First-principles Enabled Predictions of Conductive and Radiative Properties of Solids

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The Nobel Prize in Chemistry 2013

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Martin Karplus

Photo: Keilana via Wikimedia Commons

Michael Levitt

Photo: Wikimedia Commons

Arieh Warshel

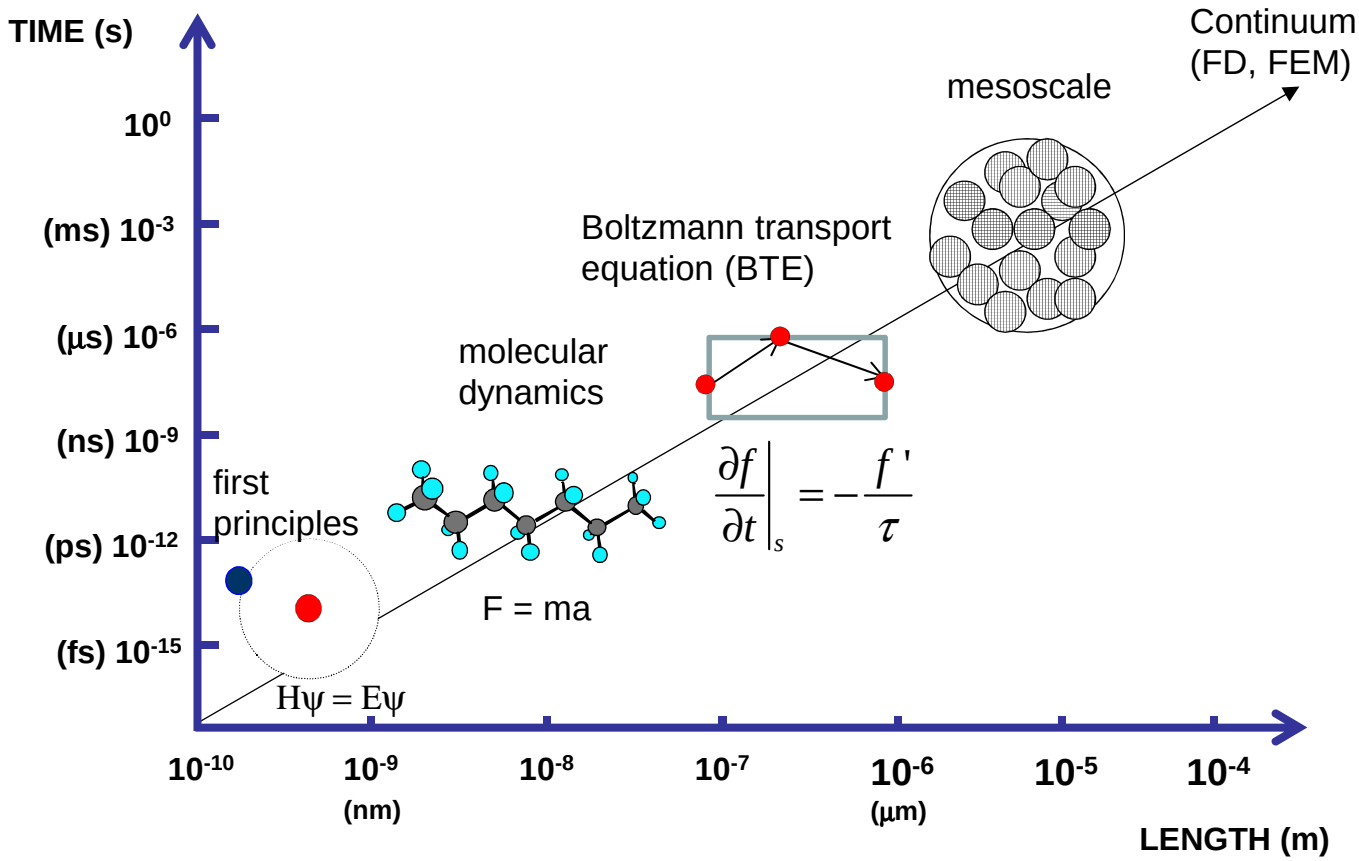
The Nobel Prize in Chemistry 2013 was awarded jointly to Martin Karplus, Michael Levitt and Arieh Warshel *"for the development of multiscale models for complex chemical systems"*.

http://www.nobelprize.org

Outline

- *Overview of multiscale multiphysics predictions*
- Thermal conductivity of thermoelectric materials
- Phonon mean free path distribution
- Radiative properties in the visible band: photon-electron interaction
- Radiative properties in the far-infrared band: photon-phonon interaction
- Summary and Acknowledgements

Length and Time Scales of Simulation Methods



- Parameters obtained in a smaller scale simulation can be fed into larger scale simulations.

Outline

- Overview of multiscale multiphysics predictions
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- Summary and Acknowledgements

Power supply

http://www.micropelt.com/products/thermogenerator.php

PC hardware

http://hothardware.com/Articles/Dell-XPS-710-H2C-Performance-Gaming-System/?page=4

Solar power converter

http://worldwide-energy.net/

Thermoelectrics

- Thermo power generation
- Thermoelectric refrigeration

Refrigerator

http://www.germes-online.com/catalog/93/460/page9/261219/thermoelectric_refrigerator.html

Space missions

http://www.abovetopsecret.com/forum/thread305010/pg1

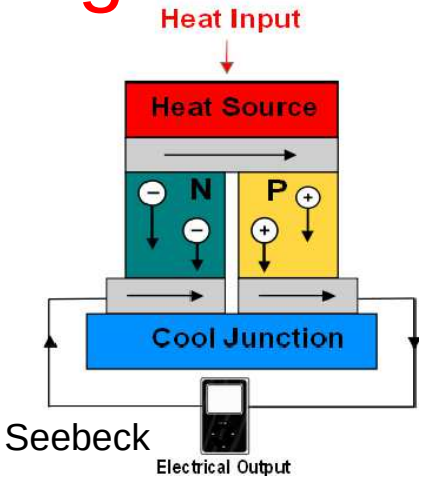
Clean energy

http://www.arxiel.com/#

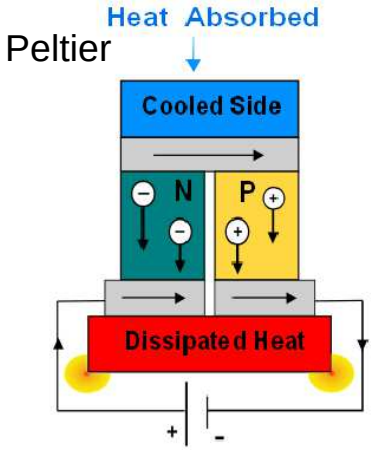
Car air conditioning

http://blogs.edmunds.com/greencaradvisor/2008/12/energy-efficient-automotive-climate-control-goal-of-federal-private-project.html

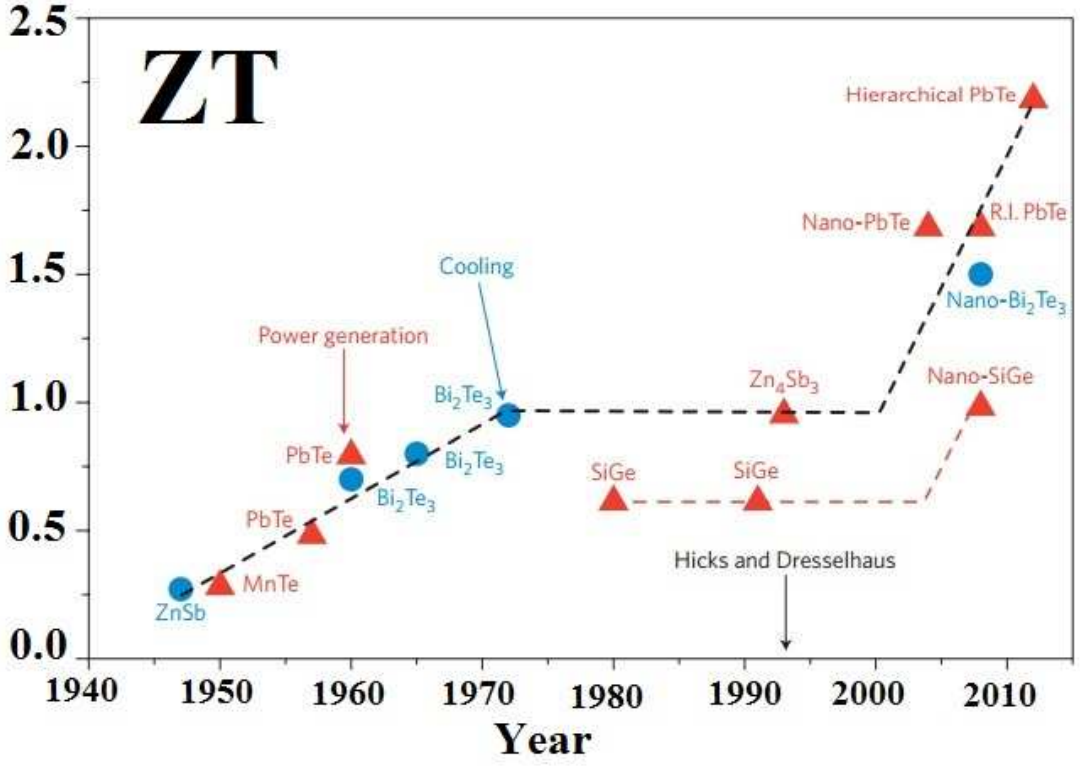
Figure of Merit *ZT*



http://www.npl.co.uk/science-technology/engineered-materials/research/nanomaterials/nanostructured-thermoelectrics

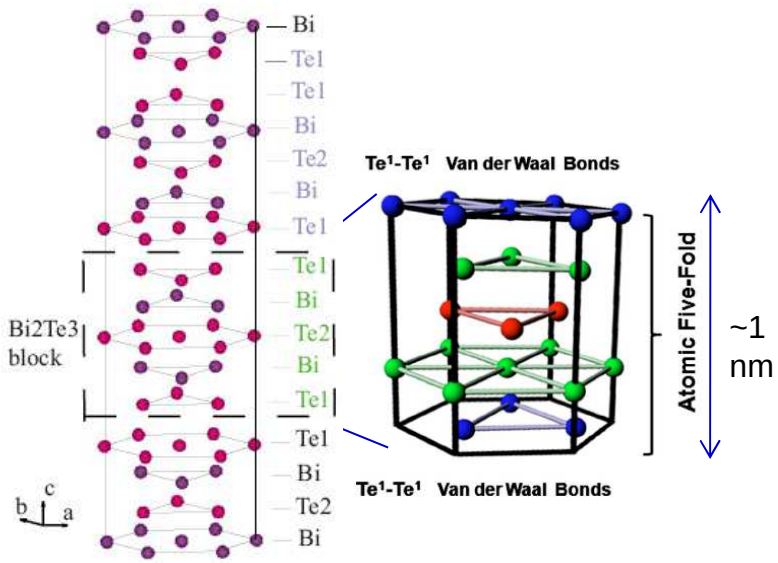


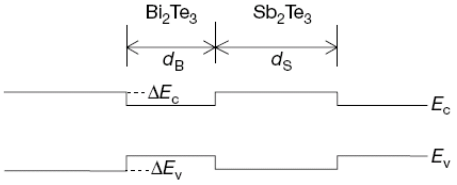
- Figure of merit: $ZT = \frac{S^2 \sigma T}{k} = \frac{S^2 \sigma T}{k_e + k_l}$
  - *S*: power factor
  - σ: electrical conductivity
  - *k*: thermal conductivity



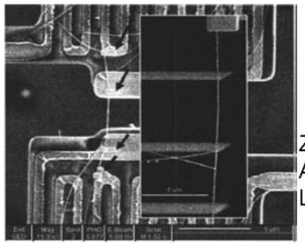
Heremans, Dresselhaus, Bell and Morelli, *Nat. Nanotech*. **8**, 471 (2013)

Bi_2Te_3 Bulk and Nanostructures

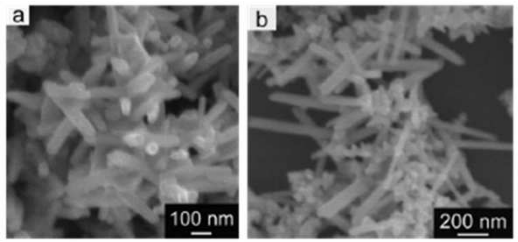




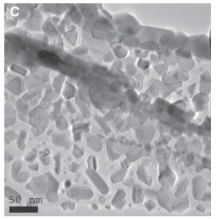
Venkatasubramanian *et al*, Nature, 2001



Zhou *et al*, Appl. Phys. Lett 2005

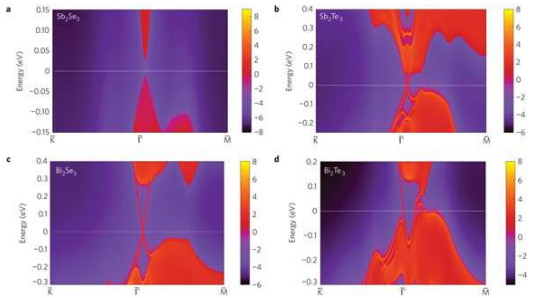


Purkayastha *et al*, Adv. Mater. 2006

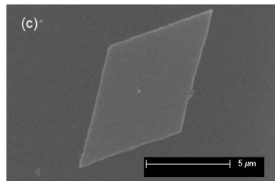


Poudel *et al*, Science, 2008

- Bi_2Te_3: Layered structure similar to graphite.
- Van Der Waals **AND** weak electrostatic interactions between quintuples.



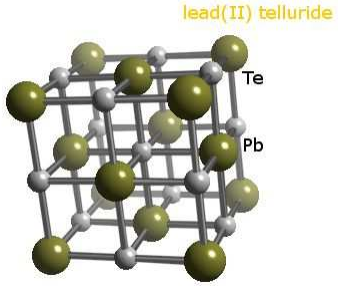
Zhang *et al*, Nat. Phys. 2009

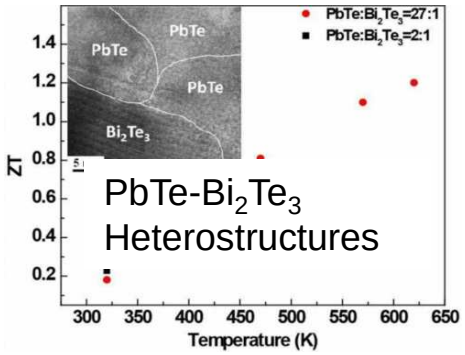


Teweldebrhan, Goyal, and Balandin, Nano Lett. 10, 1209, 2010.

PbTe Bulk and Nanostructures

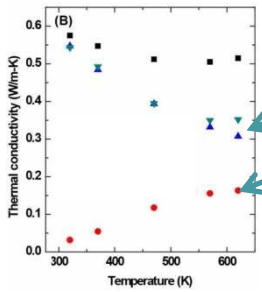
- PbTe: cubic structure similar to NaCl





PbTe-Bi_2Te_3 Heterostructures

ZT=1.2, 650K

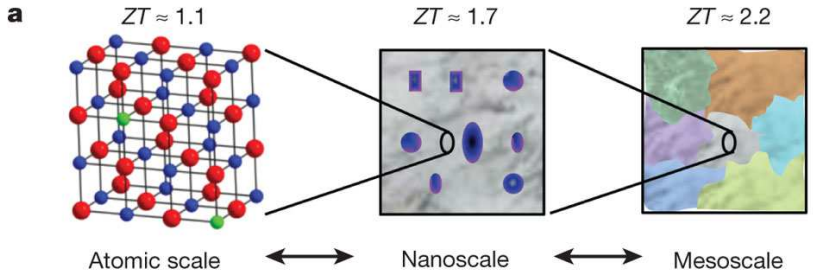


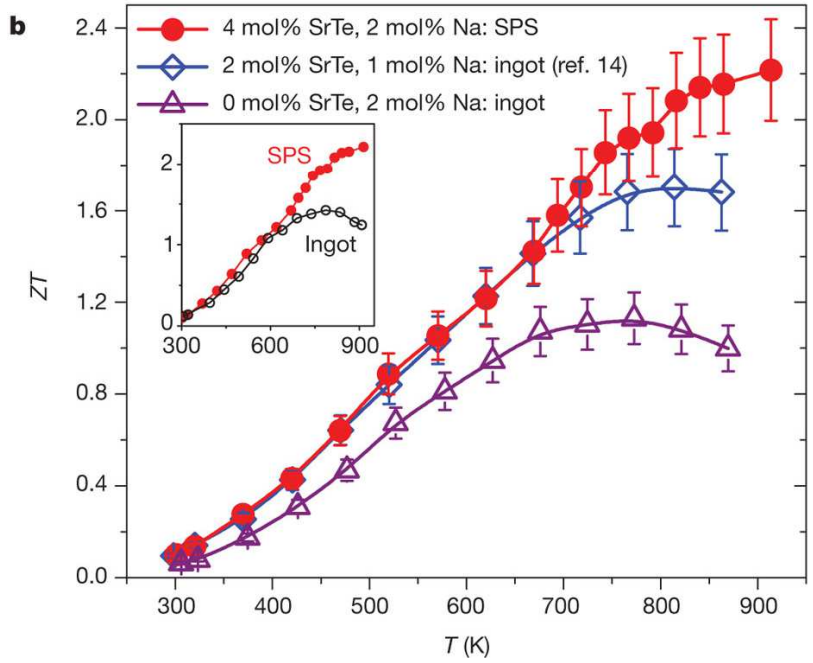
EMA

k_l

k_e

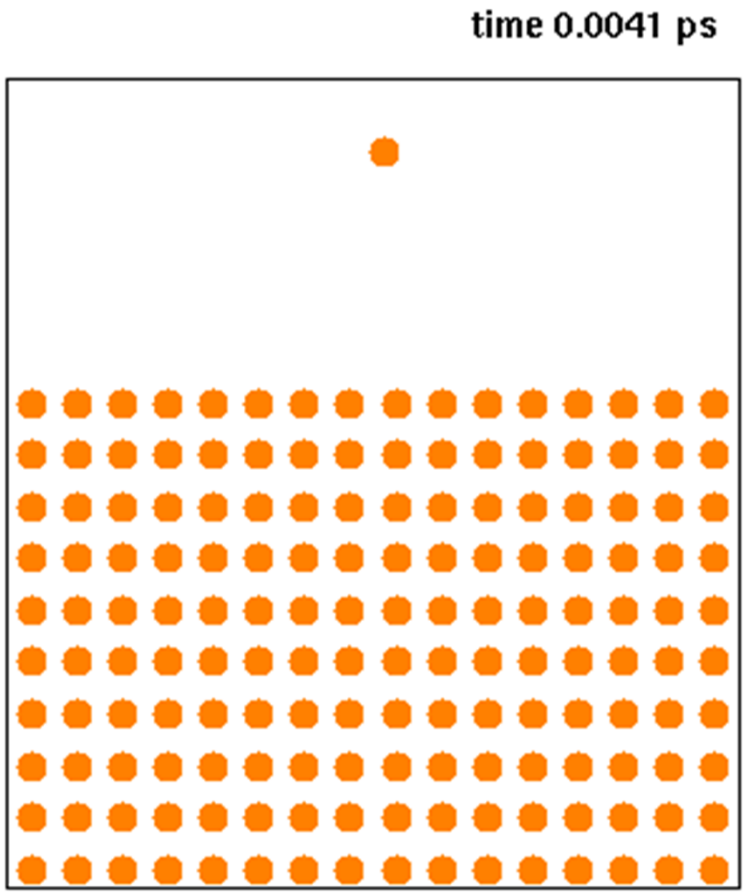
Fang, Feng, Yang, Ruan, Wu, *Nano Lett.*, (2013).





K Biswas *et al. Nature* **489**, 414-418 (2012)

A Molecular Dynamics Demo on a 2D Lattice



A falling ball and stacked balls

↓

The falling ball hits the stack

↓

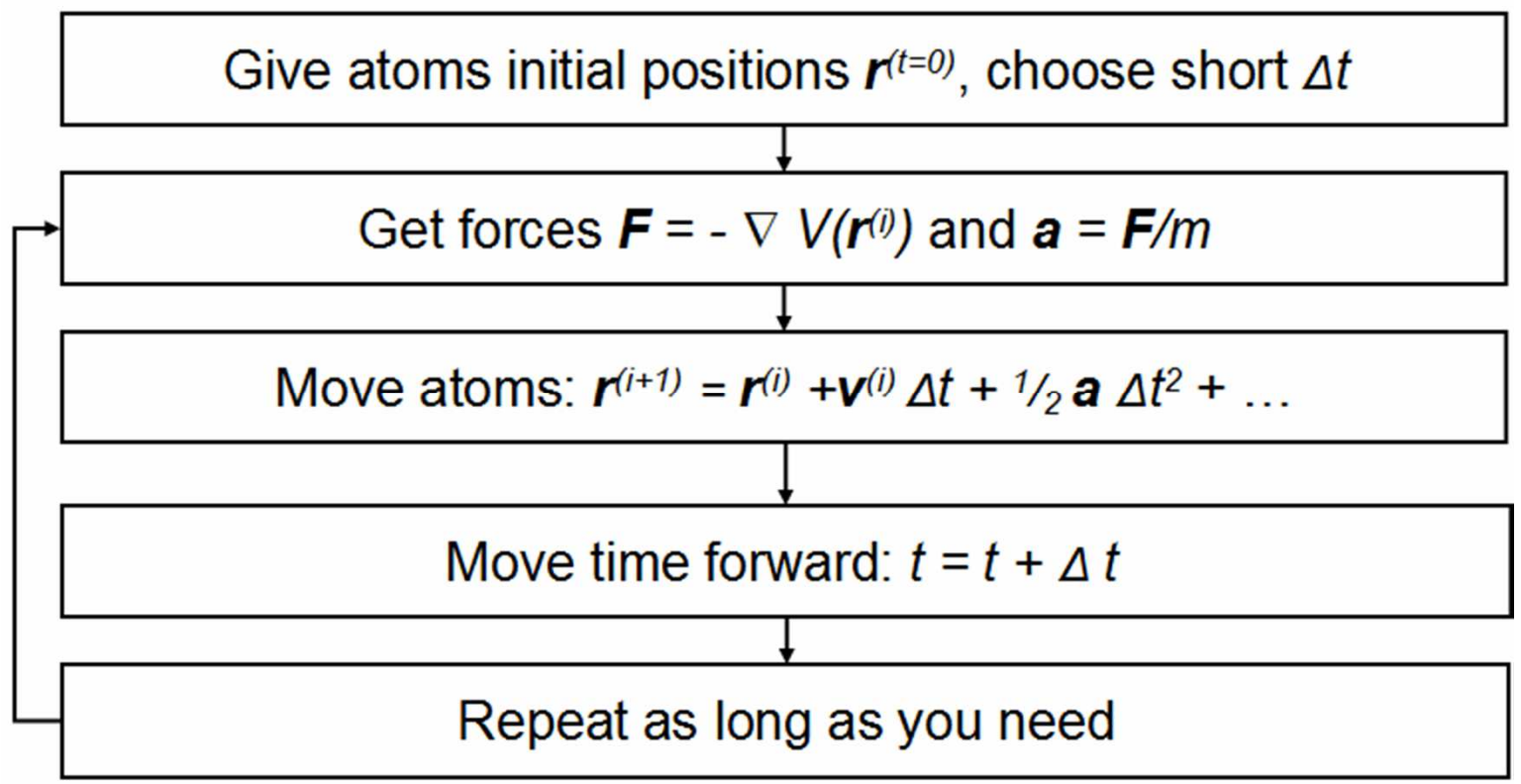
The vibration pass through the stack

↓

Those stacked balls keep Small vibrations

http://en.wikipedia.org/wiki/File:Cudeposition.gif

Basic Algorithm



Definition of Temperature in MD

- Kinetic energy per degree of freedom of a particle

$$\frac{1}{2}k_B T$$

- A particle in 3D has 3 degrees of freedom, so

$$E_k \sim \frac{3}{2}k_B T$$

- The kinetic energy for a N-particle system:

$$\left(E_k\right)_N \sim \frac{3}{2}Nk_B T$$

- Temperature is defined as:

$$\therefore \frac{1}{2}\sum_i m_i v_i^{\,2} = \frac{3}{2}Nk_B T \Rightarrow T = \frac{1}{3Nk_B}\sum_i m_i v_i^{\,2}$$

Thermal Conductivity Calculation Methods

- Non-equilibrium method: non-zero temperature gradient
  - Fourier Law

$$J_y = -k\frac{dT}{dy} \qquad k = \frac{-J_y}{dT/dy}$$

  - Size effect is more serious

- Equilibrium method: no temperature gradient needed
  - Using the fluctuation-dissipation signal of the system
  - Better control of size effect

$$\mathbf{S} = \frac{d}{dt}\sum_i \mathbf{r}_i E_i = \frac{d}{dt}\sum_i \mathbf{r}_i \left(E_{k,i} + E_{p,i}\right)$$

$$\mathbf{S} = \sum_i E_i \mathbf{v}_i + \frac{1}{2}\sum_{i,j}\left(\mathbf{F}_{ij}\cdot\mathbf{v}_i\right)\mathbf{r}_{ij}$$

$$k = \frac{1}{k_B T^2 V}\int_0^\infty \frac{\langle \mathbf{S}(t)\cdot\mathbf{S}(0)\rangle}{3}dt$$

Classical Potential Development

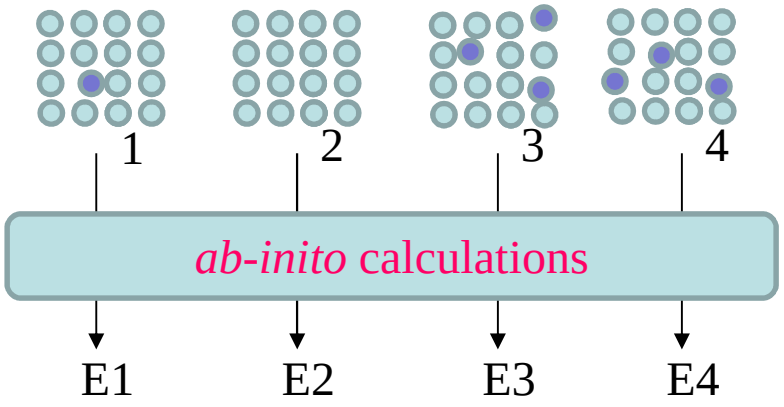
$$V(r) = D_e(1 - e^{-a(r-r_e)})^2$$

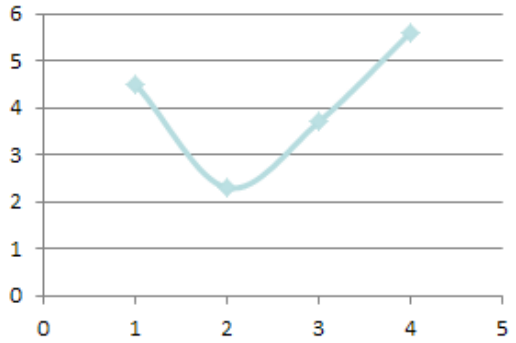
$D_e = ?, \alpha = ?, r_e = ?$

Potential parameterization

Energy surface generation

Configuration creation

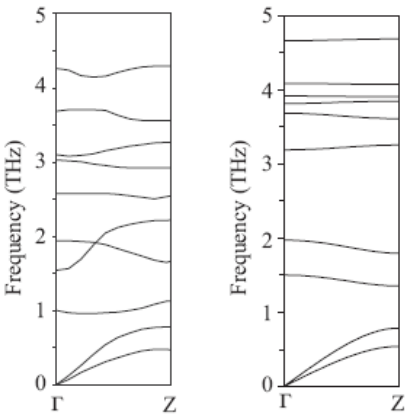




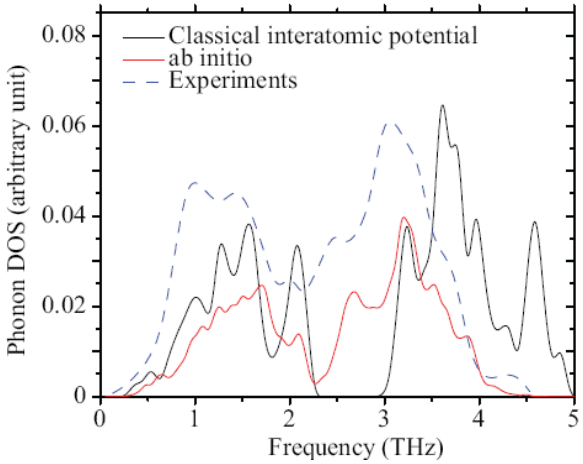
Potential Parameterization

TABLE I. The short-range interatomic pair potential for Bi_2Te_3. Here r is the separation between atom pair and r_c is the cutoff distance.

Interaction	D_e (eV)	a (1/Å)	r_0 (Å)	r_c (Å)
Te1-Bi	0.975	1.285	3.089	4.0
Te2-Bi	0.582	1.257	3.251	4.0
Te1-Te1	0.076	1.675	3.642	5.0
Bi-Bi	0.085	2.212	4.203	5.5
Te2-Te2	0.066	2.876	4.312	5.0
Te1-Te2	0.807	0.731	4.497	5.5



Phonon dispersion



Phonon DOS

TABLE II: Comparison of computed elastic constants $C_{\alpha\beta}$ and bulk modulus B with other works and experiments

	C_{11}	C_{12}	C_{14}	C_{33}	C_{44}	C_{66}	B
Ultrasonic experiment(0K)[a]	74.4	29.2	15.4	51.6	29.2	26.2	39.5
Many-body potential MD(0K)[b]	69.0	21.6	12.3	54.8	28.8	26.7	34.4
This work(0K)	75.4	23.7	11.0	49.3	23.5	25.8	37.3

Qiu and Ruan, Phys. Rev. B, 2009.

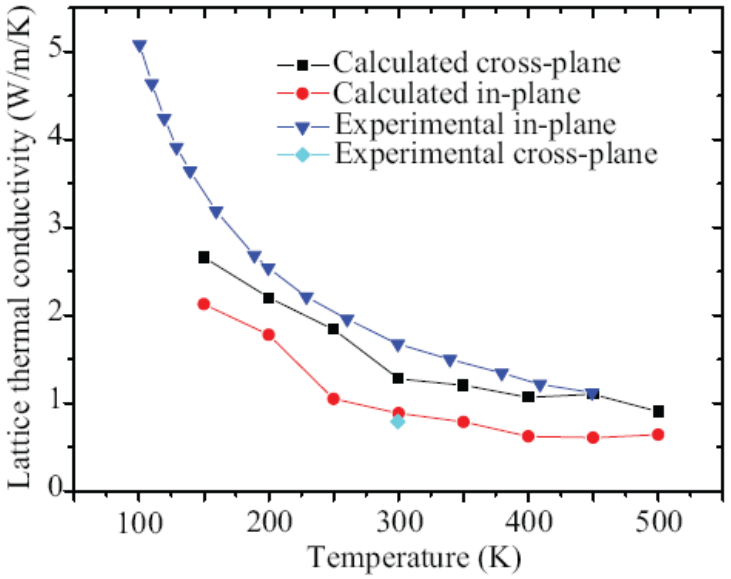
Thermal Conductivity Prediction from MD

- Equilibrium MD in the NVE ensemble.
- Green-Kubo method

General: $\mathbf{S} = \frac{d}{dt}\sum_i \mathbf{r}_i E_i = \frac{d}{dt}\sum_i \mathbf{r}_i \left(E_{k,i} + E_{p,i}\right)$

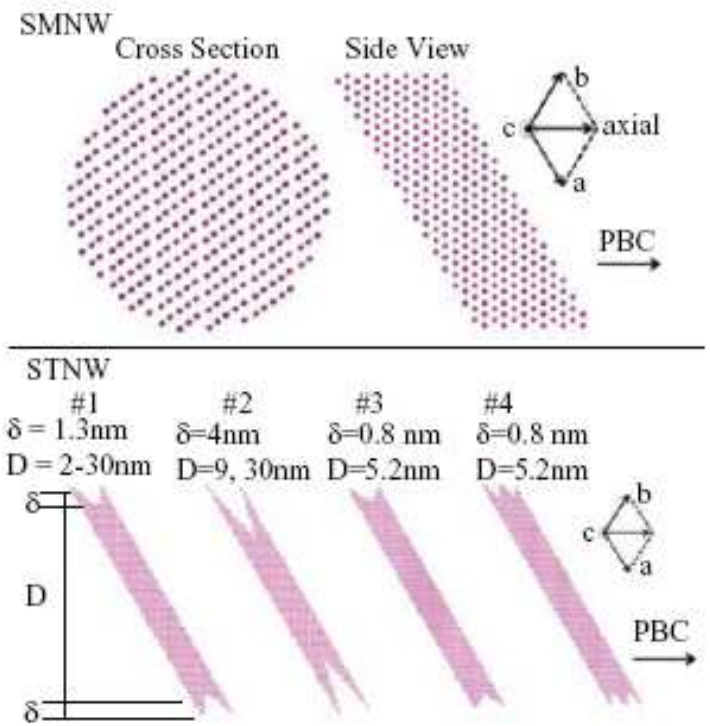
Two-body: $\mathbf{S} = \sum_i E_i \mathbf{v}_i + \frac{1}{2}\sum_{i,j}\left(\mathbf{F}_{ij}\cdot\mathbf{v}_i\right)\mathbf{r}_{ij}$

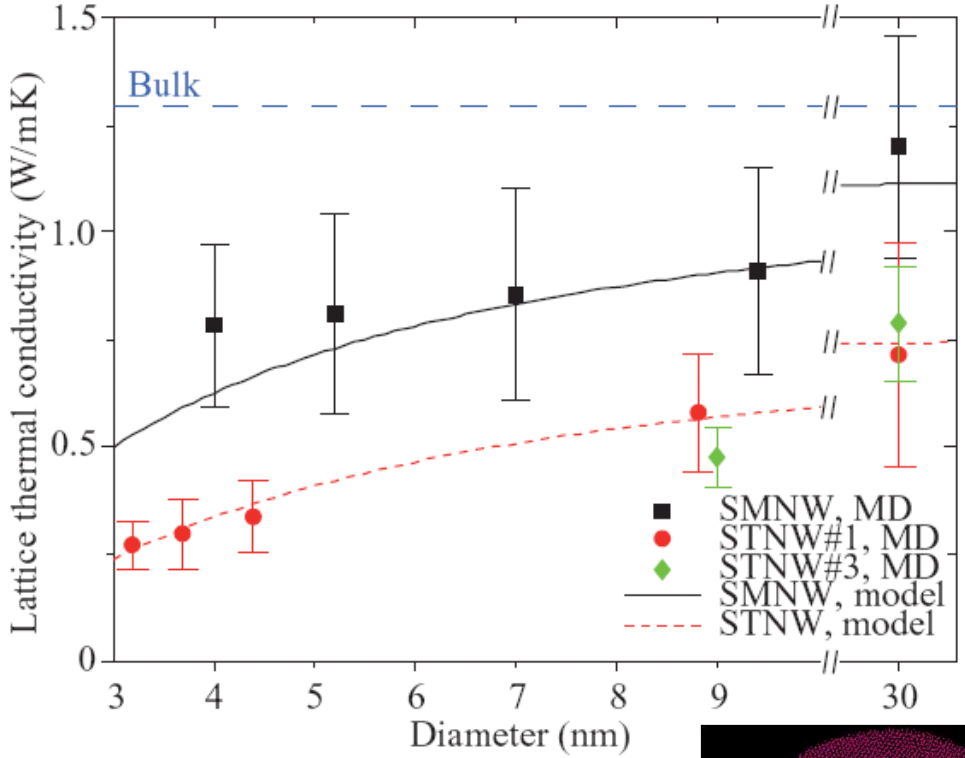
$$k = \frac{1}{k_B T^2 V}\int_0^\infty \frac{\langle \mathbf{S}(t)\cdot\mathbf{S}(0)\rangle}{3} dt$$



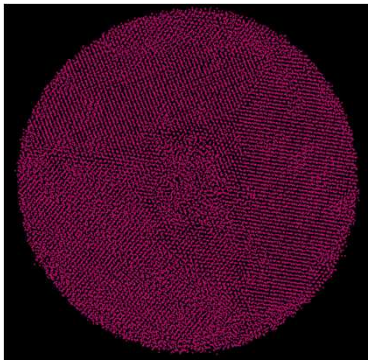
Qiu and Ruan, Phys. Rev. B, 2009.

Thermal Conductivity Reduction in Bi_2Te_3 Nanowires



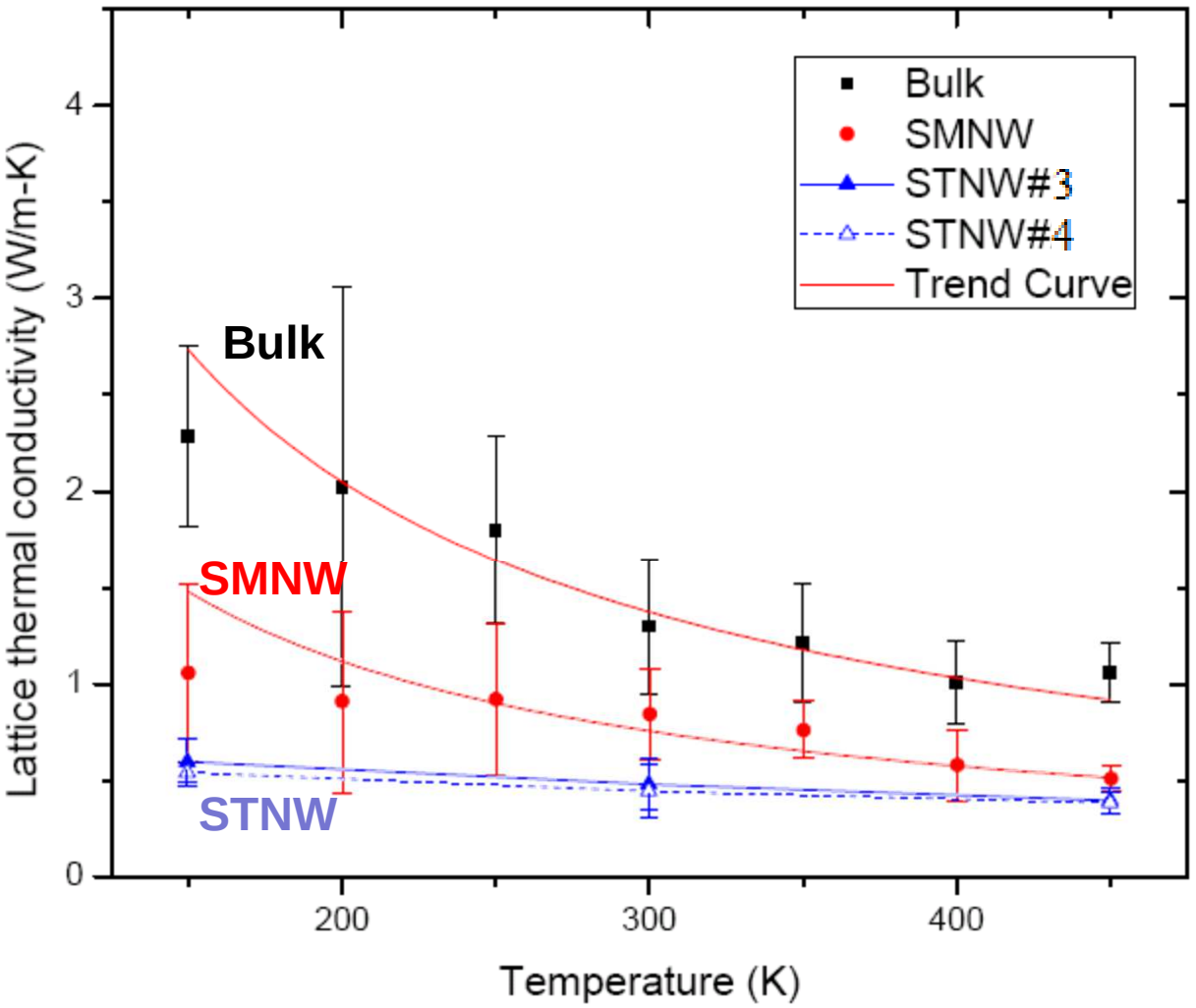


Qiu, Sun, and Ruan, *Phys. Rev. B*, **83**, 035312 (2011)



- Diameter decreases → thermal conductivity decreases
- Bulk → SMNW : 50% lower thermal conductivity
- SMNW → STNW: additional 35% lower thermal conductivity
- At 30 nm diameter, no significant reduction seen

Temperature dependence of k_l



Diameter D = 5.2 nm

T dependence:

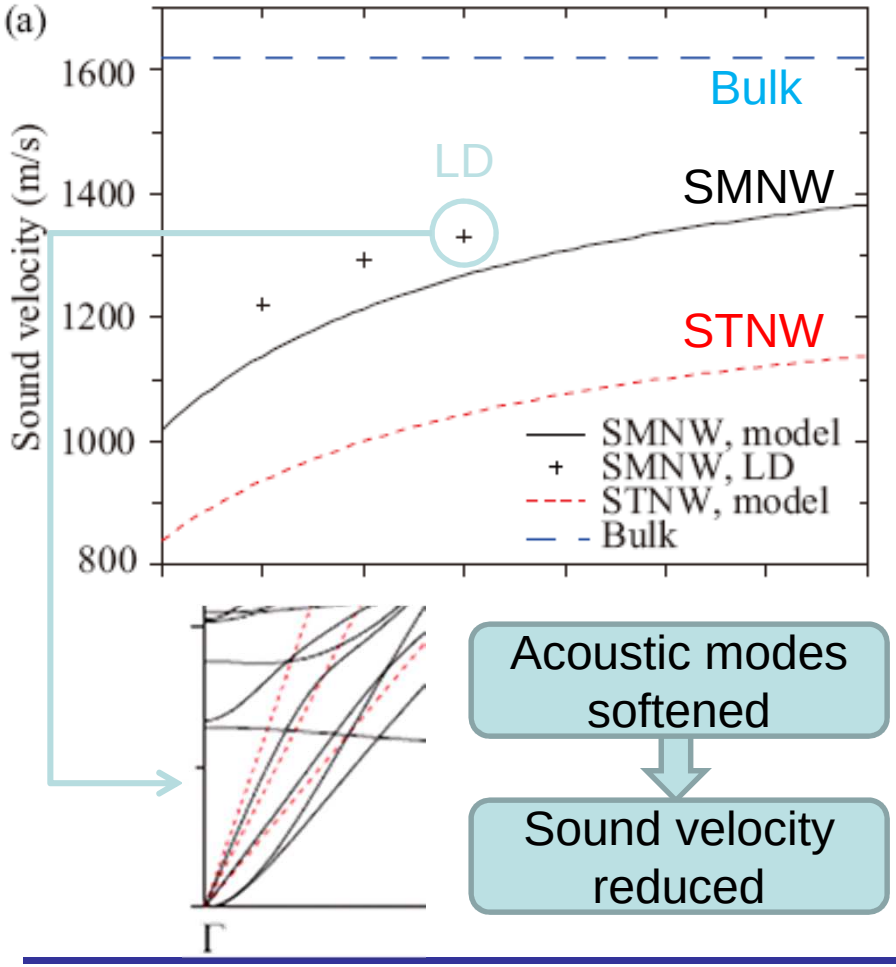
Bulk
> SMNW
> STNW

Surface roughness scattering
Independent of temperature

Qiu, Sun and Ruan, PRB 2011

Sound velocity and Relaxation time

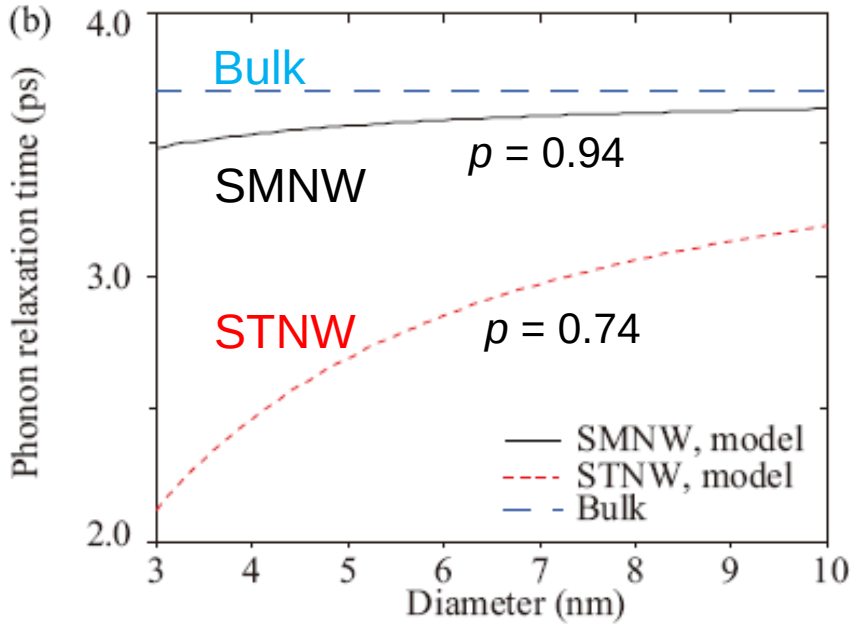
$$\kappa_l = \kappa_0 p \exp(-\alpha l_0/D) \times \frac{(1-\frac{1}{12D/L_0-1})\exp(-\frac{2S_m}{3R}\frac{1}{12D/L_0-1})}{1+(\frac{1-p}{1+p})(l_0/D)+B_{st}(\delta/D)^2}$$



Acoustic modes softened

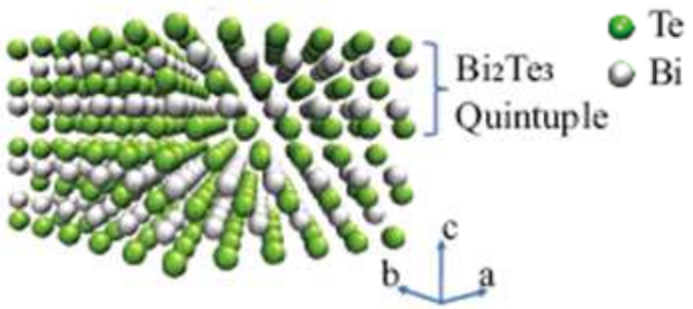
Sound velocity reduced

SMNW:
Minimal boundary scatterings
STNW:
Rough surface -> strong scattering



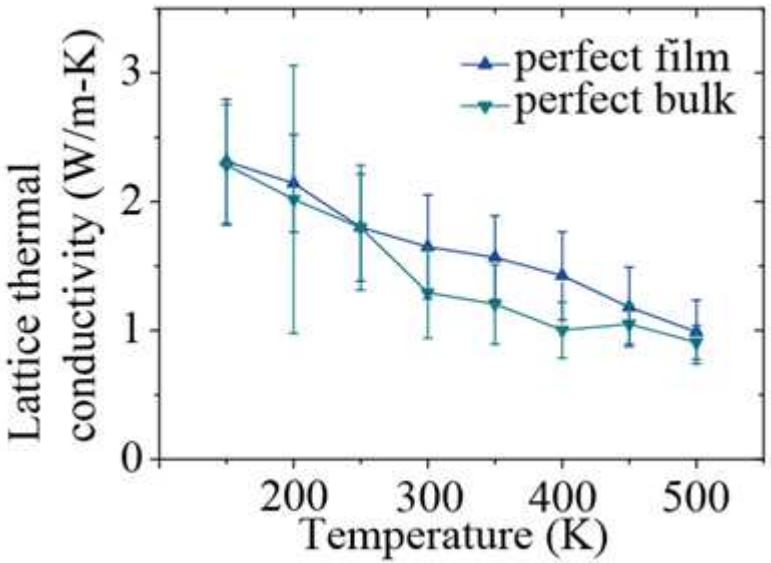
Qiu, Sun and Ruan, PRB 2011

Thermal Conductivity of Bi_2Te_3 Thin Films



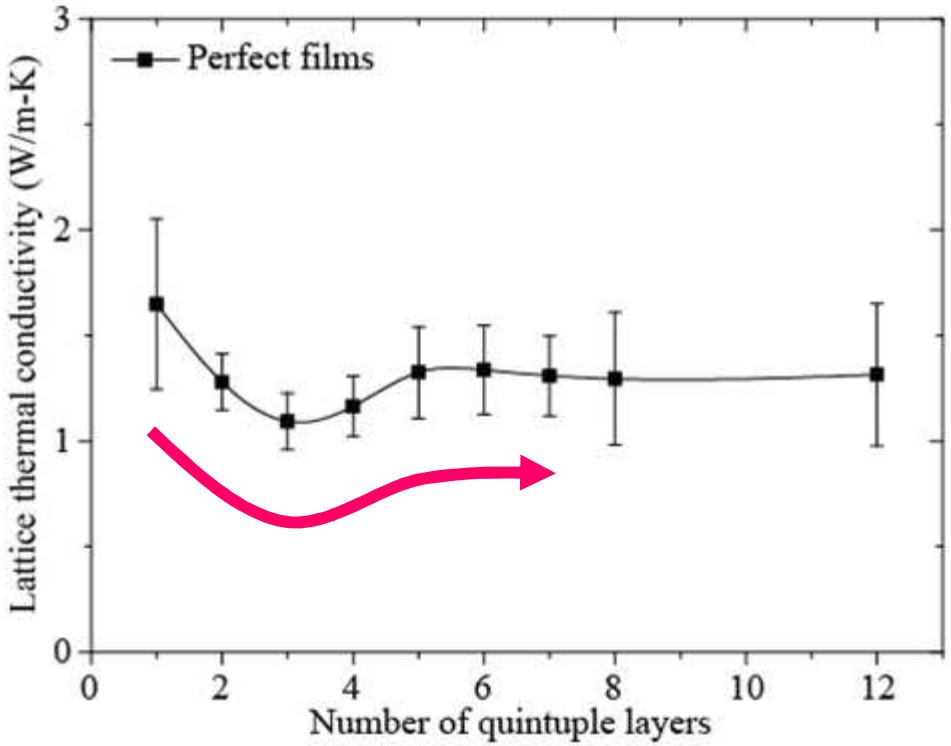
Temperature dependence

Single quintuple film



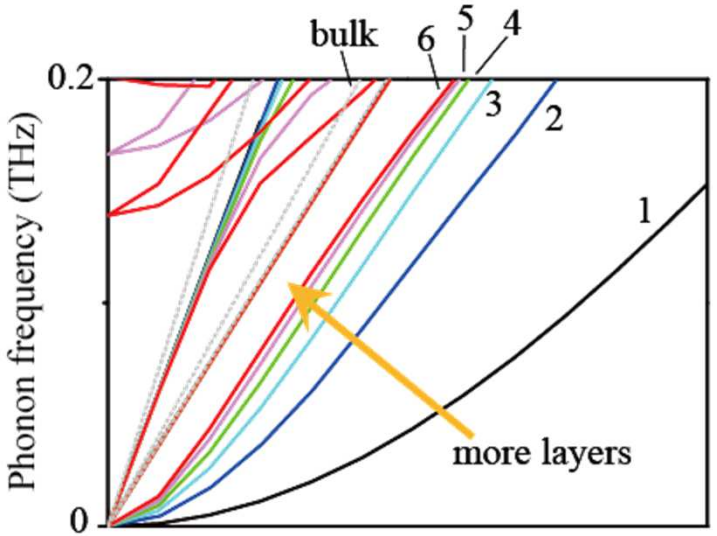
Thickness dependence

Room temperature



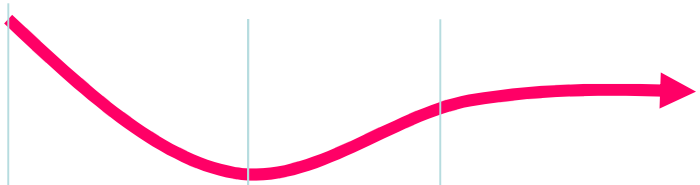
Qiu and Ruan, *Appl. Phys. Lett*. **97**, 183107 (2010)

Thickness Dependence - Phonon Point of View

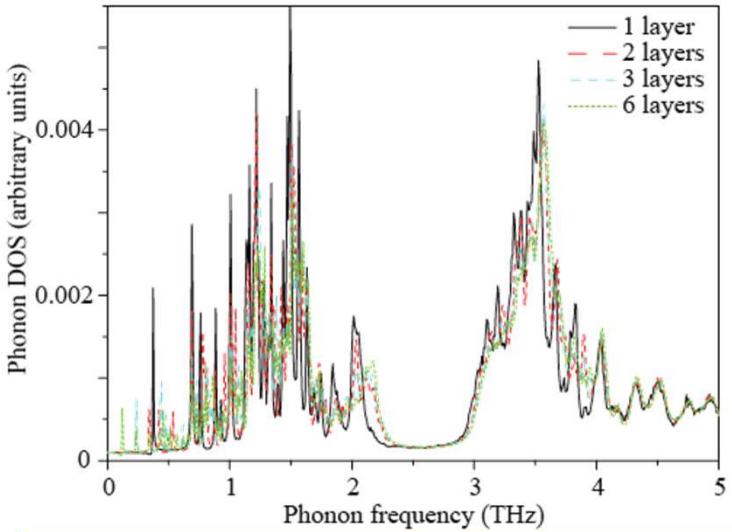


ZA mode hardening

Increased ZA group velocity



Saturate to bulk group velocity



More states for U-scattering

DOS broadening

Saturate to bulk DOS

Qiu and Ruan, *Appl. Phys. Lett*. **97**, 183107 (2010)

Outline

- Overview of multiscale multiphysics predictions
- Thermal conductivity of thermoelectric materials
- *Phonon mean free path distribution*
- Radiative properties in the visible band: photon-electron interaction
- Radiative properties in the far-infrared band: photon-phonon interaction
- Summary and Acknowledgements

Thermal Conductivity and Phonon MFP

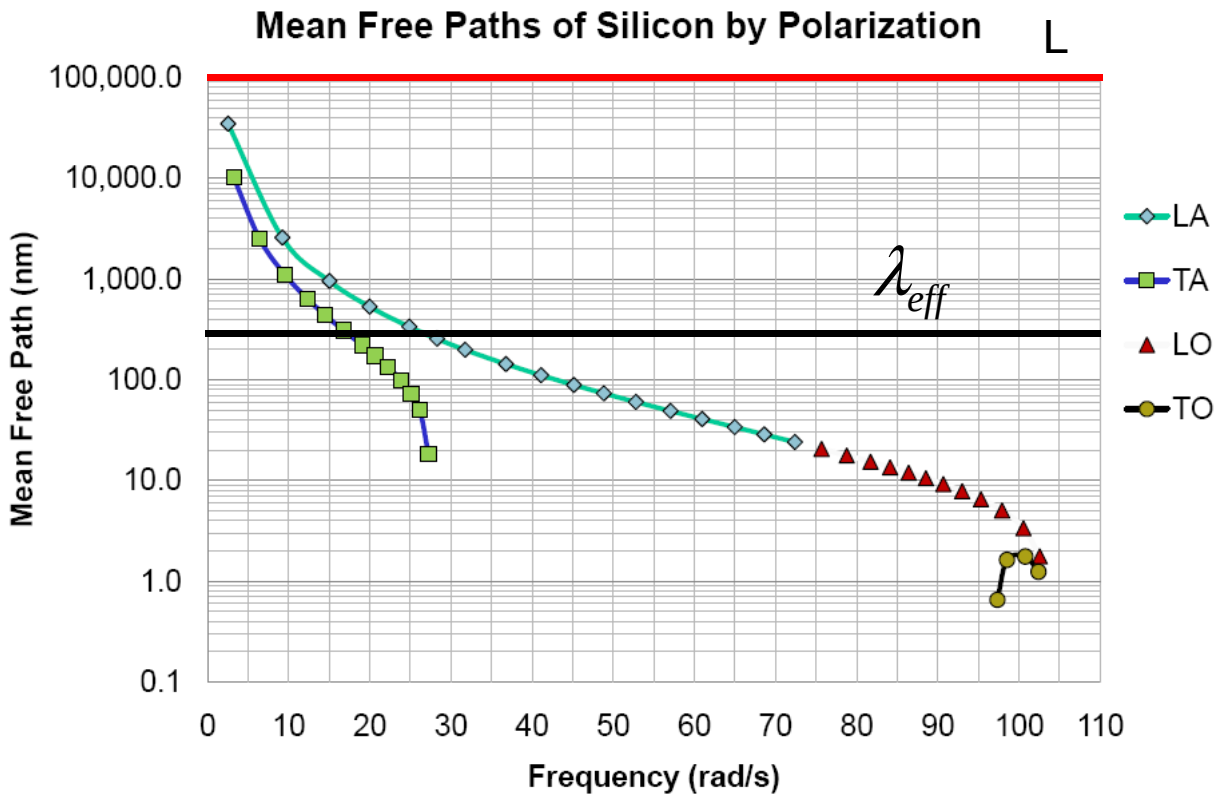
- Gray approach

$$\kappa_x = \frac{1}{3} c v \lambda_{eff}$$

$$= \frac{1}{3} c v^2 \tau_{eff}$$

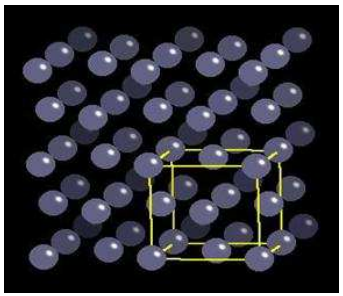
- Spectral approach

$$\kappa_x = \sum_{\nu} \sum_{\mathbf{k}} c v_{g,x}^2 \tau_{\mathbf{k},\nu}$$



(modified from Figure of Jayathi Murthy)

Phonon Normal Mode Analysis



MD simulations

↓

Atomic velocity

↓

Normal mode amplitude

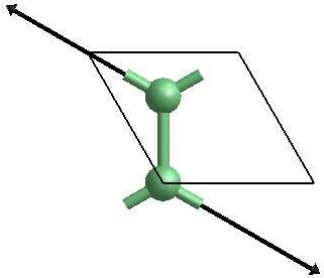
$$\dot{S}_{\mathbf{k},\nu}(t) = \sum_{\alpha,b,l}^{3,n_b,N_c} \sqrt{\frac{m_b}{N_c}} \dot{u}_\alpha^{b,l}(t) e_\alpha^{b*}(\mathbf{k},\nu) \exp(-i\mathbf{k}\cdot\mathbf{r}_0^l)$$

↑

Eigen-displacements

↑

Lattice dynamics calculations



Spectral energy density function

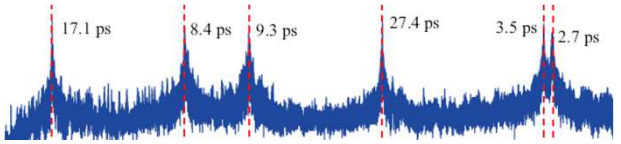
$$\Psi(\mathbf{k},\nu,f) \equiv |F[\dot{S}_{\mathbf{k},\nu}(t)]|^2$$

$$\equiv \frac{C_{\mathbf{k},\nu}}{[4\pi\tau_{\mathbf{k},\nu}(f - f^A_{\mathbf{k},\nu})]^2 + 1}$$

Lorentzian form

↓

Spectral peaks fitting



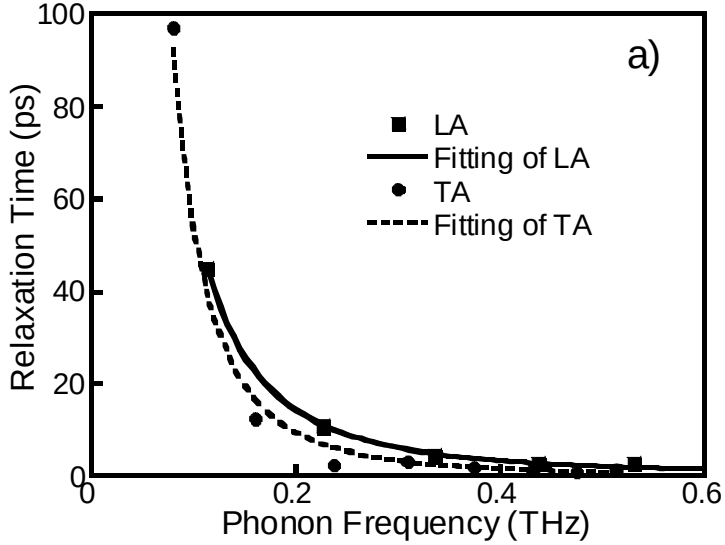
ω τ

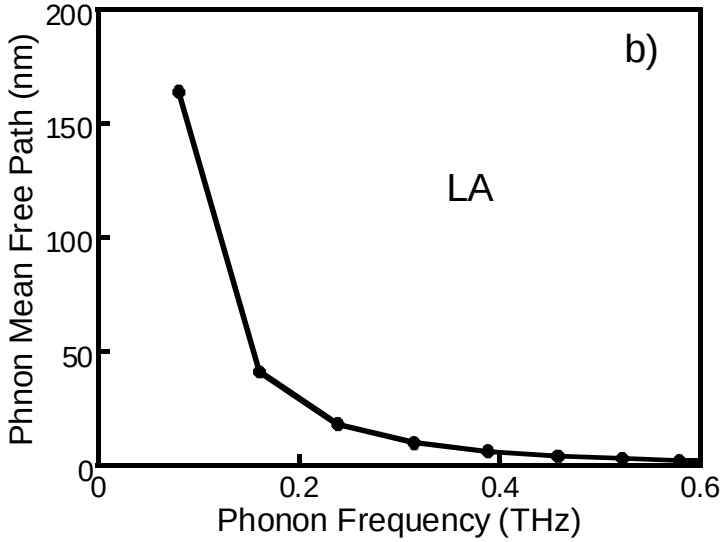
wider peak → shorter τ

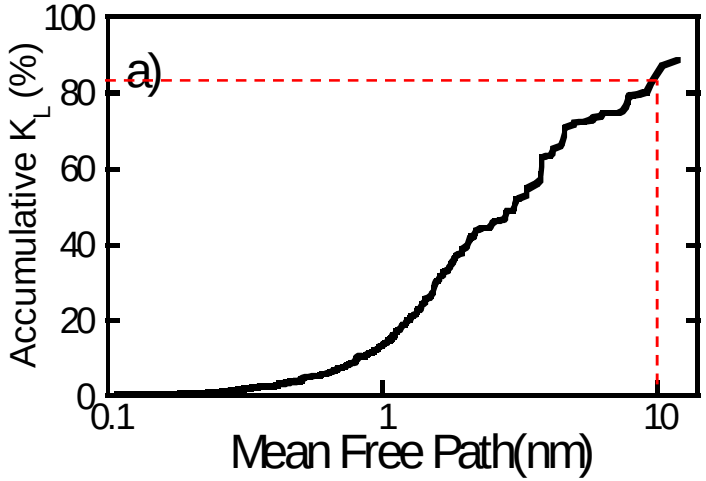
References:

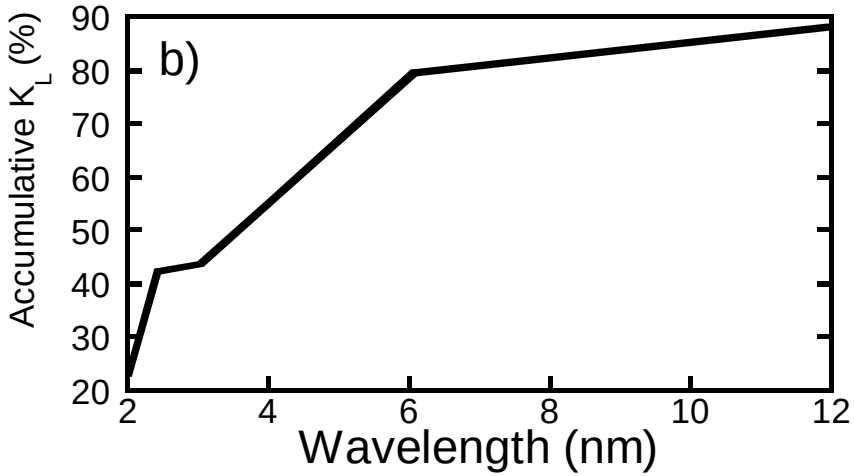
- A. J. C. Ladd, B. Moran, and W. G. Hoover, Phys. Rev. B 34, 5058 (1986).
- A.J.H. McGaughey and M. Kaviany, Phys. Rev. B, 2004.
- A. S. Henry and G. Chen, J. Comput. Theor. Nanosci. 5,1 (2008).
- N. de. Koker, Phys. Rev. Lett. 103, 125902 (2009)
- J. E. Turney, E. S. Landry, A. J. H. McGaughey, and C. H. Amon, Phys. Rev. B 79, 064301 (2009)
- J. A. Thomas, J. E. Turney, R. M. Iutzi, C. H. Amon, and A. J. H. McGaughey, Phys. Rev. B 81, 081411 (2010)
- Qiu, Zhang, Wu, and Ruan, Comp. Mat. Sci., 2012.
- Qiu and Ruan, Appl. Phys. Lett., 2012.

Relaxation Time and Mean Free Path for Bi_2Te_3





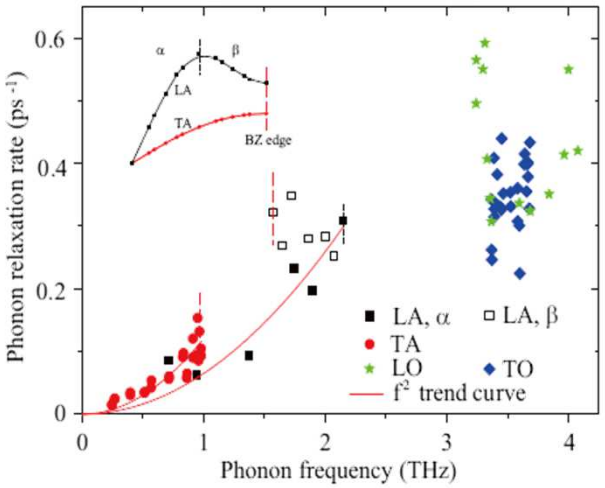




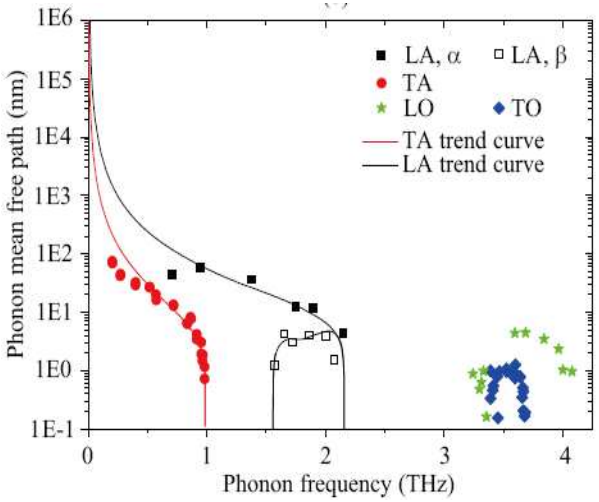
Wang, Qiu, McGaughey, Ruan, and Xu, *J. Heat Transfer* 135, 091102 (2013).

Results for PbTe

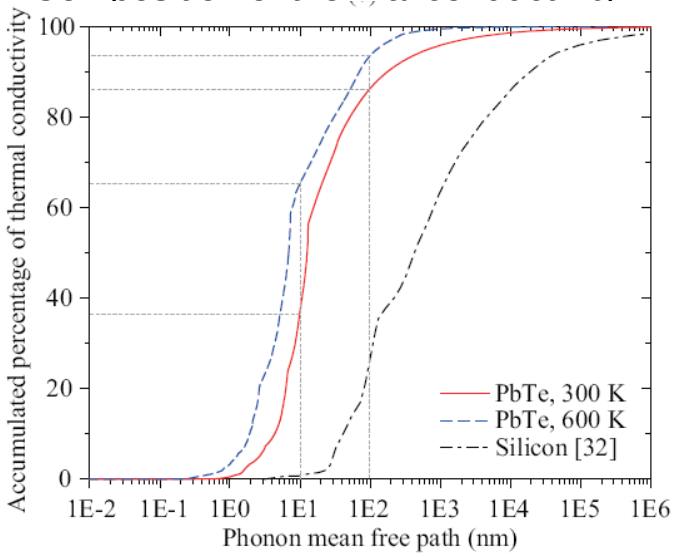
Relaxation rate



MFP



Composition of thermal conductivity



- Sub-10 nm nanostructures are needed for PbTe for size effect.

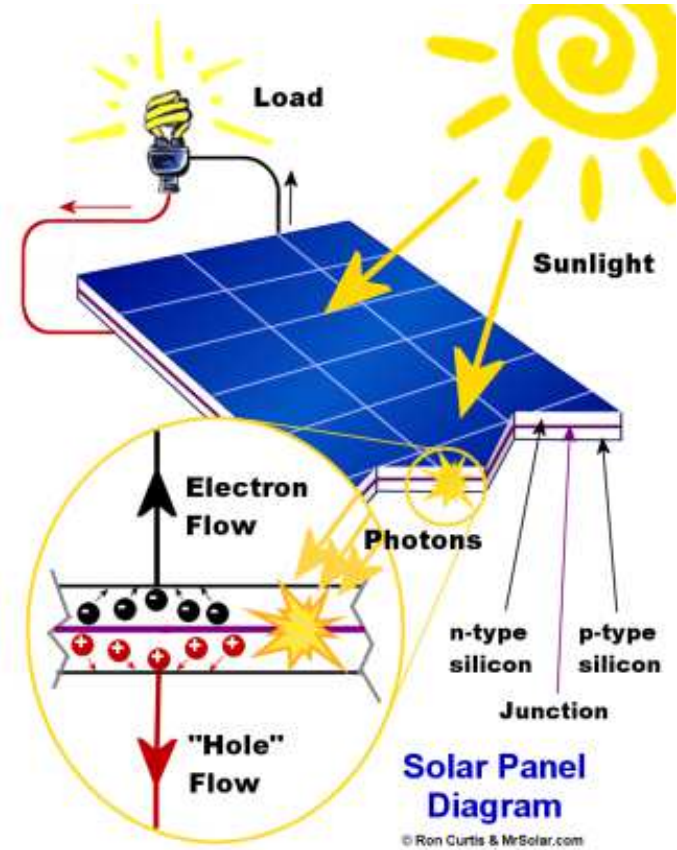
Qiu, Zhang, Wu, and Ruan, Comp. Mat. Sci., 2012.

Outline

- Overview of multiscale multiphysics predictions
- Thermal conductivity of thermoelectric materials
- Phonon mean free path distribution
- *Radiative properties in the visible band: photon-electron interaction*
- Radiative properties in the far-infrared band: photon-phonon interaction
- Summary and Acknowledgements

How Solar Cell Works

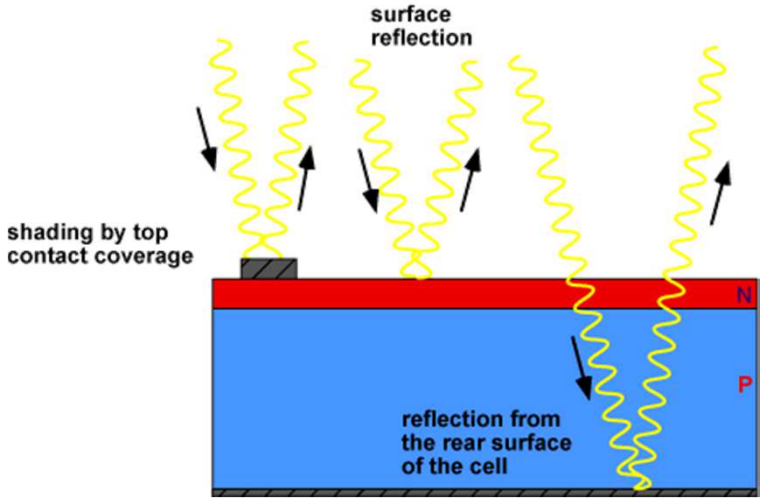
http://deviceace.com/science/266/more-efficient-solar-cells-thanks-to-cnt-films-that-transmit-infrared-light.html

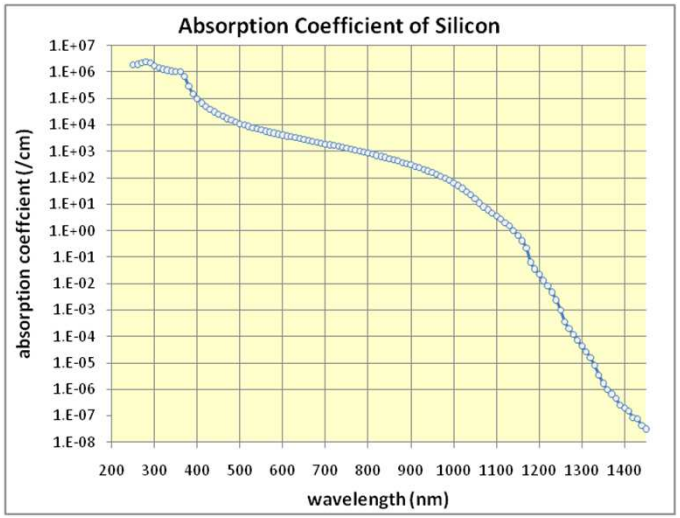


http://mrsolar.com

- Three steps: (1) Absorption of solar photons and creation of electron-hole pairs; (2) Decay of hot carriers; (3) Diffusion of carriers to electrodes.

One Loss Mechanism: Reflection



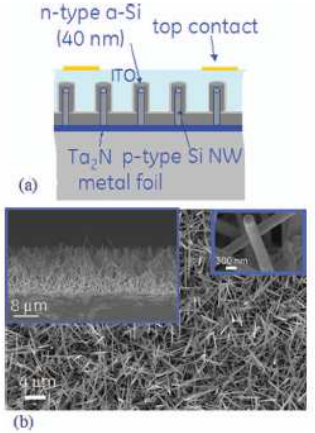


http://pvcdrom.pveducation.org/APPEND/OPTICAL.HTM

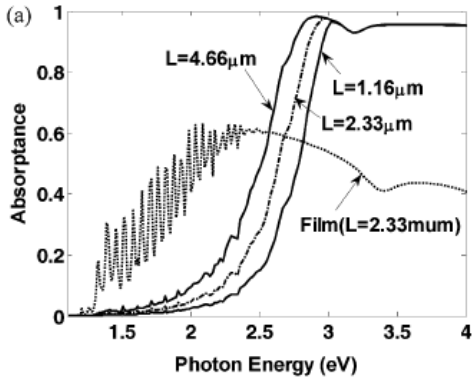
- Light is attenuated according to the Beer–Lambert law: $I = I_0 \exp(-\sigma L)$
  - σ: absorption coefficient [1/cm]
  - L: thickness of the film
- Silicon has low absorption coefficient. For example, σ is on the order of 1 cm^{-1} for λ = 1,116 nm (band gap), indicating that 7 mm thick Si film is needed to absorb 50% of the light at that wavelength.
- A major loss mechanism for both solar photovoltaics and solar thermal.

Nanoscale Control of Radiative Properties

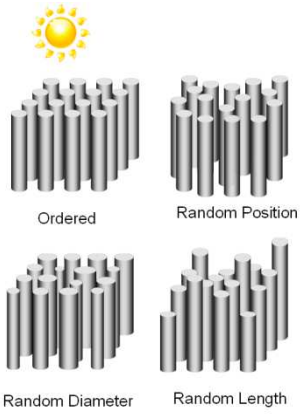
- Solar-photovoltaics: silicon nanowire arrays



Tsakalakos et al, APL, 2007.

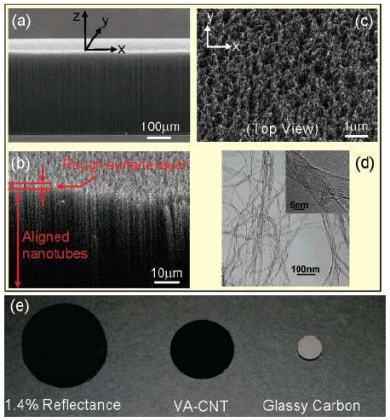


Hu et al, Nano Lett., 2007

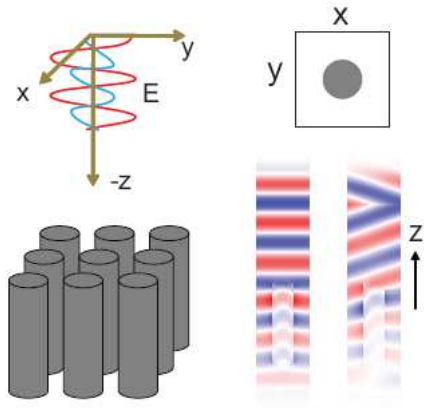


Bao and Ruan,
Opt. Lett, 2010

- Thermal radiation (such as solar thermal): CNT arrays



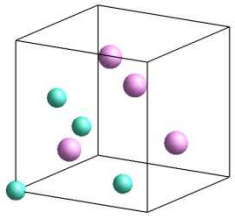
Yang et al, Nano Lett, 2008



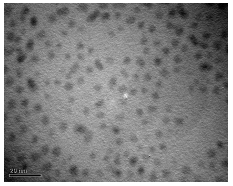
Bao, Ruan, and Fisher, Optics Express, 2010

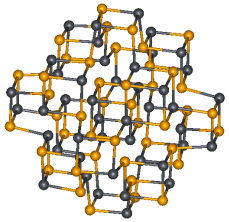
Atomic-scale Control of Radiative Properties

- Atomic-scale control: atomic structure ↔ radiative properties
  - Bulk materials
  - Nanomaterials in the quantum confinement regime: bulk dielectric function no longer applicable (quantum size effect)

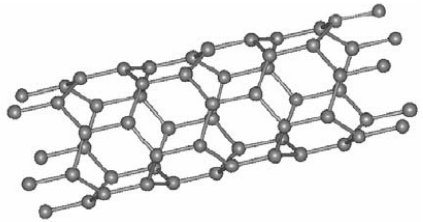


GaAs



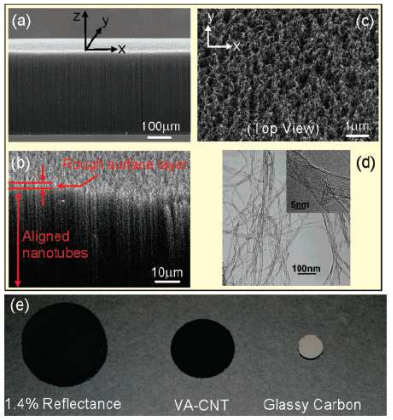


Quantum dot



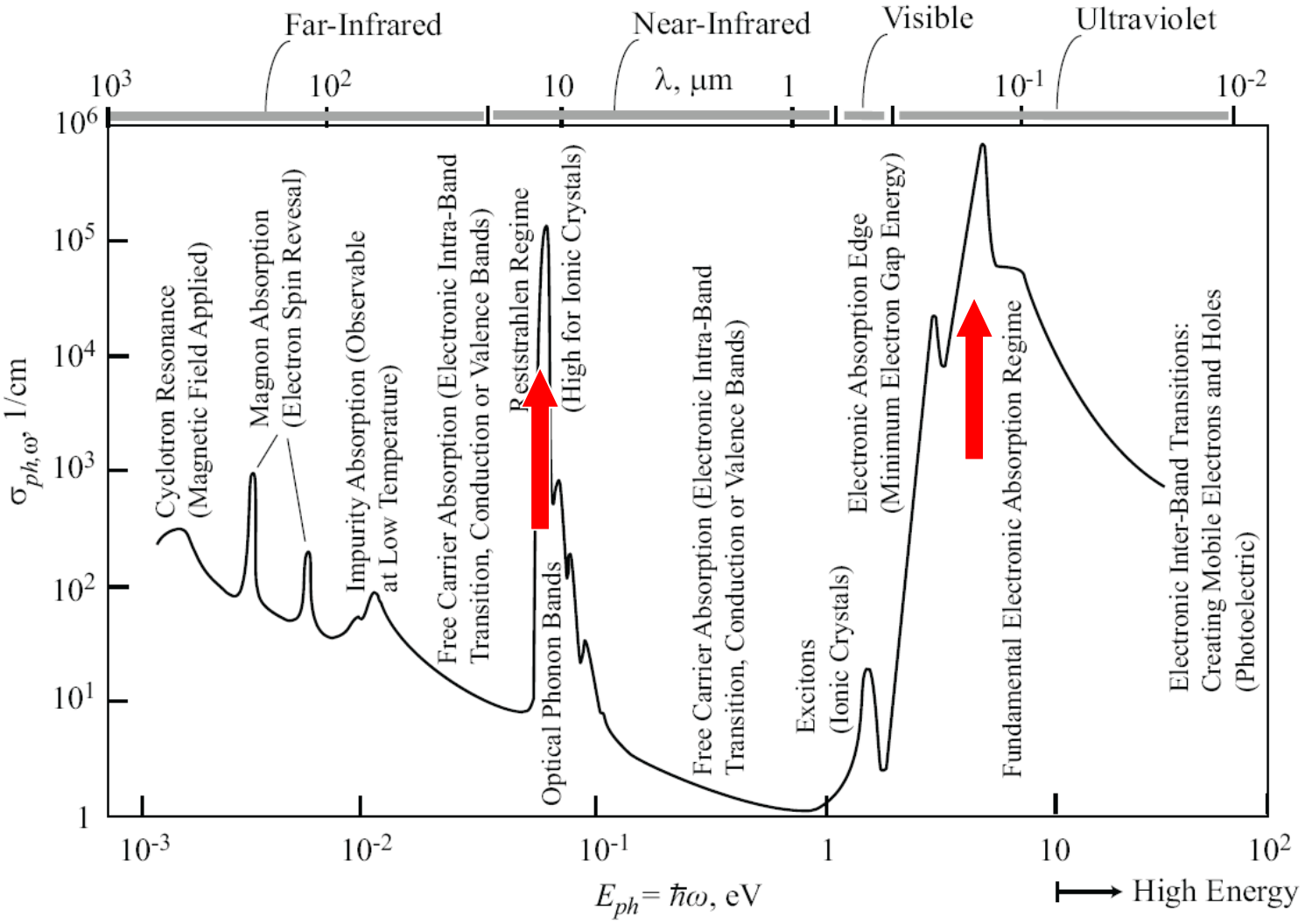
CNT

- Multiscale control:
  - Example: CNT array. The radiative properties are determined not only by the atomic structure of each individual CNT, but also by the long-range order or disorder of the array.



Yang et al, Nano Lett, 2008

Absorption Spectrum of Semiconductor



Massoud Kaviany, Heat Transfer Physics, 2008.

Ground State Ab Initio Methodology

- Density functional theory to solve the Kohn-Sham equation

$$\left[-\frac{\hbar^2\nabla^2}{2m}+V_{KS}\right]\varphi_{nk}(\mathrm{r})=\varepsilon_{nk}\varphi_{nk}(\mathrm{r})$$

- Fermi's golden rule – imaginary part of the dielectric function

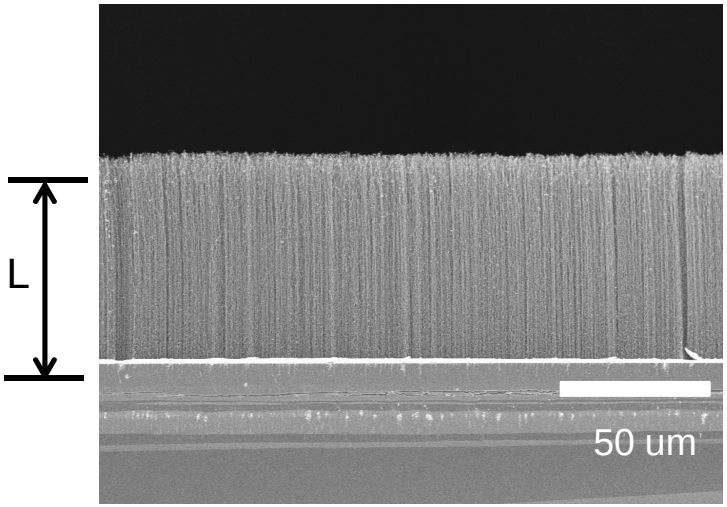
$$\epsilon''_{\alpha,\alpha}(\omega)=\frac{4\pi^2}{\Omega\omega^2}\sum_{i\in VB,j\in CB}\sum_{\mathbf{k}}w_{\mathbf{k}}\left|p^{\alpha}_{ij}\right|^2\delta(\epsilon_{\mathbf{k}j}-\epsilon_{\mathbf{k}i}-\omega)$$

$p^a_{ij}=\langle\mathbf{k}j|p_a|\mathbf{k}i\rangle$ is the transition matrix element.

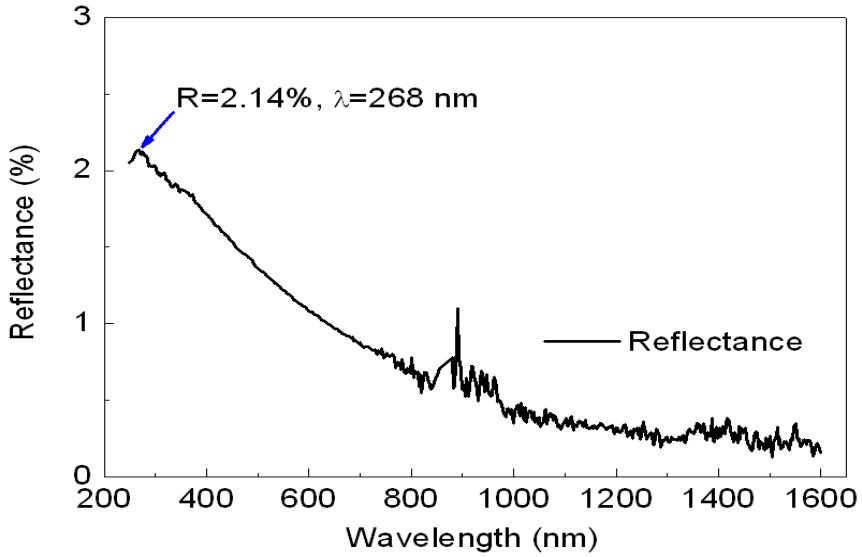
- Kramer-Kronig transformation – real part of the dielectric function

$$\epsilon'(\omega)=1+\frac{4}{\pi}\mathbf{P}\int_0^{\infty}d\omega'\frac{\omega'\epsilon''(\omega')}{\omega'^2-\omega^2}$$

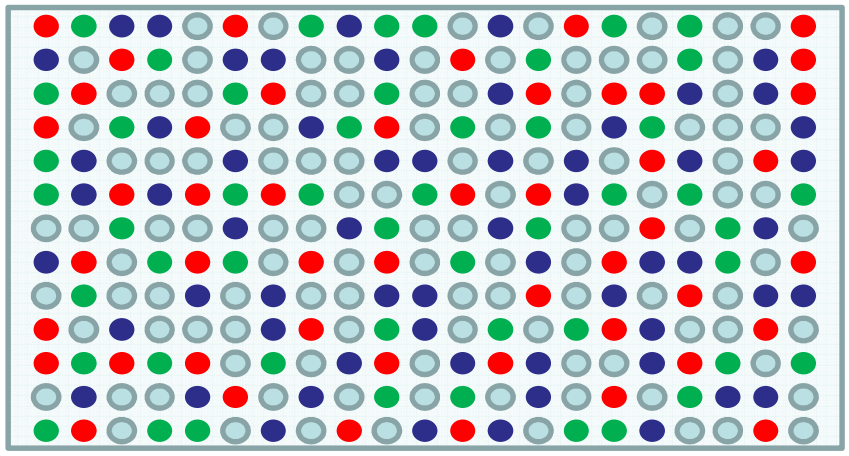
Ultra-Low Reflectance of CNT Arrays



Samples provided by Tim Fisher

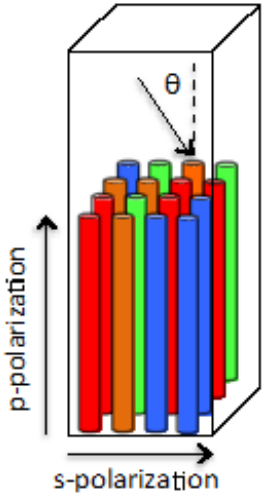


- Monte-Carlo simulation of inhomogeneous array



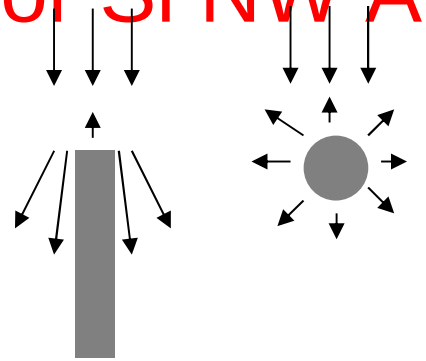
(6,6) (metallic)
(8,0)
(10,0)
(11,0)

Avg. diameter
= 0.75 nm



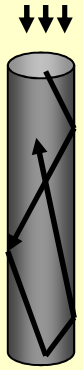
Light Trapping Mechanisms for Si NW Arrays

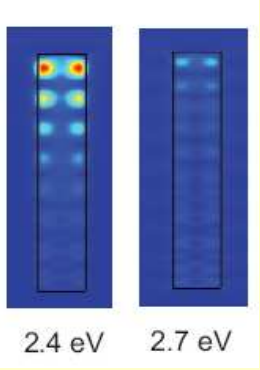
Anisotropic Scattering

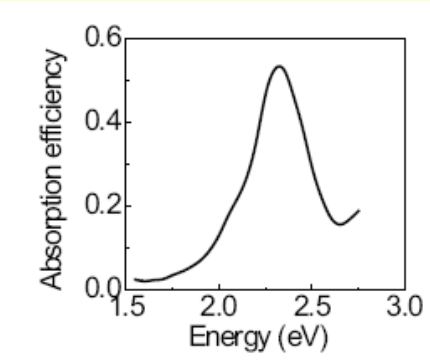


Small reflection

Internal resonance

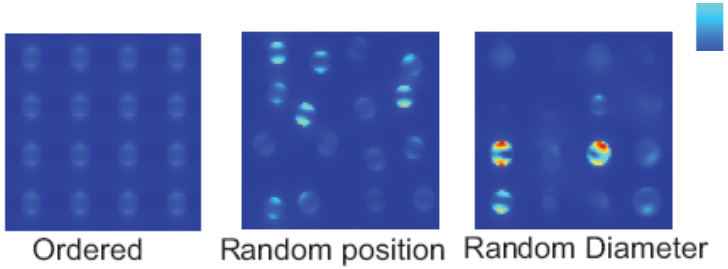






Absorption peaks,
absorption enhancement

Multiple inter-wire scattering

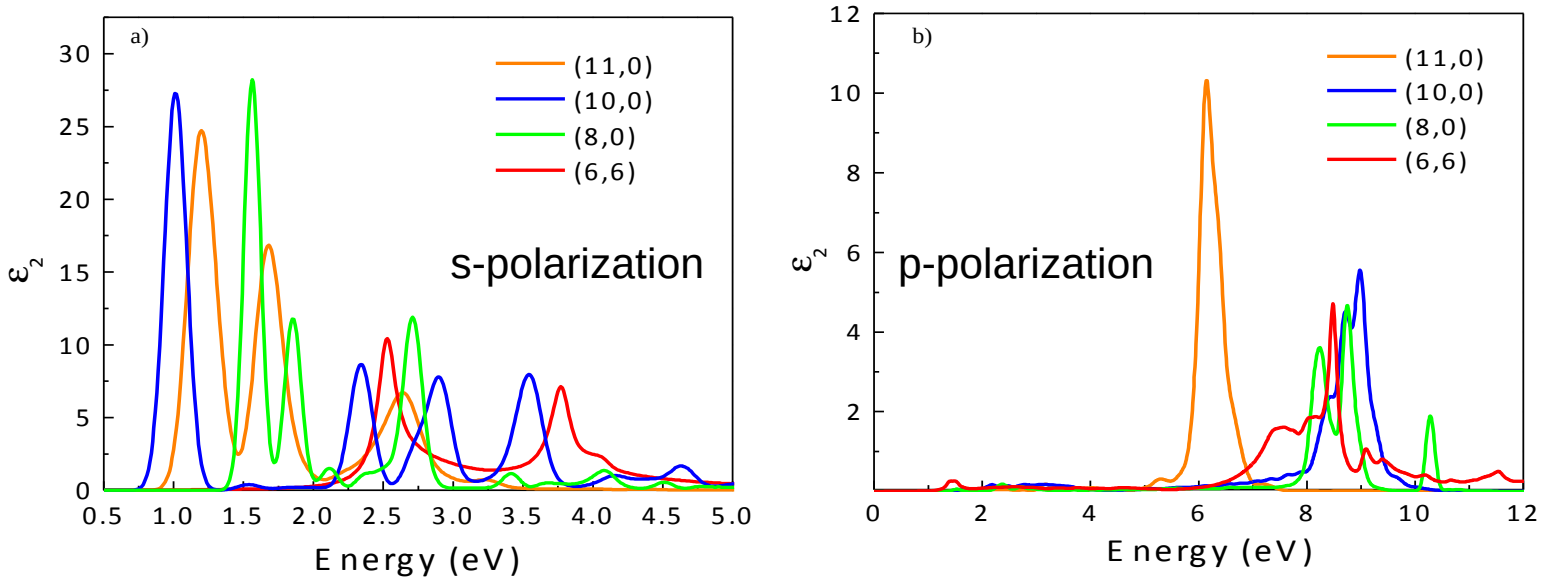


Absorption enhancement

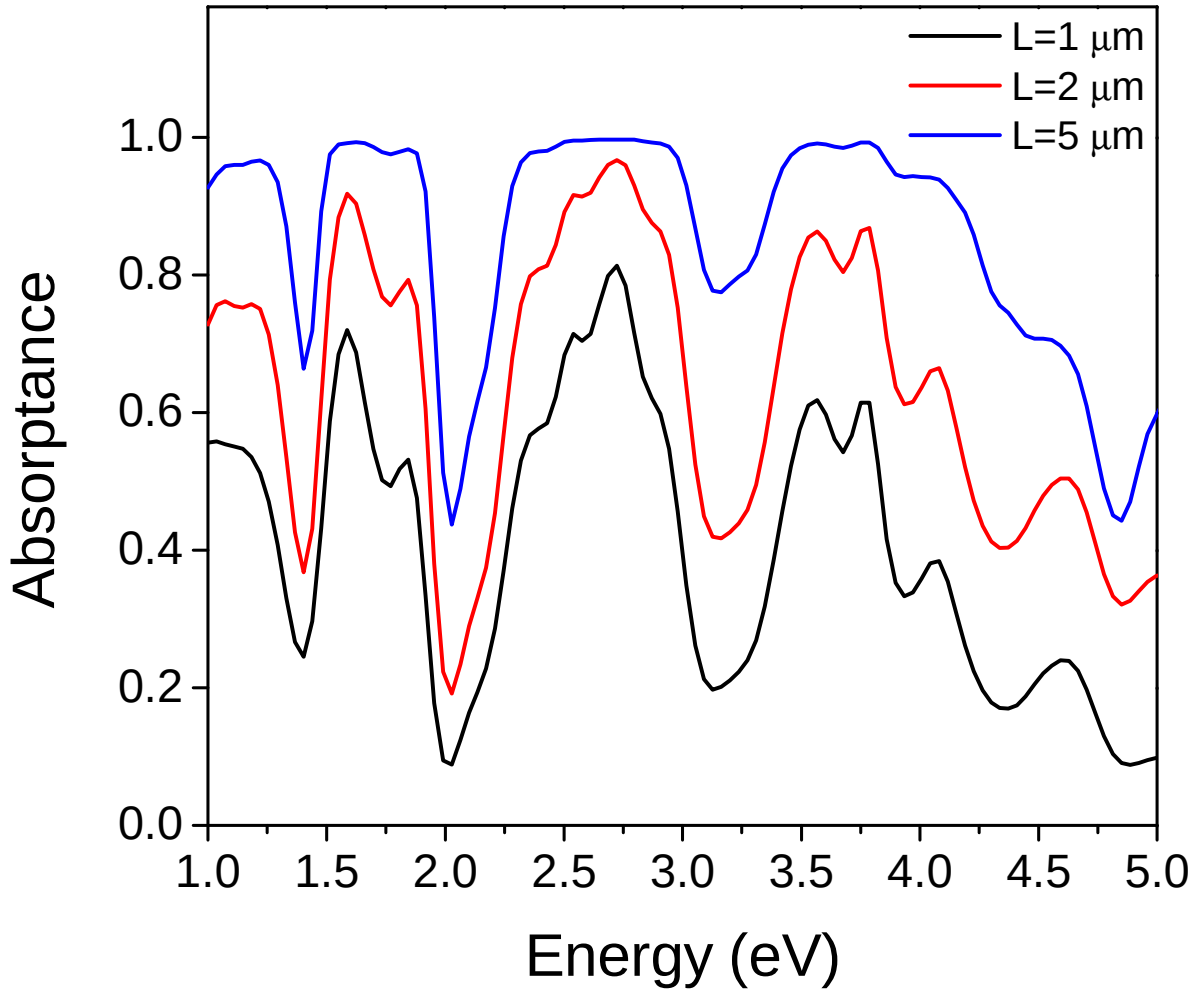
Bao and Ruan, *Opt. Lett*. **35**, 3378-3380, 2010.

Dielectric Function for Four Chiralities

S-polarization	GW/BSE (E_{11}, E_{22}) (eV)	Exp. (E_{11}, E_{22}) (eV) [1]
(11,0)	1.18, 2.67	1.21, 2.69
(10,0)	1.01, 2.34	1.11, 2.36
(8,0)	1.56, 1.85	1.62, 1.88
(6,6) - metallic	2.53, 3.77	--



Electromagnetic Simulations of Absorptance



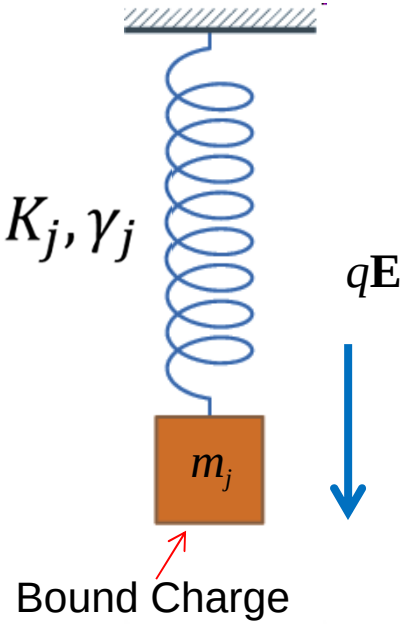
Aaron Sisto

A. Sisto, X.L. Ruan, and T.S. Fisher, *J. Heat Transfer,* in press, 2013.

Outline

- Overview of multiscale multiphysics predictions
- Thermal conductivity of thermoelectric materials
- Phonon mean free path distribution
- Radiative properties in the visible band: photon-electron interaction
- *Radiative properties in the far-infrared band: photon-phonon interaction*
- Summary and Acknowledgements

Oscillator Model

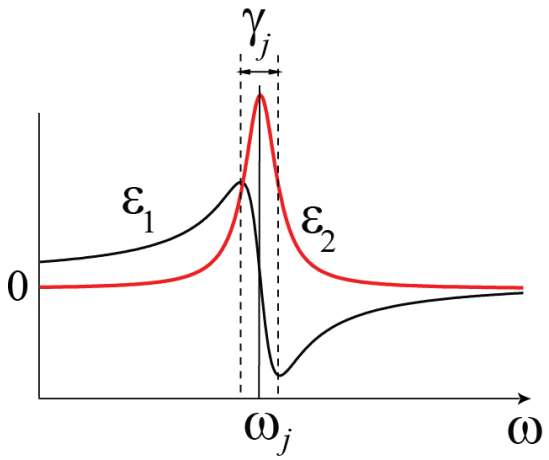


Oscillator Strength

$$\varepsilon(\omega) = \varepsilon_\infty + \sum_j \frac{S_j \omega_j^2}{\omega_j^2 - \omega^2 - i\gamma_j \omega}$$

Resonant Frequency

Damping Factor



$$m_j \ddot{\mathbf{x}} - m_j \gamma_j \dot{\mathbf{x}} + K_j \mathbf{x} = q\mathbf{E}$$

- To determine the dielectric function, the **resonant frequency**, **oscillator strength** and **damping factor** need to be obtained.
- These parameters are usually obtained by fitting to experiments.

Oscillator Model and Phonon Properties

Born and Huang's formalism,

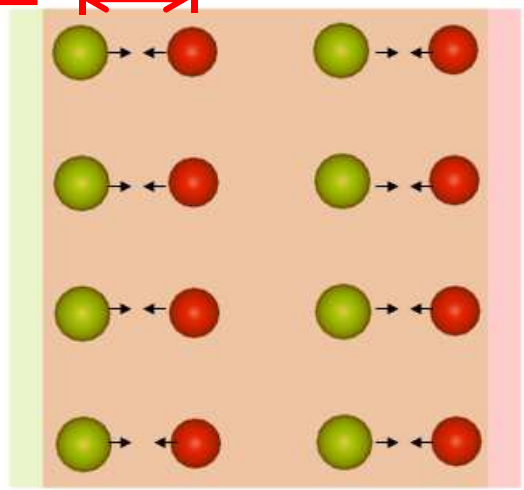
$$\mathbf{P} = b_{21}\mathbf{w} + b_{22}\mathbf{E}$$

$$\ddot{\mathbf{w}} = b_{11}\mathbf{w} - \gamma\dot{\mathbf{w}} + b_{12}\mathbf{E}$$

$$\varepsilon(\omega) = \frac{\varepsilon_0\mathbf{E} + \mathbf{P}}{\varepsilon_0\mathbf{E}}$$

$$\frac{\varepsilon(\omega)}{\varepsilon(\infty)} = 1 + \frac{\omega_0^2(\varepsilon(0) - \varepsilon(\infty))}{\omega_0^2 - \omega^2 - i\omega\gamma}$$

$$\mathbf{w} = \left(\frac{\bar{M}}{\Omega}\right)^{\frac{1}{2}} (\mu_+ - \mu_-)$$



P

Macroscopic Polarization

When **E**=0, and define $\omega_1 = (\omega_0^2 - \gamma^2/4)^{1/2}$

$$\mathbf{w} = \mathbf{A}e^{-\gamma t/2}\cos(\omega_1 t)$$

TO phonon in relaxation time approximation

$$q_{TO} = \mathbf{B}e^{-\Gamma t}\cos(\omega_{TO} t)$$

Therefore, $\omega_{TO} \approx \omega_0$

$$\Gamma = \gamma/2$$

Lyddano-Sachs-Teller (LST) relationship

$$\frac{\omega_{LO}}{\omega_{TO}} = \left[\frac{\varepsilon(0)}{\varepsilon(\infty)}\right]^{\frac{1}{2}}$$

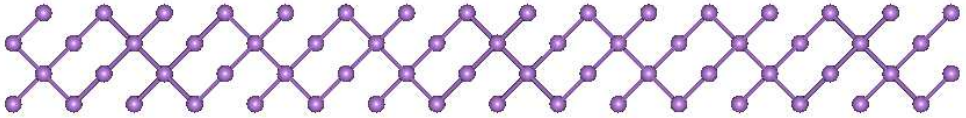
$$\frac{\varepsilon(\omega)}{\varepsilon(\infty)} = 1 + \frac{\omega_{LO}^2 - \omega_{TO}^2}{\omega_{TO}^2 - \omega^2 - i(2\Gamma)\omega}$$

TO LO Frequencies

Phonon Linewidth

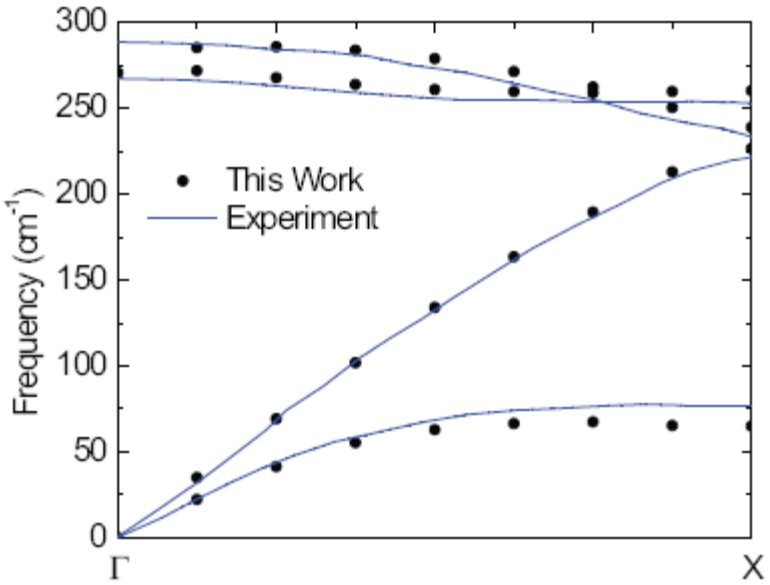
Phonon Dispersion

Using an 8×1×1 conventional cell of GaAs



Hua Bao

***Ab initio* molecular dynamics** implemented in VASP, 80 ps NVE trajectory at 300 K

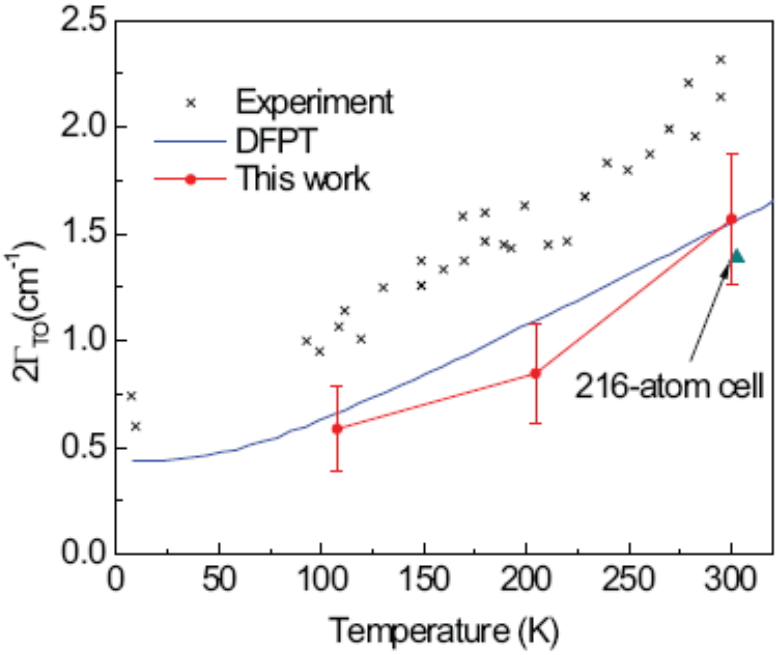


Parameters	This work	Neutron	Infrared
ω_{TO}	271	267.5	268.2
ω_{LO}	286	285.2	291.5

- Our calculation agrees well with experimental results.

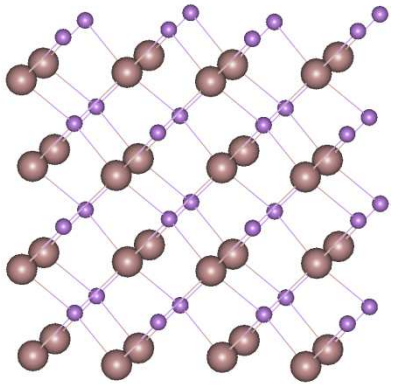
Bao, Qiu, Zhang, and Ruan, *J. Quant. Spec. Rad. Trans.*, 2012.

Damping Factor



Bao, Qiu, Zhang, and Ruan, *J. Quant. Spec. Rad. Trans.,* 2012.

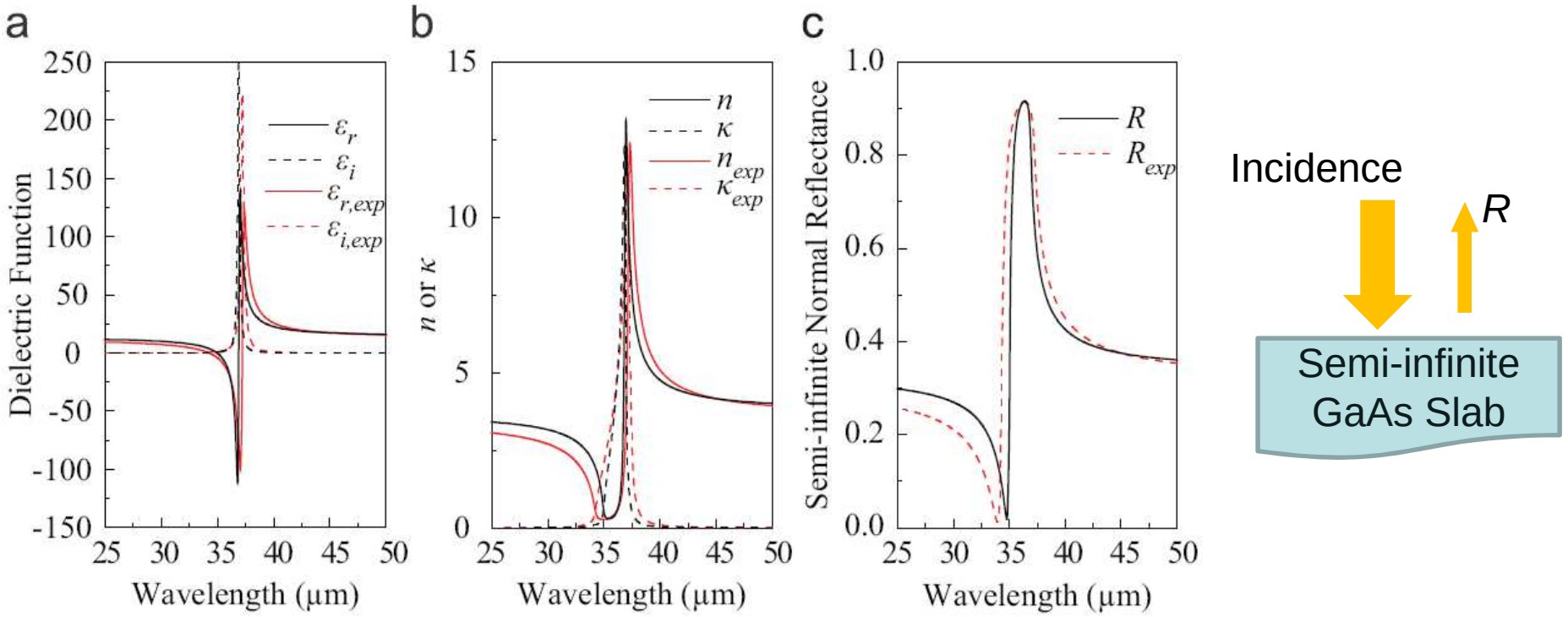
(DFPT from Debernardi A. Phys Rev B 1998;57:12847)



A 64 atom 2×2×2 supercell is used for the calculation.

- The first direct comparison between the predicted phonon line-width (reciprocal of relaxation time) from phonon normal mode analysis and experimental data.
- Discrepancy between our work and experimental results is probably due to the size effect of the MD simulation.
- Also, impurities in the experimental materials can give larger linewidth.

Dielectric Function and Normal Reflectance



- Implications: engineering infrared properties through the manipulation of optical phonon lifetimes.

Summary

- Multiscale multiphysics approaches can be used to link macroscopic thermal properties with atomic level structure. Such approaches are very helpful for a deep understanding of thermal properties.

- Thermal transport property manipulation that is not possible at the bulk scale can be achieved at the nanoscale, by taking advantage of boundary, interface, and quantum confinement effects.

- Nanoscale control of thermal transport can potentially enhance the efficiencies of energy transfer and conversion.

Outlook

- More sophisticated interatomic potentials for use in classical MD simulations.

- Direct first-principles methods that can bypass the need of using empirical interatomic potentials
  - DFT-BTE-MC
  - Ab initio MD
  - …

Acknowledgements

- Students:

Bo Qiu

Aaron Sisto

Hua Bao

- Collaborators:

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