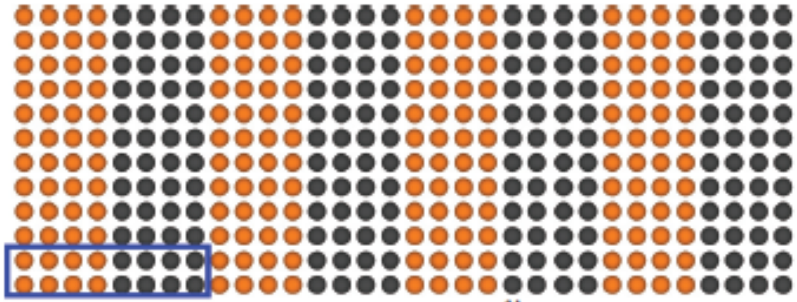

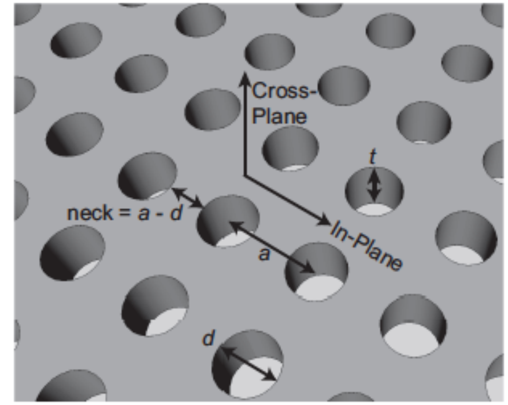

Phonon Transport in Periodic Materials with Feature Sizes of 1 nm to 1 μm

Alan McGaughey
Department of Mechanical Engineering
Carnegie Mellon University, Pittsburgh PA

CMU: Ankit Jain, Jason Larkin, Eric Landry
U. Toronto: Sam Huberman, Cristina Amon

Support: NSF, AFOSR

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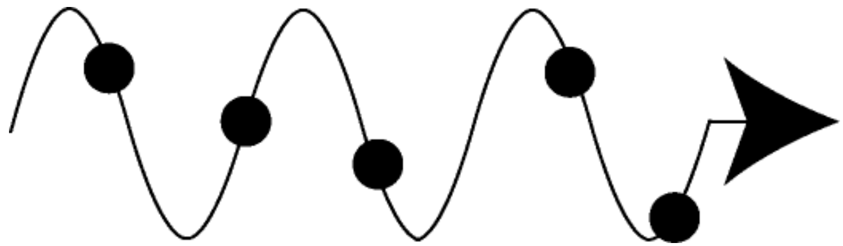
What is a Phonon?

- Quantized lattice vibration in a periodic material with energy $\hbar\omega$



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

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

Phonon Formula for Thermal Conductivity

Boltzmann transport equation + Fourier law

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

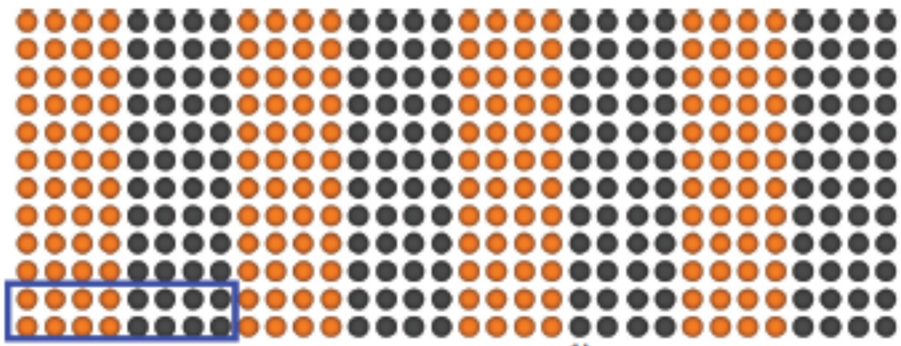
i : indexes over all phonon modes

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

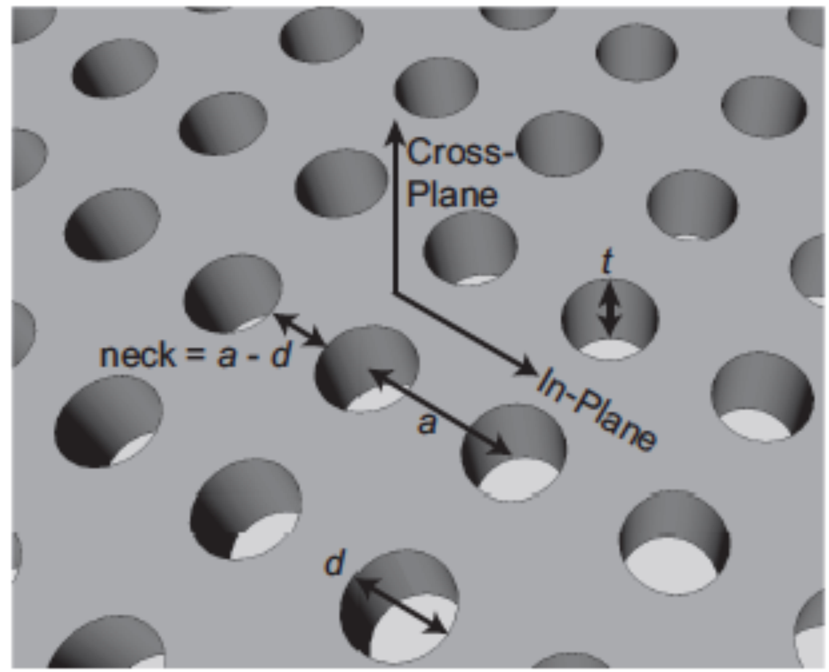
Λ_i : mean free path

Application to Periodic Materials

Superlattice



Porous Film



How to define the phonons?
What dispersion relation to use?

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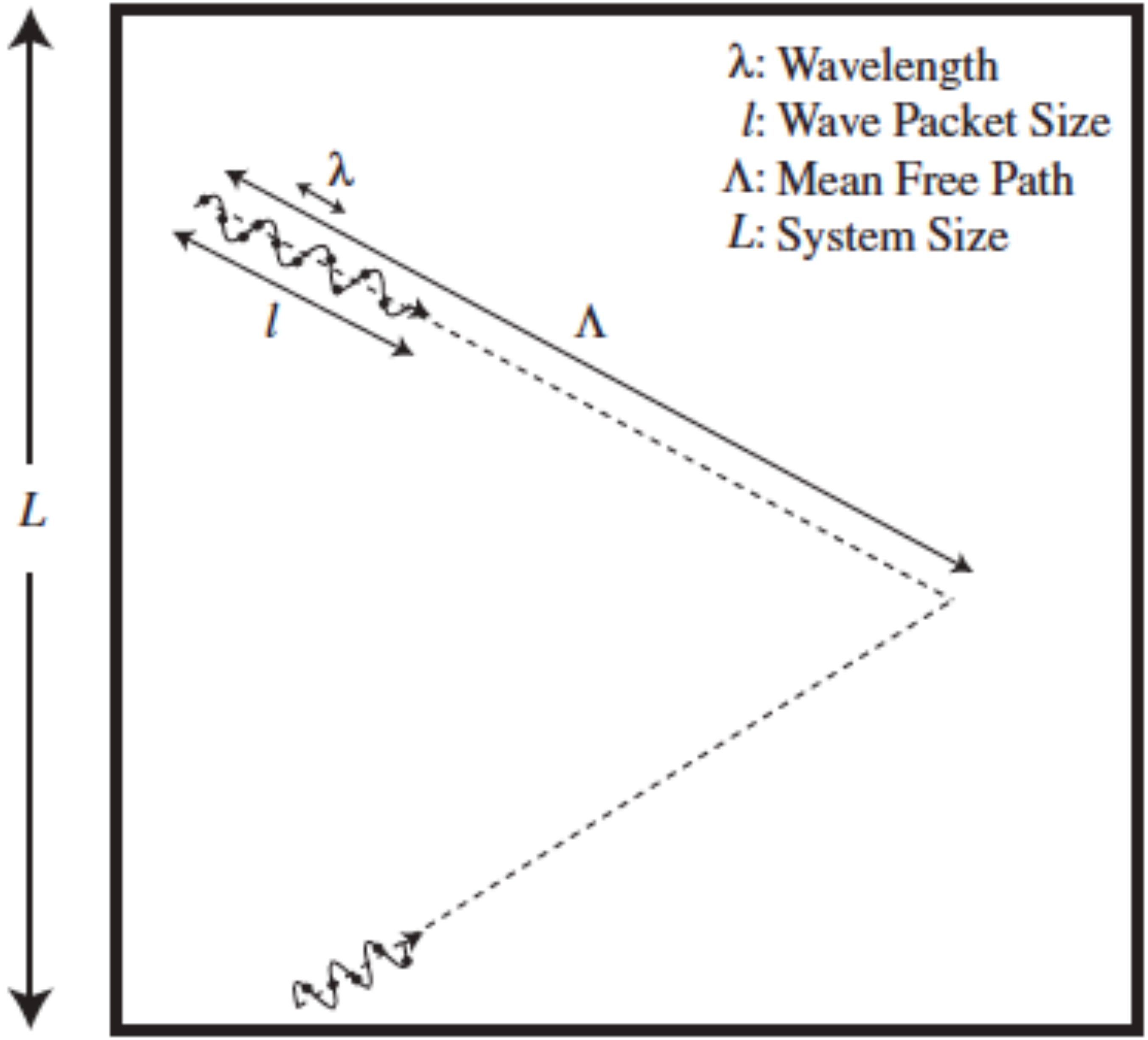
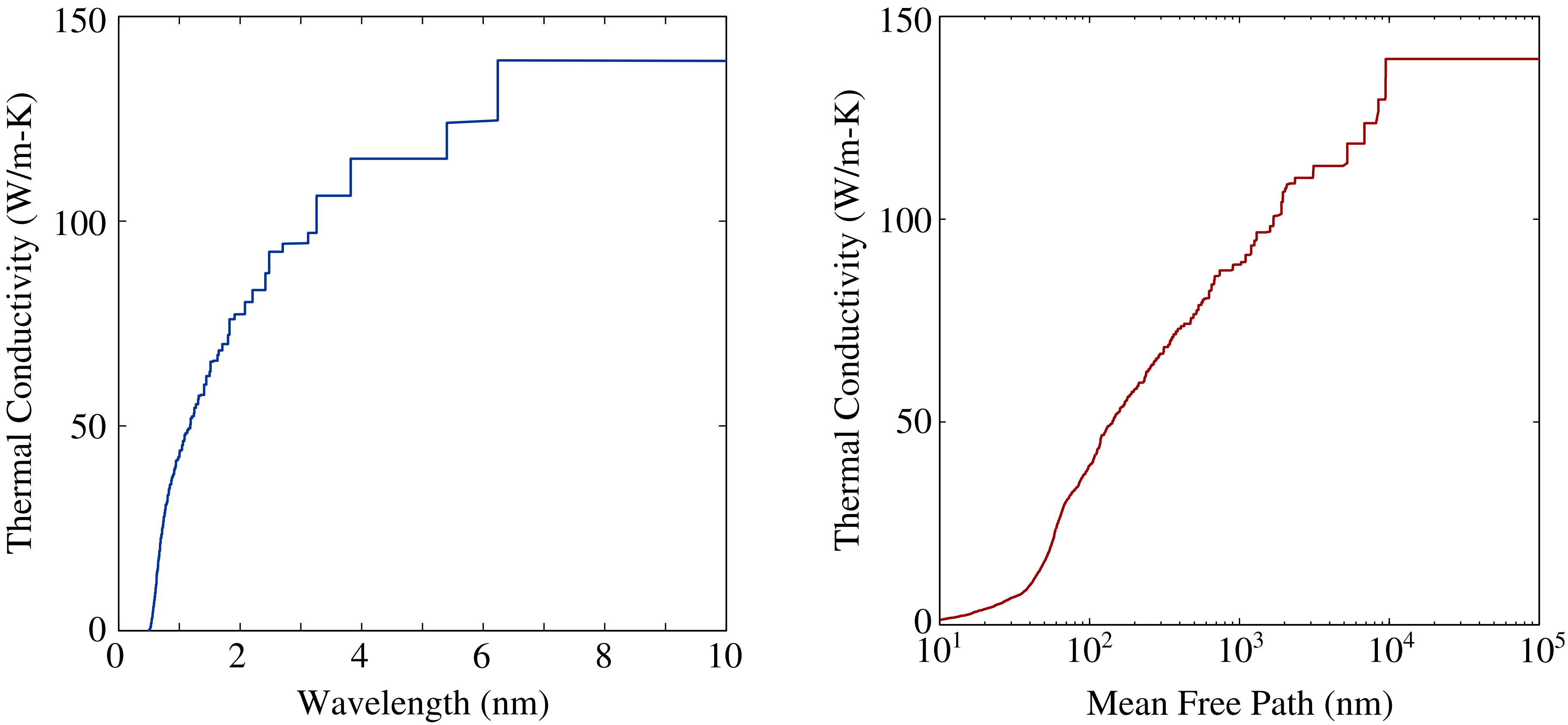
Length Scales in Phonon Transport



Bulk Silicon Accumulation

Phonon properties from first-principles calculations.



Boundary scattering important when mean free path > system size.

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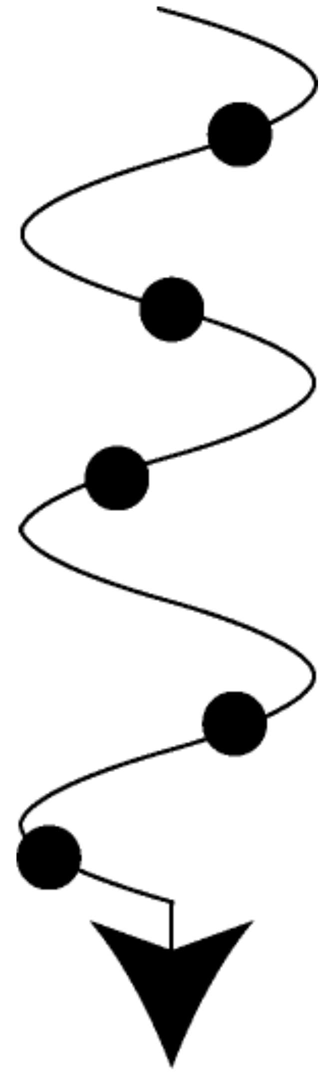
Outline



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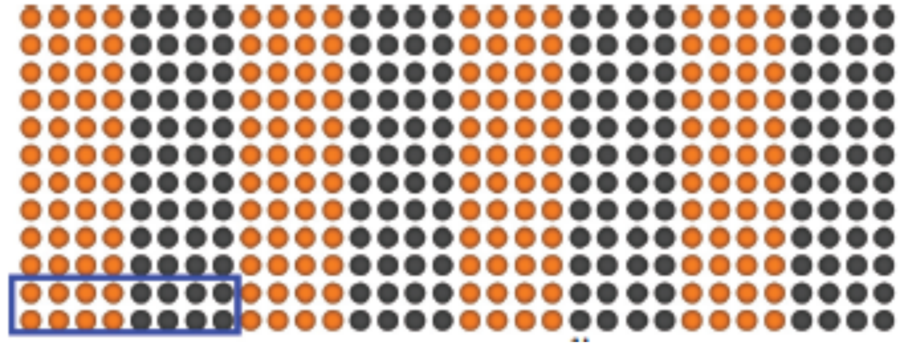
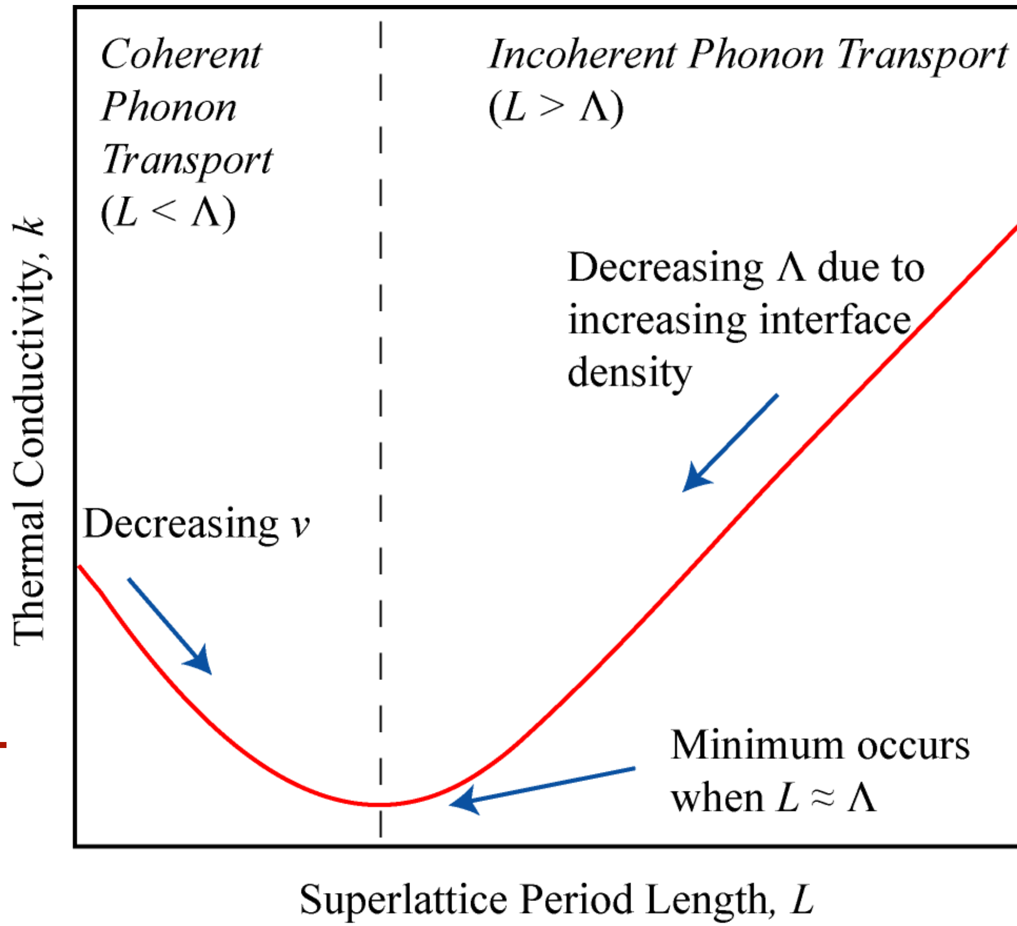
Proposed Phonon Transport Regimes





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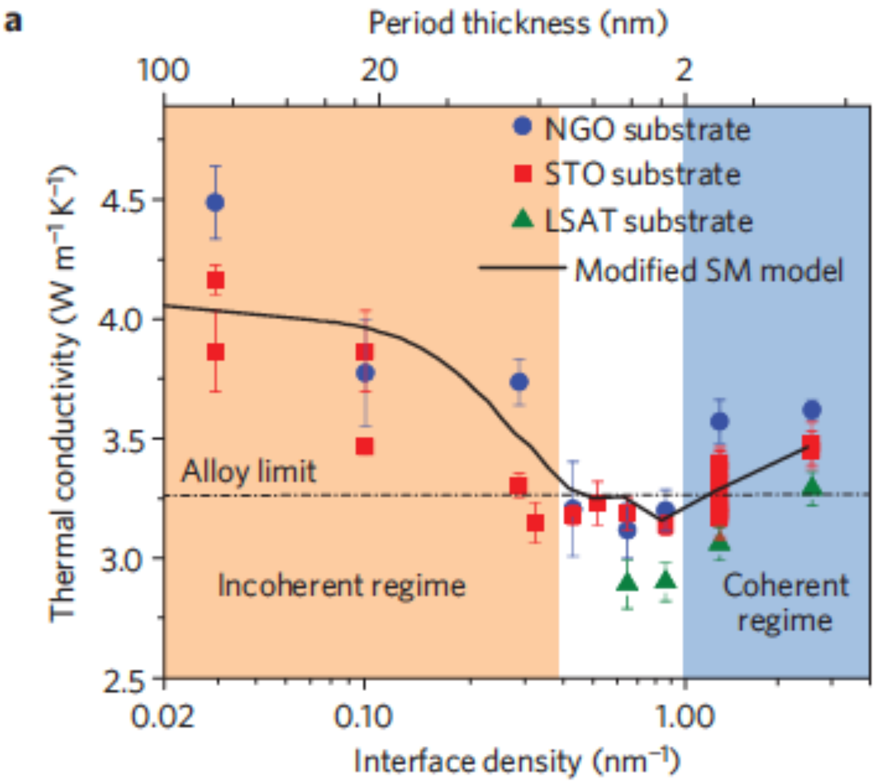
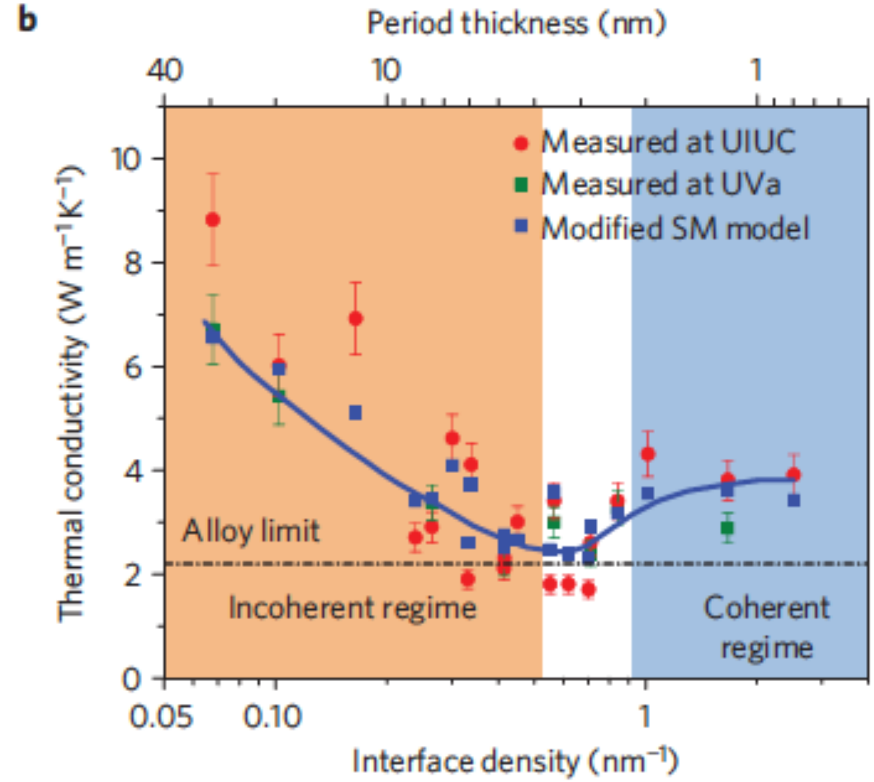
Experimental Evidence in Oxide Superlattices

$SrTiO_3/CaTiO_3$

$SrTiO_3/BaTiO_3$





Need interfaces of extremely high quality.

Ravichandran et al., *Nature Materials* **13**, 168-172 (2013)

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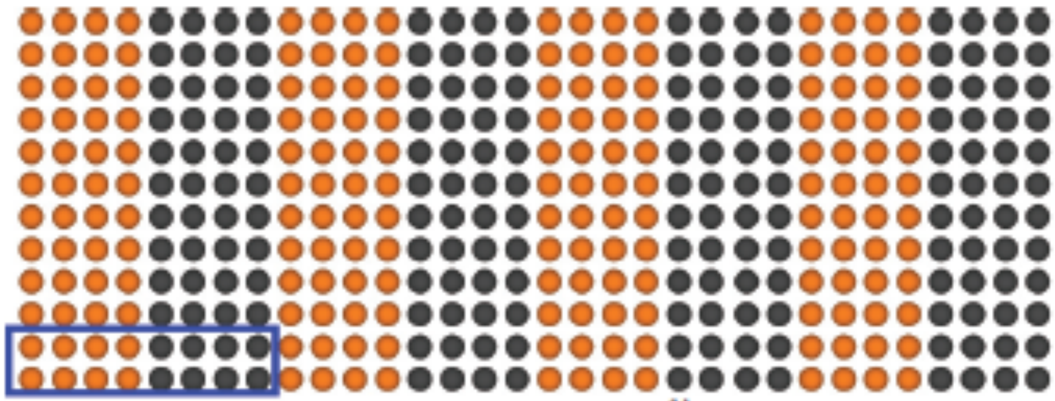
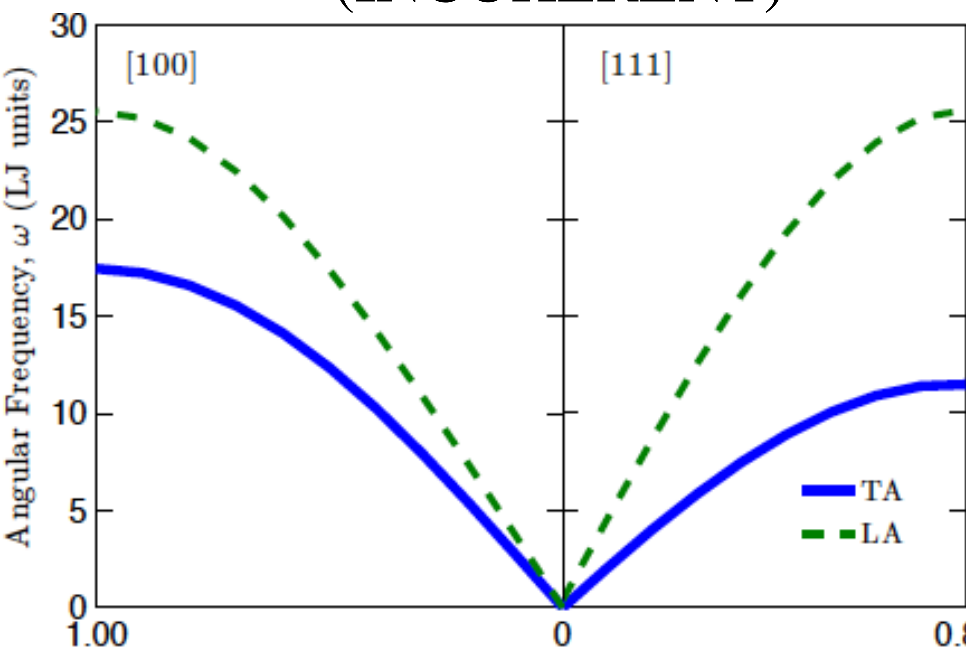
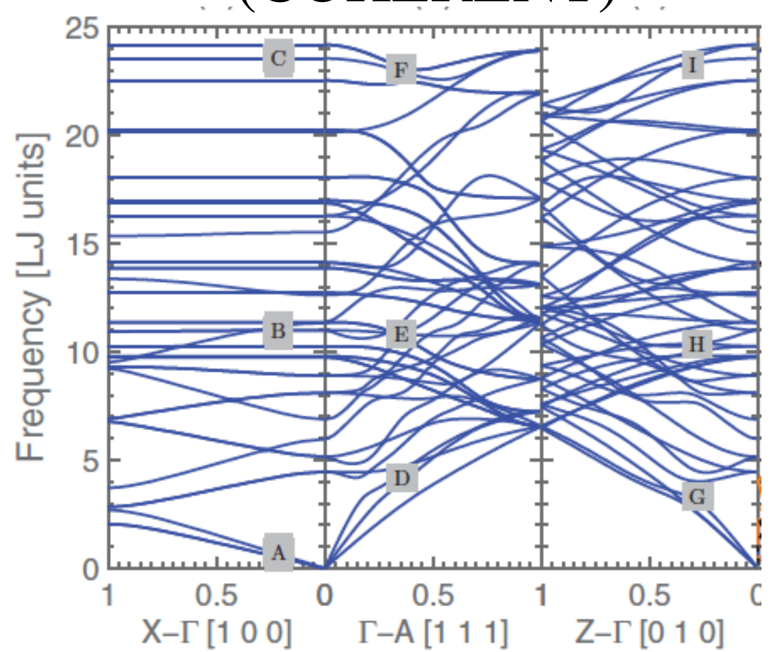
What Dispersion to Use?



Layer Lattice Constant
(INCOHERENT)



Superlattice Period
(COHERENT)



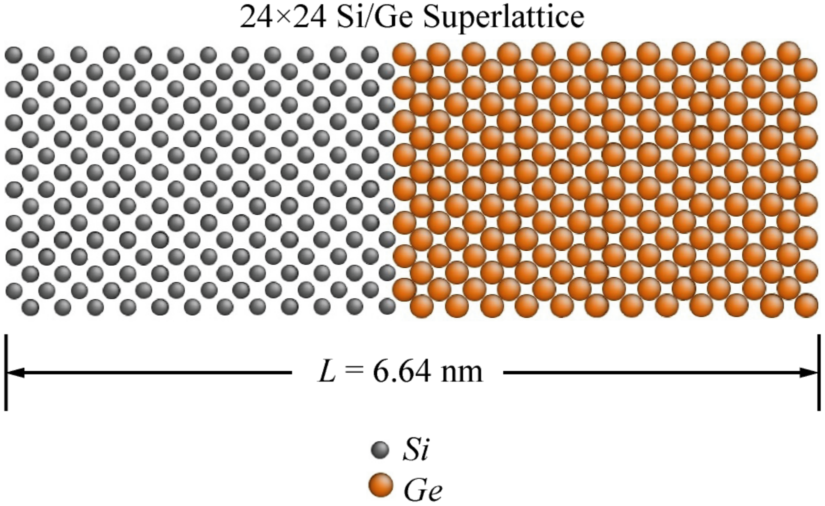
Silicon/Germanium Superlattices

Questions:

- Can we predict experimental trends?
- How does sample quality affect phonon transport?

Samples:

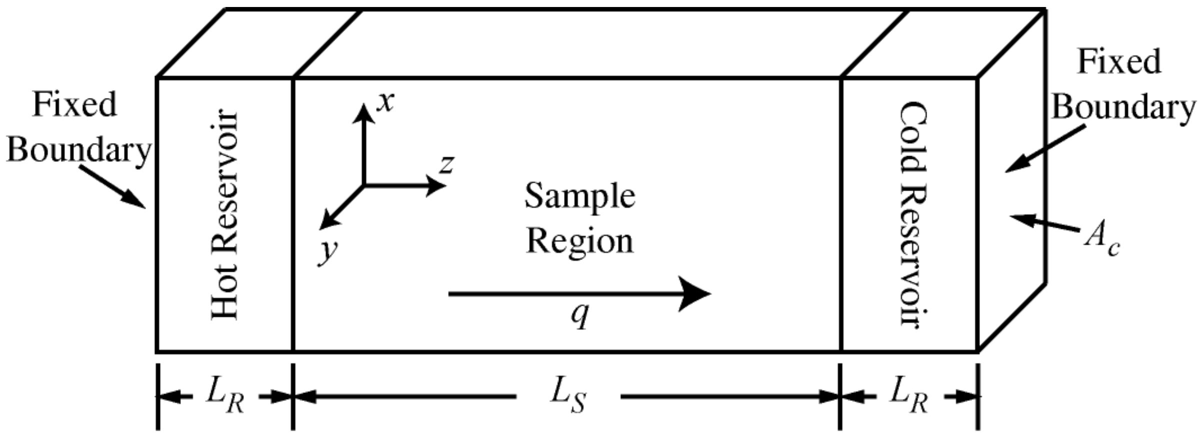
- Si/Ge superlattices
- Stillinger-Weber potential
- $T = 500$ K

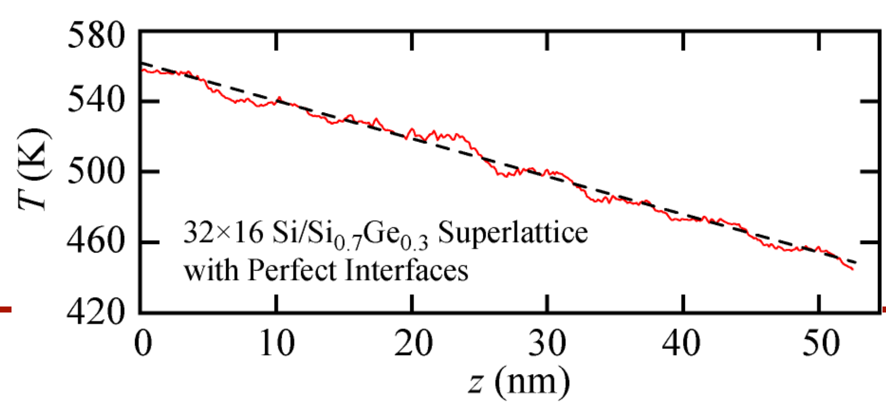


Landry and McGaughey, *Physical Review B* **79**, 075316 (2009).

Molecular Dynamics (MD) Simulations

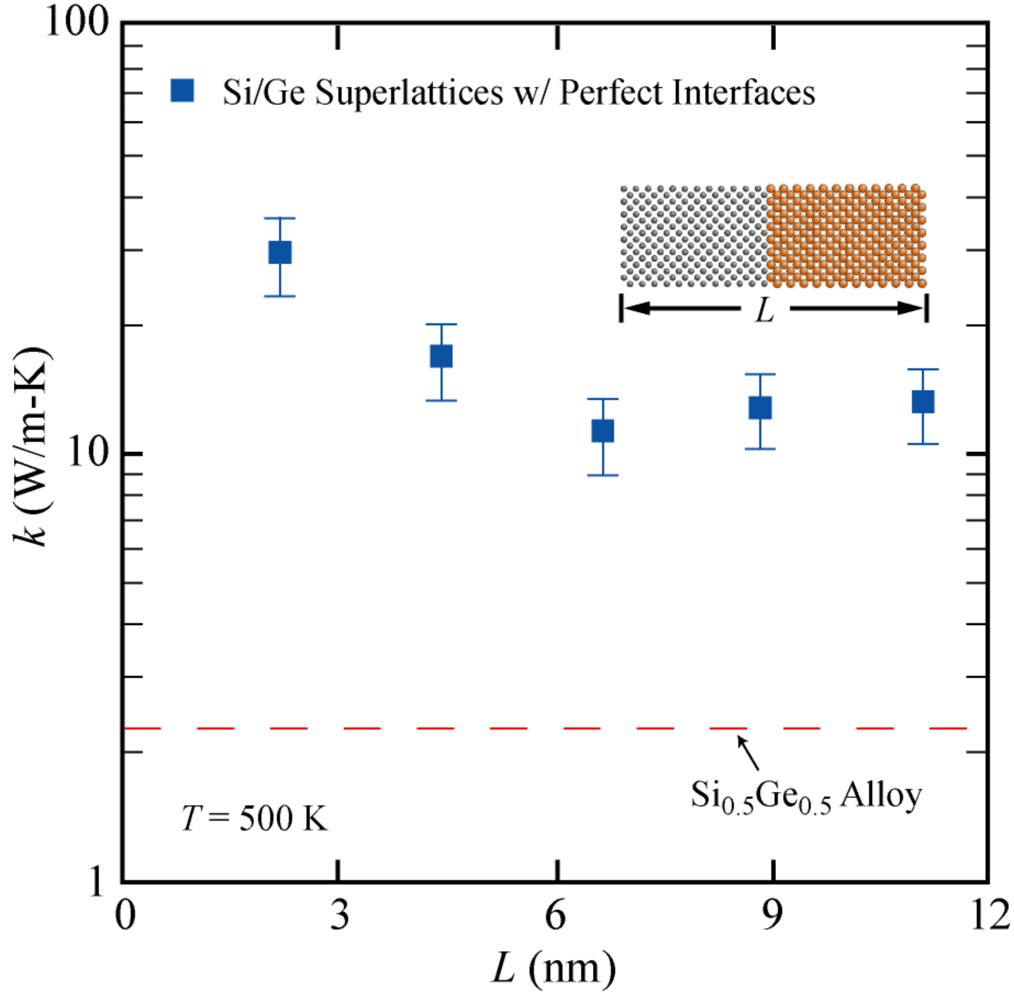
- Predict evolution of atomic positions/momentum using Newton's laws of motion.
- No assumptions about nature of phonon transport.





$$k = \frac{-q}{\partial T / \partial z}$$

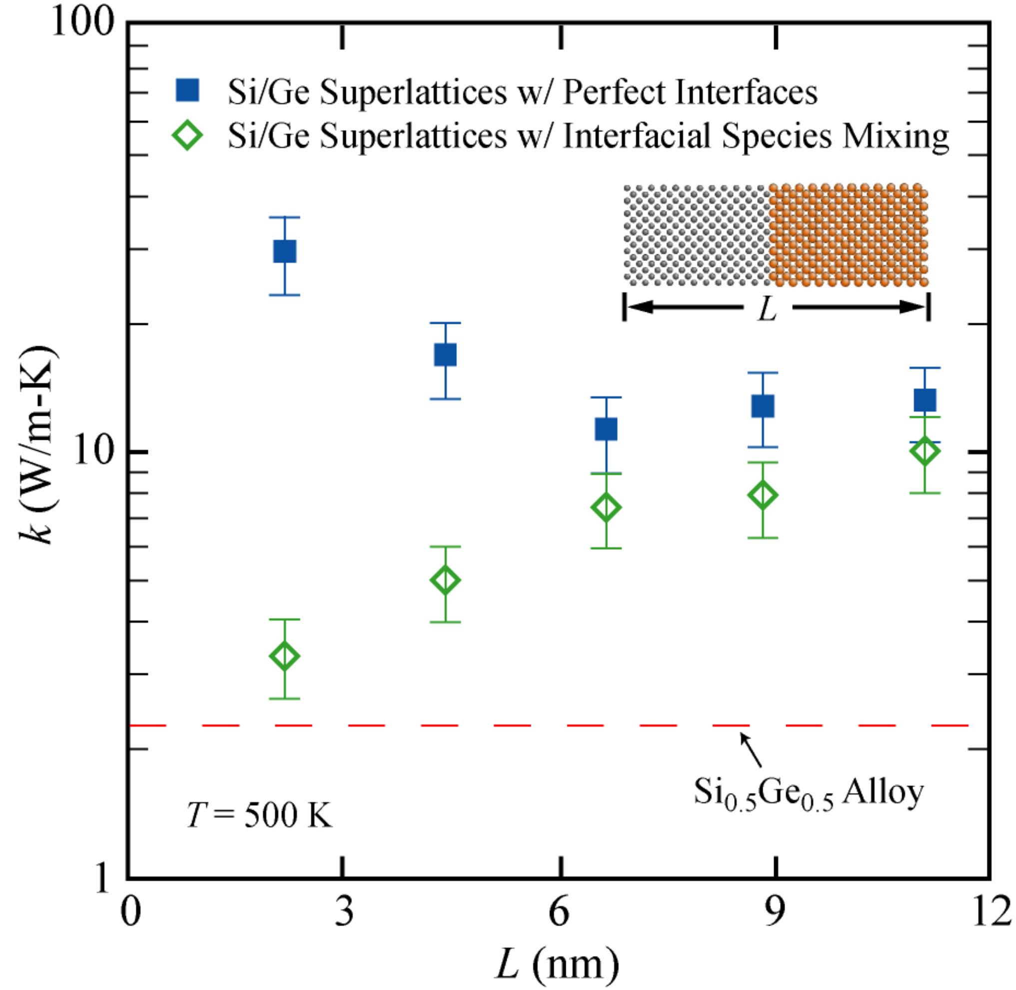
Si/Ge Superlattices with Perfect Interfaces



Thermal conductivity *decreases* with increasing period length.

Landry and McGaughey, *Physical Review B* **79**, 075316 (2009).

Si/Ge Superlattices with Interfacial Mixing



Thermal conductivity *increases* with increasing period length.

Landry and McGaughey, *Physical Review B* **79**, 075316 (2009).

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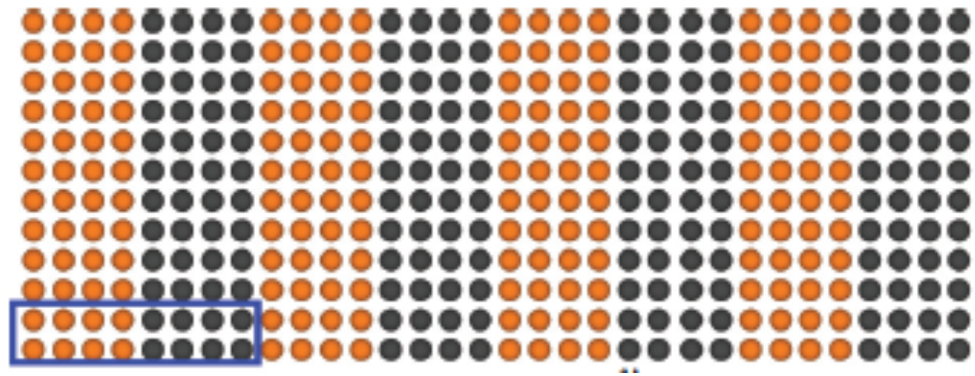
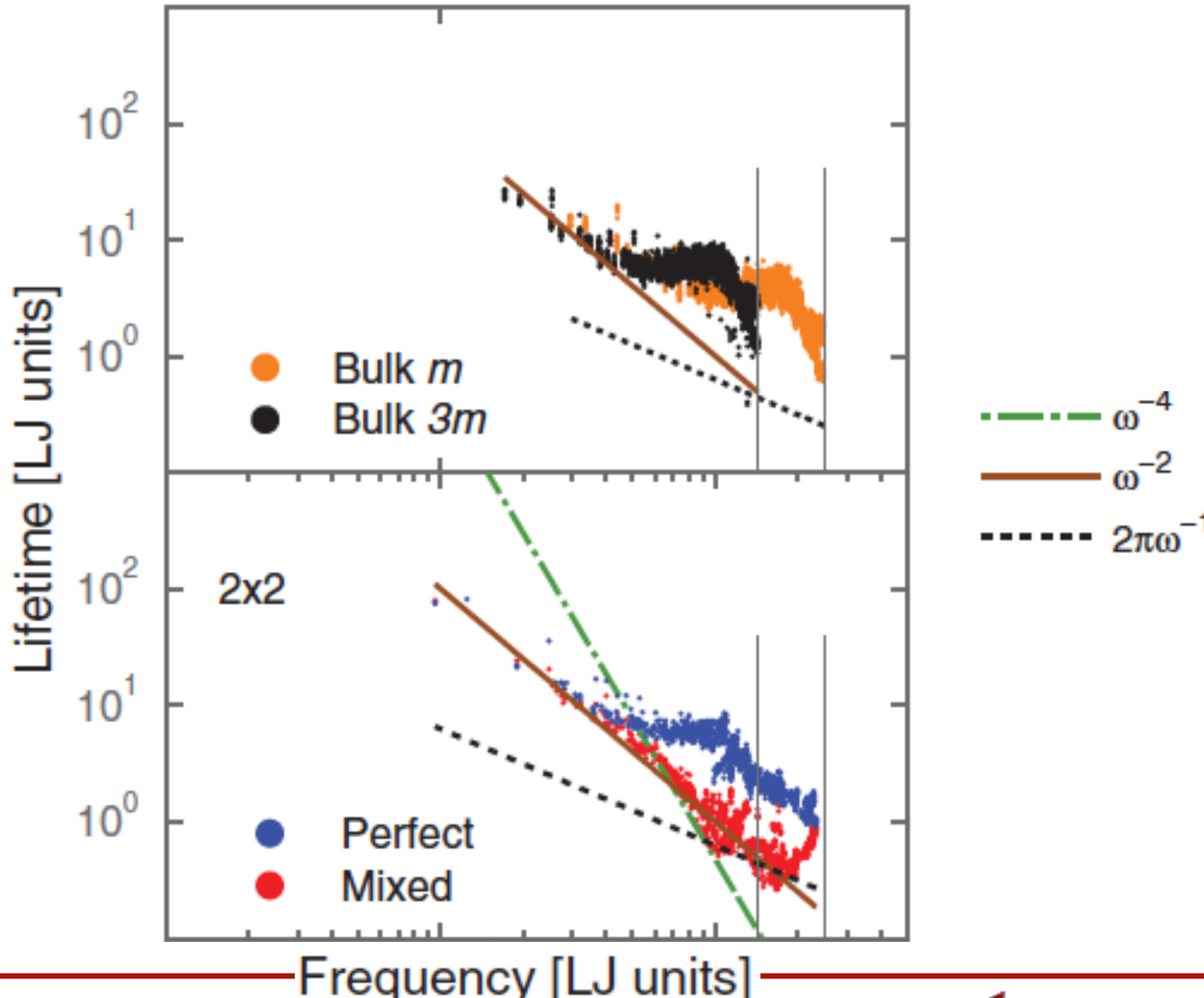
Lennard-Jones Superlattices

- Base: argon, $T = 20$ K, species differ only in mass
- Predict phonon properties and thermal conductivity
- MD simulations and lattice dynamics calculations
- Perfect and mixed interfaces



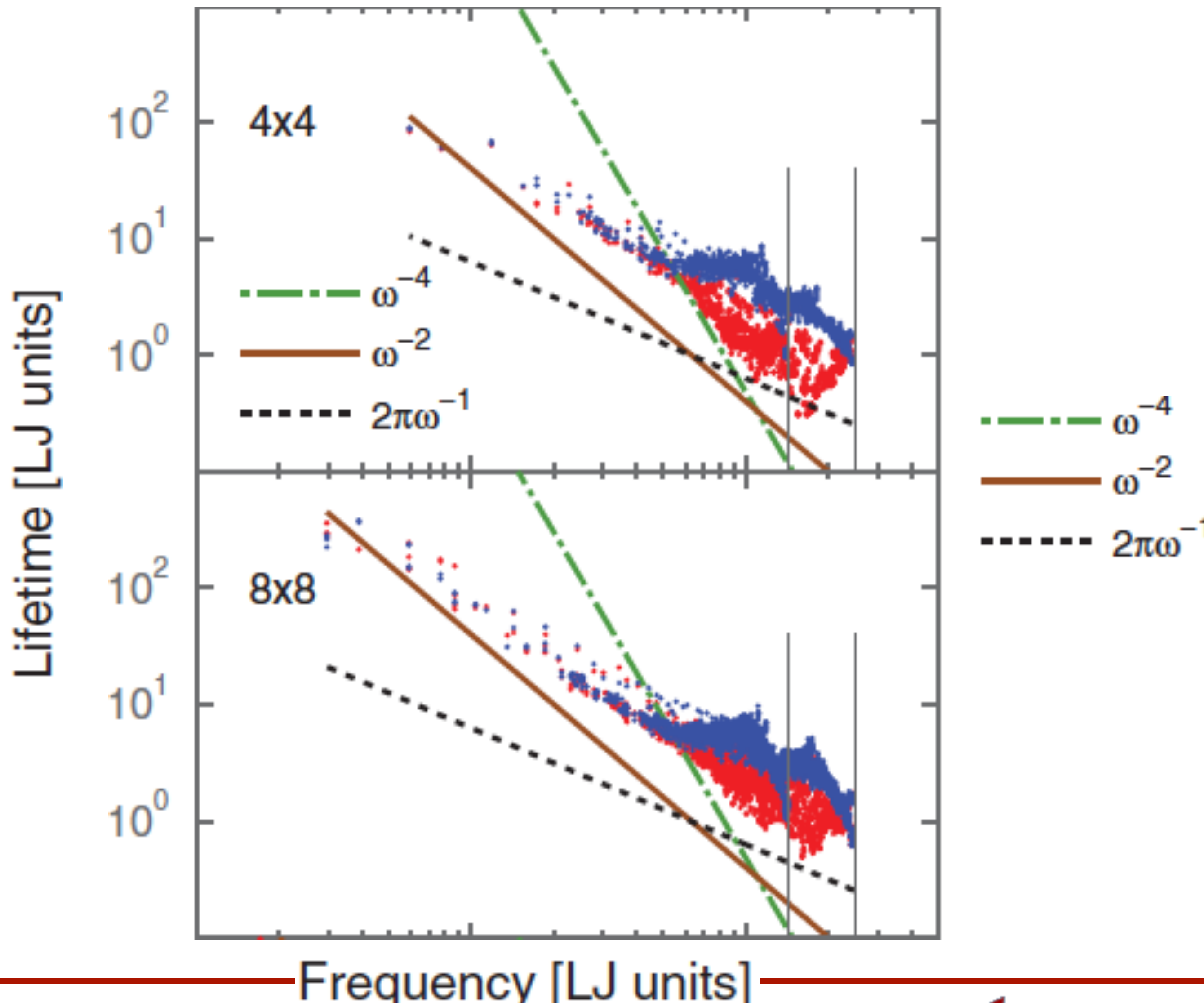
Huberman, Larkin, McGaughey & Amon, *Physical Review B* **88**, 155311 (2013).

Phonon Lifetimes



Huberman, Larkin, McGaughey & Amon, *Physical Review B* **88**, 155311 (2013).

More Phonon Lifetimes



Huberman, Larkin, McGaughey & Amon, *Physical Review B* **88**, 155311 (2013).

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Phonon Transport in Superlattices

- Superlattice dispersion always valid for perfect systems
- Interface mixing affects high frequency (short wavelength) modes
  - Superlattice dispersion a good approximation for most modes
- Bulk dispersion only a good approximation when period length >> wavelength (mode dependent effect)

Outline

1. Introduction
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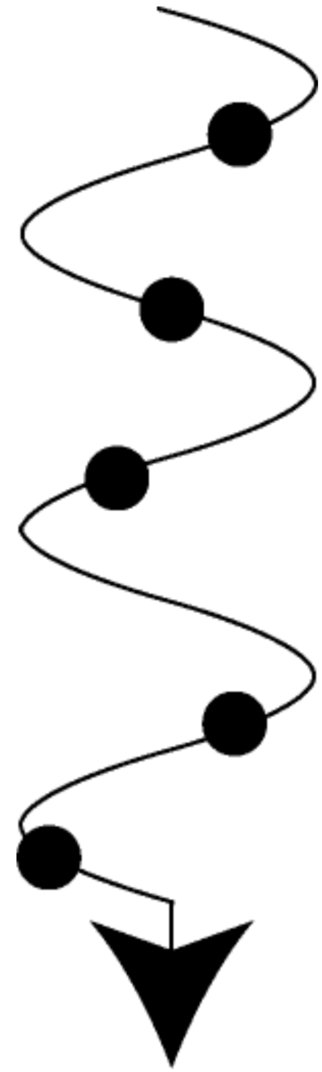

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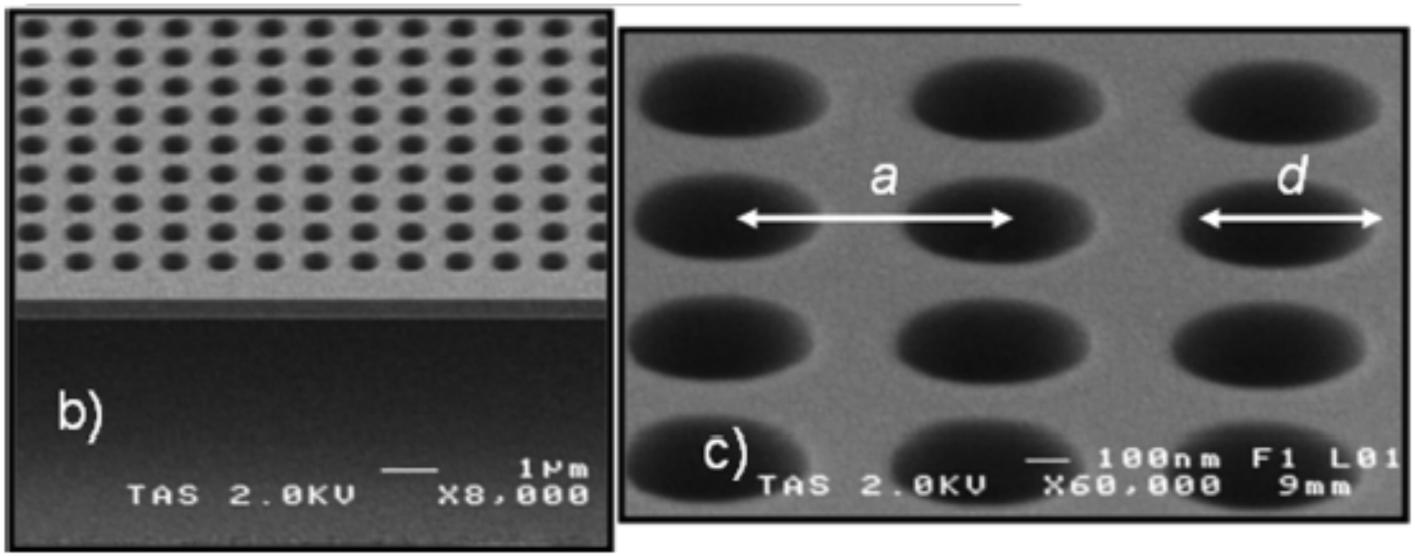
Objective

Predict the thermal conductivity of a silicon structure like this:



in a few seconds.

Hopkins et al., *Nano Letters* **11**, 107 (2011)

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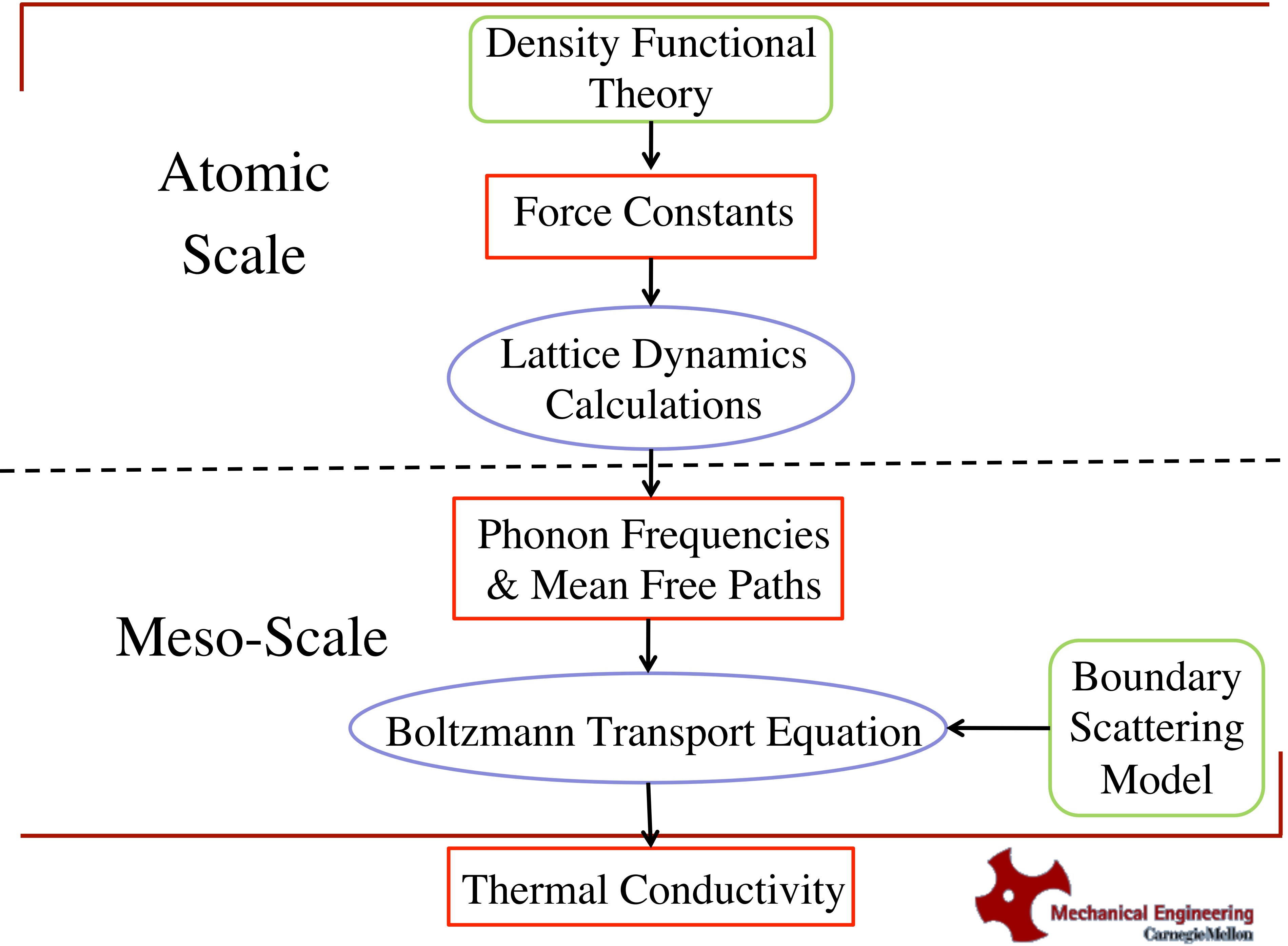
Density Functional Theory
Atomic Scale
Force Constants
Lattice Dynamics Calculations
Phonon Frequencies & Mean Free Paths
Meso-Scale
Boltzmann Transport Equation
Boundary Scattering Model
Thermal Conductivity
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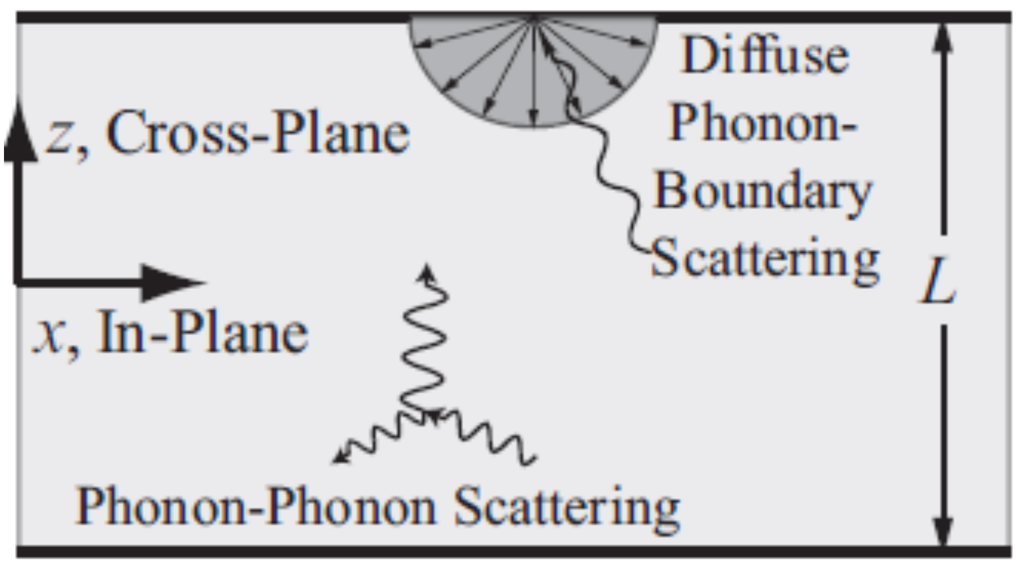
Thin Film Model

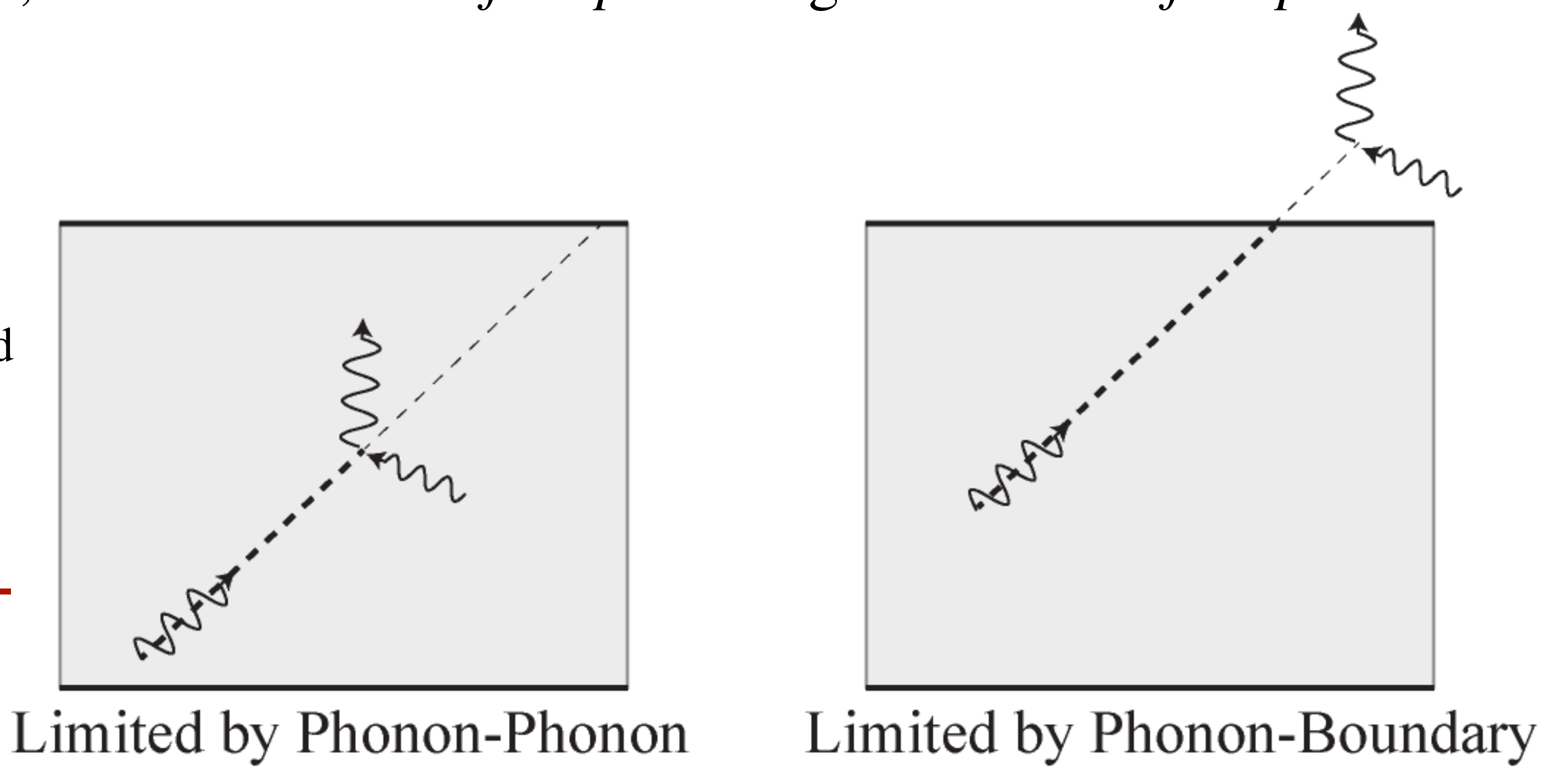


Turney et al., *JAP* **107**, 024317 (2010)

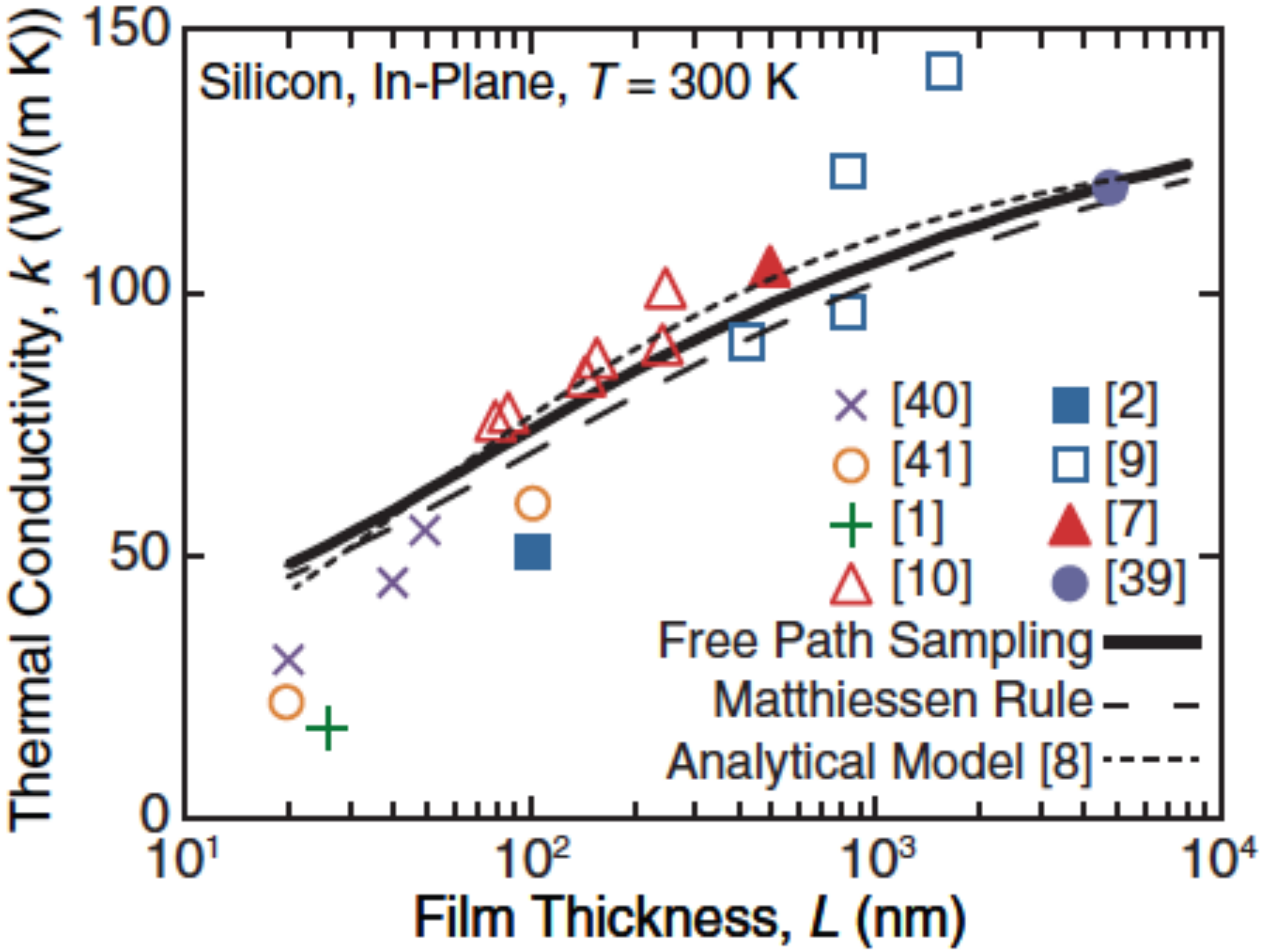
Random Sampling of Free Paths

- For every phonon mode, do the following 1,000 times:
  1. Phonon-phonon free path from a Poisson distribution.
  2. Randomly select a starting point. Use group velocity vector to calculate phonon-boundary free path.
  3. Smaller of these two quantities is the nanostructure free path
- Average 1,000 nanostructure *free paths* to give the *mean free path*.

McGaughey and Jain, *APL* **100**, 061911 (2012).



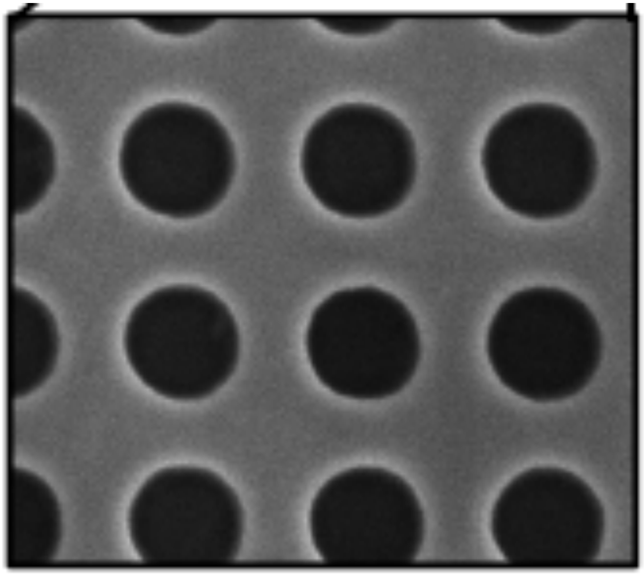
In-Plane: Comparison to Experiments



Jain, Yu, and McGaughey, *Physical Review B* **87**, 195301 (2013).

Sandia: Experimental Measurements @ 300 K

- In-Plane Measurements: 16 samples, 500 nm thick
  - Pore separation: 500-900 nm
  - Pore diameter: 213-535 nm
  - Porosity: 0.07-0.38
  - Steady-state measurement
  - SAND2012-0127



- Cross-Plane Measurements: 4 samples, 500 nm thick
  - Pore separation: 500-800 nm
  - Pore diameter: 300-400 nm
  - Porosity: 0.20-0.28
  - Time-domain thermoreflectance
  - Hopkins et al., *Nano Letters* **11**, 107 (2011)

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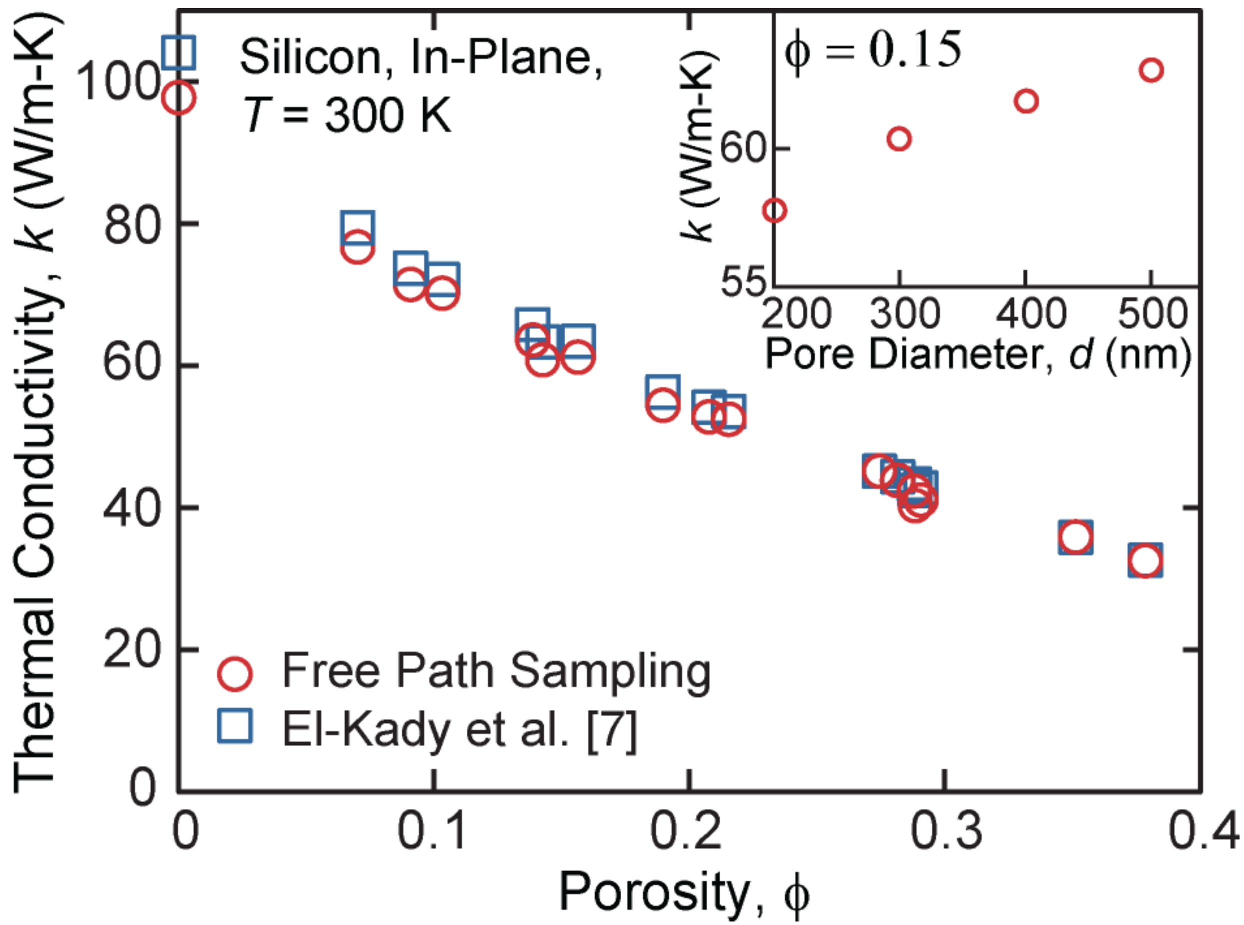
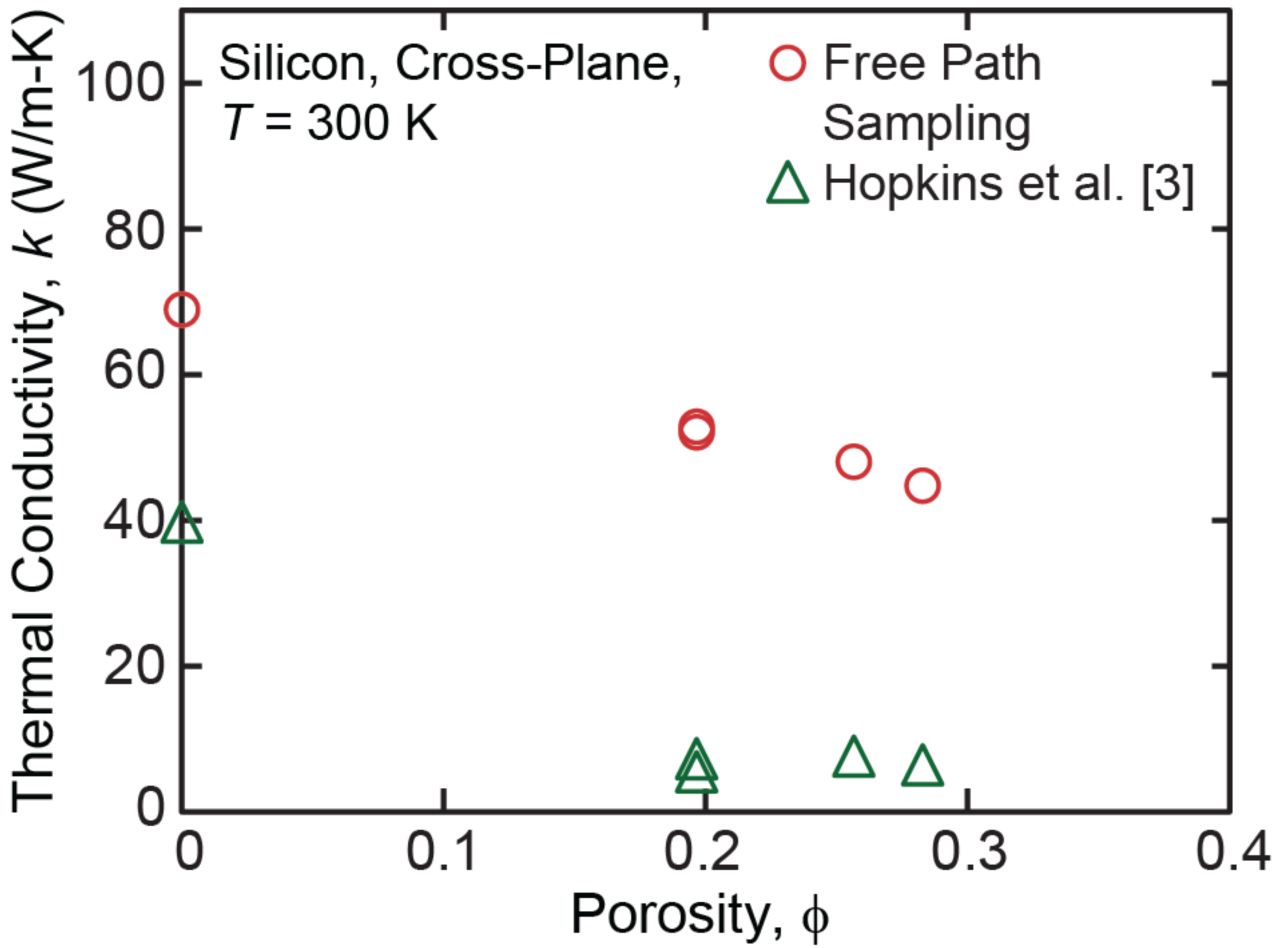
In-Plane Comparison



No evidence of coherent effects.

Jain, Yu, and McGaughey, *Physical Review B* **87**, 195301 (2013).

Cross-Plane Comparison



Jain, Yu, and McGaughey, *Physical Review B* **87**, 195301 (2013).

Phonon Transport in Porous Films

- Phonon properties obtained from first-principles can predict the measured thermal conductivities of silicon thin films.
- No evidence for coherent transport in in-plane direction for porous films.
- Unexplained cross-plane porous film thermal conductivities.

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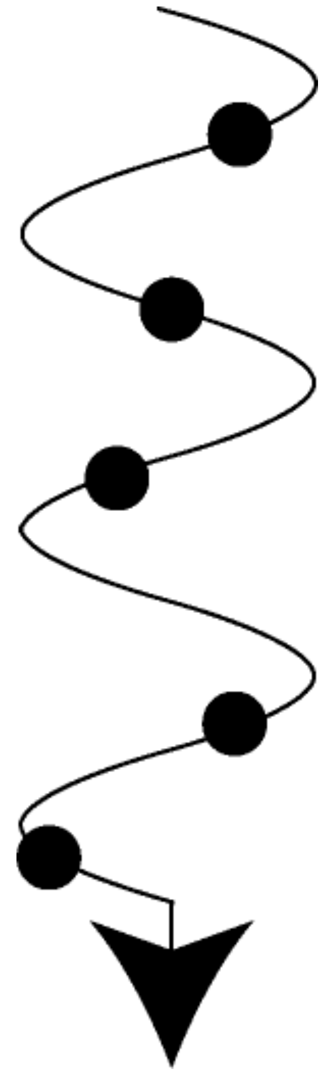

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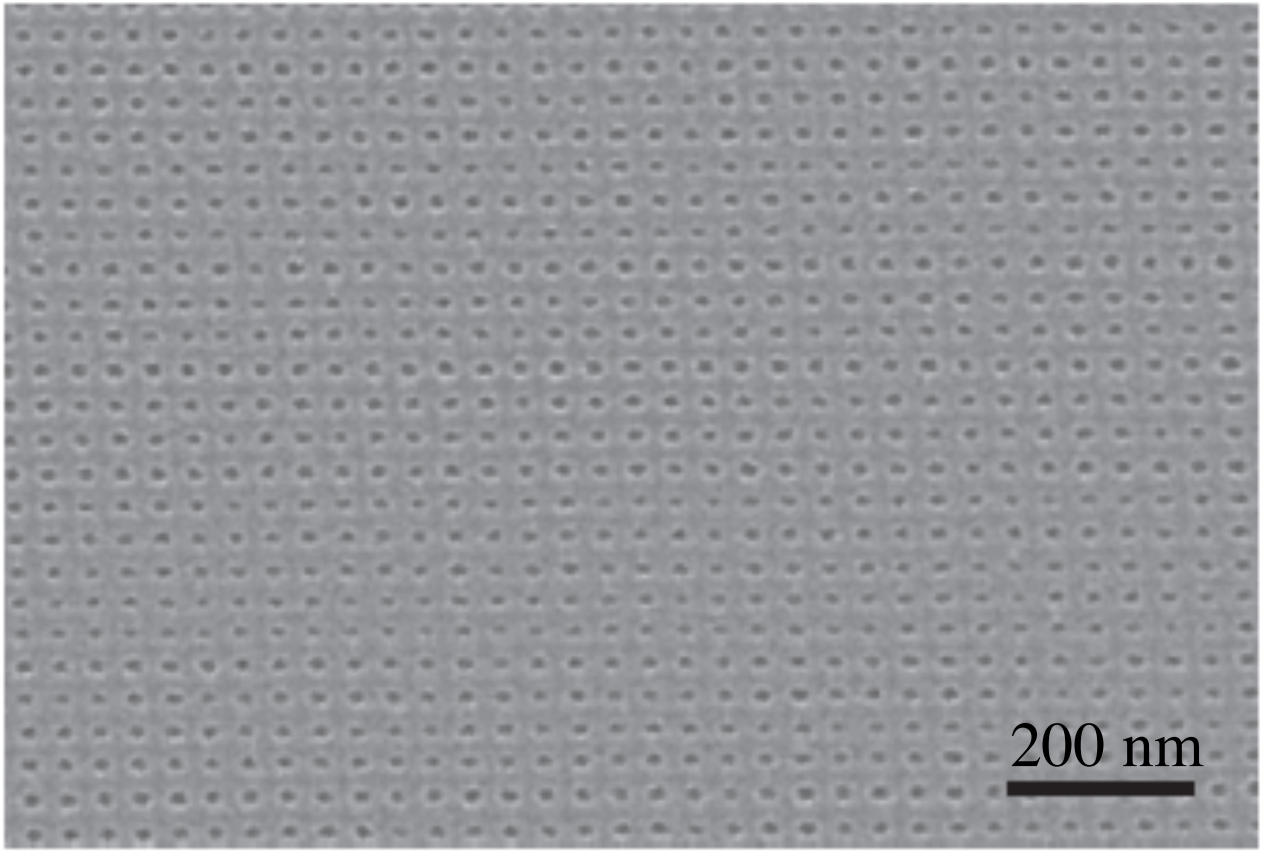
Summary

- "Coherent" phonons follow dispersion of secondary periodicity
  - Relevant length scale: wavelength (<10 nm at 300 K)
  - Evidence in experimental and modeling on high-quality superlattices

- "Incoherent" phonons scatter with boundaries
  - Interface or free surface
  - Relevant length scale: mean free path (<10 μm at 300 K in Si)

Bridge Length Scales to Promote Coherence



But what about variability in the pore size and surface roughness?

Use temperature to adjust what phonon wavelengths are important.

Yu et al., *Nature Nanotech.* **5**, 718 (2010)

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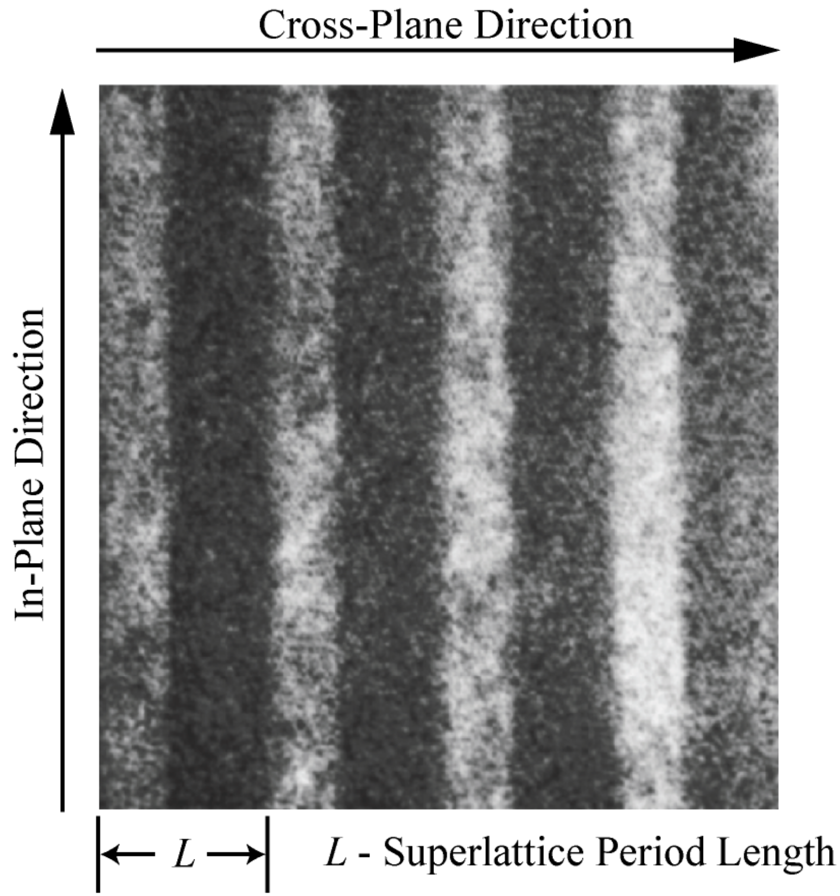
Semiconductor superlattices

- Periodic, composite material with layers as thin as 1-10 nanometers.
- *Phonons* (quantized lattice vibrations) are the dominant thermal energy carriers.
- The electrical energy is carried by either *electrons* or *holes*.
- Phonon scattering at interfaces reduces k without degrading the charge transport, leading to high ZT.

$$ZT = \frac{S^2 \sigma}{k} T$$



Dark grey: Si (5.9 nm)
Light grey: $Si_{0.78}Ge_{0.22}$ (7.4 nm)

TEM image from D. B. Aubertine and P. C. McIntyre, *J. Appl. Phys.* **97** (2005) 013531.

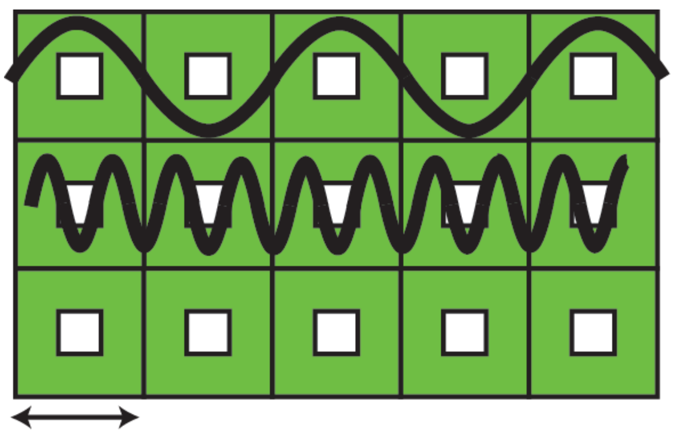
Interest in Porous Films

ENGINEERING: Thermoelectric Energy Conversion

$$ZT = \frac{S^2 \sigma T}{k_e + k_p}$$

Is it small?

SCIENCE: "Coherent" Phonon Effects and Role in Thermal Transport



Vibrational Modes Emerge Based on Supercell Periodicity

Supercell Lattice Constant >> Primitive Cell Lattice Constant

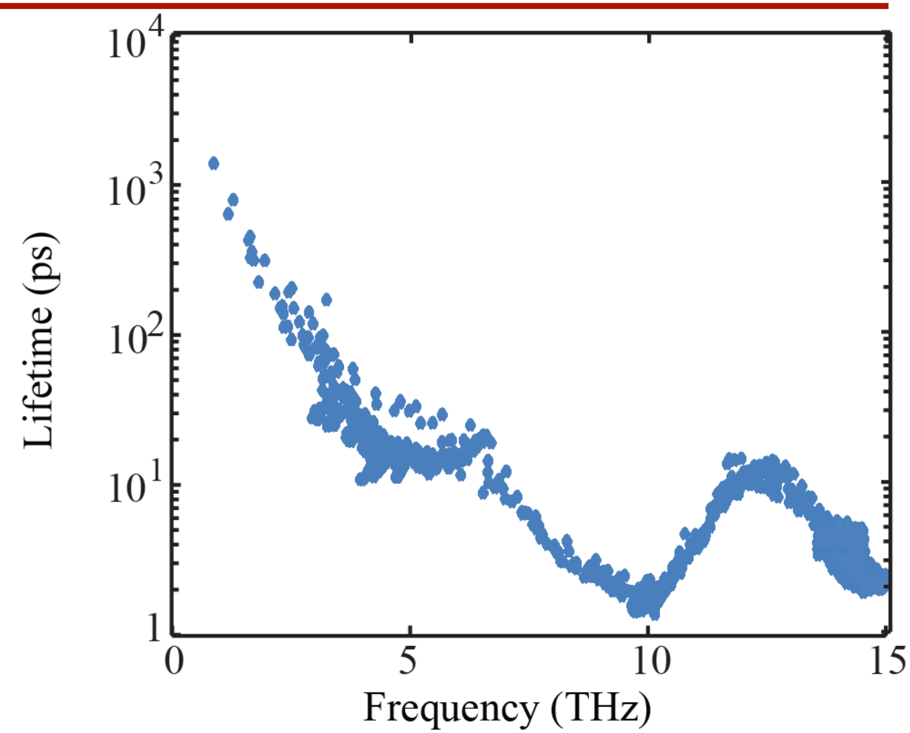
Bulk Silicon from First Principles

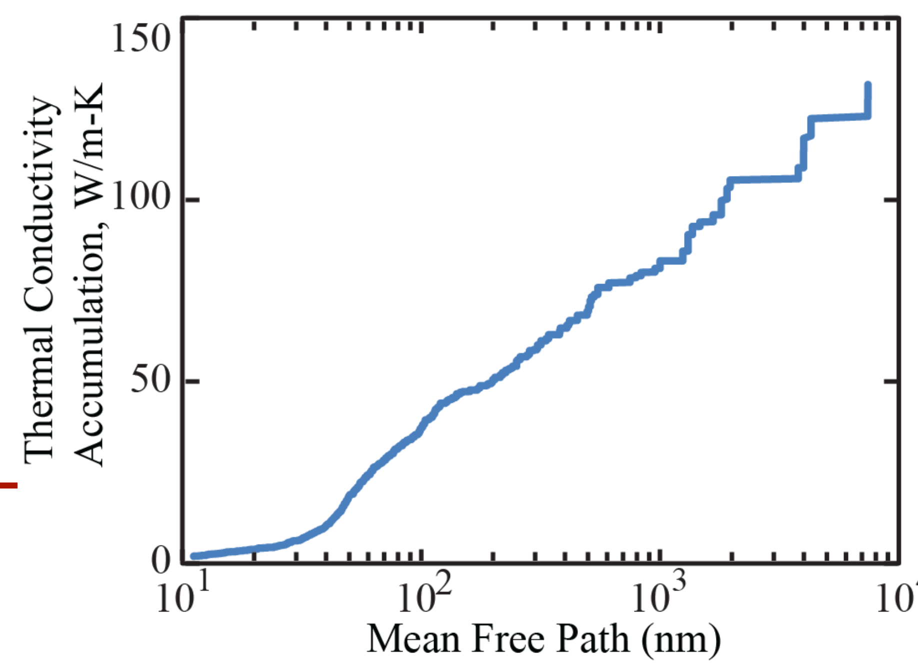
- Harmonic & anharmonic lattice dynamics calculations for 34,992 phonons in the first Brillouin zone

- T = 300 K

$$k_{theory} = 132 \text{ W/m-K}$$
$$k_{bulk,\ experiment} = 145 \text{ W/m-K}$$

Silicon phonon properties courtesy of Keivan Esfarjani, MIT.





Thermal Conductivity Prediction

Predicted from theory →

$$k_{CP,solid} = \sum_i c_{v,i} v_{g,i,CP}^2 \frac{\Lambda_i}{|\mathbf{v}_{g,i}|}$$

Measured experimentally →

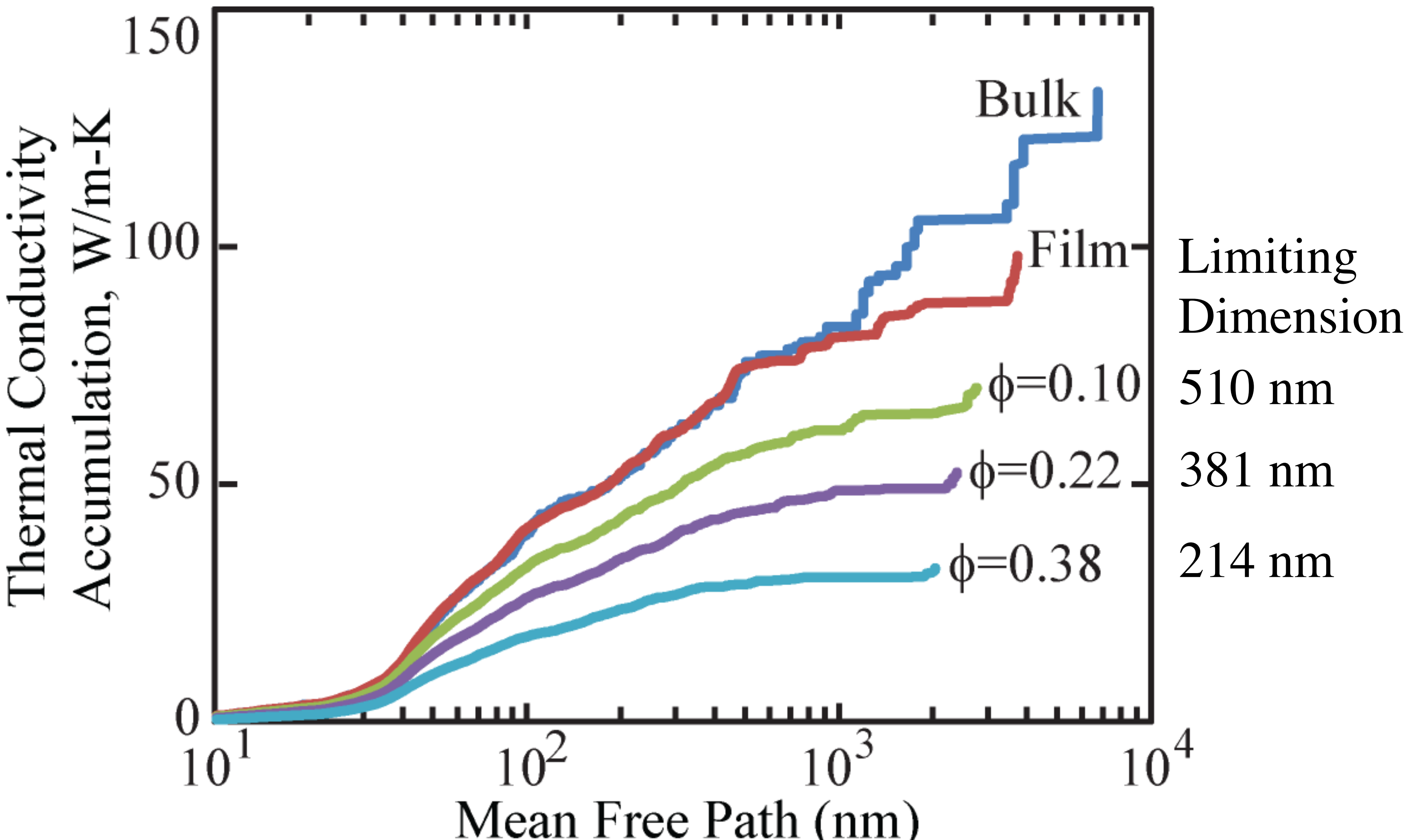
$$k_{CP,matrix} = k_{CP,solid} \times (1-\phi), \quad \phi = \text{porosity}$$

$$k_{IP,solid} = \sum_i c_{v,i} v_{g,i,IP}^2 \frac{\Lambda_i}{|\mathbf{v}_{g,i}|}$$

$$k_{IP,matrix} = k_{IP,solid} \times \frac{1-\phi}{1+\phi}$$

← Hashin Factor

Thermal Conductivity Accumulation



Jain, Yu, and McGaughey, *Physical Review B* **87**, 195301 (2013).