

## An Introduction to First Principles Thermal Transport

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### Collaborators

## Funding

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#### **Thermal Transport in Materials**

(CBET-0651427 and CBET-01066406)

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#### 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)

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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











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Pop and Goodson, <u>J. of Electronic Packaging, 2006</u>

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#### 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.** 





## Energy Lost in Automobiles



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



#### 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 MgSiO<sub>3</sub> in Earth's D<sup>r</sup> layer

#### Artem R. Oganov<sup>1</sup> & Shigeaki Ono<sup>2</sup>

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#### Nature, 430, 445 (2004).

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







Figure 1 Structure of the post-perovskite phase of MgSiO<sub>3</sub> (calculated at 120 GPa). SiO<sub>6</sub> octahedra and Mg atoms (spheres) are shown. Similar structures are known for Fe<sub>2</sub>O<sub>3</sub>, CalrO<sub>3</sub>, FeUS<sub>3</sub>, PbTII<sub>3</sub>, USCS<sub>3</sub>, KTmI<sub>3</sub>, AgTaS<sub>3</sub> and CalnBr<sub>3</sub>.

# 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:



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

where **q** is the phonon wavevector and v is the phonon branch. The phonon **Bose** distribution is given by  $n(\mathbf{q}, v)$ .



## 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 **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



**Specific heat** *Cp* **versus temperature** from 20 K to 300 K (<u>DeSorbo [1953]</u>) and *Cp* and *Cv* from 273 K

to 1073 K (Viktor [1962]).

 $F = E - TS \approx E_{gs}(V)\Big|_{T=0} + \Delta F_{vib}(V,T)$  $\Delta F_{vib}(V,T) = k_B T \sum_{i,\mathbf{q}} \log\{2\sinh[\hbar\omega_{i,\mathbf{q}}(V)/2k_B T]\}$ 

Other properties Infrared absorption, Raman Electron-phonon coupling for transport Estimates for Tc for Superconductivity

Phase Diagrams

#### Phonon Modes in a General Crystal



$$ma = F$$

$$Equation of Motion$$

$$m_{s}\ddot{u}_{s}^{\alpha}(\ell) = -\frac{\partial E}{\partial u_{s}^{\alpha}(\ell)}$$

$$m_{s}\ddot{u}_{s}^{\alpha}(\ell) = -\sum_{\beta tm} \frac{\partial^{2}E}{\partial u_{s}^{\alpha}(\ell)\partial u_{t}^{\beta}(m)} u_{t}^{\beta}(m)$$
$$C_{st}^{\alpha\beta}(\ell,m) = \frac{\partial^{2}E}{\partial u_{s}^{\alpha}(\ell)\partial u_{t}^{\beta}(m)}$$
IFCs

Assume u has a wave solution

$$u_{s}^{\alpha}\left(l\right) = \frac{1}{\sqrt{m_{s}}} u_{s}^{\alpha} \cdot e^{i\left(\mathbf{q}\cdot\mathbf{x}-\omega t\right)}$$

$$\det \omega^2 \delta_{\alpha\beta} \delta_{st} - D_{st}^{\alpha\beta} (\mathbf{q}) = 0$$

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



Ion and Core electrons

#### 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!





#### DFT+Phonons = Thermal Transport







#### DFT+Phonons = Thermal Transport







Heat Transfer in Nanostructures

$$G^{R}(\omega) = \left[\omega^{2}\mathbf{I} - \mathbf{H} - \boldsymbol{\Sigma}_{\mathbf{L}} - \boldsymbol{\Sigma}_{\mathbf{R}}\right]^{-1}$$

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...

$$H = \frac{-\hbar^2}{2m_e} \sum_{i} \nabla_i^2 - \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r} - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{I} \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}$$



...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.

Huge savings in computational costs which results in an approach that helps describe known systems and also predict new systems, scaling as N<sup>3</sup>. For an N interacting particle system, this moves us from 3N variables to a single function of x, y, and z.

1998: Nobel prize awarded for Density Functional Theory

Hohenberg & Kohn, Phys. Rev., **136**, B864 (1964). – Density functional foundation

Kohn & Sham, Phys. Rev., **140**, A1133 (1965). – transform problem to set of non-interacting quasi-particles

## Interactions for a full crystal

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

Harmonic terms: 
$$\Phi_{\alpha_1\alpha_2}^{\kappa_1\kappa_2}(\mathbf{R}_1,\mathbf{R}_2) = \frac{\partial^2 E_{tot}}{\partial u_{\alpha_1}^{\kappa_1}(\mathbf{R}_1)\partial u_{\alpha_2}^{\kappa_2}(\mathbf{R}_2)} = -\frac{\partial F_1}{\partial u_{\alpha_2}^{\kappa_2}(\mathbf{R}_2)}$$

Anharmonic terms: 
$$\Phi_{\alpha_1\alpha_2\alpha_3}^{\kappa_1\kappa_2\kappa_3}(\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3) = \frac{\partial^3 E_{tot}}{\partial u_{\alpha_1}^{\kappa_1}(\mathbf{R}_1)\partial u_{\alpha_2}^{\kappa_2}(\mathbf{R}_2)\partial u_{\alpha_3}^{\kappa_3}(\mathbf{R}_3)}$$

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)

3rd 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 is self-consistently converged.



This then gives us  $\mathbf{n}_{\text{scf}}$  and  $\mathbf{V}_{\text{scf}}$ 





#### Calculating IFCs from first principles in q-space

#### 2 Throw a phonon into the mix

We have some phonon going through a crystal  $e^{i(qx-\omega t)}$  q

which induces a perturbing potential  $\Delta V_{ion}$  that is periodic with wavevector **q**.

In this case, it is better to consider  $\Delta n(q+G)$  rather than  $\Delta n(r)$ . All calculations are done in the first Brillouin zone!

Sample different **q** values in the BZ and FFT back to real space IFCs.

With enough calculated **q** points, you can interpolate to other **q** values.

With this, we also get phonon dispersion, phonon density of states.





## Density Functional Perturbation Theory

3

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

$$\Delta \rho(\mathbf{r}) = 4 \operatorname{Re} \sum_{n=1}^{N/2} \psi_n^{0*}(\mathbf{r}) \Delta \psi_n(\mathbf{r})$$

$$\downarrow$$

$$\Delta V(\mathbf{r}) = \Delta V_{ext}(\mathbf{r}) + e^2 \int \frac{\Delta \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{dv_{xc}}{dn} \Big|_{n=n(r)} \Delta \rho(\mathbf{r})$$

$$\downarrow$$

$$(H - \varepsilon_n) |\Delta \psi_n\rangle = -(\Delta V - \Delta \varepsilon) |\psi_n^0\rangle$$

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#### Ab-initio Phonon Dispersions



### **Thermal Transport in InAs Nanowires**



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!

F. Zhou et al, Phys. Rev. B, 83, 205416 2011



ZB Experimental Data: N. S. Orlova, *Phys. Stat. Solidi (b)* **119**, 541 (1983).

Kohn Anomaly in [ $\zeta\zeta$ 0]



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)).

D. A. Stewart, New J. of Phys. 10, 043025 (2008)

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#### Very difficult for shell model or empirical potentials to catch this.



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## 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

$$n_{\lambda} = n_{0\lambda} + n_{1\lambda}$$
 for mode  $\lambda$   $\lambda = (j, q)$ 

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

$$\mathbf{v}_{\lambda} \cdot \nabla T \frac{\partial n_{0\lambda}}{\partial T} = \frac{\partial n_{\lambda}}{\partial t} \bigg|_{collisidential}$$

on

For three phonon scattering:

T<sub>c</sub>

$$\frac{\partial n}{\partial t}\Big|_{collision} = \sum_{\lambda'\lambda''} W^{+}_{\lambda\lambda'\lambda''} (\Phi_{\lambda''} - \Phi_{\lambda'} - \Phi_{\lambda}) + \frac{1}{2} W^{-}_{\lambda\lambda'\lambda} (\Phi_{\lambda''} + \Phi_{\lambda'} + \Phi_{\lambda})$$
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.



Tн



## 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



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);

D. A. Broido et al, Phys Rev B, 72, 014308 (2005)





## 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

## Iterative Solution of the Boltzmann Equation

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.

![](_page_25_Figure_4.jpeg)

Number of Iterations

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![](_page_25_Picture_6.jpeg)

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

### Thermal conductivity for Si and Ge

![](_page_26_Figure_1.jpeg)

![](_page_26_Picture_2.jpeg)

D. A. Broido, M. Malorny, G. Birner, N. Mingo, & D. A. Stewart, Appl. Phys. Lett. **91**, 231922 (2007)

## Thermal Conductivity for Diamond

![](_page_27_Figure_1.jpeg)

![](_page_27_Picture_2.jpeg)

## Thermal Conductivity for Diamond

![](_page_28_Figure_1.jpeg)

![](_page_28_Picture_2.jpeg)

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## 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.

- Full calc
- – – No optic phonon scattering

# This detailed scattering info is lost in relaxation time models.

![](_page_29_Figure_6.jpeg)

![](_page_29_Picture_7.jpeg)

## Effect of Isotopes on **Diamond Thermal Conductivity**

99.93% C<sup>12</sup>, 0.07% C<sup>13</sup>  $W^{iso}_{\lambda\lambda'} \propto g$ Λ 99.90 %C<sup>12</sup>, 0.10% C<sup>13</sup> -attice thermal conductivity (W/m-K) 10000 +,x, ◊ Natural Distribution Scattering rate of phonons due Isotopically pure to isotopes is proportional to the mass variance  $g = \frac{\sum c_{i}M_{i}^{2} - (\sum c_{i}M_{i})^{2}}{(\sum c_{i}M_{i})^{2}}$ 1000 Natural Isotope Distribution where  $c_i$  and  $M_i$  are the 98.9% C<sup>12</sup> 1.1% C<sup>13</sup> concentration and mass of isotope i. 200 400 600 800 1000

Temperature (K)

![](_page_30_Picture_3.jpeg)

## Brillouin Zone Contributions to $\kappa$

#### **Isotopically Pure Silicon**

$$\kappa_{zz} = \frac{1}{(2\pi)^3} \int \kappa_{zz}(\mathbf{q}) d\mathbf{q}$$
$$\kappa_{zz}(\mathbf{q}) = \sum C_j(\mathbf{q}) v_{jz}(\mathbf{q})^2 \tau_{jz}(\mathbf{q})$$

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

![](_page_31_Figure_4.jpeg)

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

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Thermal Gradient in z direction

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

## **Phonon Velocity Effects**

![](_page_32_Figure_1.jpeg)

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## Predicting Thermal Conductivity of Thermoelectrics

![](_page_33_Figure_1.jpeg)

#### Radioisotope Thermoelectric system

have powered deep space probes:

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

![](_page_33_Figure_6.jpeg)

Thermoelectric Refrigerators:

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

#### What makes a good thermoelectric?

Electrical

![](_page_34_Figure_1.jpeg)

need fast charges and slow phonons,

#### **Electron crystal – phonon glass**

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

# Boosting ZT with nanostructuring

![](_page_35_Figure_1.jpeg)

# Using nanostructures in alloys to reduce thermal conductivity

![](_page_36_Figure_1.jpeg)

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  $\sim$  1.6 at 800K

![](_page_36_Picture_4.jpeg)

# SiGe alloy thermoeletrics

- Many thermoelectrics are made from toxic or scarce materials that are difficult to integrate into silicon fabrication – i.e. Bi<sub>2</sub>Te<sub>3</sub>, 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).

![](_page_37_Picture_4.jpeg)

## Add nanoparticles...

![](_page_38_Figure_1.jpeg)

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

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Mingo et al., Nano Lett. 9, 711 (2009).

### Which works better? Si or Ge nanoparticles?

Scattering Rate 
$$\frac{1}{\tau_{\lambda}^{np}} = \frac{\Omega}{2\omega^{2}} \frac{f_{np}}{V_{np}} \operatorname{Im}\left[\left\langle \lambda | \mathbf{T}(\omega^{2}) \lambda \right\rangle\right]$$
$$\mathbf{T}(\omega^{2}) = \left[\mathbf{I} - \mathbf{V}\mathbf{g}^{+}(\omega^{2})\right]^{-1} \mathbf{V} \qquad \mathbf{T} = \mathbf{V} + \mathbf{V}\mathbf{g}\mathbf{V} + \dots$$
$$\mathbf{T} \approx \mathbf{V} \qquad \text{Born approximation}$$
$$\frac{1}{\tau_{\lambda}^{np}} \propto \frac{\left(M - M_{np}\right)^{2}}{M^{2}} \qquad \text{Born approximation} \qquad \text{Perturbation matrix due to nanoparticle}$$
$$(\mathbf{M} - \mathbf{M}_{np})^{2}/\mathbf{M}^{2} \qquad \mathbf{M}_{Si} = 28.086 \ \mathbf{M}_{Ge} = 72.61 \ \mathbf{M}_{Si0.5Ge0.5} = 50.348$$

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?

![](_page_39_Picture_3.jpeg)

# **Calculation Details**

- Use ab-initio force constants from Si and Ge to generate force constants for Si<sub>0.5</sub>Ge<sub>0.5</sub> 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.

![](_page_40_Picture_4.jpeg)

## SiGe alloys & Si or Ge nanoparticles

Si<sub>0.5</sub>Ge<sub>0.5</sub> thermal conductivity without nanoparticles

	Theory	Ехр	
300K	10.62 W/m-K	7.5-8 W/m-K	<b>←</b>
800K	6.07 W/m-K	4.5-5 W/m-K	

Let's first look at the predicted thermal conductivity for the SiGe alloy

#### Possible reasons for differences:

- 1. Defects in experimental samples
- 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

A Kundu, N. Mingo, D. A. Broido, D. A. Stewart, Phys. Rev. B, **84**, 125426 (2011).

## SiGe alloys & Si or Ge nanoparticles

Si<sub>0.5</sub>Ge<sub>0.5</sub> thermal conductivity without nanoparticles

	Theory	Ехр
300K	10.62 W/m-K	7.5-8 W/m-K
800K	6.07 W/m-K	4.5-5 W/m-K

Possible reasons for differences:

- 1. Defects in experimental samples
- 2. Use of VCA
- 3. Enhanced scattering due to changes in elastic constants.

![](_page_42_Figure_7.jpeg)

A. Kundu, N. Mingo, D. A. Broido, D. A. Stewart, Phys. Rev. B, 84, 125426 (2011).

## Thermal Conductivity ratio

![](_page_43_Figure_1.jpeg)

**Conclusion**: Ge nanoparticles can give a higher ZT value than Si nanoparticles A. Kundu, N. Mingo, D. A. Broido, D. A. Stewart, Phys. Rev. B, **84**, 125426 (2011).

# Scattering Rate comparison

![](_page_44_Figure_1.jpeg)

![](_page_44_Picture_2.jpeg)

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A. Kundu, N. Mingo, D. A. Broido, D. A. Stewart, Phys. Rev. B, **84**, 125426 (2011).

# Why is there a difference?

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

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

![](_page_45_Figure_5.jpeg)

#### Green's Functions for Nanoscale Phonon Transmission

What does it mean to transport energy on the nanoscale?

$$\begin{array}{c} \sum_{\mathbf{L}} & H_{\mathbf{J}} \\ \hline \mathbf{T}_{\mathbf{h}} & \overline{\mathbf{T}_{\mathbf{c}}} & \overline{\mathbf{T}_{\mathbf{c}}} \end{array} \end{array} \begin{array}{c} \sum_{\mathbf{R}} & Ballistic Transport \\ \hline \mathbf{H} = \frac{1}{2} \sum_{i} M_{i} \dot{\varphi}_{i} \dot{\varphi}_{i} + \frac{1}{2} \sum_{ij} K_{ij} \varphi_{i} \varphi_{j} + \sum_{ijk} V_{ijk}^{(3)} \varphi_{i} \varphi_{j} \varphi_{k} + O^{(4)}_{anh} \end{array}$$

![](_page_46_Picture_3.jpeg)

$$G^{R}(\omega) = \left[\omega^{2}\mathbf{I} - \mathbf{H}_{J} - \boldsymbol{\Sigma}_{\mathbf{L}} - \boldsymbol{\Sigma}_{\mathbf{R}}\right]^{-1} \qquad \Xi(\omega) = \operatorname{Tr}\left[\Gamma_{L}(\omega)G^{R}_{1N}(\omega)\Gamma_{R}(\omega)G^{A}_{1N}(\omega)\right]$$
  
Phonon Transmission

Thermal conductance

$$\sigma = \left(1/k_B T^2\right) \int_{0}^{\infty} \frac{d\omega}{2\pi} (\hbar\omega)^2 \Xi(\omega) \frac{e^{\hbar\omega/k_B T}}{\left(1 - e^{\hbar\omega/k_B T}\right)^2}$$

![](_page_46_Picture_7.jpeg)

Cornell University 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

![](_page_47_Figure_1.jpeg)

IFC calc for simple crystal

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.

![](_page_47_Picture_11.jpeg)

N. Mingo et al, Phys. Rev. B, 77 033418 (2008)

![](_page_47_Picture_14.jpeg)

# Which DFT approach makes sense for nanostructures?

#### **Q-Space Approach (DFPT)**

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** 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)

![](_page_48_Picture_11.jpeg)

![](_page_48_Figure_12.jpeg)

Codes available – Phonon (Keblinski), Vibra (Andrei Postnikov), Phon (Dario Alfe)

![](_page_48_Picture_14.jpeg)

![](_page_48_Picture_16.jpeg)

# Phonon transmission through defective (7,0) carbon nanotubes

![](_page_49_Figure_1.jpeg)

18% TC reduction at RT

![](_page_49_Picture_3.jpeg)

Cornell University

N. Mingo et al, Phys. Rev. B, 77 033418 (2008).

How does phonon transmission change as the disordered region increases? T+dT L T

Isotopically disordered region (blue atoms)

![](_page_50_Picture_3.jpeg)

I. Savic, D. A. Stewart, N. Mingo, *Phys. Rev. Lett.* **101**, 165502 (2008)

![](_page_51_Figure_1.jpeg)

![](_page_51_Picture_2.jpeg)

I. Savic, D. A. Stewart, N. Mingo, *Phys. Rev. Lett.* **101**, 165502 (2008)

![](_page_52_Figure_1.jpeg)

![](_page_53_Figure_1.jpeg)

![](_page_54_Figure_1.jpeg)

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

Cornell University

I. Savic, D. A. Stewart, N. Mingo, *Phys. Rev. Lett.* **101**, 165502 (2008)

#### 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.

![](_page_55_Figure_5.jpeg)

# Thank you for your attention!

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

![](_page_56_Picture_2.jpeg)

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