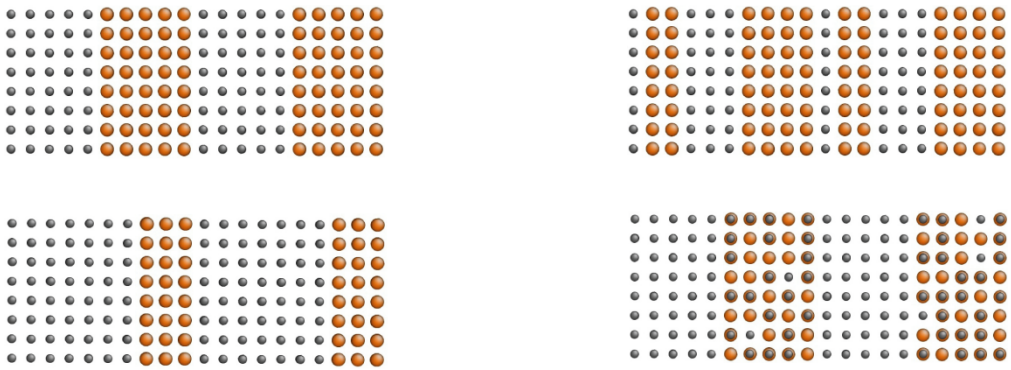
Why Simulations and Calculations?

- Nanoscale phenomena are challenging to observe experimentally
  - Small length (10^{-10} m) and time (10^{-15} s) scales



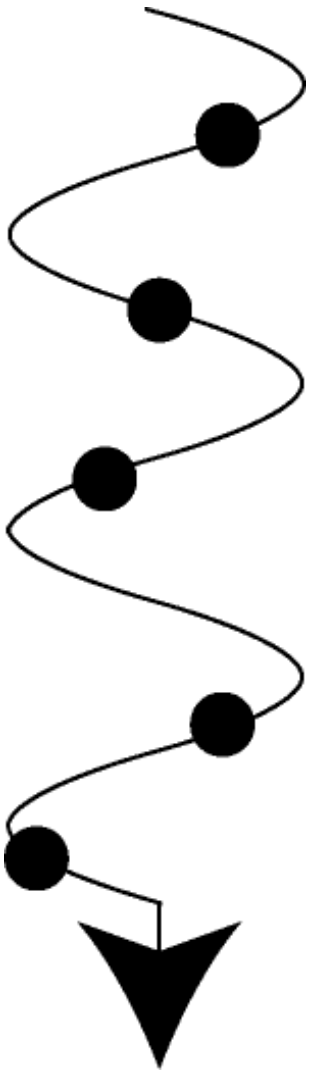


Why does one material have higher thermal conductivity than another?

Can thermal conductivity be tailored by nanostructuring?

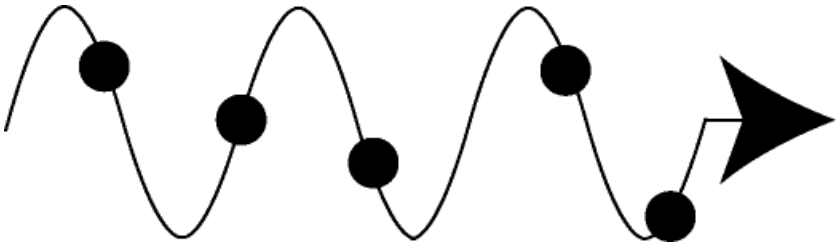
Outline

1. Thermal Conductivity
2. Phonons
3. Computational Tools
4. Impactful Research



What is a Phonon?

- Quantized lattice vibration with energy $\hbar\omega$



- Wave number (=2π/wavelength), frequency, polarization
  → Define the *phonon mode*

- Primary carriers of thermal energy in semiconductors and dielectrics (Si, GaN, graphene, quartz).

- *There is a spectrum of phonons in every material.*

Phonon Formula for Thermal Conductivity

Boltzmann transport equation + Fourier law

$$\Longrightarrow k_n = \sum_i c_{v,i} v_{g,i,n}^2 \tau_i = \sum_i c_{v,i} v_{g,i,n}^2 \frac{\Lambda_i}{\left|\mathbf{v}_{g,i}\right|}$$

i : indexes over all phonon modes

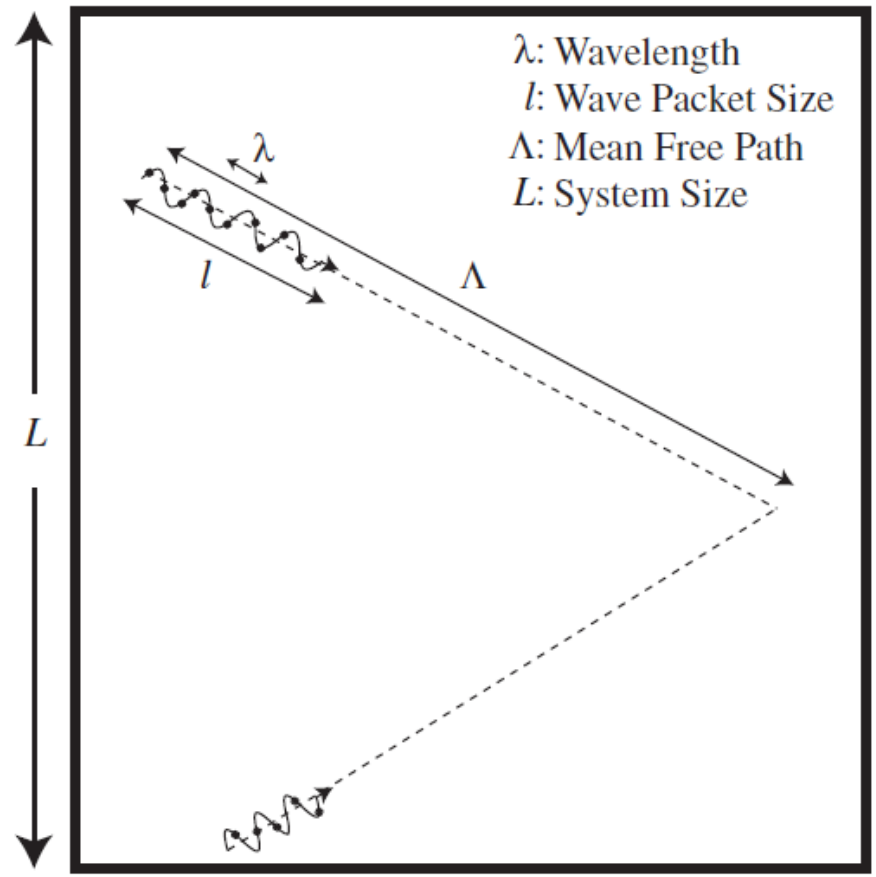
$c_{v,i}$: heat capacity $\mathbf{v}_{g,i}$: group velocity

τ_i: lifetime Λ_i: mean free path

Transport and Scattering

Phonons scatter with:

- other phonons
- grain boundaries, interfaces, surfaces
- electrons
- defects (isotopes, vacancies, …)



McGaughey and Kaviany, *PRB* **71**, 184305 (2005).

Outline

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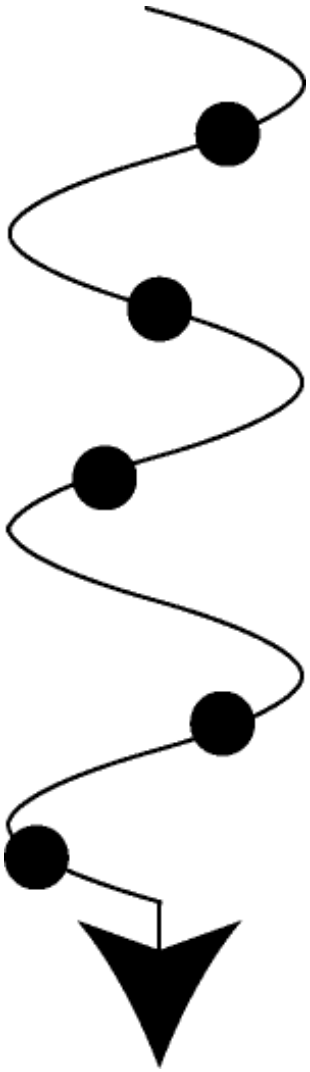


How are atomic trajectories & dynamics related to thermal conductivity?

Atom → Real

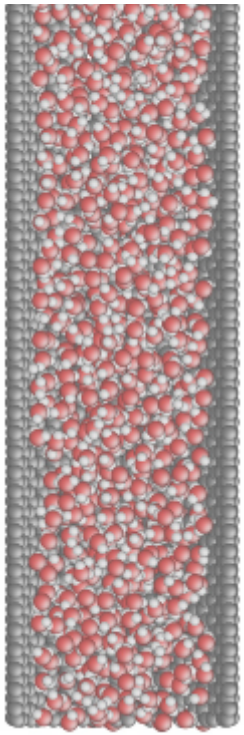
Molecular Dynamics

Phonon → Abstraction

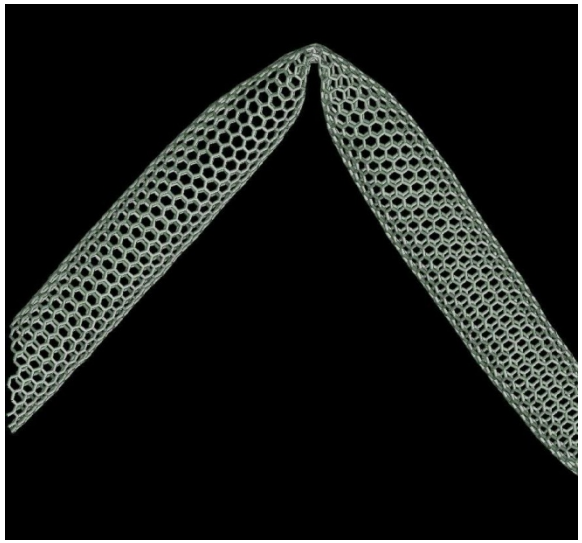
Lattice Dynamics

What is Molecular Dynamics Simulations?

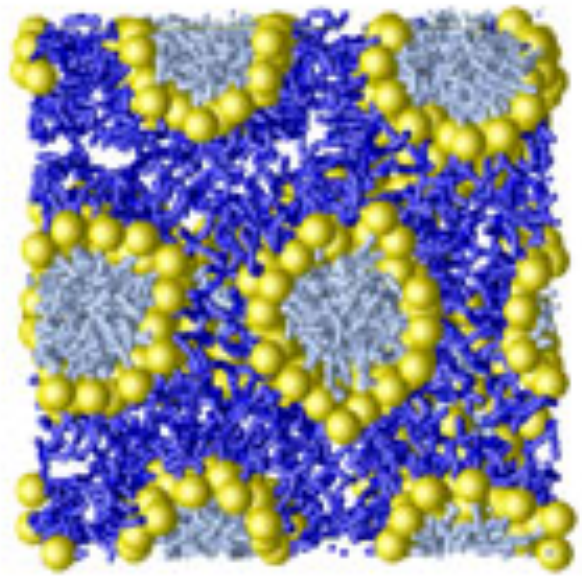
- Real-space technique (atoms, positions, velocities)
- Generate trajectories: Newton's laws of motion & empirical potential



Water flow in a CNT
A. McGaughey, CMU

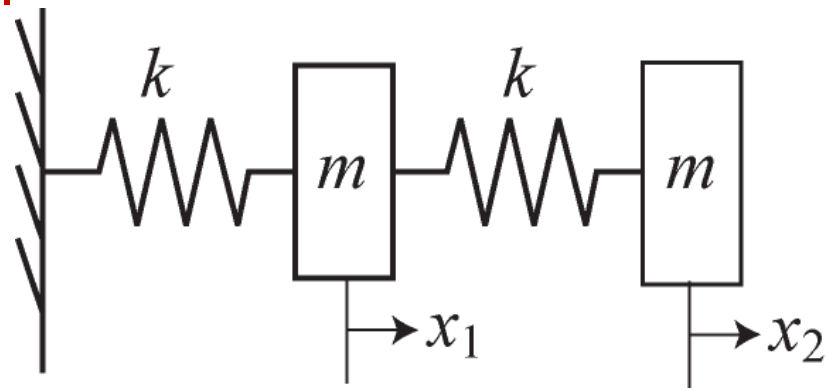


Bending a carbon CNT
J. Li, MIT



Assembling tethered nanoparticles
S. Glotzer, UMichigan

MD is Like a Mass-Spring System



1. Equations of Motion:

$$\begin{bmatrix} \ddot{x}_1 \\ \ddot{x}_2 \end{bmatrix} = \begin{bmatrix} -2 & 1 \\ 1 & -1 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \end{bmatrix}$$

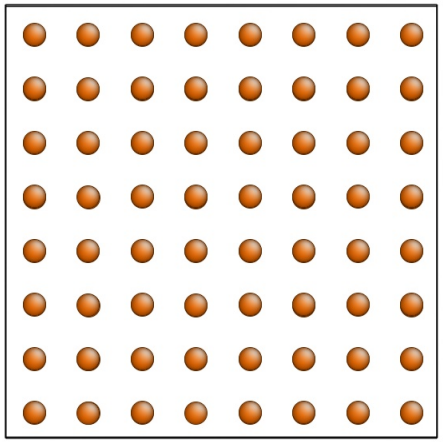
2. Convert to 1st order equations:

$$\begin{bmatrix} \dot{x}_1 \\ \dot{x}_2 \\ \dot{x}_3 \\ \dot{x}_4 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ -2 & 1 & 0 & 0 \\ 1 & -1 & 0 & 0 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{bmatrix}$$

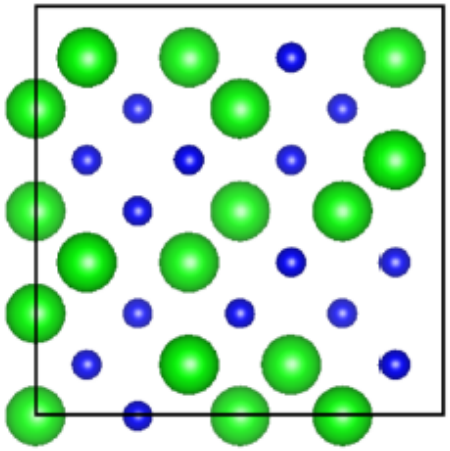
3. Solve numerically

What is Lattice Dynamics Calculations?

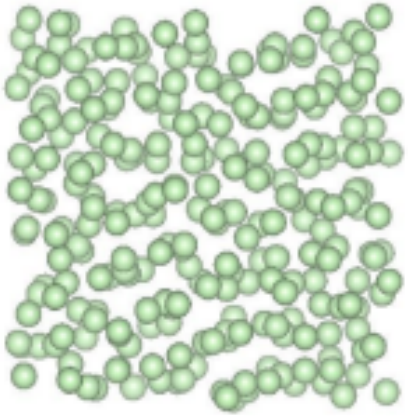
- Reciprocal-space technique (vibrational modes)
- Taylor series of potential energy around equilibrium
  - Empirical potential or density functional theory



Crystal

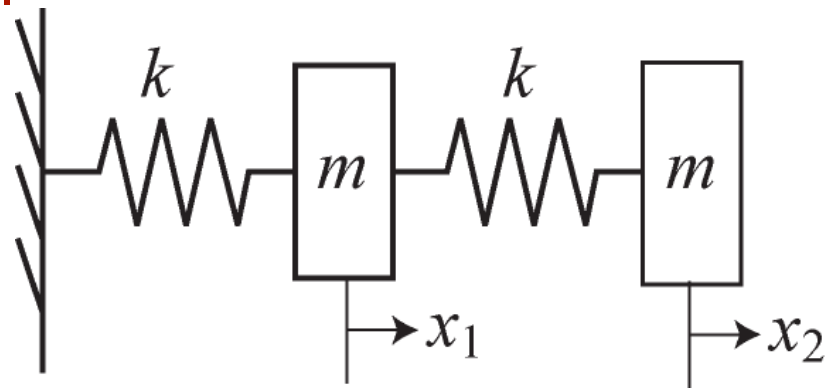


Alloy



Amorphous

Harmonic Formulation



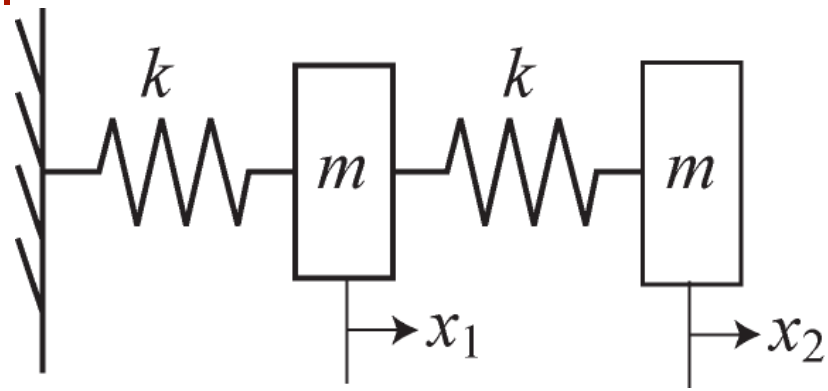
Find the natural frequencies and mode shapes for $m = k = 1$.

1. Equations of motion: $$\begin{bmatrix} \ddot{x}_1 \\ \ddot{x}_2 \end{bmatrix} = \begin{bmatrix} -2 & 1 \\ 1 & -1 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \end{bmatrix}$$

2. Assume harmonic solution: $$\omega^2 \begin{bmatrix} e_1 \\ e_2 \end{bmatrix} = \begin{bmatrix} 2 & -1 \\ -1 & 1 \end{bmatrix} \begin{bmatrix} e_1 \\ e_2 \end{bmatrix}$$

3. Eigenvalue problem:
   Solution 1: $\omega = 0.618, e_2 = 1.618\, e_1$
   Solution 2: $\omega = 1.618, e_2 = -0.618\, e_1$

Normal Modes



Solution of form: $\mathbf{x} = A\mathbf{e}_I + B\mathbf{e}_{II}$

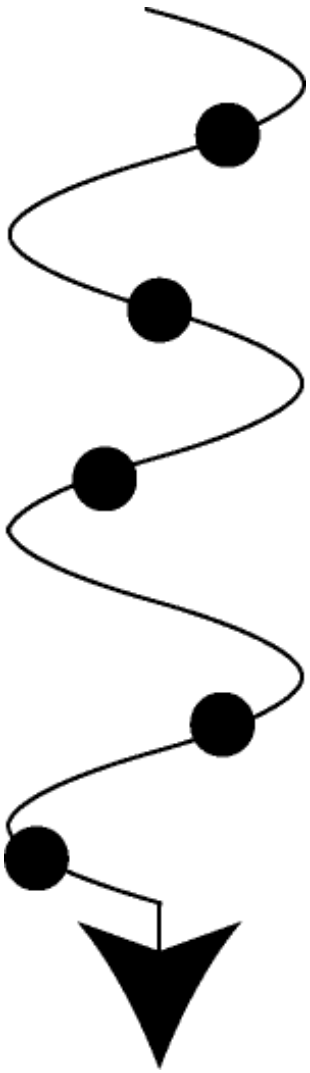
(coordinate transform)

Total potential energy = $x_1^2 + (x_2 - x_1)^2 = 0.383A^2 + 2.62B^2$

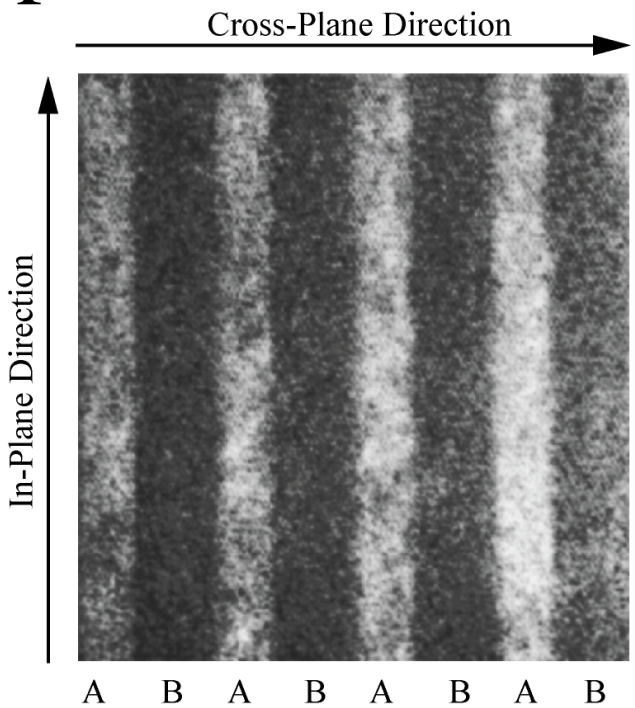
Coordinates decoupled!

Outline

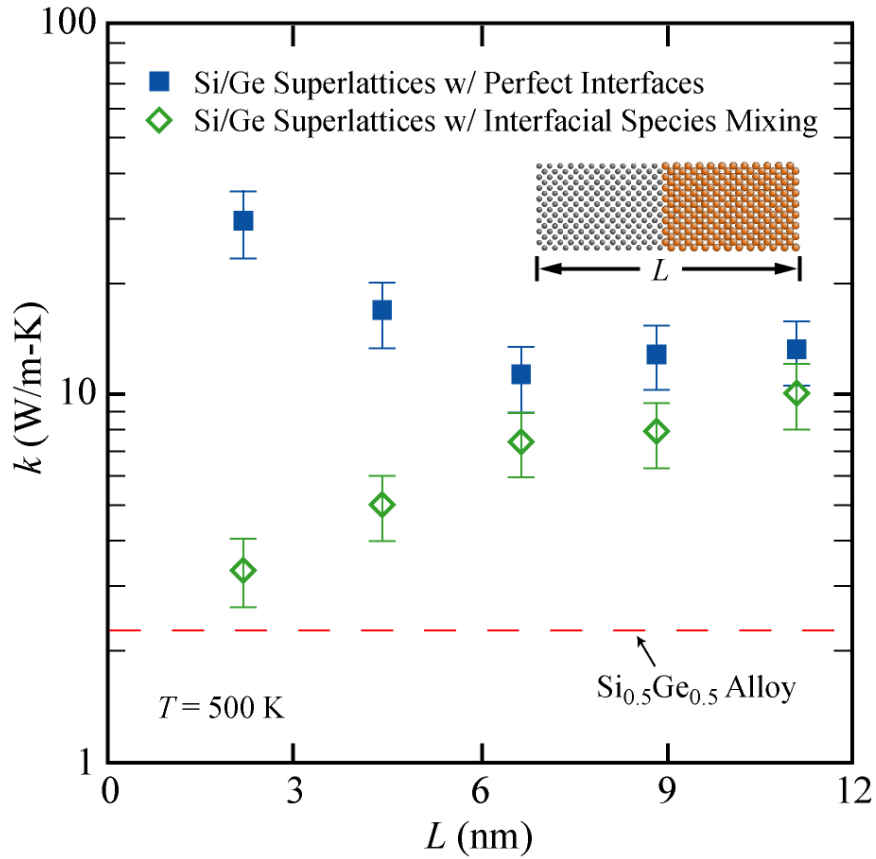
1. Thermal Conductivity
2. Phonons
3. Molecular Dynamics and Lattice Dynamics
4. Impactful Research

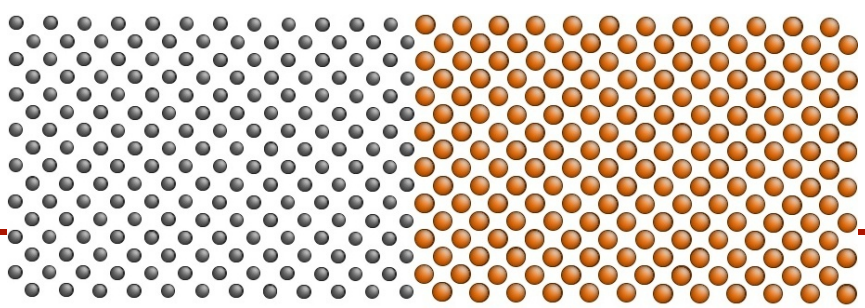


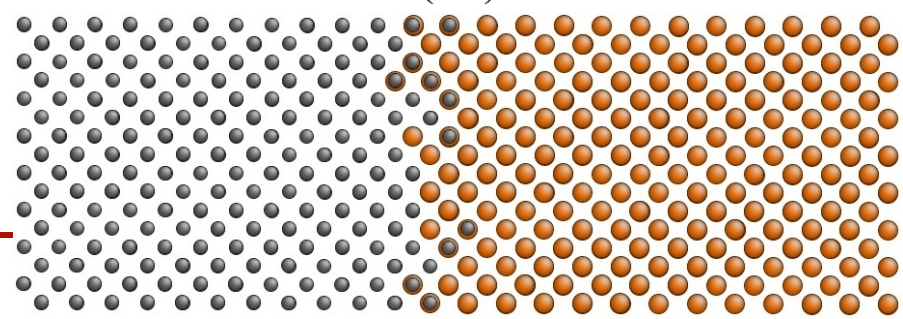
Superlattices



A: Si (5.9 nm)
B: $Si_{0.78}Ge_{0.22}$ (7.4 nm)

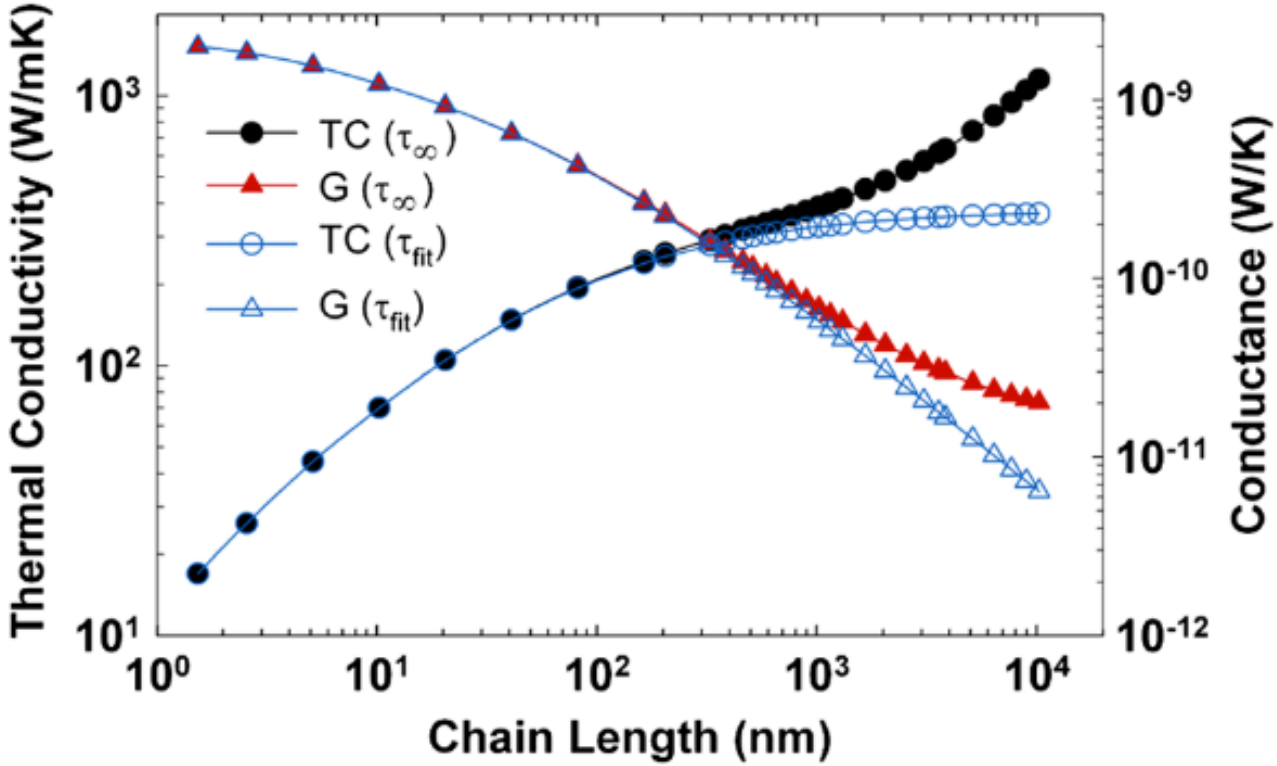


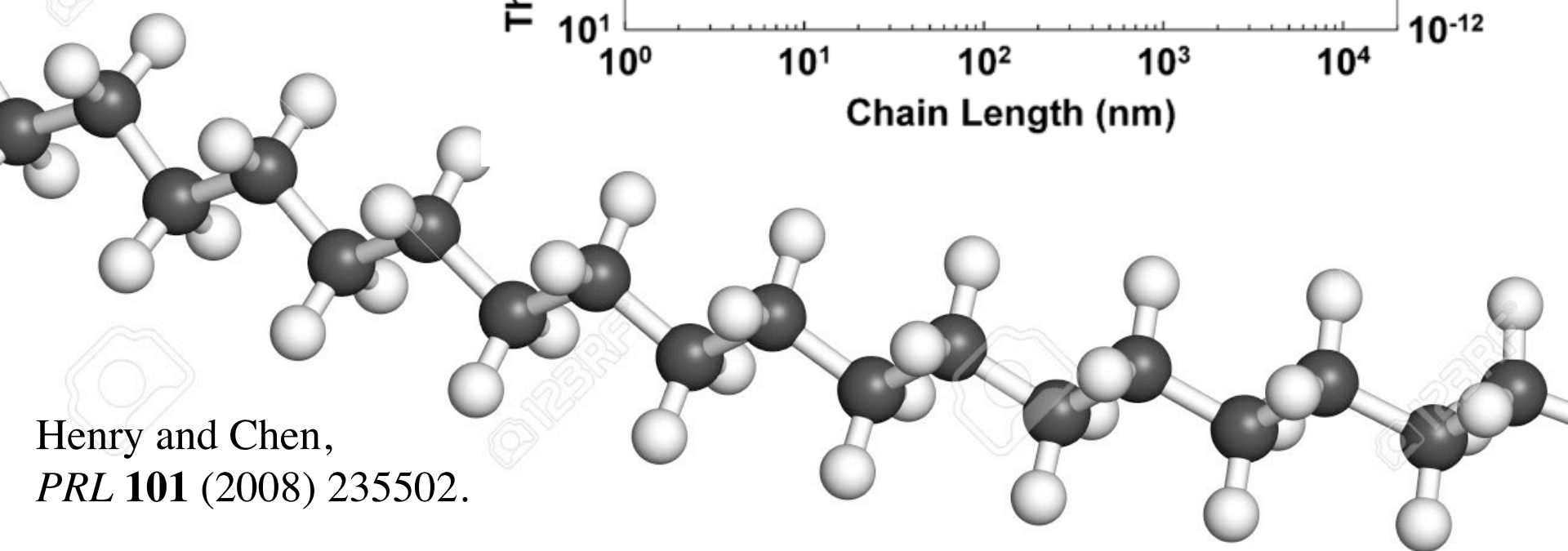




Landry and McGaughey, *PRB* **79** (2009) 075316.

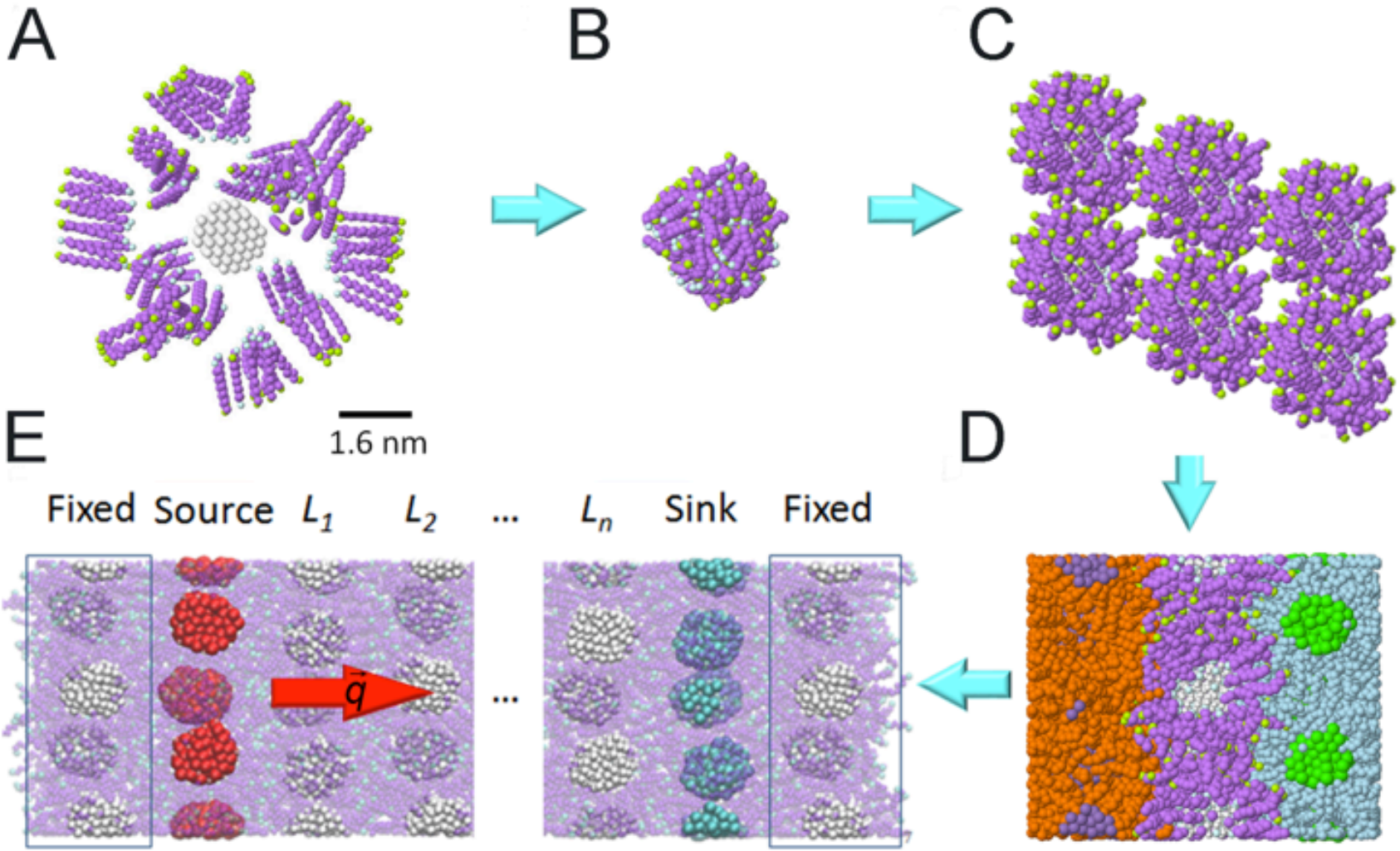
Divergent Thermal Conductivity of Polyethylene





Henry and Chen,
PRL **101** (2008) 235502.

Complex Hybrid Materials



Ong et al., *Journal of Physical Chemistry C* **118**, 7288 (2014).

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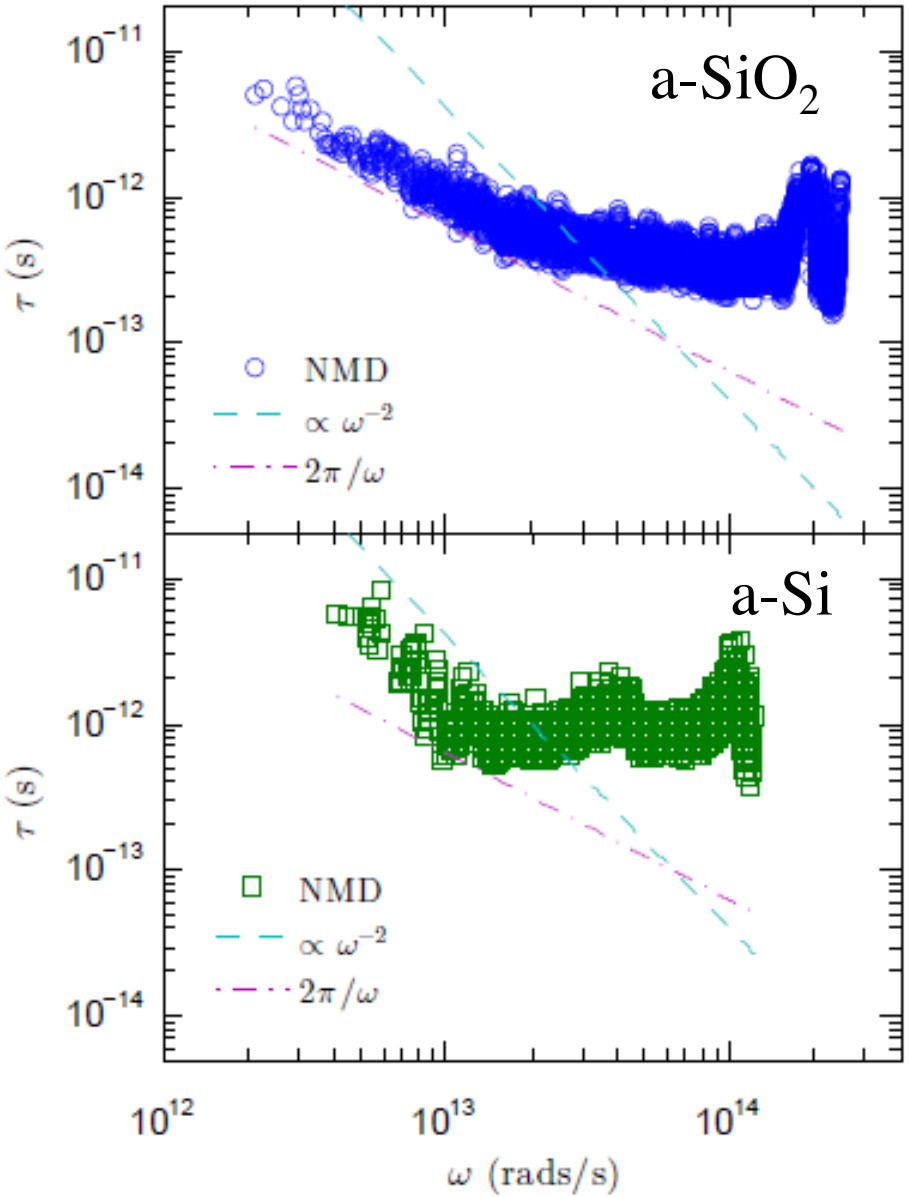
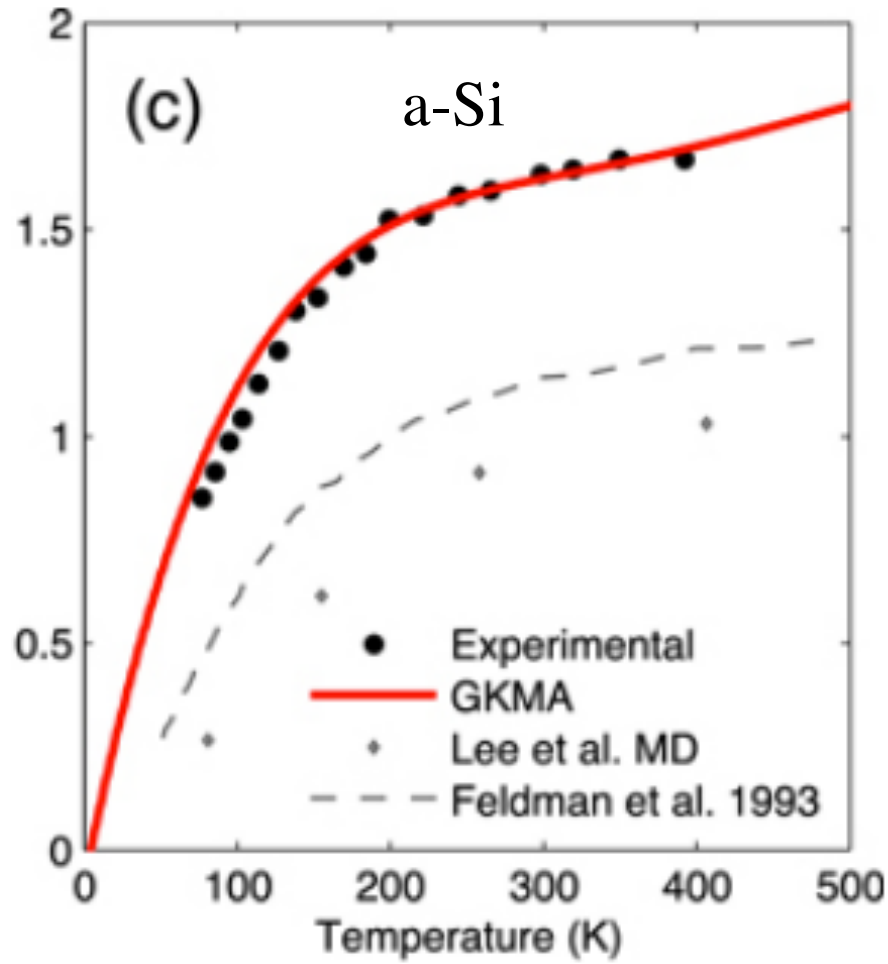
Amorphous Materials

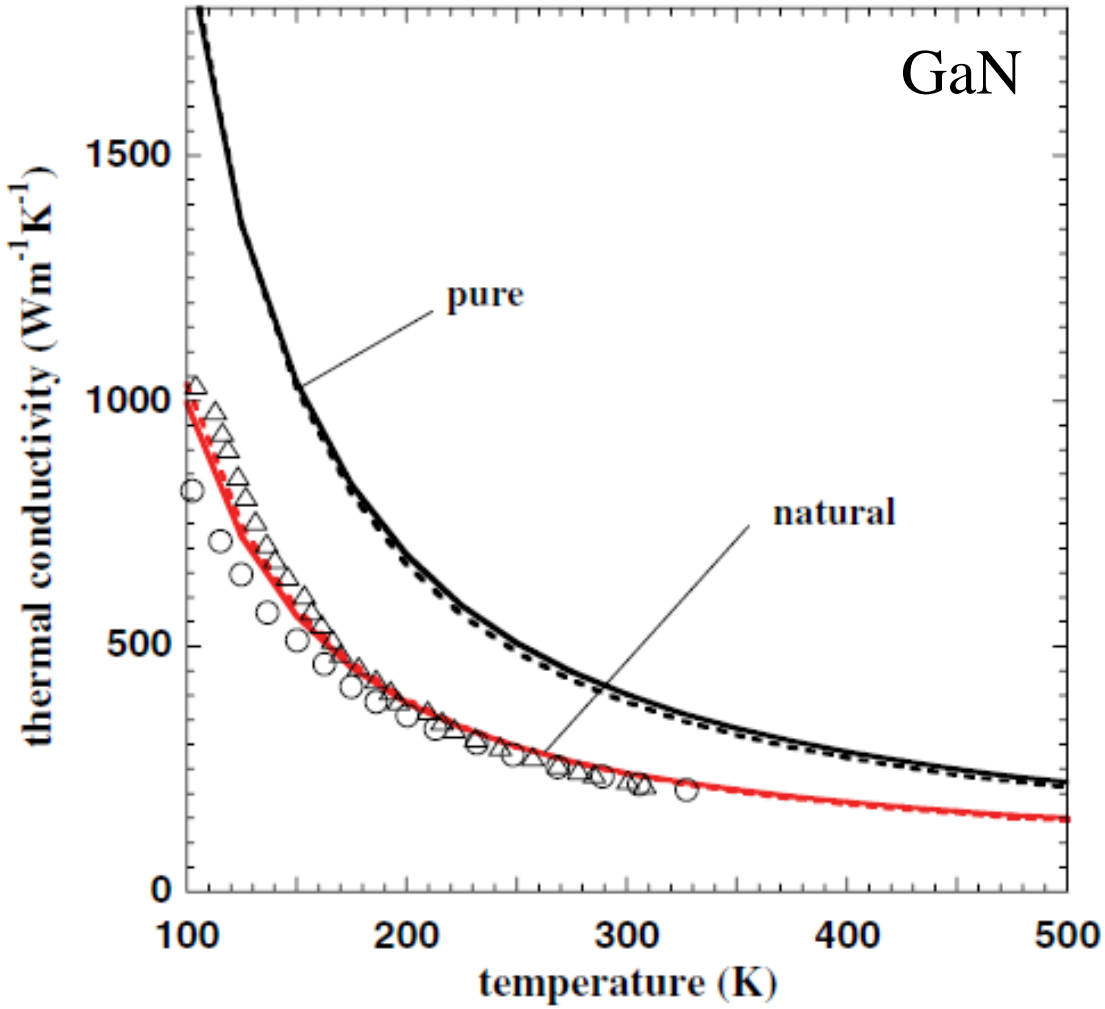




Lv and Henry, *NJP* **18** (2016) 013028.

Larkin and McGaughey, *PRB* **89** (2014) 144303.

Thermal Conductivity from First Principles



Lindsay et al., *PRL* **109** (2012) 095901.

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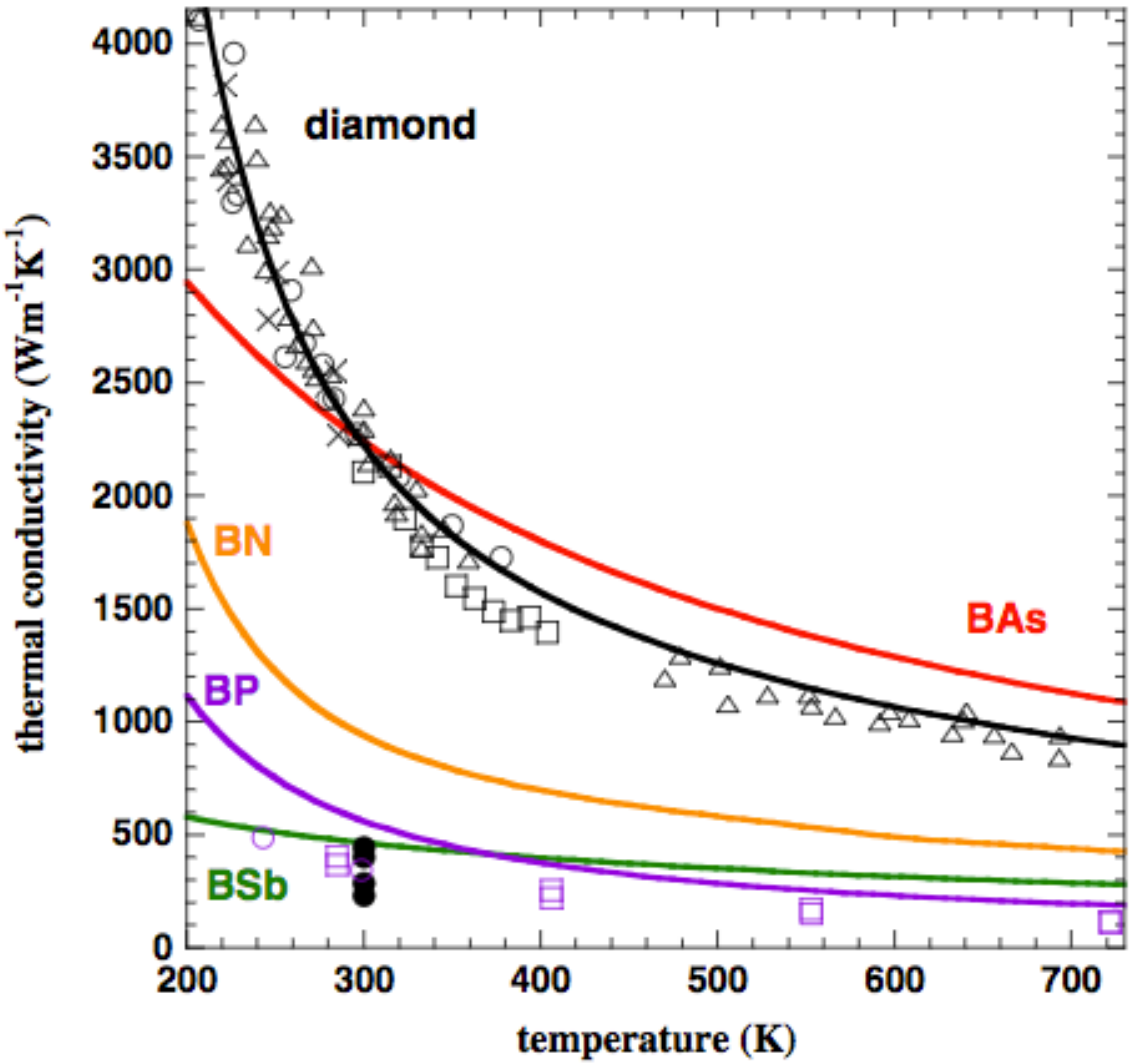
Ultra-High Thermal Conductivity of BAs



Lindsay et al., *PRL* **111** (2013) 025901.

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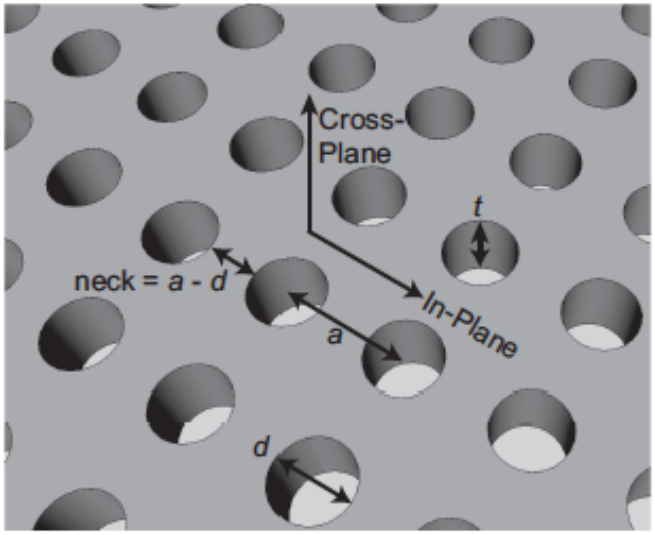
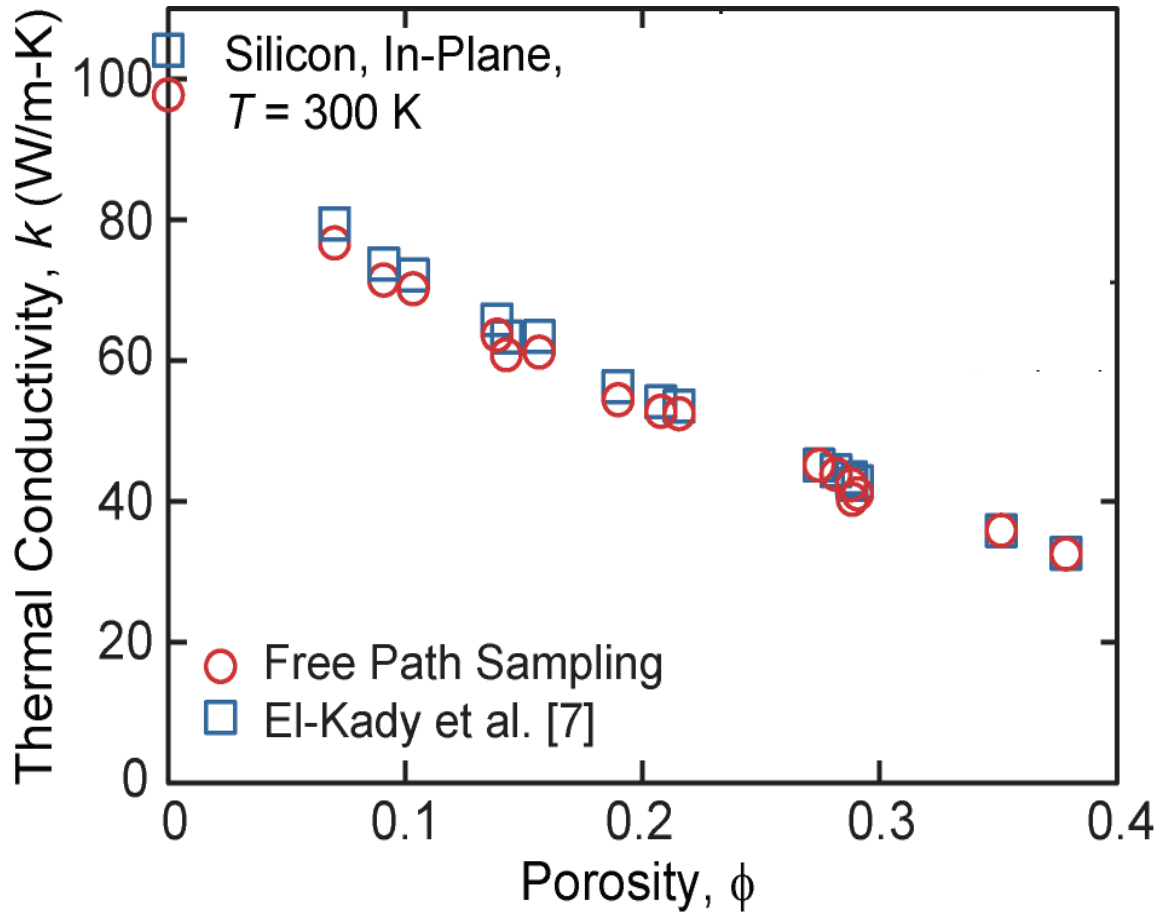
Nanostructure Thermal Conductivity





Jain, Yu, and McGaughey, *PRB* **87**, 195301 (2013)

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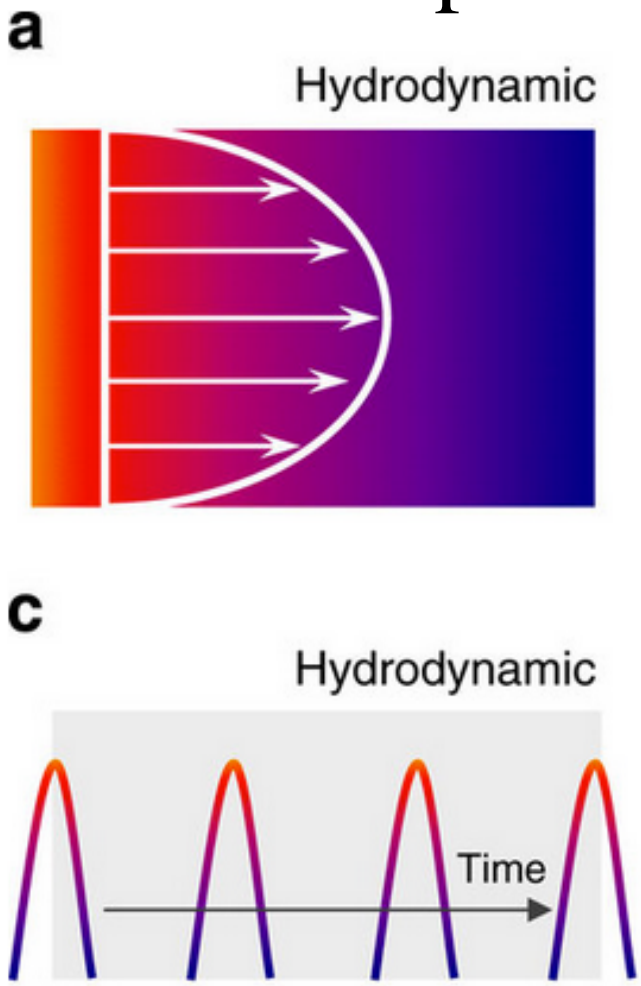
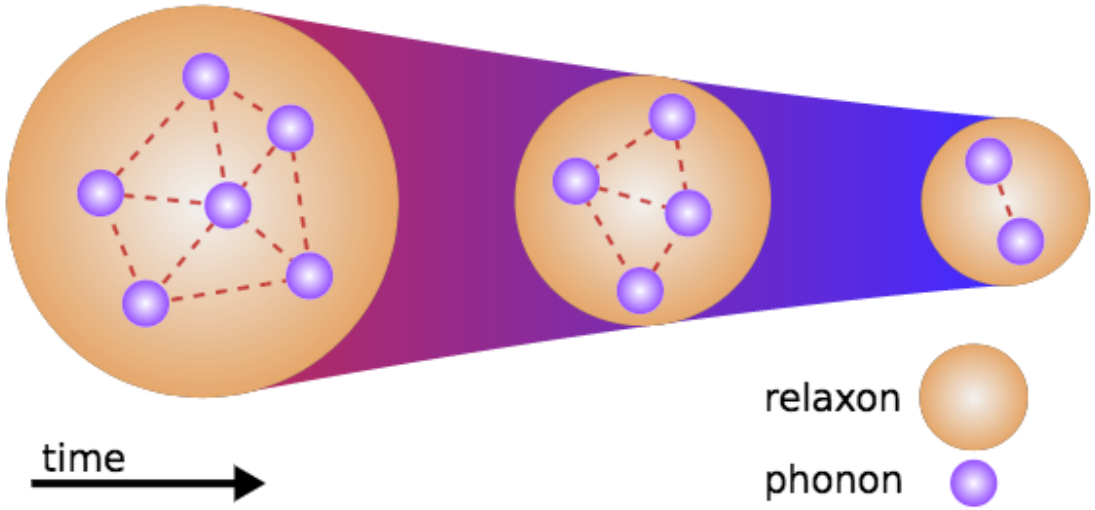
New Descriptions of Thermal Transport



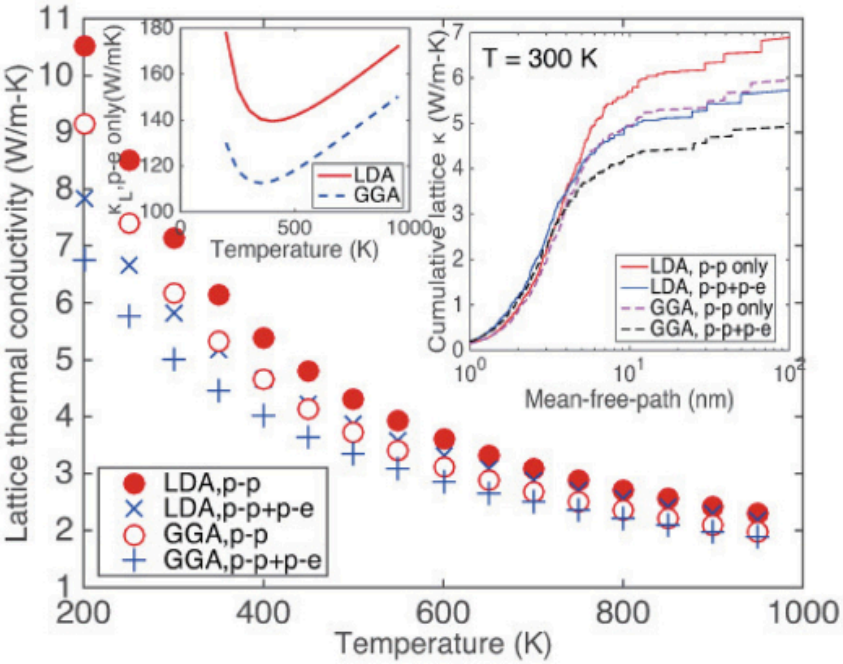
Lee et al.,
Nat. Comm. **6** (2015) 6290.

Relaxons

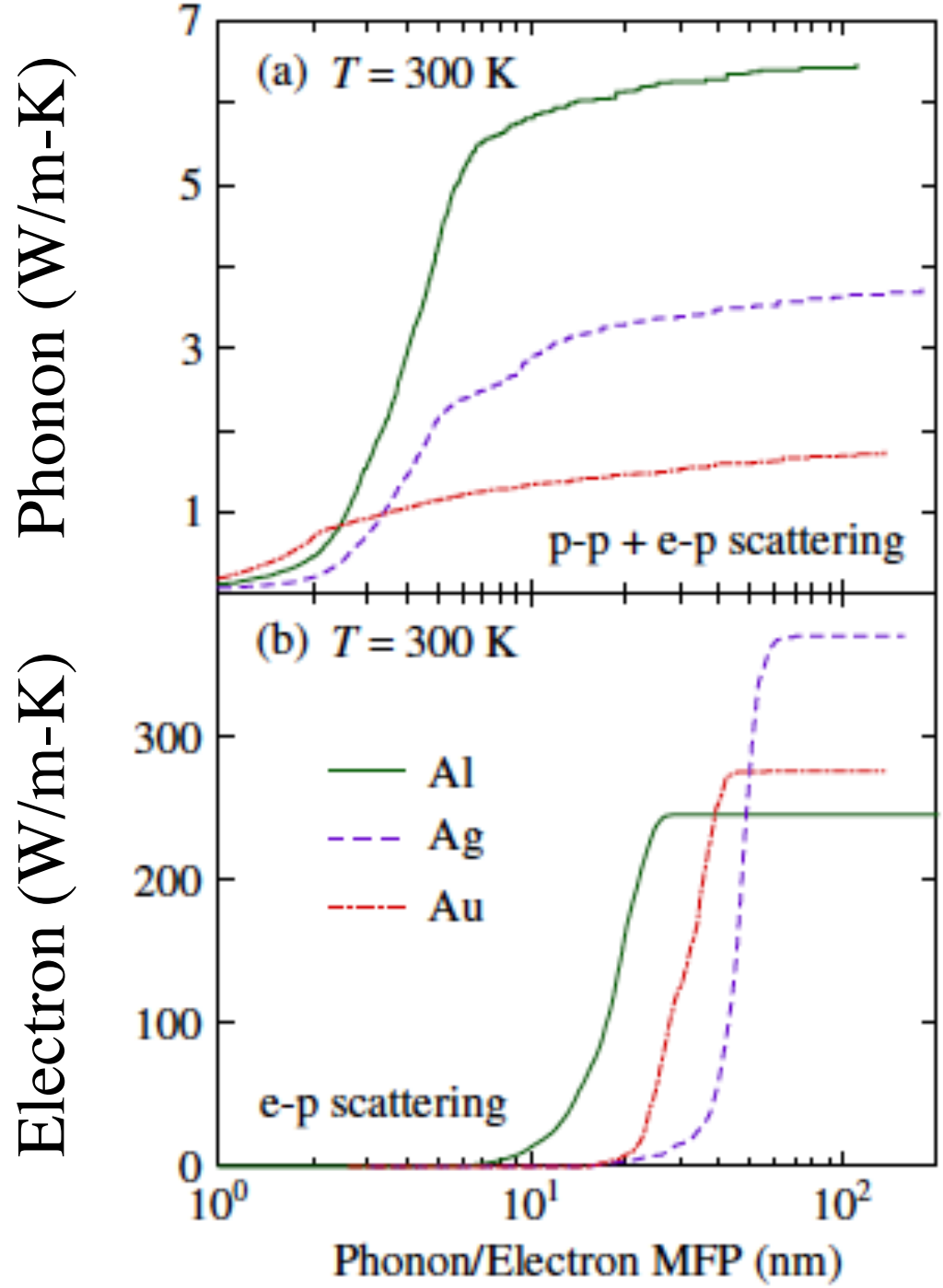


Cepellotti and Marzari, *PRX* **109** (2016) 041013.

Thermal Transport in Metals



Wang, Lu, and Ruan,
JAP **119** (2016) 225109.



Jain and McGaughey,
PRB **93** (2016) 081206(R).

A Huge Field! We Can't Cover Everything.

- Focus on bulk crystals using MD and LD
- Disordered materials (alloys and amorphous)
- Solving the Boltzmann transport equation (key for interpreting experiments)
  - Theoretical and numerical approaches
  - Austin Minnich, Gang Chen, Sandip Mazumder
- Interfaces (will discuss a bit)
- Fluids (no phonons, but can apply MD)