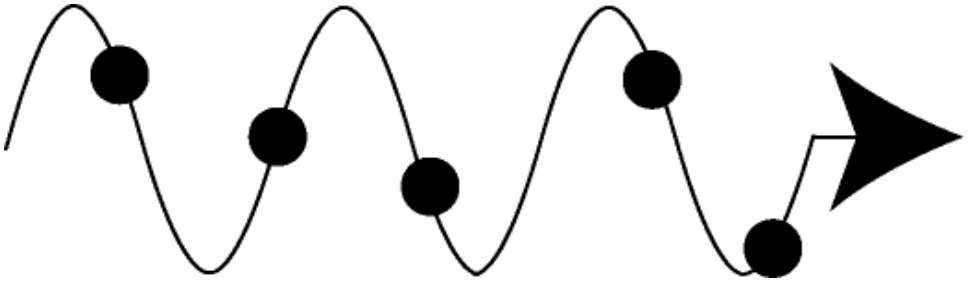

Molecular-Level Modeling of Phonon Transport: Formulation, Implementation, and Applications

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Mechanical Engineering
CarnegieMellon

Outline

Session I

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

Session II

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

Phonon Formula for Thermal Conductivity

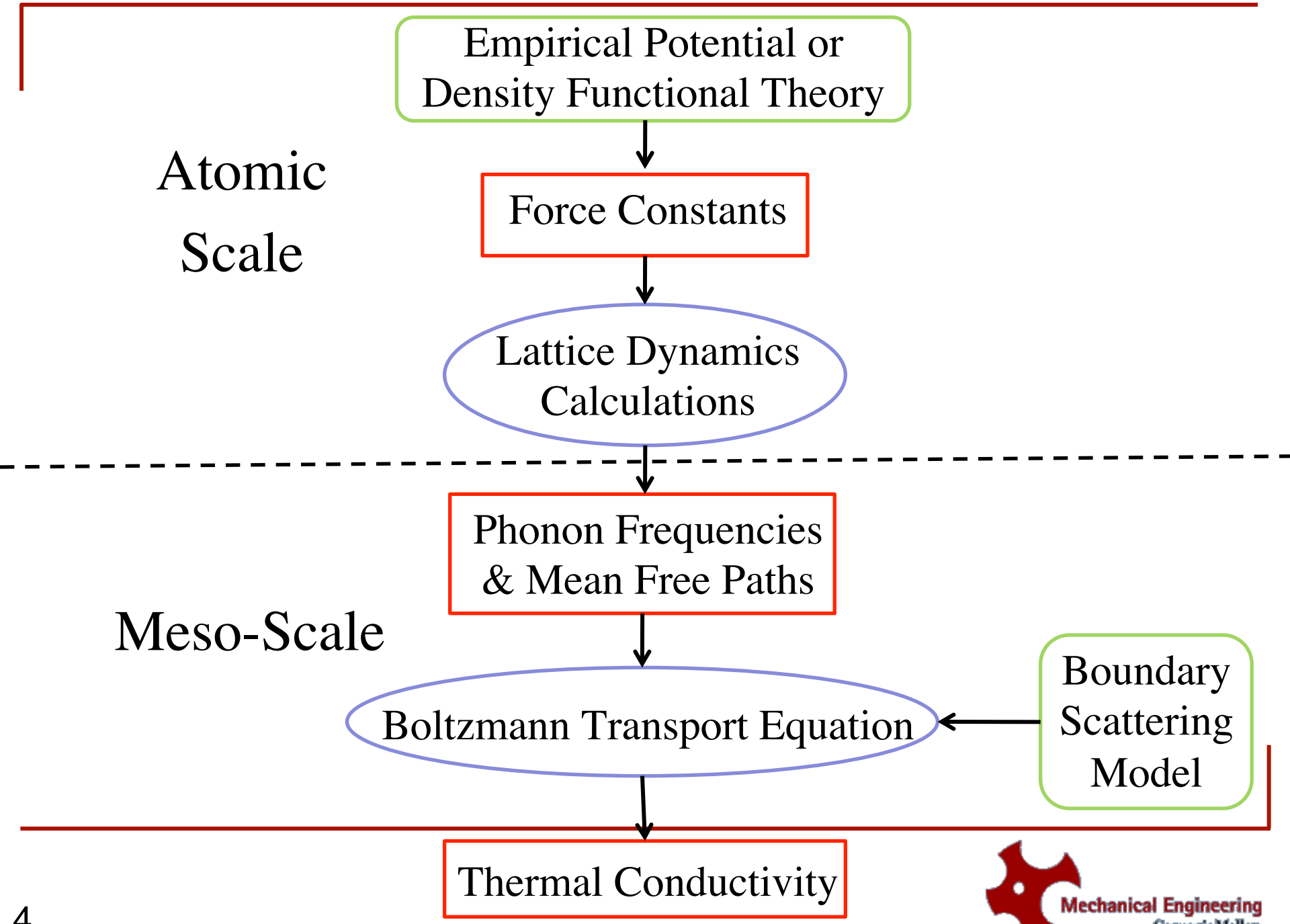
Boltzmann transport equation + Fourier law

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

i : indexes over all phonon modes

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

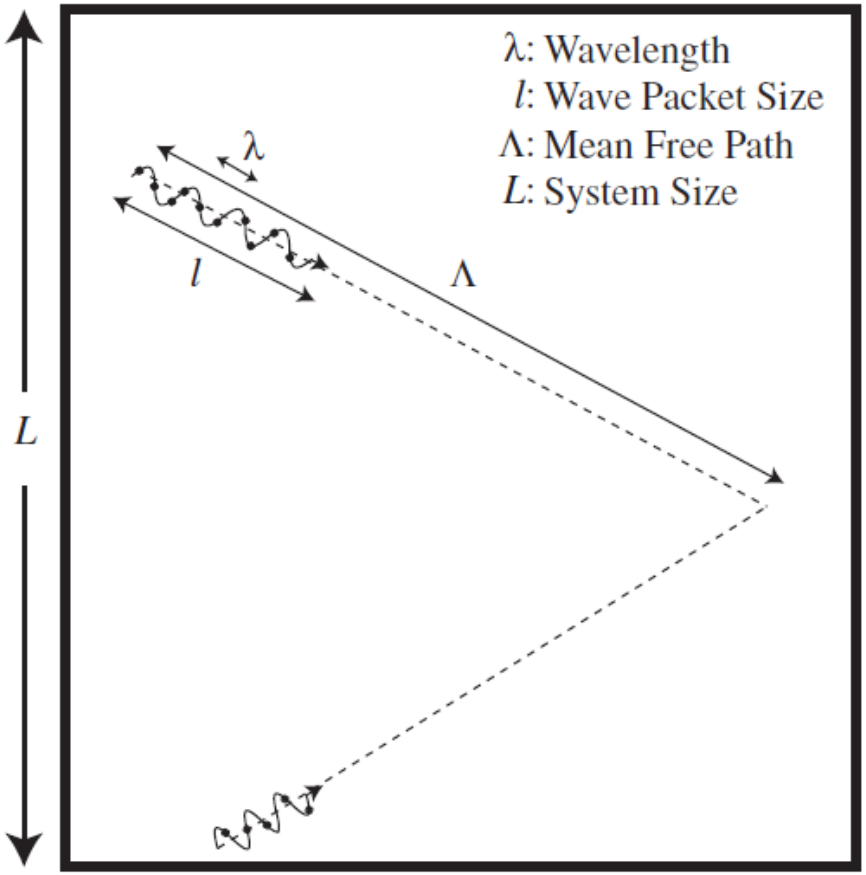
τ_i : lifetime $\quad$ Λ_i : mean free path



Transport and Scattering

Phonons scatter with:

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



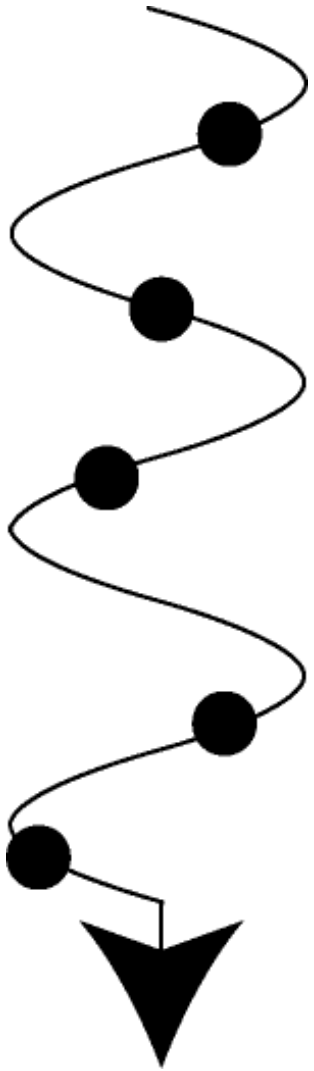
McGaughey and Kaviany, *PRB* **71**, 184305 (2005).

Outline

1. Force Constants, Phonons, and Thermal Conductivity

2. First Principles Approach

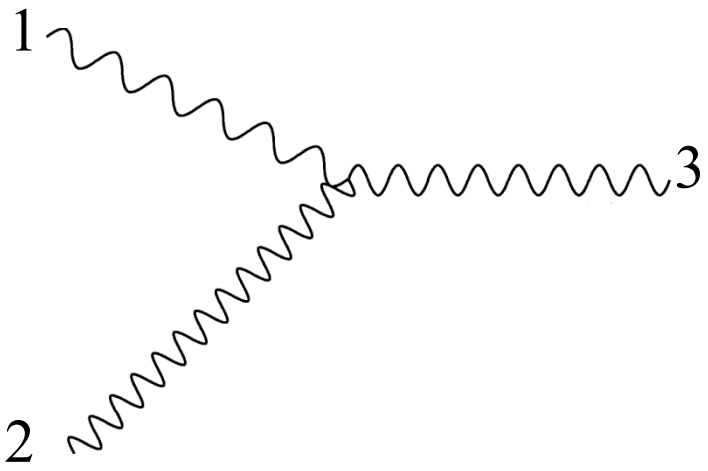
3. Impactful Research



Phonon-Phonon Scattering

Two phonons can combine to form a third

(and vice-versa)



- Energy conservation: $\hbar\omega_1 + \hbar\omega_2 = \hbar\omega_3$

- Translational invariance of the lattice: $\kappa_1 + \kappa_2 = \kappa_3 + \mathbf{G}$

Reciprocal lattice vector

- Interactions with > 3 phonons possible, rates increase with temperature

Lattice Dynamics on a Crystal Lattice

- Building from the mass-spring system, include:
  - Motion in three-dimensions
  - More than nearest-neighbor interactions
  - Non-linear interactions
  - Periodic boundary conditions
- Expand the system potential energy as a Taylor series:

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

0

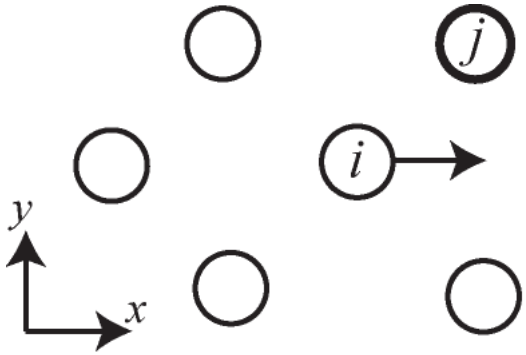
2nd Order Force Constant

3rd Order Force Constant

E = potential energy

$u_{i,\alpha}$ = displacement of atom i in direction α

Force Constant Calculation



Harmonic Force Constant

1. Move i in x-direction.
2. Calculate force on j in y-direction.

$$\frac{\partial^2 E}{\partial u_{i,x}\partial u_{j,y}} = \frac{\partial}{\partial u_{i,x}}\frac{\partial E}{\partial u_{j,y}} = -\frac{\partial F_{j,y}}{\partial u_{i,x}}$$

- From an empirical interatomic potential
  - Analytically
  - Numerically
- From first-principles calculations
  - Density functional perturbation theory [Baroni et al., *RMP* **73**, 515 (2001)]
  - Numerically

Significant work by David Broido and colleagues.

Harmonic Force Constants

- Dynamical matrix -> eigenvalue problem
  - Frequencies and mode shapes
  - Group velocities

$$\mathbf{v}_{g,i} = \frac{\partial \omega_i}{\partial \boldsymbol{\kappa}}$$

$$v_{g,i,n} = \frac{1}{2\omega_i}\left[\mathbf{e}_i^{+}\frac{\partial \mathbf{D}(\boldsymbol{\kappa})}{\partial \kappa_n}\mathbf{e}_i\right]$$

Wang et al., *Eur. Phys. J. B* **62**, 381 (2008)

Cubic Force Constants

- Anharmonic + frequencies & mode shapes
  - RTA - > phonon lifetimes

$$\frac{1}{\tau_{\mathbf{q}\nu}^{pp}} = \frac{\pi\hbar}{16N} \sum_{\mathbf{q}'\nu'} \sum_{\mathbf{q}''\nu''} \left| V_{\nu\nu'\nu''}^{\mathbf{q}\mathbf{q}'\mathbf{q}''} \right|^2 \left\{ (n_{\mathbf{q}'\nu'}^o + n_{\mathbf{q}''\nu''}^o + 1)\delta(\omega_{\mathbf{q}\nu} - \omega_{\mathbf{q}'\nu'} - \omega_{\mathbf{q}''\nu''}) + (n_{\mathbf{q}'\nu'}^o - n_{\mathbf{q}''\nu''}^o) \right.$$

$$\left. \times \left[\delta(\omega_{\mathbf{q}\nu} + \omega_{\mathbf{q}'\nu'} - \omega_{\mathbf{q}''\nu''}) - \delta(\omega_{\mathbf{q}\nu} - \omega_{\mathbf{q}'\nu'} + \omega_{\mathbf{q}''\nu''}) \right] \right\},$$

  - BTE full solution (many flavors) -> scattering rates

Quantum vs. Classical Statistics

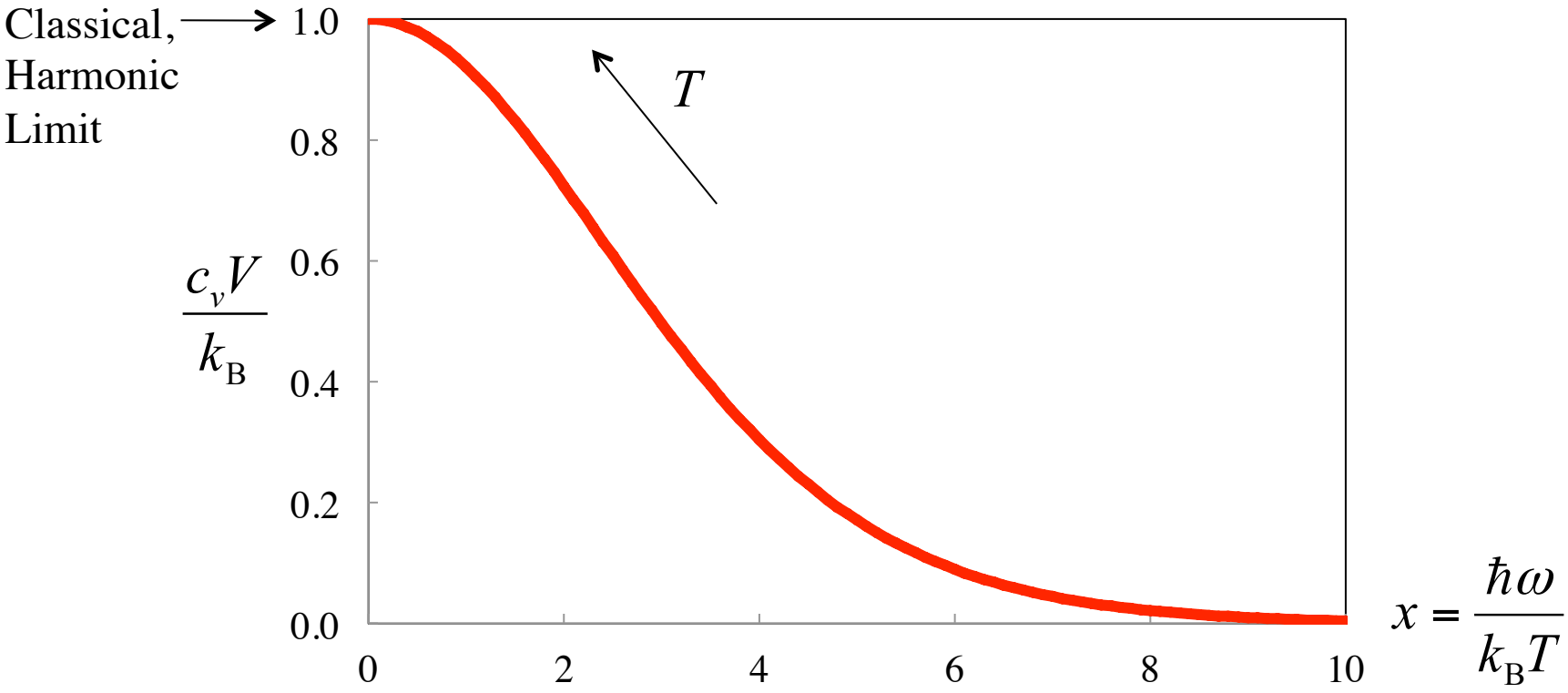
MD simulations are classical

- High temperature limit of Bose-Einstein, $x = \hbar\omega/k_B T \rightarrow 0$
- Equipartition of energy in a harmonic system

	Quantum	Classical
f	$1/(e^x-1)$	$1/x$
$c_v V$	$k_B\, x^2 e^x/(e^x-1)^2$	k_B

Heat Capacity

- Phonons are bosons, described by Bose-Einstein statistics
- Energy of phonon mode i is $E_i = \hbar\omega_i f_i$
- Heat capacity is $c_{v,i} = \frac{1}{V}\frac{\partial E_i}{\partial T} = \frac{k_B x_i^2}{V}\frac{\exp(x_i)}{[\exp(x_i)-1]^2}$



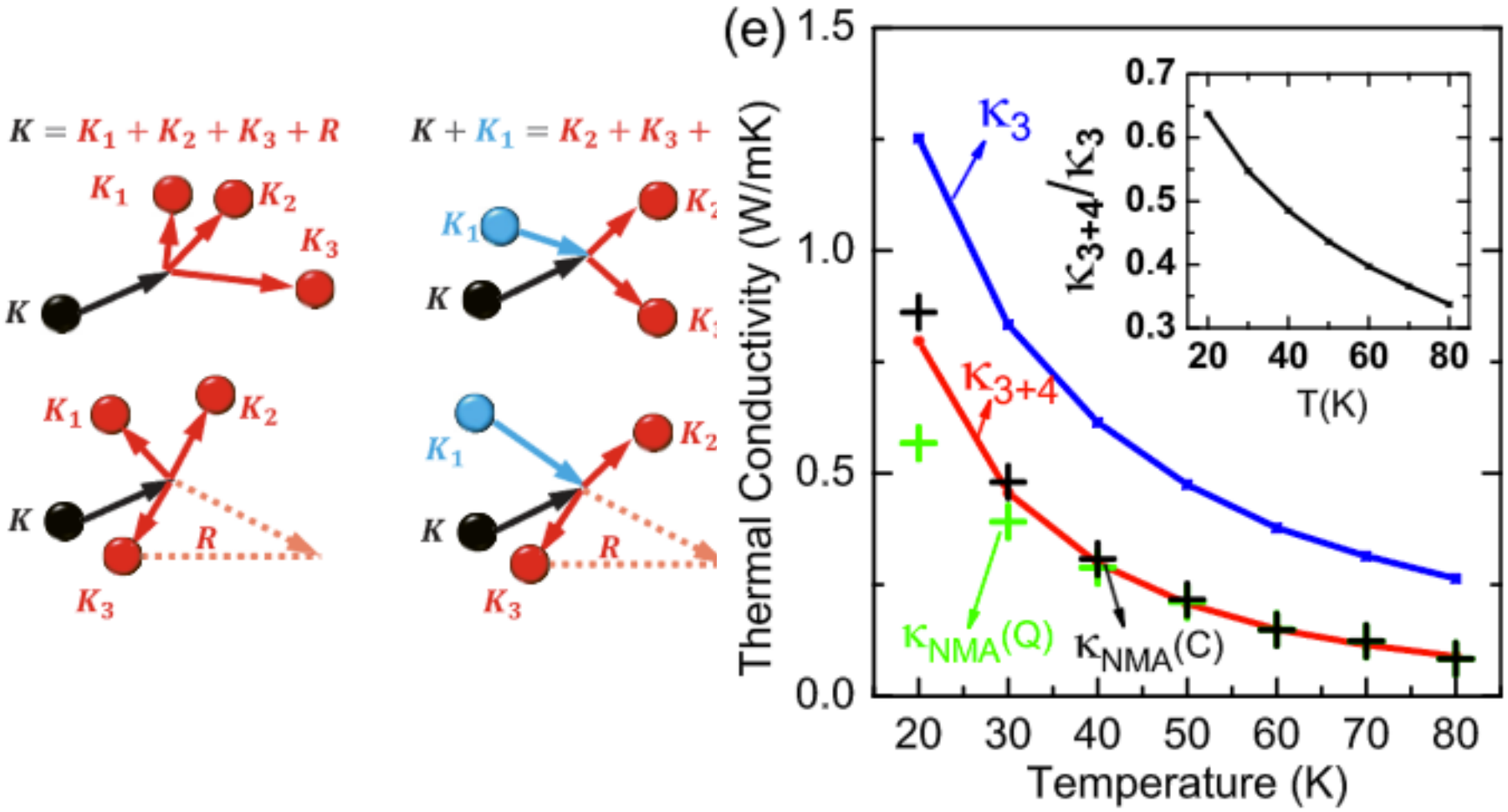
LJ Crystal Self-Consistent Comparison

T (K)	GK-MD[a]	Direct-MD	BTE-MD	BTE-LD
20	1.2	1.4	1.3	1.4
30	0.72	0.76	0.69	0.89
40	0.47	0.50	0.49	0.63
50	0.32	0.34	0.30	0.49
60	0.26	0.29	0.20	0.38
70	0.20	0.21	0.13	0.31
80	0.16	0.17	0.086	0.26

- Limited to low/medium temperatures
- Cannot include disorder explicitly
- Computational challenges for large unit cells

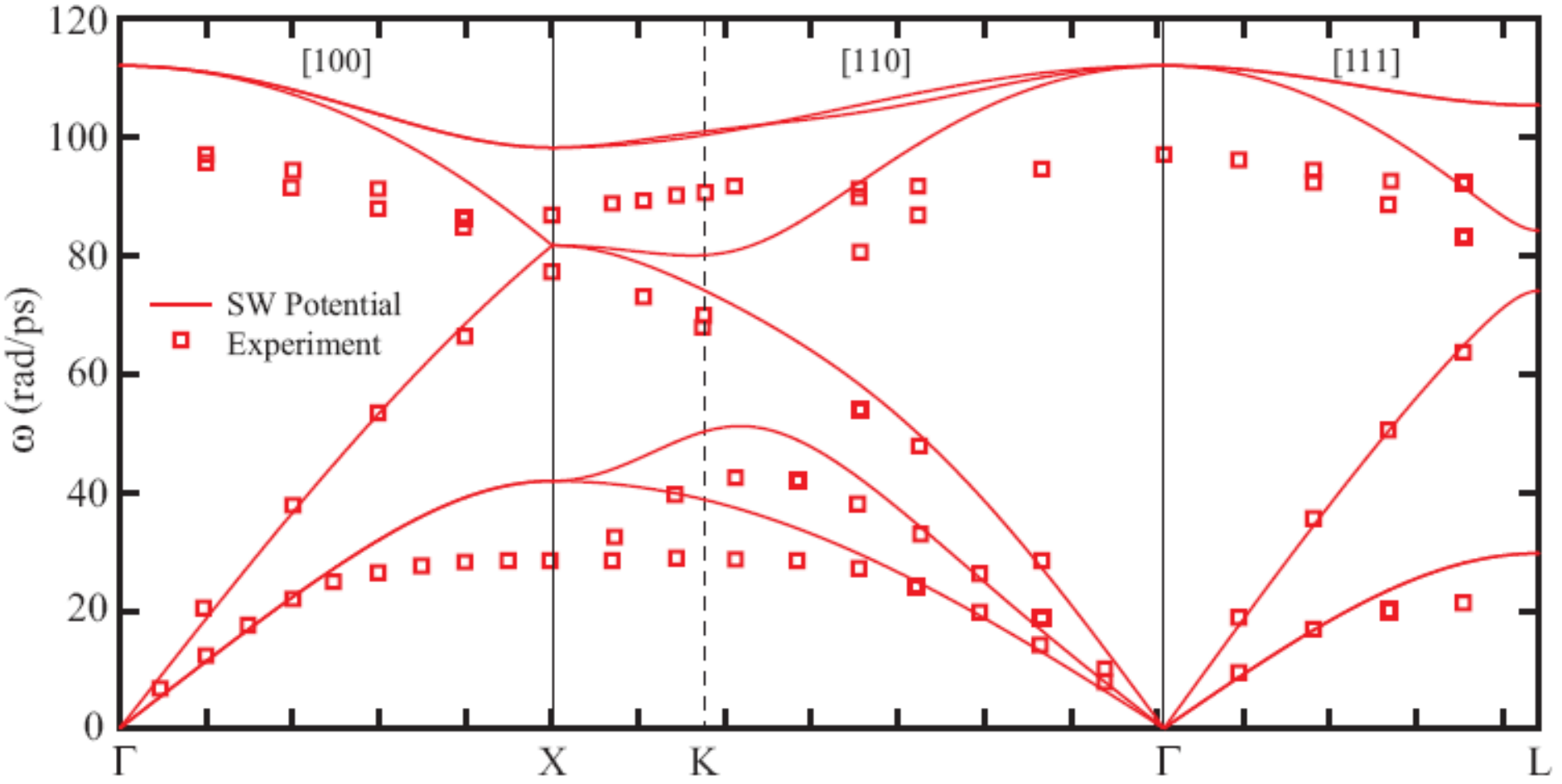
Turney et al., *PRB* **79**, 075316 (2009)

Inclusion of Four-Phonon Processes



Feng and Ruan, *PRB* **93**, 045202 (2016)

Failure of Empirical Potentials: Dispersion



Eric Landry PhD thesis (CMU, 2009).

Failure of Empirical Potentials: Thermal Conductivity

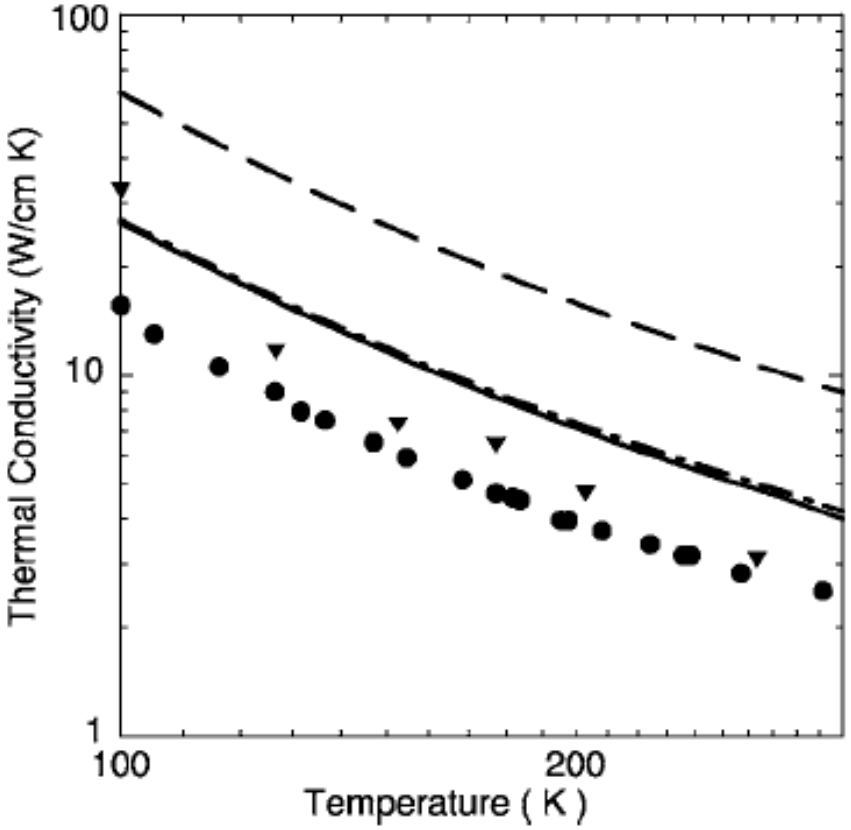


FIG. 5. Calculated lattice thermal conductivity for isotopically enriched Si using SW (dashed line), Tersoff (dashed-dotted line) and ED (solid line) models in the temperature range between 100 K and 300 K compared to measured values.

Broido et al., *PRB* **72** (2005) 014308.

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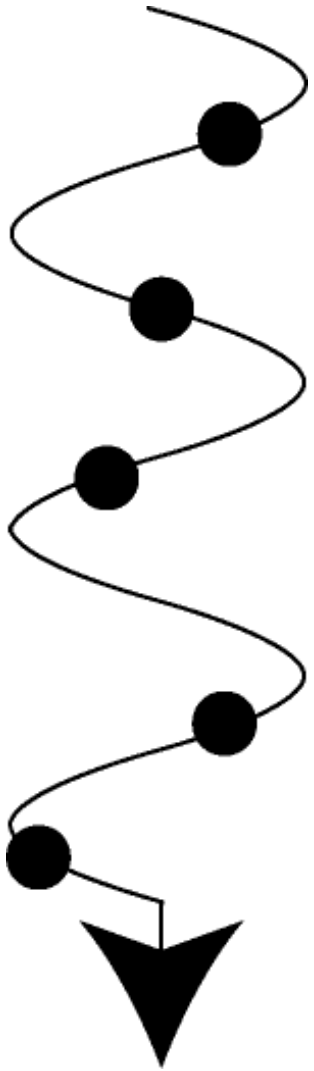


Density Functional Theory

- Approximate numerical solution to the many-body Schrödinger equation
  (bodies = electrons and ions)

- Theoretically and computationally complex
  (large number of degrees of freedom)

- Expertise is needed to set up and run the calculations.

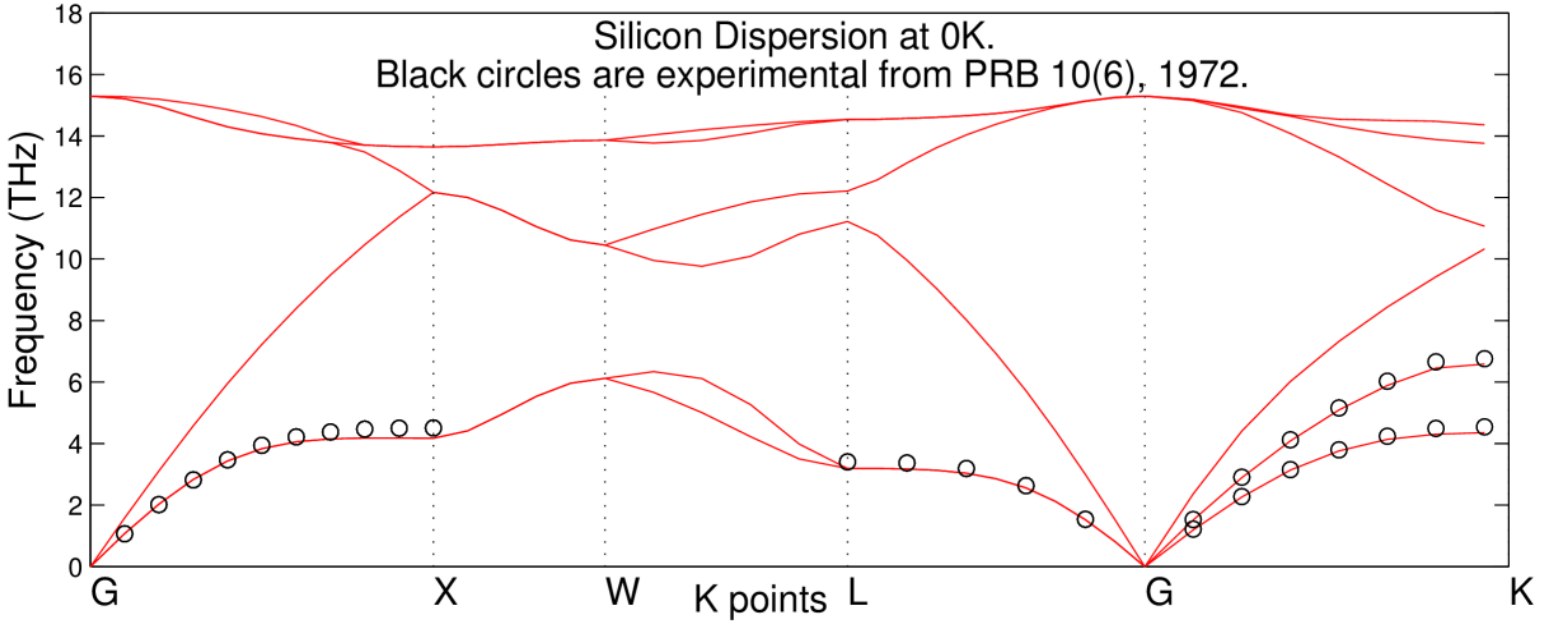
- Graduate students can write a molecular dynamics or harmonic lattice dynamics code in a one-semester class.
  (not possible for DFT)

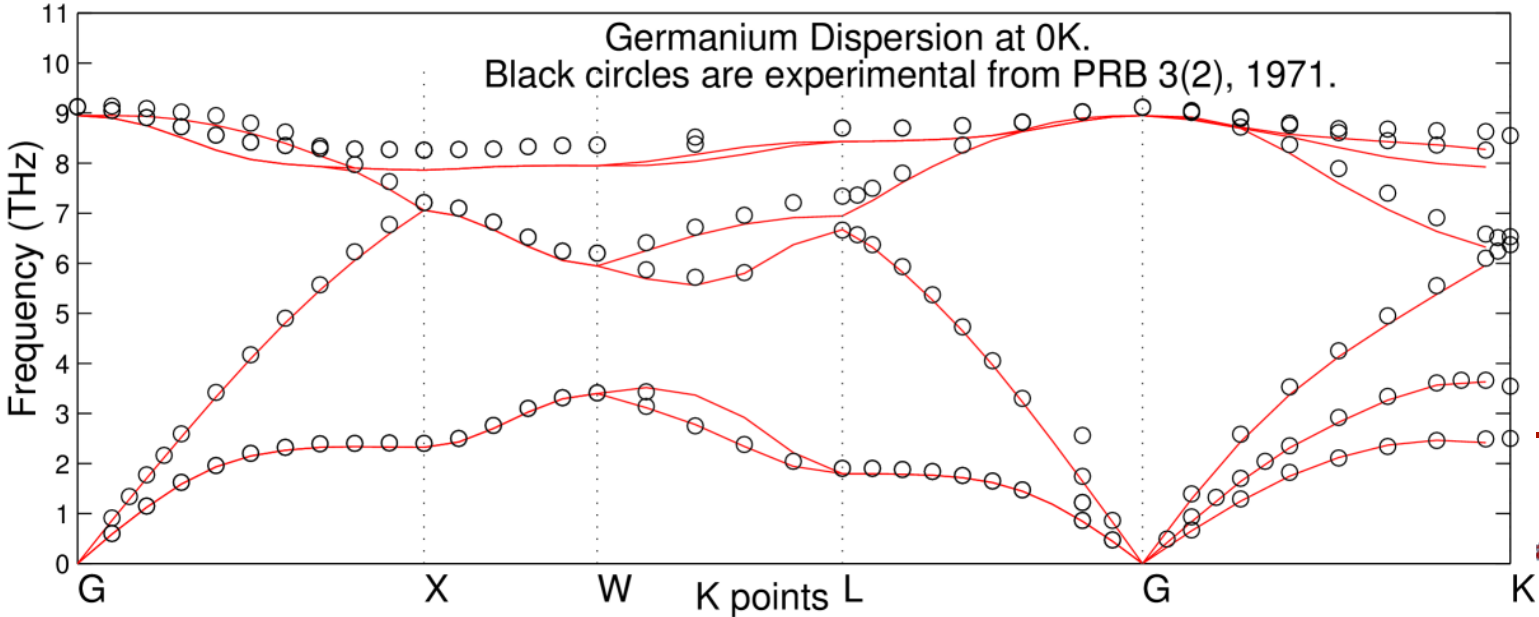
DFT -> Force Constants

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

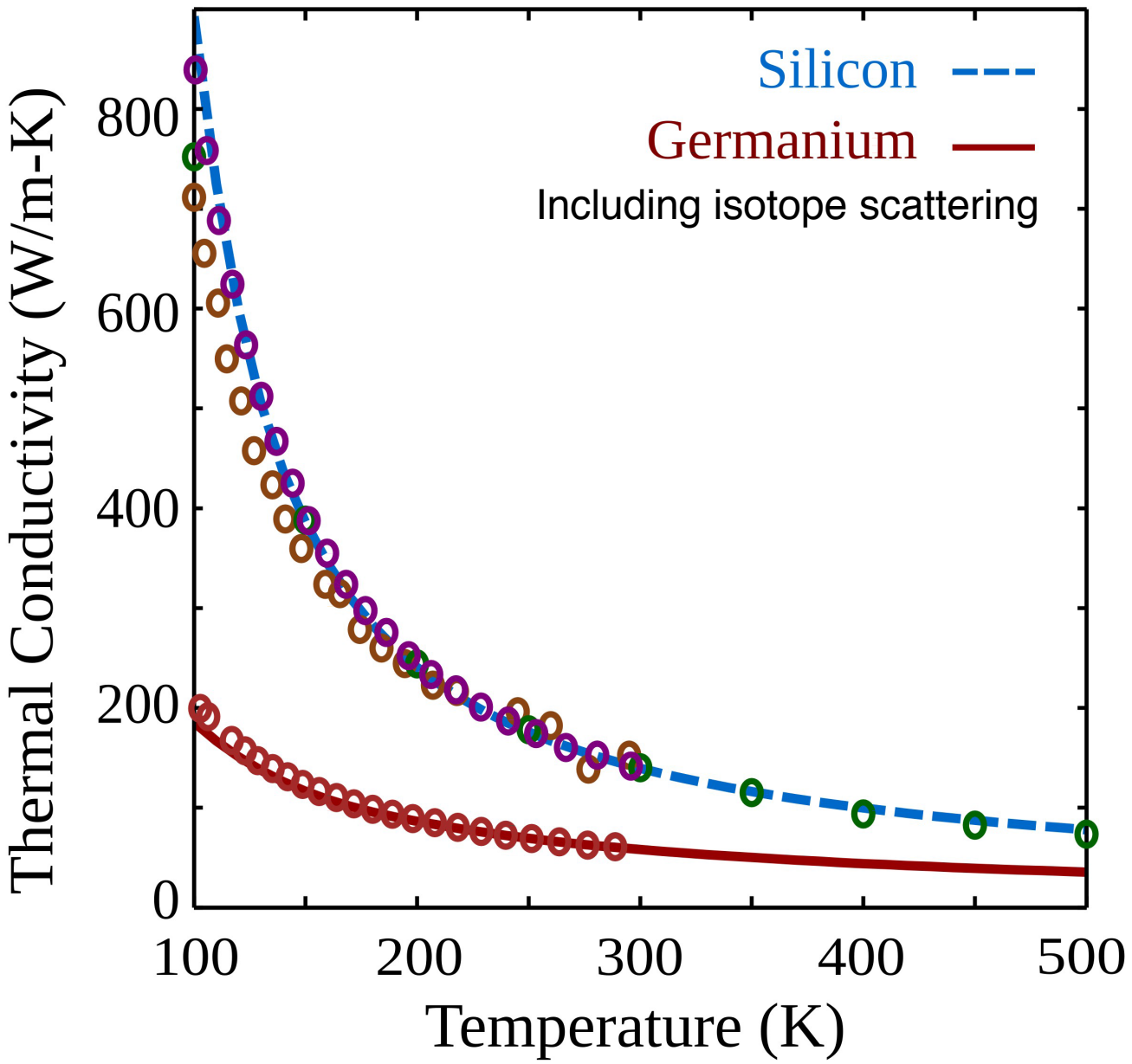
- Density functional perturbation theory or finite differences
  - Symmetry reduction, translational invariance
- Harmonic: **DFPT (standard)**, FD (convergence issues)
- Anharmonic: DFPT (non-standard), **FD (tractable)**

Si and Ge Dispersion from First Principles



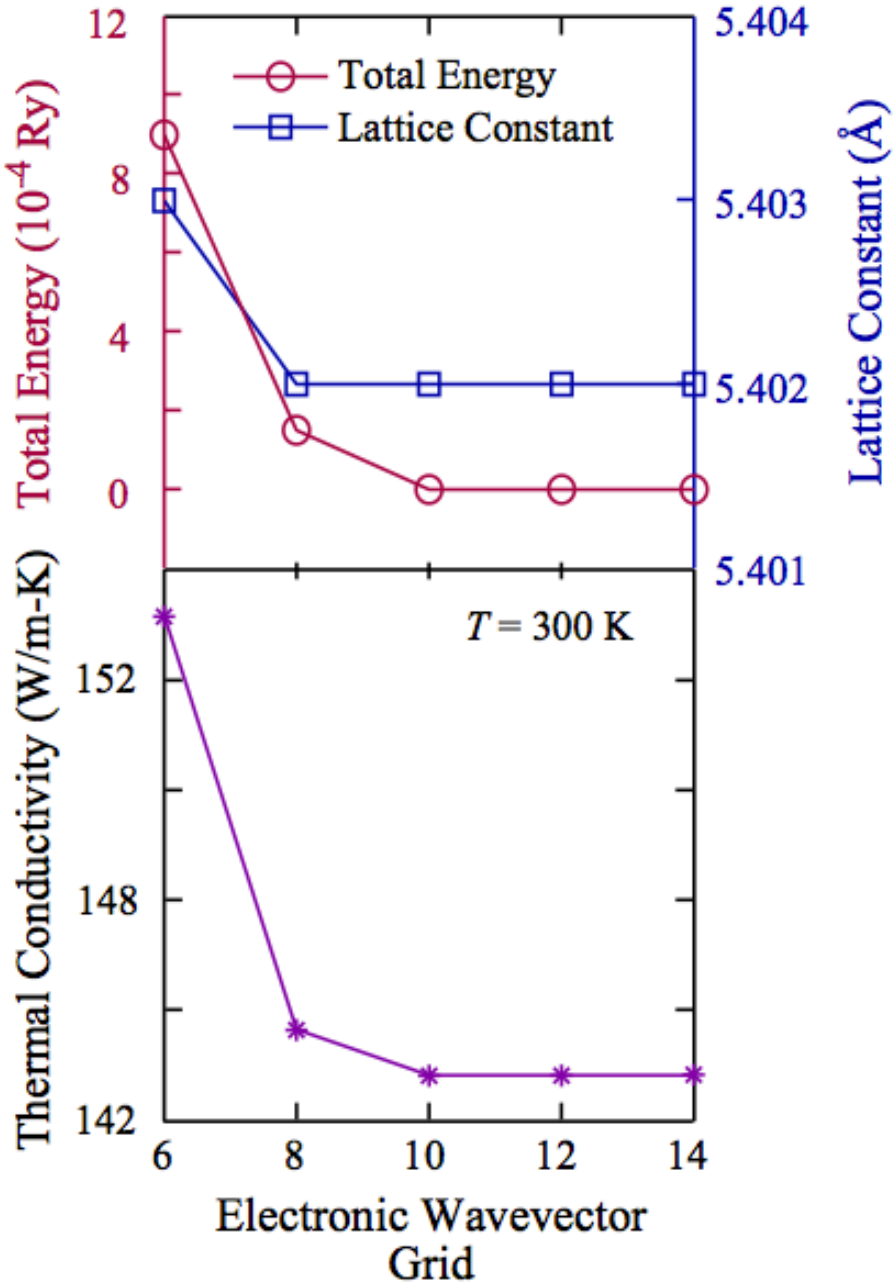


Si and Ge Thermal Conductivity from First Principles



Convergence (1)

- DFT and DFPT calculations on isotopically pure silicon
  - Quantum Espresso
- Thermal conductivity < 2%
- Electron wave vector grid
  - Total energy (< 0.2 mRy), lattice constant (< 0.001 A)
  - Converged at 8x8x8
- Plane wave energy cutoff converged at 60 Ry



Jain and McGaughey, *Comp. Mat. Sci.* **110** (2015) 115.

Convergence (2)

- Phonons
  - 8x8x8 wave vector grid for DFPT (harmonic force constants)
  - 216 atom supercell (cubic force constants)
  - 24x24x24 wave vector grid for thermal conductivity

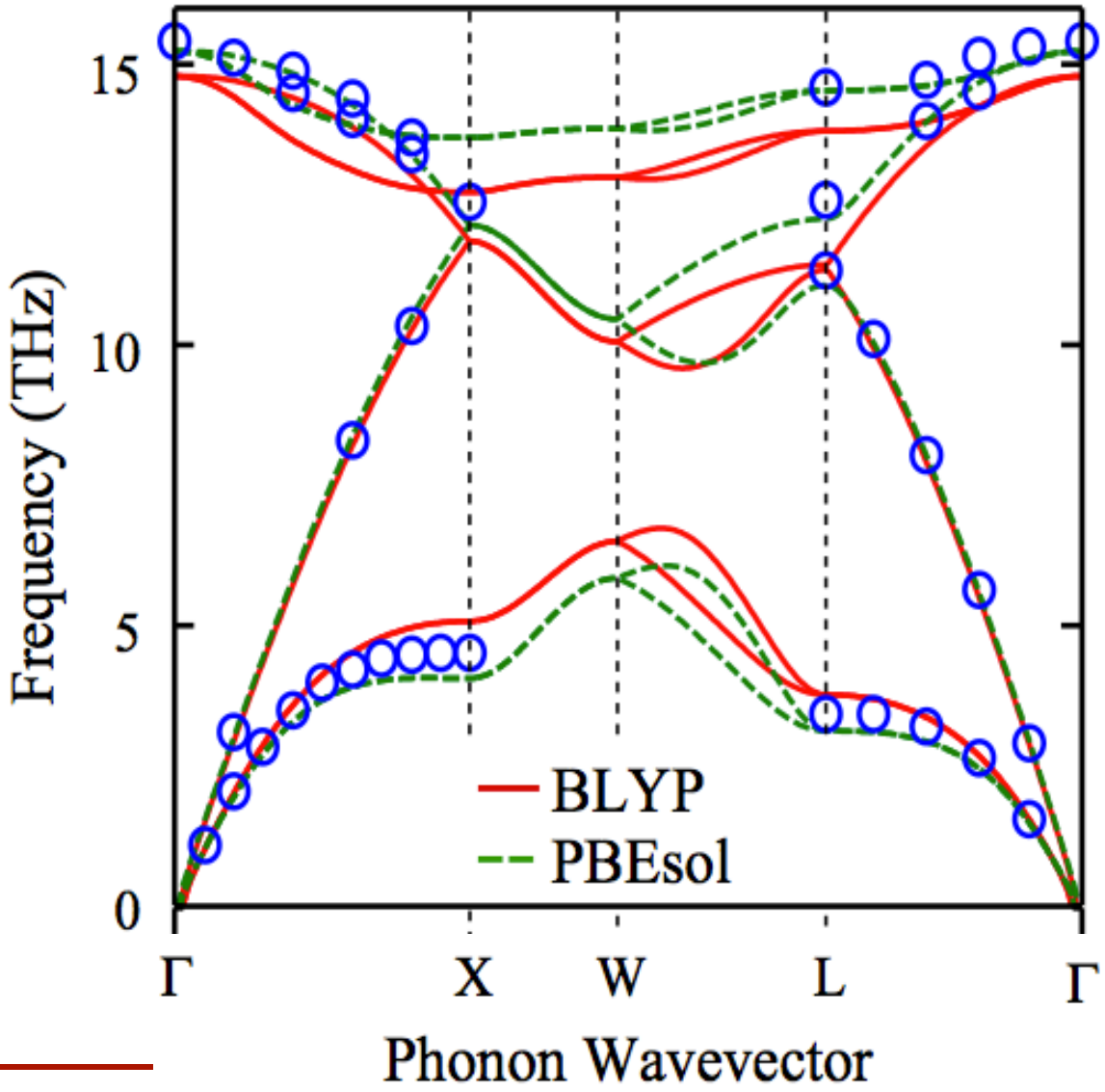
- Pseudopotential: Core electron model
  - Norm conserving, ultrasoft, PAW

- Exchange correlation: Many-body interaction closure
  - LDA, PBE, PBEsol, PW91, BLYP

Pseudopotential and Exchange Correlation

Pseudopotential type [24]	Exchange correlation [24]	Lattice constant (Å)	Sound velocity (m/s)
Experiment		5.430 [27]	8430 [30]
Ultrasoft	LDA	5.399	8320
	PBE	5.468	8120
	PBEsol	5.430	8330
	PW91	5.466	5970
Norm-conserving	LDA	5.402	7560
	PBE	5.461	8150
	BLYP	5.505	8510
PAW	LDA	5.400	8340
	PBE	5.466	7830
	PBEsol	5.430	8320

Dispersion



Expts: Nillson and Nelin, *PRB* **6** (1972) 3777.

Pseudopotential and Exchange Correlation

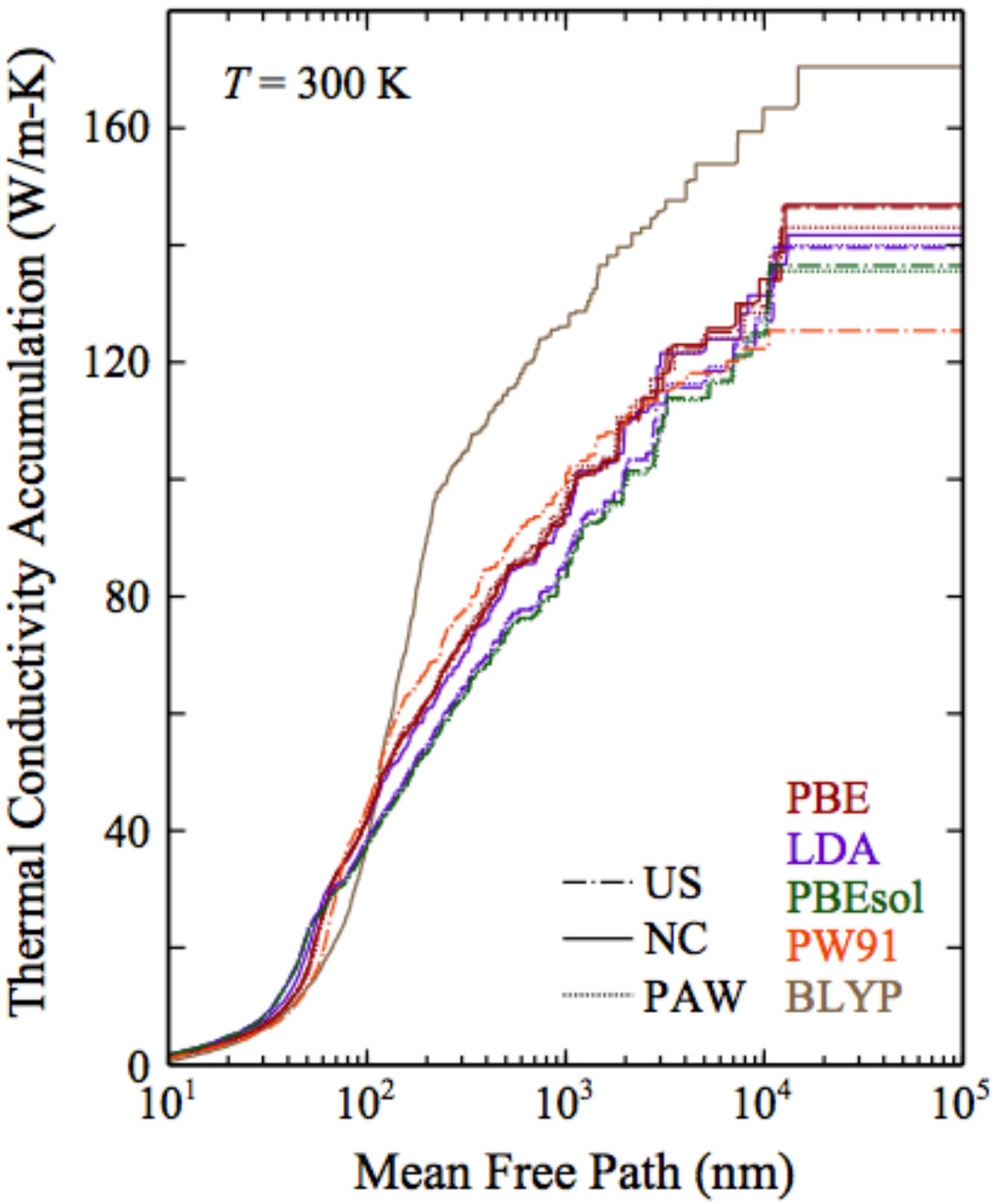
Pseudopotential type [24]	Exchange correlation [24]	Lattice constant (Å)	Sound velocity (m/s)	Thermal conductivity (W/m K) at 300 K
Experiment		5.430 [27]	8430 [30]	153 [19]
Ultrasoft	LDA	5.399	8320	142
	PBE	5.468	8120	148
	PBEsol	5.430	8330	140
	PW91	5.466	5970	127
Norm-conserving	LDA	5.402	7560	144
	PBE	5.461	8150	148
	BLYP	5.505	8510	172
PAW	LDA	5.400	8340	142
	PBE	5.466	7830	145
	PBEsol	5.430	8320	137

Our values: 127-148 W/m-K

Experiment: 153 W/m-K [Inyushkin, *Phys. Stat. Sol. (c)* **1** (2004) 2995]

Literature DFT: 132-155, 172 W/m-K

Thermal Conductivity Accumulation



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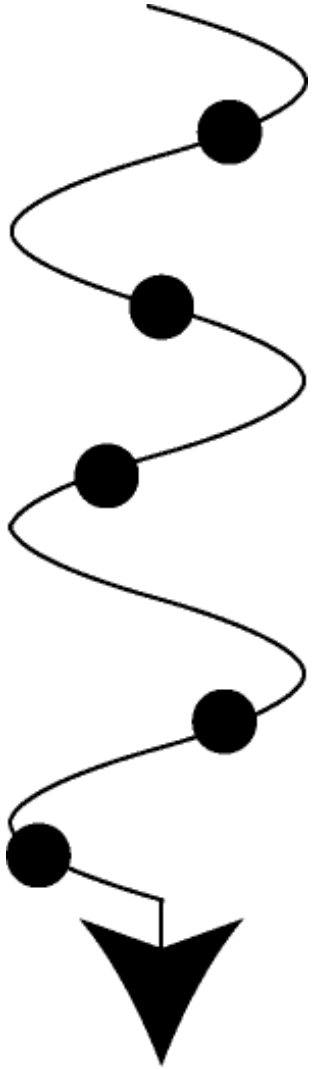
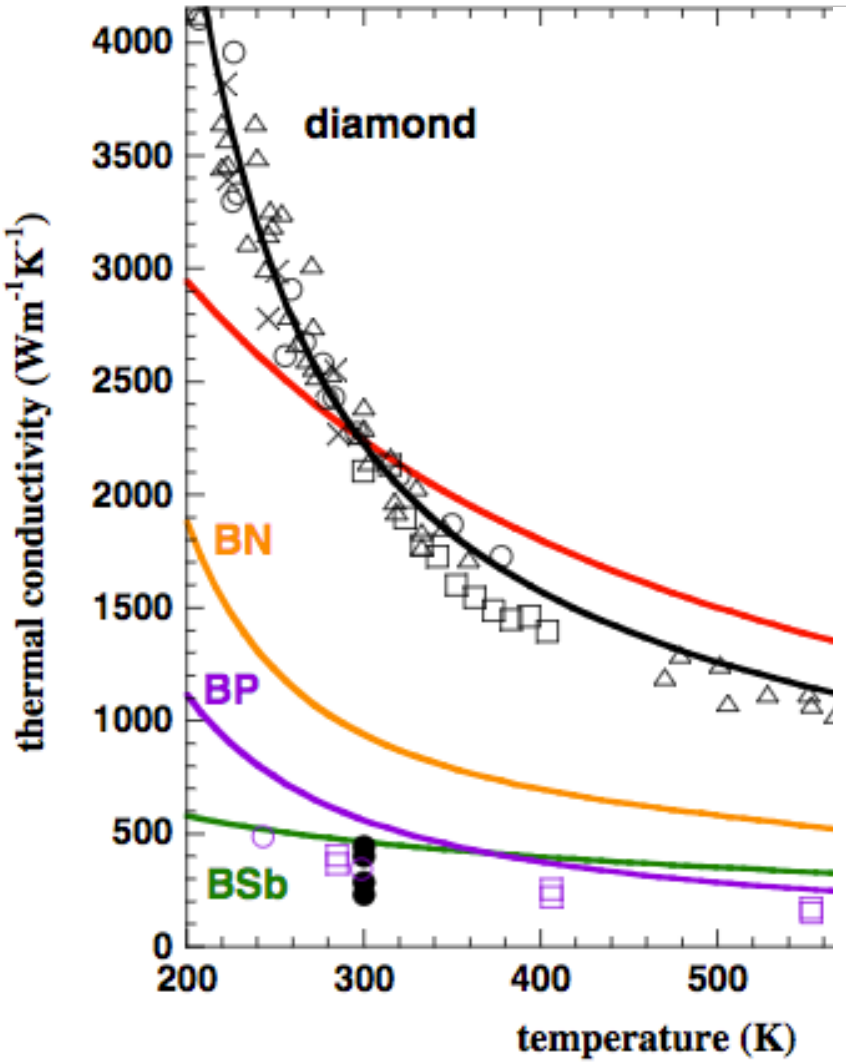


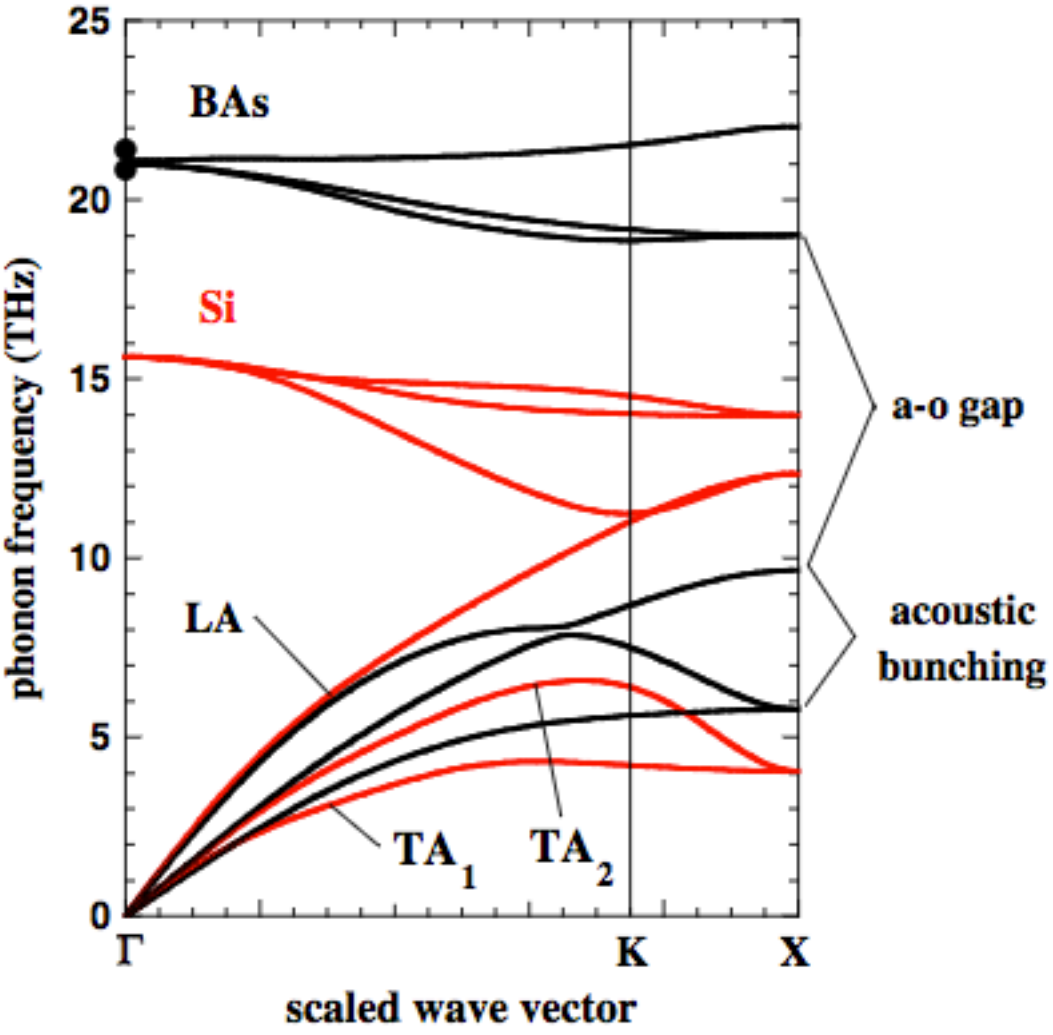
Extensive Work Across Many Materials Systems

	a_{calc} (a_{exp}) (Å)	g_{cation} (g_{anion}) ($\times 10^{-4}$)	κ_{pure} (W m^{-1} K^{-1})	$\kappa_{natural}$ (W m^{-1} K^{-1})	P	S
Diamond[a]	3.53 (3.57)	0.75 (0.75)	3450	2290	51	50
Si	5.37 (5.43)	2.01 (2.01)	155	144	8	2.4
Ge	5.61 (5.65)	5.87 (5.87)	74	60	23	6.9
3C-SiC	4.34 (4.36)	2.01 (0.75)	572	479	20	6.7
AlP	5.40 (5.45)	– (–)	90	–	–	3.0
AlAs	5.61 (5.66)	– (–)	105	–	–	0.5
AlSb	6.10 (6.14)	– (0.66)	118	86	36	39
c-GaN[b]	4.42 (4.50)	1.97 (–)	362	215	68	13
GaP[c]	5.34 (5.45)	1.97 (–)	153	131	16	4.8
GaAs[c]	5.55 (5.65)	1.97 (–)	56	54	4	5.6
GaSb[c]	6.00 (6.10)	1.97 (0.66)	48	45	6	3.1
InP[b]	5.79 (5.87)	0.12 (–)	91	89	2	2.4
InAs[b]	5.97 (6.06)	0.12 (–)	36	36	.5	2.8
InSb[b]	6.39 (6.48)	0.12 (0.66)	20	20	2	3.9
w-GaN[b,d]	3.13 (3.19) 5.10 (5.19)[e] 0.377 (0.377)[f]	1.97 (–)	401 (385)[g]	242 (239)[g]	66	7.2
w-AlN	3.05 (3.11) 4.81 (4.98)[e] 0.387 (0.382)[f]	– (–)	322 (303)[g]	–	–	14

Lindsay et al., *PRB* **87** (2013) 165201.

Ultra-High Thermal Conductivity of BAs





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

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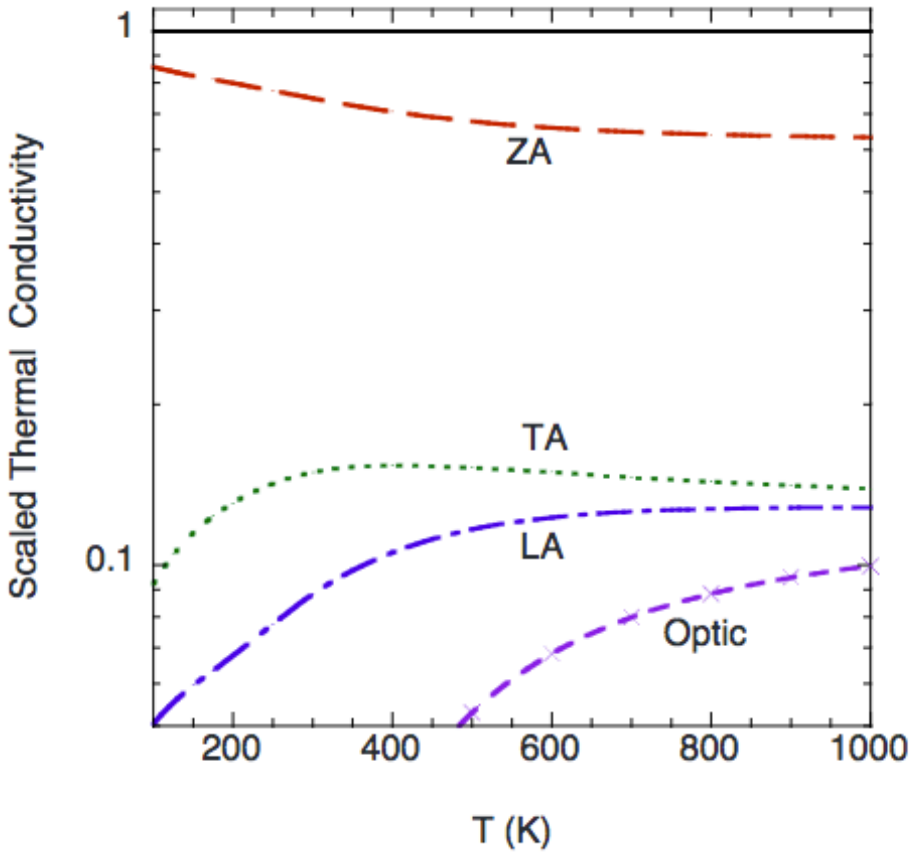
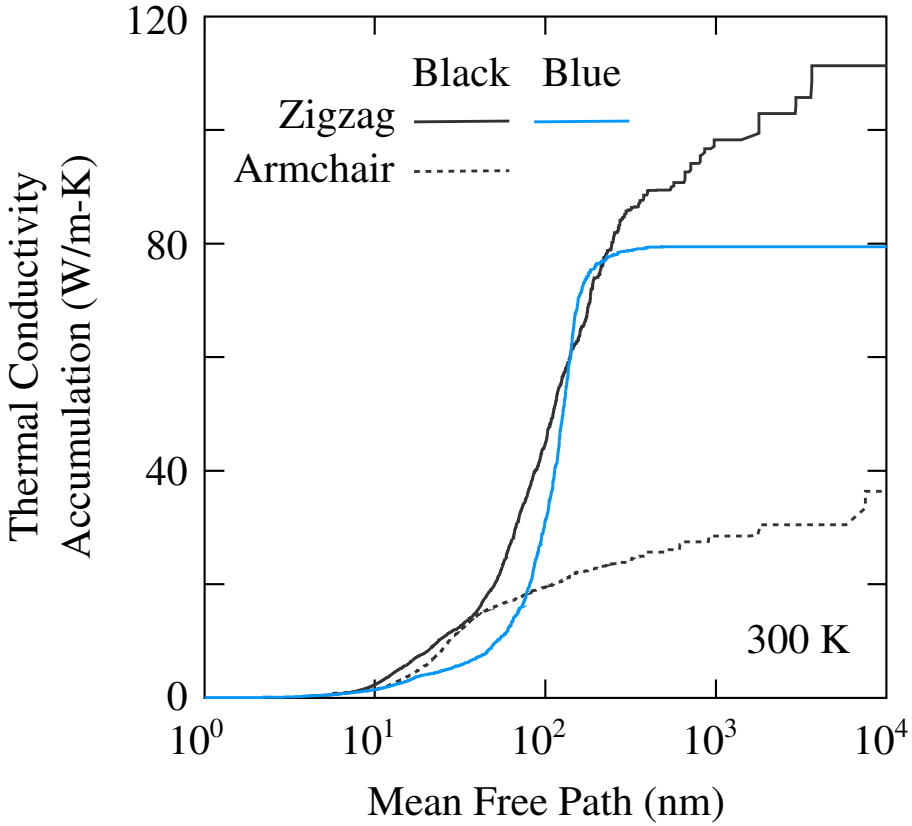
Two Dimensional Materials



Origin of graphene's high thermal conductivity.

Lindsay et al. *PRB* **82** (2010) 115427.



Anisotropic thermal conductivity in phosphorene.

Jain and McGaughey, *Sci. Rep.* **5** (2015) 8501.

Many Others…

- Strain
  - Parrish et al., *PRB* **90** (2014) 235201
  - Mukhopadhyay et al., *PRL* **113** (2014) 025901

- Electrons (next lecture)
  - Liao et al., *PRL* **114** (2015) 115901
  - Jain and McGaughey, *PRB* **93** (2016) 081206(R)
  - Wang et al., *JAP* **119** (2016) 225109.

- BTE Methodology
  - Fugallo et al., *PRB* **88** (2013) 045430
  - Cepellotti and Marzari, *PRX* **109** (2016) 041013

Advantages and Disadvantages

- Naturally incorporate quantum statistics
- Integrate with input from first principles calculations
- Essentially the same framework for all materials

- Thermal conductivity prediction limited by unit cell size, N
  - Scales as N^4, $N < 20$
- Anharmonicity typically to 3rd order

Recommendations

- Some codes freely available, but be careful!
  - GULP, Phonopy, ShengBTE, …
  - We write our own codes

- Many subtle decisions to make
  - How to enforce energy conservation
  - Convergence/size effects

Summary of Lecture 4

- Phonon-phonon mean lifetimes from anharmonic lattice dynamics
  - Theoretical and computational challenges

- Force constants from first principles
  - Better agreement with experiments compared to empirical potentials
  - But, there is still uncertainty!