An Introduction to First Principles Thermal Transport

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dft4nano
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University of Wisconsin
Collaborators

**Thermal Transport in Materials**

David Broido (Boston College)
Alistair Ward, Lucas Lindsay (Boston College)
Gernot Deinzer, Michael Malorny (Univ. of Regensburg)

**Thermal Transport in Nanostructures**

*Theory*
Natalio Mingo (CEA-Grenoble, UC Santa Cruz)
Wu Li, Anupam Kundu (CEA-Grenoble)
Ivana Savić (CEA-Grenoble, now at Tyndall Natl. Institute, Ireland)
Keivan Esfarjani (UC Santa Cruz, now at MIT)

*Experimental*
Arden Moore, Li Shi (Univ. of Texas at Austin)
Lars Samuelson’s group (Lund University, Sweden)

Funding

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Talk Outline

- The need for predictive thermal transport?
- A brief review of phonons
- A first principles approach to calculating harmonic and anharmonic force constants
- Predicting thermal conductivity of crystals & nanostructured alloys
- Thermal transport in nanostructures
Importance of Nanoscale Heat Transfer

**Cost burdens:**
HP estimate:
Data center with 100 server racks

Cooling cost per year: $1.2 million dollars

Effective transfer of heat may be the limiting factor for nanoscale electronics.

Pop and Goodson, J. of Electronic Packaging, 2006
Reducing Heat Transfer in Jet Engine Blades

Thermal barrier coatings

By coating metal turbine blades in jet engines with a thermally grown oxide, the temperature of the metal blade can be kept lower.

This reduces thermal fatigue and helps prevent blade failure.

High thermal resistance at interfaces is required, but predicting the thermal resistance of an interface is very difficult.

§ Derek Hass, Univ. of Virginia, Ph.D Dissertation. (2000)
Energy Lost in Automobiles

Using Energy Scavenging to Boost Efficiency

Typical Energy Split in Gasoline Internal Combustion Engines

100% Applied Fuel Energy (Combustion)

25% Effective Power: Mobility and Accessories

5% Friction and Parasitic Losses

30% Coolant

40% Exhaust Gas

Energy equivalent of 46 billion gallons of gasoline is lost each year down the exhaust pipe.

Can we design new materials or nanostructures that can be used as new thermoelectrics?

QuickSnap® Thermoelectric Device, Hi-Z Technology, Inc.
Journey to the Center of the Earth

DFT style

New mineral found near the center of the Earth

Seismic boundary layers indicate phase transitions

Theoretical and experimental evidence for a post-perovskite phase of MgSiO₃ in Earth’s D'' layer

Artem R. Oganov¹ & Shigeaki Ono²

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Can we use density functional theory to explore thermal transport for crystals under pressure deep within the earth?
A review of phonons

What carries the heat in many systems? **Lattice vibrations aka phonons.**

Take a crystal consisting of a periodic lattice of atoms

We can treat the solid as a collection of coupled quantum harmonic oscillators.

Phonons are the quantized lattice vibrations in the crystal:

\[
E(q, v) = \hbar \omega(q, v) \left[ \frac{1}{2} + n(q, v) \right]
\]

where \(q\) is the phonon wavevector and \(v\) is the phonon branch. The phonon **Bose** distribution is given by \(n(q, v)\).
Acoustic versus Optical Phonons

Assume we have $Z$ atoms in the unit cell

**Acoustic Branches**
All atoms move in phase

For a given phonon vector $\mathbf{q}$, always 1 longitudinal (LA) and 2 transverse acoustic (TA) waves possible

**Optical Branches**
Occurs when there are multiple atoms in an unit cell.

Different atoms vibrate out of phase

For a unit cell with $Z$ atoms, there are $3(Z-1)$ optical branches
If you know the phonons...

Phonons are essential for explaining numerous material properties at $T > 0$:

**Acoustic properties**
- sound velocity

**Thermal properties**
- Heat capacity
- Specific heat
- Thermal expansion

**Thermal conductivity**

\[
F = E - TS \approx E_{gs}(V)_{T=0} + \Delta F_{vib}(V, T)
\]

\[
\Delta F_{vib}(V, T) = k_B T \sum_{i,q} \log \left[ 2 \sinh \left( \frac{\hbar \omega_{i,q}(V)}{2k_B T} \right) \right]
\]

**Other properties**
- Infrared absorption, Raman
- Electron-phonon coupling for transport
- Estimates for $T_c$ for Superconductivity
- Phase Diagrams

**Specific heat $C_p$ versus temperature** from 20 K to 300 K ([DeSorbo [1953]](https://doi.org/10.1063/1.1706415)) and $C_p$ and $C_v$ from 273 K to 1073 K ([Viktor [1962]](https://doi.org/10.1063/1.1706415)).
Phonon Modes in a General Crystal

\[ m\dddot{u}_s^\alpha (\ell) = - \frac{\partial E}{\partial u_s^\alpha (\ell)} \]

\[ m_s \dddot{u}_s^\alpha (\ell) = - \sum_{\beta \tau \mu} \frac{\partial^2 E}{\partial u_s^\alpha (\ell) \partial u_t^\beta (m)} u_t^\beta (m) \]

\[ C_{st}^{\alpha\beta} (\ell, m) = \frac{\partial^2 E}{\partial u_s^\alpha (\ell) \partial u_t^\beta (m)} \]

IFCs

Assume \( u \) has a wave solution

\[ u_s^\alpha (\ell) = \frac{1}{\sqrt{m_s}} u_s^\alpha \cdot e^{i(q \cdot x - \omega t)} \]

\[ \det \left| \omega^2 \delta_{\alpha\beta} \delta_{st} - D_{st}^{\alpha\beta}(q) \right| = 0 \]

where \( D(q) \) is the Fourier Transform of the real space IFCs.
Routes to Model Phonons

**Spring and Shell Models**
Can be used to fit phonon dispersions
Difficult to interpret
Little predictive information

**Empirical potentials**
Fit to material properties
Provides phonon dispersion
Limited to similar structures
Used in both lattice and Molecular dynamic calculations
Easy to implement and fast.

**Density Functional Approach**
*(Our Focus)*
Good agreement for phonon dispersions
Information on electron-phonon interactions
Able to describe interactions between different types of atoms
However, more time consuming!

Ion and Core electrons
Valence electrons
DFT+Phonons = Thermal Transport

First principles **harmonic** and **anharmonic** interatomic force constants calculated using DFT

\[
\omega_j(q) \pm \omega_j(q') = \omega_j(q'') \quad q \pm q' = q'' + K
\]

**Thermal Conductivity in Bulk Materials**

\[
\frac{df}{dt} = \left( \frac{\partial f}{\partial t} \right)_{\Delta T} + \left( \frac{\partial f}{\partial t} \right)_{\text{Collisions}} = 0
\]

**Boltzmann Equation**

**Density Functional Perturbation IFCs**

**Heat Transfer in Nanostructures**

\[
G^R(\omega) = \left[ \omega^2 \mathbf{I} - \mathbf{H} - \Sigma_L - \Sigma_R \right]^{-1}
\]

**Green’s Function Approach**

**Real Space IFCs**

Cornell University
DFT+Phonons = Thermal Transport

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Boltzmann Equation
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Heat Transfer in Nanostructures
\[
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\]

Green’s Function Approach
Real Space IFCs
What is density functional theory?

“The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known…

\[ H = \frac{-\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_{i,j} \frac{Z_i e^2}{|\mathbf{r}_i - \mathbf{R}_j|} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 + \frac{1}{2} \sum_{i,j} \frac{Z_i Z_j e^2}{|\mathbf{R}_i - \mathbf{R}_j|} \]

…the exact application of these laws leads to equations much too complicated to be soluble”, Dirac (1929)

Use electron density as the fundamental parameter that defines all properties of a system instead.

For an N interacting particle system, this moves us from 3N variables to a single function of x, y, and z.

Huge savings in computational costs which results in an approach that helps describe known systems and also predict new systems, scaling as \(N^3\).

1998: Nobel prize awarded for Density Functional Theory


Interactions for a full crystal

We consider interactions between a large number of atoms, in terms of displacements, \( u \), from equilibrium positions.

**Harmonic terms:**

\[
\Phi_{\alpha_1\alpha_2}(R_1, R_2) = \frac{\partial^2 E_{tot}}{\partial u_{\alpha_1}(R_1) \partial u_{\alpha_2}(R_2)} = -\frac{\partial F_1}{\partial u_{\alpha_2}(R_2)}
\]

**Anharmonic terms:**

\[
\Phi_{\alpha_1\alpha_2\alpha_3}(R_1, R_2, R_3) = \frac{\partial^3 E_{tot}}{\partial u_{\alpha_1}(R_1) \partial u_{\alpha_2}(R_2) \partial u_{\alpha_3}(R_3)}
\]

Density functional perturbation theory (linear response due to phonon \( q \))

Giannozzi et al., PRB 43, 7231 (1991); Quantum Espresso – harmonic terms

**2n+1 theorem:** With 1\( st \) derivative of \( \Psi \), we can calculate the 2\( nd \) and 3\( rd \) derivative of the energy – Gonze, Vigneron, PRB 39, 13120, (1989)

3\( rd \) order terms: G. Deinzer, G. Birner and D. Strauch, PRB 67, 144304 (2003)
Calculating IFCs from first principles

1. **Get the Charge Density**

Do your standard density functional calculation till everything is self-consistently converged.

This then gives us $n_{SCF}$ and $V_{scf}$
Calculating IFCs from first principles in q-space

2. Throw a phonon into the mix

We have some phonon going through a crystal

\[ e^{i(qx - \omega t)} \]

which induces a perturbing potential \( \Delta V_{\text{ion}} \) that is periodic with wavevector \( \mathbf{q} \).

In this case, it is better to consider \( \Delta n(\mathbf{q}+\mathbf{G}) \) rather than \( \Delta n(\mathbf{r}) \).

All calculations are done in the first Brillouin zone!

Sample different \( \mathbf{q} \) values in the BZ and FFT back to real space IFCs.

With enough calculated \( \mathbf{q} \) points, you can interpolate to other \( \mathbf{q} \) values.

With this, we also get phonon dispersion, phonon density of states.
Density Functional Perturbation Theory

Second self-consistent loop to find changes in potential and charge

\[
\Delta \rho(r) = 4 \text{Re} \sum_{n=1}^{N/2} \psi_n^0(r) \Delta \psi_n(r)
\]

\[
\Delta V(r) = \Delta V_{\text{ext}}(r) + e^2 \int \frac{\Delta \rho(r')}{|r-r'|} dr' + \frac{d\nu_{xc}}{dn} \bigg|_{n=n(r)} \Delta \rho(r)
\]

\[
(H - \epsilon_n) \langle \Delta \psi_n \rangle = - (\Delta V - \Delta \epsilon) \langle \psi_n^0 \rangle
\]
Ab-initio Phonon Dispersions

**Si**

Experiment Nilsson and Nelin
PRB 6 3777 (1972)

Experiment Sangster et al.

Theory: Harmonic ab initio IFC’s (QE plane wave DFT package)

**Ge**

Brillouin Zone


**Pd**

Experiment: Harmonic ab initio IFC’s (QE plane wave DFT package)
Bulk InAs is zincblende. For diameters smaller than 70 nm, InAs nanowires grow in the wurtzite structure.

However, bulk wurtzite InAs does not exist and the phonon dispersion has never been measured. Use DFPT to calculate it!


ZB Experimental Data:
For low frequency lattice vibrations, electrons can shield the positive charge induced by the phonons. But when $q$ spans Fermi sheets and connects different electronic states, this breaks down (Kohn, PRL, 2 393 (1959)).

Very difficult for shell model or empirical potentials to catch this.
Moving on to the Thermal Conductivity

\[ \kappa_{\alpha\beta} = \sum_\lambda C_\lambda v_{\lambda\alpha} v_{\lambda\beta} \tau_{\lambda\beta}^{scf} \]

Temperature gradient, \( \nabla T \), perturbs the phonon distribution

\[ n_{\lambda} = n_{0\lambda} + n_{1\lambda} \quad \text{for mode } \lambda \quad \lambda = (j, q) \]

**Iteratively** solve the linearized Boltzmann equation given by:

\[ \mathbf{v}_\lambda \cdot \nabla T \left. \frac{\partial n_{0\lambda}}{\partial t} \right|_{\text{drift}} = \left. \frac{\partial n_{\lambda}}{\partial t} \right|_{\text{collision}} \]

For three phonon scattering:

\[ \left. \frac{\partial n}{\partial t} \right|_{\text{collision}} = \sum_{\lambda', \lambda''} W_{\lambda\lambda'\lambda''}^+ (\Phi_{\lambda''} - \Phi_{\lambda'} - \Phi_\lambda) + \frac{1}{2} W_{\lambda\lambda'\lambda''}^- (\Phi_{\lambda''} + \Phi_{\lambda'} + \Phi_\lambda) \]

Scattering rates needed to get \( \tau \)

\[ \Phi_\lambda = n_{1\lambda} / (n_{0\lambda} (n_{0\lambda} + 1)) \]

Specific heat, \( C \), needs equilibrium phonon frequencies and distributions.
Ab-initio Harmonic and Anharmonic Terms

**Harmonic terms** provide phonon frequencies and eigenvectors for Boltzmann Equation

**Anharmonic terms** provide the scattering rates, $W^{+-}$, for three phonon processes

Iterative solution is required to accurately account for normal phonon scattering processes.

First iterative Solutions to BTE was done using empirical potentials:

- **Omini & Sparavigna**, Phys Rev B, 53, 9064 (1996);
Iterative Solution of Boltzmann Equation

**Step 1:** Non-equilibrium distribution for each independent phonon mode is calculated (similar to relaxation time approximation).

**Step 2:** Iterative procedure accounts for the fact that the non-equilibrium distribution functions for all phonons are actually coupled together.

In RTA, both normal and Umklapp processes are independent and treated as resistive. However, normal scattering events do not provide resistance.
Relaxation time approximation **underestimates** the thermal conductivity of material because Normal scattering processes are treated as resistive.

For materials where normal scattering is dominant, this can have a big impact.

You typically need to be careful when you have high thermal conductivity materials.

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Thermal conductivity for Si and Ge

4x4x4 q-point grid, 4096 possible q-pairs for zb
symmetry reduces this to 42 q-pairs!
Equivalent to 3rd order force constants
to 7th nearest neighbors

Experimental Data:
[Ge] V. I Ozhogin et al. (1996)
Thermal Conductivity for Diamond

A. Ward, D. A. Broido, D. A. Stewart, G. Deinzer
Much of the experimental work on diamonds was done at Cornell by Robert Pohl’s group in the 1990s. Diamonds supplied by DeBeers Corp. (worth $2 million then!)
Importance of Optic Modes

Since optical phonon branches have small group velocities, they are neglected in many thermal conductivity models.

However, they provide an important scattering channel.

This detailed scattering info is lost in relaxation time models.

A. Ward, D. A. Broido, D. A. Stewart, G. Deinzer
Effect of Isotopes on Diamond Thermal Conductivity

$W^{iso}_{\lambda \lambda'} \propto g$

Scattering rate of phonons due to isotopes is proportional to the mass variance

$$g = \frac{\sum c_i M_i^2 - \left(\sum c_i M_i \right)^2}{\left(\sum c_i M_i \right)^2}$$

where $c_i$ and $M_i$ are the concentration and mass of isotope $i$.  

A. Ward, D. A. Broido, D. A. Stewart, G. Deinzer
Brillouin Zone Contributions to $\kappa$

Isotopically Pure Silicon

\[ \kappa_{zz} = \frac{1}{(2\pi)^3} \int \kappa_{zz}(q) dq \]

\[ \kappa_{zz}(q) = \sum_j C_j(q) \nu_{jz}(q)^2 \tau_{jz}(q) \]

$q$ values near $q=0$ contribute the most to thermal conductivity. They have high group velocities and act mainly in normal processes.

Umklapp processes will reduce contribution to thermal conductivity of larger $q$-vectors.

Thermal Gradient in $z$ direction

"Ab-Initio Thermal Transport", (Book Chapter) Mingo, Broido, Stewart, to be published (2012)
Phonon Velocity Effects

TA Branch Velocity drops

Cornell University
Predicting Thermal Conductivity of Thermoelectrics

Radioisotope Thermoelectric system have powered deep space probes:

- Pioneer 10 (30 yrs operations)
- Voyager 1&2 (32 yrs and still going!)

Thermoelectric Refrigerators:

- Used in electronics to lower or maintain temperature
- Cooling in car seats, beer can coolers

Active Cooling

Heat sink

Apply a voltage to cool a surface
What makes a good thermoelectric?

\[ ZT = \frac{\alpha^2 \sigma T}{\kappa_e + \kappa_{ph}} \]

- **Seebeck coefficient**
- **Electrical conductivity**
- **Thermal conductivity**

**ZT** - Measure of the Efficiency of a Thermoelectric Device at given \( T \)

To get a high \( ZT \sim 1 \), need fast charges and slow phonons,

**Electron crystal – phonon glass**

Materials Options (increase power factor \((\alpha^2\sigma)\) or reduce thermal conductivity)

Standard thermoelectrics were discovered in the 1950s and 1960s

- \( \text{Bi}_2\text{Te}_3 \) (400K) \( ZT \sim 0.8-1.0 \)
- \( \text{PbTe} \) (600K), \( \text{SiGe} \) (1200K) \( ZT \sim 0.9 \) at high \( T \)
Boosting ZT with nanostructuring

Using nanostructures in alloys to reduce thermal conductivity

ErAs nanoparticles epitaxially embedded in InGaAs

Zide et al., APL, 87, 112102 (2005)
Kim et al., PRL, 96, 045901 (2006)

ZT increases by a factor of 2 compared to InGaAs, largest ZT ~ 1.6 at 800K

SiGe alloy thermoelectrics

- Many thermoelectrics are made from toxic or scarce materials that are difficult to integrate into silicon fabrication – i.e. Bi$_2$Te$_3$, PbTe

- SiGe alloys could provide an on-chip cooling for electronic hot-spots (easy to integrate, low thermal resistance at interfaces), however they suffer from low ZT (~0.1) at RT.

- If we can boost SiGe alloy ZT to 0.5 at RT, we can cool hotspots by 15-30K, much better than current technology (7K cooling).
Add nanoparticles…

Calculation based on interpolation between Born approximation and geometric scattering regime

\[ \frac{1}{\sigma} \approx \frac{1}{\sigma_{\text{Born}}} + \frac{1}{\sigma_{\text{geom}}} \]

The reduction is not as great for crystalline Si. Why?

Nanoparticles (scatters low frequency phonons)
Substitutional Disorder in alloys (scatters high frequency phonons)

Mingo et al., Nano Lett. 9, 711 (2009).
Which works better?
Si or Ge nanoparticles?

\[
\frac{1}{\tau_{\lambda}^{np}} = \frac{\Omega}{2\omega^2} \frac{f_{np}}{V_{np}} \text{Im}\left[ \langle \lambda | T(\omega^2) | \lambda \rangle \right]
\]

\[
T(\omega^2) = \left[ I - V g^+ (\omega^2) \right]^{-1} V
\]

\[
T \approx V + V g V + \ldots
\]

According to the Born approximation, substituting a Si or Ge cluster has the same effect on the scattering rate! If we calculate the full T matrix, does this remain true?

\[
\frac{1}{\tau_{\lambda}^{np}} \propto \left( M - M_{np} \right)^2
\]

\[
\frac{(M-M_{np})^2}{M^2} \quad M_{Si} = 28.086 \quad M_{Ge} = 72.61 \quad M_{Si0.5Ge0.5} = 50.348
\]
Calculation Details

- Use ab-initio force constants from Si and Ge to generate force constants for Si$_{0.5}$Ge$_{0.5}$ using the virtual crystal approximation (7 nn).

- Calculate full T matrix for phonon scattering from Si or Ge nanoparticles (low concentrations)

- Determine the thermal conductivity using the Boltzmann transport equation.
Si$_{0.5}$Ge$_{0.5}$ thermal conductivity without nanoparticles

<table>
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Let’s first look at the predicted thermal conductivity for the SiGe alloy.

Possible reasons for differences:

1. Defects in experimental samples
2. VCA may underestimate phonon scattering in SiGe, J. Garg et al. *Phys Rev Lett*, 106, 045901 (2011)
   Enhanced scattering due to changes in elastic constants.
3. Phase separation in experimental samples

SiGe alloys & Si or Ge nanoparticles

$\text{Si}_{0.5}\text{Ge}_{0.5}$ thermal conductivity without nanoparticles

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Possible reasons for differences:
1. Defects in experimental samples
2. Use of VCA
3. Enhanced scattering due to changes in elastic constants.

$K(\text{Si np})$ 20% greater than $K(\text{Ge np})$

**Conclusion:** Ge nanoparticles can give a higher ZT value than Si nanoparticles

Scattering Rate comparison

Higher scattering rate for Ge at low phonon frequencies

At higher frequencies, wavelengths comparable to nanoparticle diameter (geometric regime)

Si scattering rate is higher, but in an alloy this frequency range does not contribute significantly to thermal transport

3.3 nm diameter nanoparticles

Why is there a difference?

Born approximation is valid when our scatterer is weak, $T \ll V$

We can think of an analogy with electrons scattering from a potential well or a potential barrier of the same magnitude.

From scattering theory, the cross-section of a potential well is greater than the cross-section of a potential barrier at low energies or for phonons (frequencies).

**Well** - Born approx. underestimates **Barrier** - Born approx. overestimates for potential.

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Electron scattering
M. Zebarjadi et al.
Green’s Functions for Nanoscale Phonon Transmission

What does it mean to transport energy on the nanoscale?

\[
H = \frac{1}{2} \sum_i M_{ii} \dot{\varphi}_i \dot{\varphi}_i + \frac{1}{2} \sum_{ij} K_{ij} \varphi_i \varphi_j + \sum_{ijk} V_{ijk}^{(3)} \varphi_i \varphi_j \varphi_k + O^{(4)}_{anh}
\]

**Ballistic Transport**

\[
G^R(\omega) = \left[\omega^2 \mathbf{I} - H_J - \Sigma_L - \Sigma_R \right]^{-1}
\]

\[
\Xi(\omega) = \text{Tr} \left[ \Gamma_L(\omega) G^R_{1N}(\omega) \Gamma_R(\omega) G^A_{1N}(\omega) \right]
\]

**Phonon Transmission**

Thermal conductance

\[
\sigma = \left(1 / k_B T^2 \right) \int_0^\infty \frac{d\omega}{2\pi} (\hbar \omega)^2 \Xi(\omega) \frac{e^{\hbar \omega / k_B T}}{(1 - e^{\hbar \omega / k_B T})^2}
\]

Mingo & Yang, PRB 68 245406 (2003) Si Nanowires
Yamamoto and Watanabe, PRL 96, 255503 (2006) NTs w/ Brenner potential,
Some notes about IFC calculations for nanostructures

First obtain relaxed crystal structures

DFT calculations with Siesta, double zeta polarized (DZP) basis set

Calculate IFCs directly in real space

Shift one atom and then calculate the forces on all other atoms in the system and repeat

Large supercell required to get sufficient IFC terms

Calculate phonon dispersion, phonon DOS

**Acoustic Sum Rule (ASR):** We need to insure that translational and rotational invariance is satisfied. For NTs, 4 eigenmodes with zero frequency at $\Gamma$ (3 translational, 1 rotational)

We developed an efficient ASR symmetrization technique based on Lagrangian multipliers.

Which DFT approach makes sense for nanostructures?

Q-Space Approach (DFPT)  \[ \text{Better for 3D systems} \]

**Phonon Dispersions**
Currently available in a few plane wave codes

Quantum Espresso, Abinit, and CASTEP

Sergei Savrasov: LMTO version for phonon dispersions

Real space approaches  \[ \text{Order-N Advantages for 1D} \]

**Phonon Dispersions**
Any code that can determine Hellmann-Feynmann forces on atoms will do.

DFT Codes that work with real space phonon utilities (VASP, WIEN2K, SIESTA, etc)

Codes available – **Phonon** (Keblinski), **Vibra** (Andrei Postnikov), **Phon** (Dario Alfe)
Phonon transmission through defective (7,0) carbon nanotubes


- Nitrogen doped nanotube: 3.5% TC reduction at RT
- Stone-Wales Defect: 18% TC reduction at RT

**Thermal conductance at RT**
- Pristine: 2.26 nW/K
- Nitrogen: 2.18 nW/K
- SW defect: 1.85 nW/K
Isotope Disorder in Nanotubes: Localization?

How does phonon transmission change as the disordered region increases?

Isotopically disordered region (blue atoms)
Isotope Disorder in Nanotubes: Localization?

How does phonon transmission change as the disordered region increases?

Isotopically disordered region (blue atoms)
Isotope Disorder in Nanotubes: Localization?

How does phonon transmission change as the disordered region increases?

Isotopically disordered region (7,0) NT with 10.7% $^{14}$C isotopes

**Ballistic and Diffusive Region**
(low – mid frequencies)

$T(\omega) = N/(1+L/\lambda_e(\omega))$

$(T/N)-1 = L/\lambda_e$
Isotope Disorder in Nanotubes: Localization?

How does phonon transmission change as the disordered region increases?

Isotopically disordered region (7,0) NT with 10.7% $^{14}$C isotopes

**Ballistic and Diffusive Region**

(low – mid frequencies)

$T(\omega) = N/(1+L/\lambda_e(\omega))$

$(T/N)-1 = L/\lambda_e$

**Phonon localization**

(only high frequencies)

$\ln T(\omega) = -L/\zeta(\omega)$

Isotopically pure nanotubes

Impact on Thermal Conductivity?

Solid lines are exact calculations
Dashed lines are approximate calculations that do not include localization effects

Localization due to isotopes has little effect on thermal conductivity. Why?

*Phonons are bosons (all modes contribute) compared to electrons (fermions) where effects at Fermi energy is paramount*

I. Savic, D. A. Stewart, N. Mingo,
Conclusions

A predictive framework for thermal transport can help address: nanoscale heat transfer, thermoelectric design, and thermal barrier coatings.

We have developed a new density functional approach to thermal transport in:

**Materials**: Calculated thermal conductivity is in excellent agreement with experiment for Si, Ge, diamond and SiGe alloys with nanoparticles.

**Nanostructures**: Model shows phonon localization due isotope scattering is not important for thermal transport.

http://sites.google.com/dft4nano
Thank you for your attention!

To learn more:
http://sites.google.com/site/dft4nano
or just google dft4nano