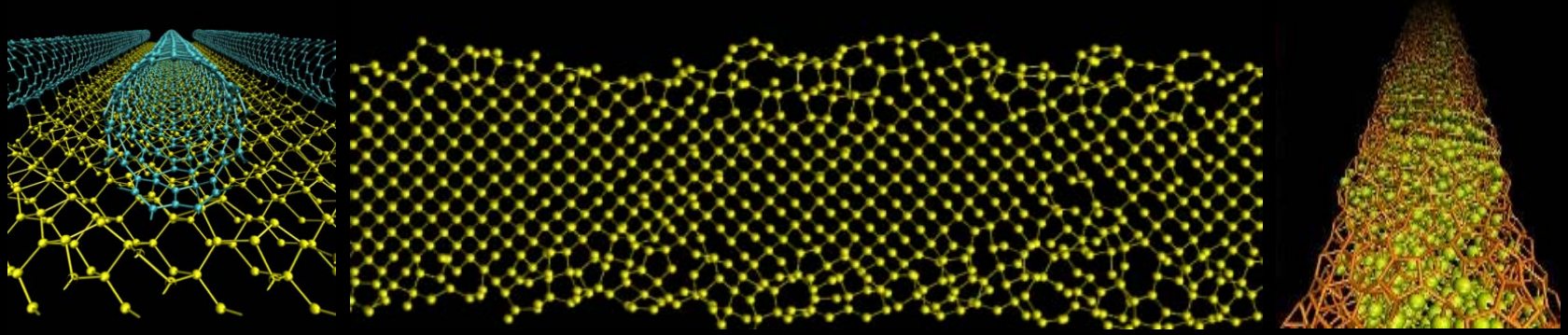


Thermal transport in simple systems

Giulia Galli

University of California, Davis

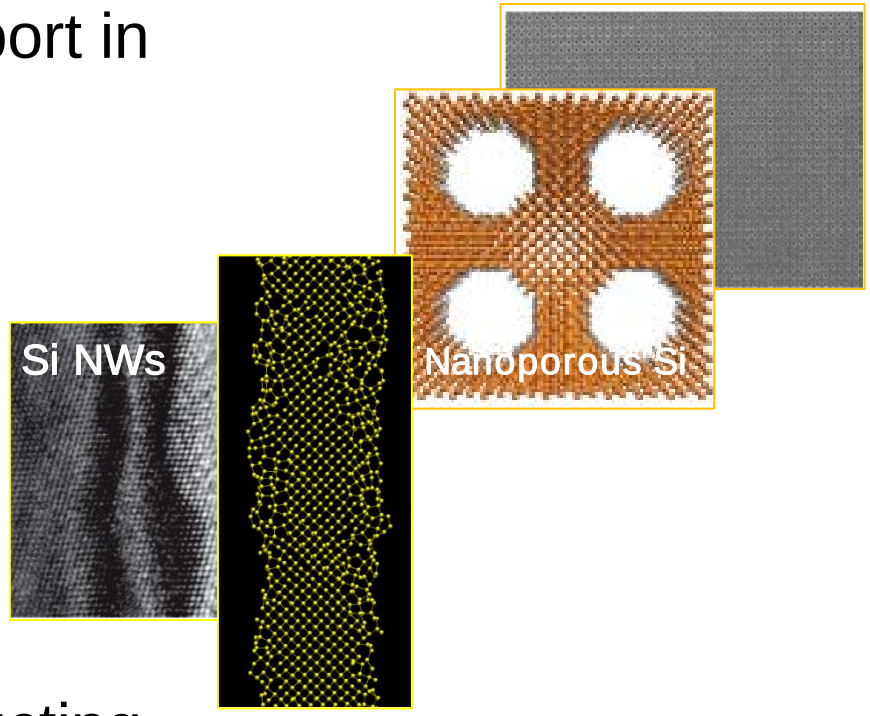
gagalli@ucdavis.edu

http://angstrom.ucdavis.edu/

KITP, Santa Barbara, October 21st, 2009

Outline

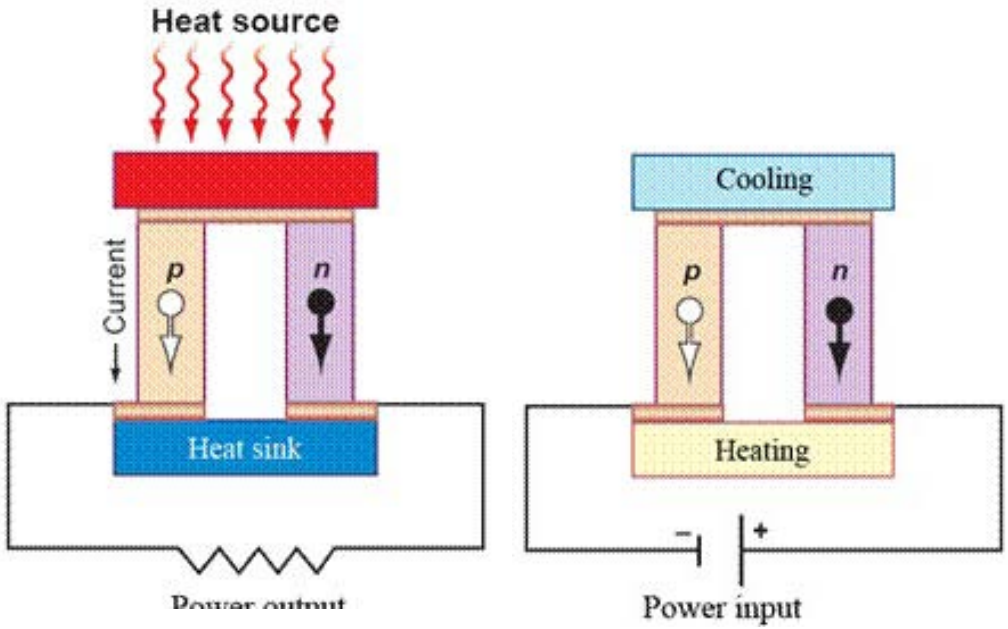
- Introduction: thermal transport in nanostructured materials
- Theoretical approaches and difficulties in using *ab-initio* techniques
- Thermoelectric properties of SWCNT and semi-conducting nanowires



Thermoelectric properties at the nanoscale

Can nanostructuring help to improve efficiency in harvesting thermal energy?

- **Power generation**
(Seebeck effect): maintain ΔT and convert heat into current
- **Cooling**
(Peltier effect): Supply electrical current and pump (transfer) heat



Seebeck, T.J., 1822, Magnetische Polarisation der Metalle und Erzedurch Temperatur-Differenz. Abhand Deut. Akad. Wiss. Berlin, 265-373.

Peltier, J.C., 1834, Nouvelles experiences sur la caloriecete des courans electriques. Ann. Chem., LVI, 371-387

Thermoelectric properties at the nanoscale

Can nanostructuring help to improve figure of merit, ZT?

$$S = \frac{\pi k^2 T}{3e}\left[\frac{\partial \ln \sigma(E)}{\partial E}\right]_{E_F}$$

Seebeck coefficient = $\Delta V/\Delta T$

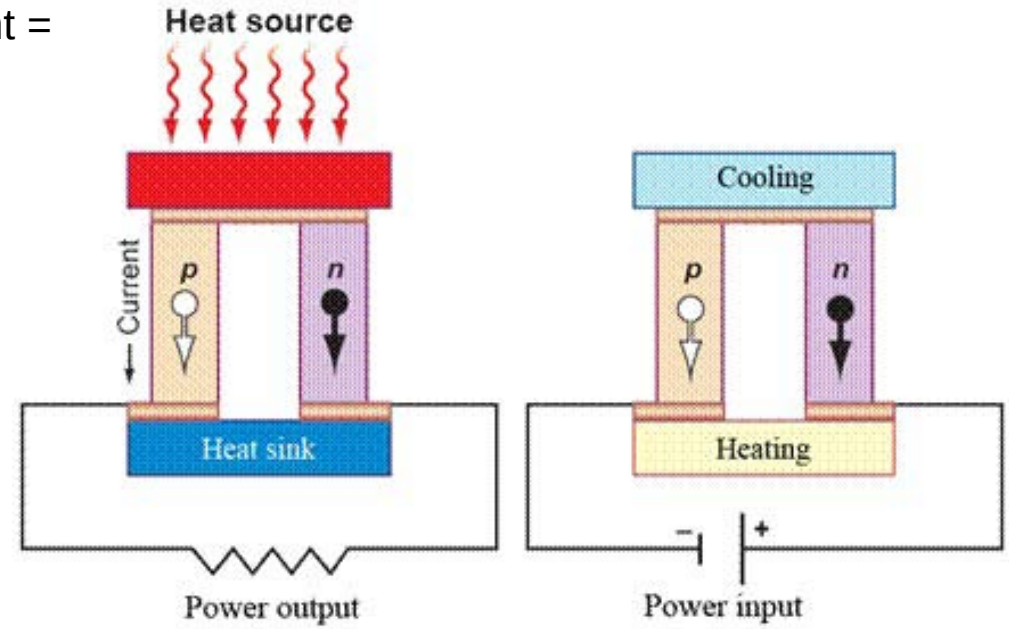
Electrical conductivity

Figure of merit

$$ZT = \frac{\sigma S^2}{\kappa_e + \kappa_l} T$$

Electronic thermal conductivity

Ionic thermal conductivity



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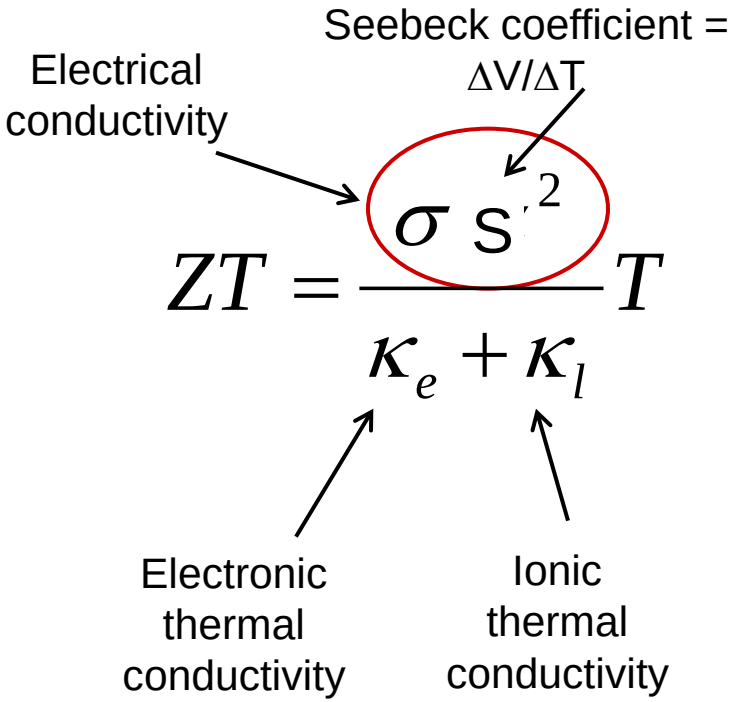
Thermoelectric properties at the nanoscale

Can nanostructuring help to improve figure of merit, ZT?



$$\eta = \frac{\Delta T}{T_{Hot}} \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+\frac{T_{Cold}}{T_{Hot}}}$$

Efficiency = Ratio between work (output) and heat (input)

Max efficiency for ZT going to infinity

Thermoelectric properties at the nanoscale

Can nanostructuring help to improve figure of merit, ZT?

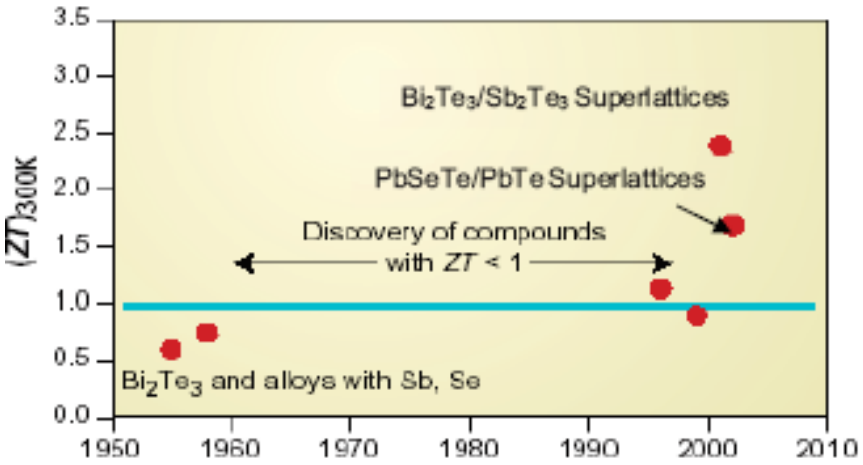
Seebeck coefficient = $\Delta V/\Delta T$

Electrical conductivity

$$ZT = \frac{\sigma S^2}{\kappa_e + \kappa_l} T$$

Electronic thermal conductivity

Ionic thermal conductivity



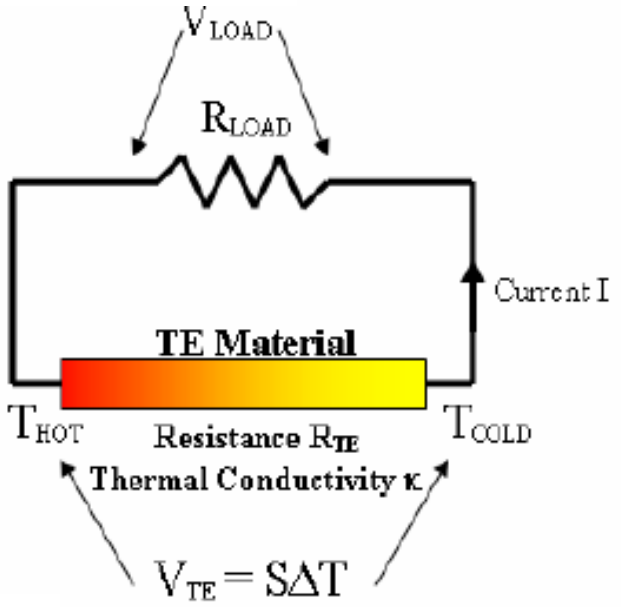
A. Majumdar, Science, 2004.

"An inconvenient truth about thermoelectrics", C.B.Vining, Nature Materials 8, 83 (2009)

Carnot Efficiency

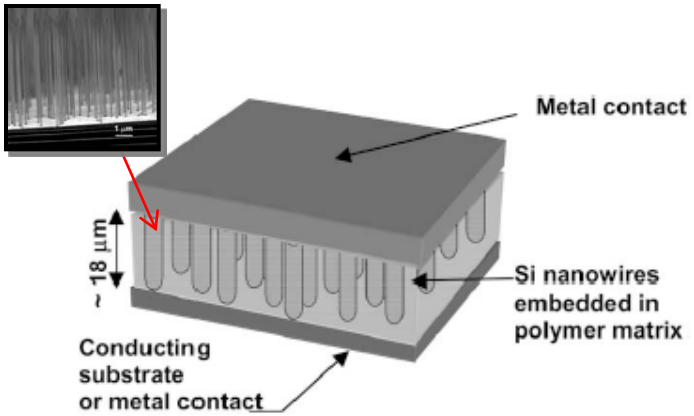
The efficiency η is given by: $\eta = \frac{W}{Q}$ where W is the work output of the TE generator and Q is the heat input into the hot reservoir.

$$S = \frac{\pi k^2 T}{3e}\left[\frac{\partial \ln \sigma(E)}{\partial E}\right]_{E_F}$$

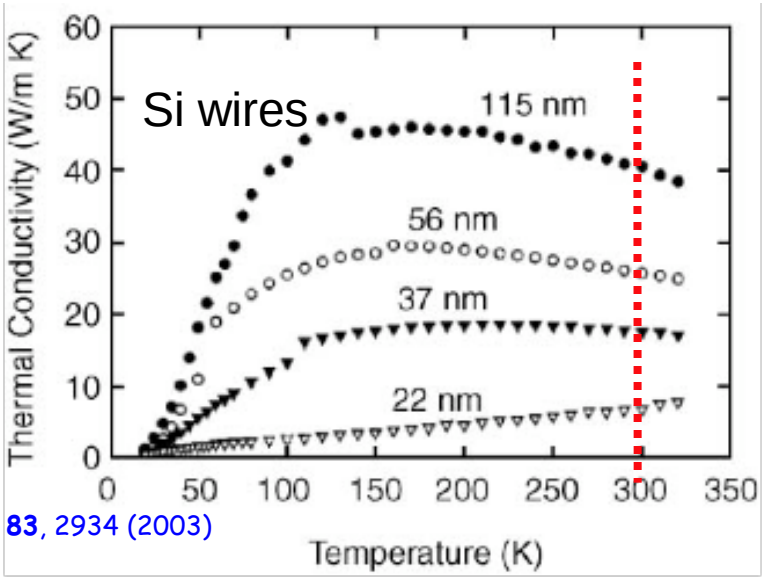


$$Z\overline{T} \to \infty, \quad \eta_{max} = \frac{\Delta T}{T_{HOT}} \text{ (the Carnot efficiency)}$$

Design materials with high figure of merit by using semiconductor nanostructures

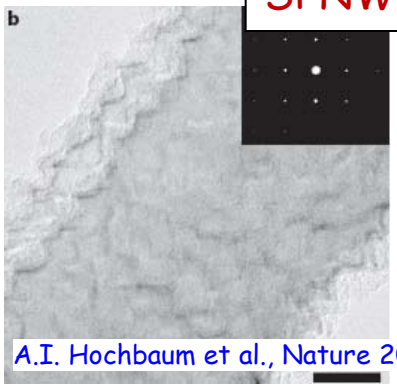


Abramson *et al.* J. Micro-Electrochemical Sys **13** 505 (2004)

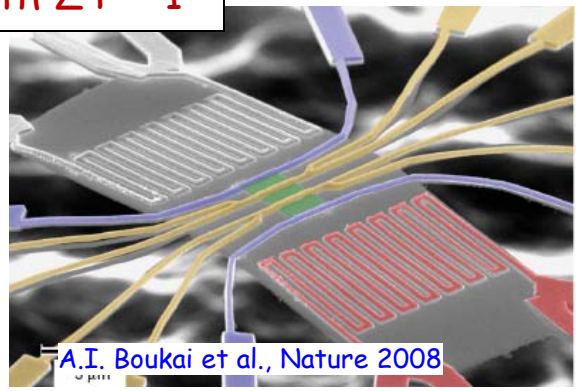


D. Li *et al.*, APL **83**, 2934 (2003)

Si NW with ZT ~ 1



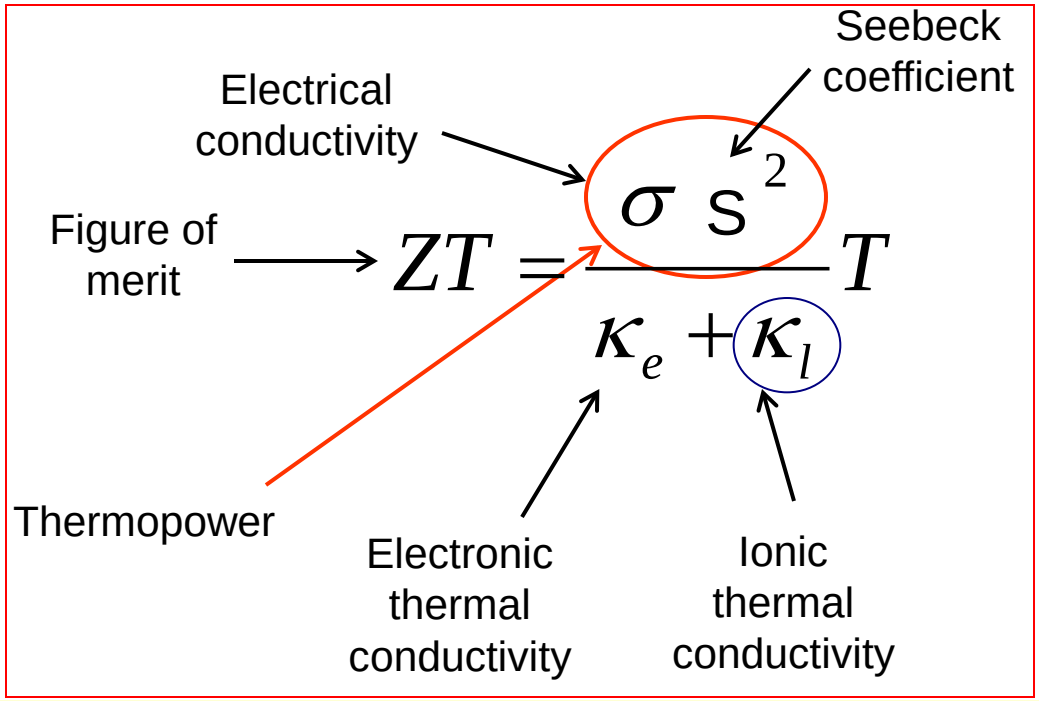
A.I. Hochbaum et al., Nature 2008



A.I. Boukai et al., Nature 2008

Observed, improved efficiency (ZT) not well understood—different interpretations provided by different groups

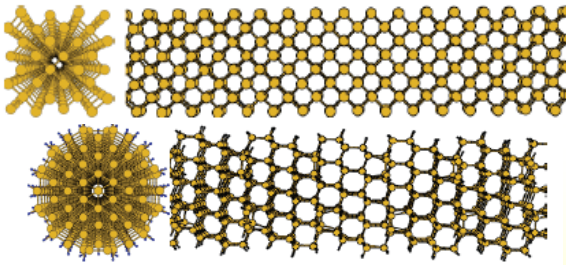
Design materials with high figure of merit by using semiconductor nanostructures



- **S σ** and $\mathbf{k_e}$ from *ab-initio* calculations within Density Functional Theory (DFT).

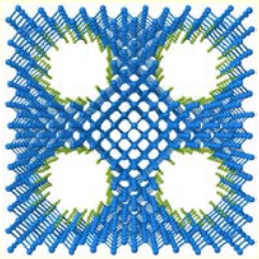
- $\mathbf{k_l}$: **How do we compute thermal conductivity?**

Si Nanowires



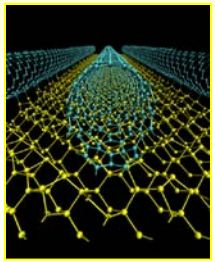
T.Vo, A.Williamson, V.Lordi and G.G. Nanolett. 08; D.Donadio, G.G. PRL 09 and Nanolett. (submitted)

Nanoporous Si



J.Lee, J.Grossman, J.Reed and G.G. APL 07
J.Lee, G.G. and J.Grossman Nanolett.08

Carbon Nanotubes



D.Donadio and G.G. PRL 07

Several techniques are available to compute k_l

- Green-Kubo formulation and calculation of heat current from equilibrium Molecular Dynamics (MD)

- Non-equilibrium MD to compute heat flux (or temperature gradient) from applied temperature gradient (or heat flux)

- Boltzman Transport Equation (BTE) to compute deviation of phonon occupation distribution from equilibrium distribution

- Green's functions approach: Landauer-Buttiker transmission function formalism

Each approach is challenging in the case of *ab-initio* Hamiltonians

Calculations of thermal conductivity using MD and fluctuation-dissipation theorem

- At equilibrium, the net heat flow of an isolated system fluctuates around zero. Using a Green-Kubo formulation, one relates κ to how long it takes for fluctuations of the heat flux to dissipate.

$$\kappa = \frac{1}{V k_b T^2} \int_0^\infty \langle J(t) J(0) \rangle \, dt$$

- Use MD to compute J(t):
  - Define J:

$$J = \frac{dR(t)}{dt} = \frac{d}{dt} \sum_i^N r_i e_i$$

  - Choose numerical method to obtain κ from J (direct integration, Einstein relation)

$$R(t) - R(0) = \int_0^t J(t') \, dt'$$

$$\kappa = \frac{1}{V k_b T^2} \lim_{t \to \infty} \frac{1}{2t} \langle (R(t) - R(0))^2 \rangle$$

Main issues:
- **Boltzman distribution, instead of Bose-Einstein is used for phonon occupation ($T > \theta_D$)**
- **Definition of energy density to obtain J not straightforward**

Calculations of thermal conductivity using MD and fluctuation-dissipation theorem

- **Theoretical issues for low dimensional (1D-2D) systems:**
  - For momentum conserving 1D systems, κ diverges as a function of L; ongoing debate on exponent of divergence; for momentum conserving 2D systems, $\kappa \sim \log(L)$ (O.Narayan and S.Ramaswamy, PRL 2002; R.Livi and S.Lepri, Nature 2003)

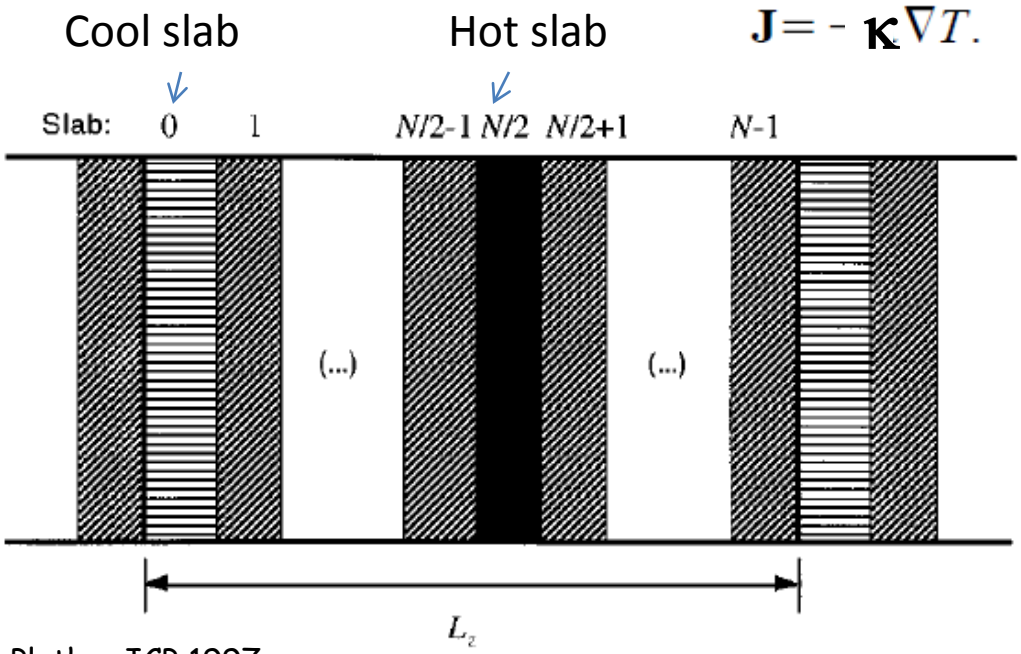
- **Computational issues in obtaining converged values of κ from MD simulations:**
  - Convergence as a function of simulation time, for fixed size (including time over which statistics is collected and number of independent runs)
  - Convergence as a function of system size (e.g. nanowire length)

No calculations using *ab-initio* Hamiltonians

Calculations of thermal conductivity using non-equilibrium MD

•Either apply T gradient to the system and compute current or:

•Impose a heat flux onto the system and compute T gradient



F.Mueller-Plathe, *JCP* 1997

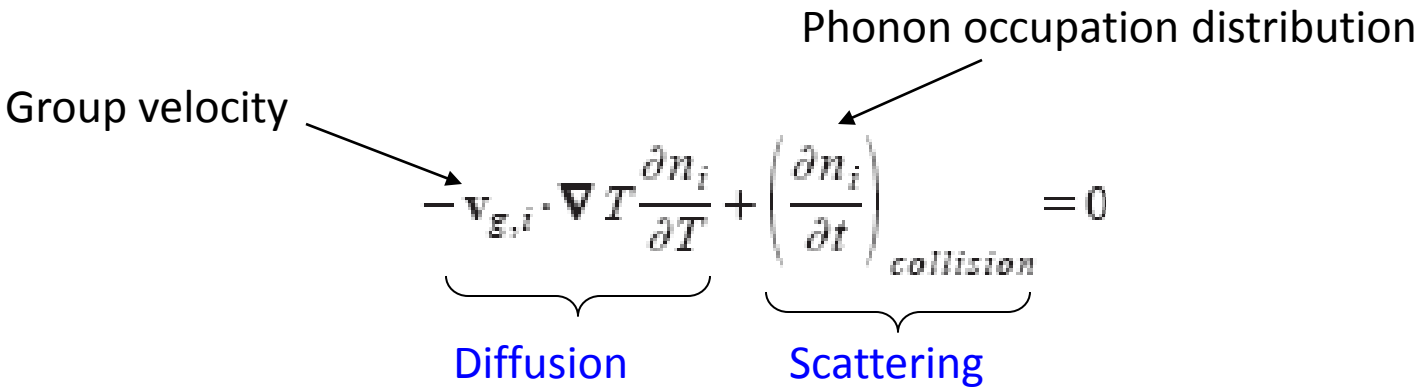
Kinetic energy artificially transferred from cool to hot slab ➔ it is then transferred back by thermal conduction

$$\kappa = -\frac{\sum_{\text{transfers}} \frac{m}{2}(v_h^2 - v_c^2)}{2tL_xL_y\langle \partial T/\partial z \rangle}.$$

PBC preserved; no need to define energy density➔ in principle, technique straightforward to implement with *ab-initio* Hamiltonians

No calculations using *ab-initio* Hamiltonians

Calculations of thermal conductivity using Boltzman transport equation (BTE)



- **Single mode relaxation time approximation (SMRT) for linearized BTE:** single relaxation time is assigned to each phonon mode (accounting for net effect of different scattering mechanisms):

$$\left(\frac{\partial n_i}{\partial t}\right)_{collision}=\frac{n_{i,o}-n_i}{\tau_{i,r}}$$

- Use **Fourier law**, i.e. assume heat flux J is proportional to temperature gradient

Note: equation written for phonon distribution, that is for distribution of propagating vibrations ($\mathbf{v}_g \neq 0$)

Calculations of thermal conductivity using Boltzman transport equation (BTE)

BTE in the SMRT approximation :

$$k = \sum_i \sum_q k_i(\mathbf{q})$$

$$k_i(\mathbf{q}) = C_i(\mathbf{q}) {v_i}^2(\mathbf{q}) {\tau_i}^{ph}(\mathbf{q})$$

Group velocity — Lifetime

$$C_i^{QM}(\mathbf{q}) = \frac{1}{V} k_b x^2 \frac{e^x}{(e^x - 1)^2}$$

$$x = \hbar\omega_i(\mathbf{q})/k_b T$$

Phonon frequency

In principle, κ may be obtained *ab-initio*, using Density Functional Perturbation Theory (DFPT) and n-phonon scattering processes (n=3,4…) may be included (imply calculation of 3rd, 4th, etc. order anharmonic interactions).

In practice, *ab-initio* phonon lifetimes have been computed so far only for a limited number of small systems, including 3-phonon processes only.

Phonon lifetimes at all orders from MD trajectories

- Compute and diagonalize dynamical matrix → eigenmodes e_i
- Compute the energy E_i of each eigenmode by projecting on e_i displacement vectors (u) in a NVE trajectory:

$$S_i(q) = N^{-1/2} \sum_j^N \sqrt{M} e^{-iqr_{j,0}} e_i^*(q) \cdot u_j \qquad E_i = \frac{\omega_i^2 S_i^* S_i}{2}$$

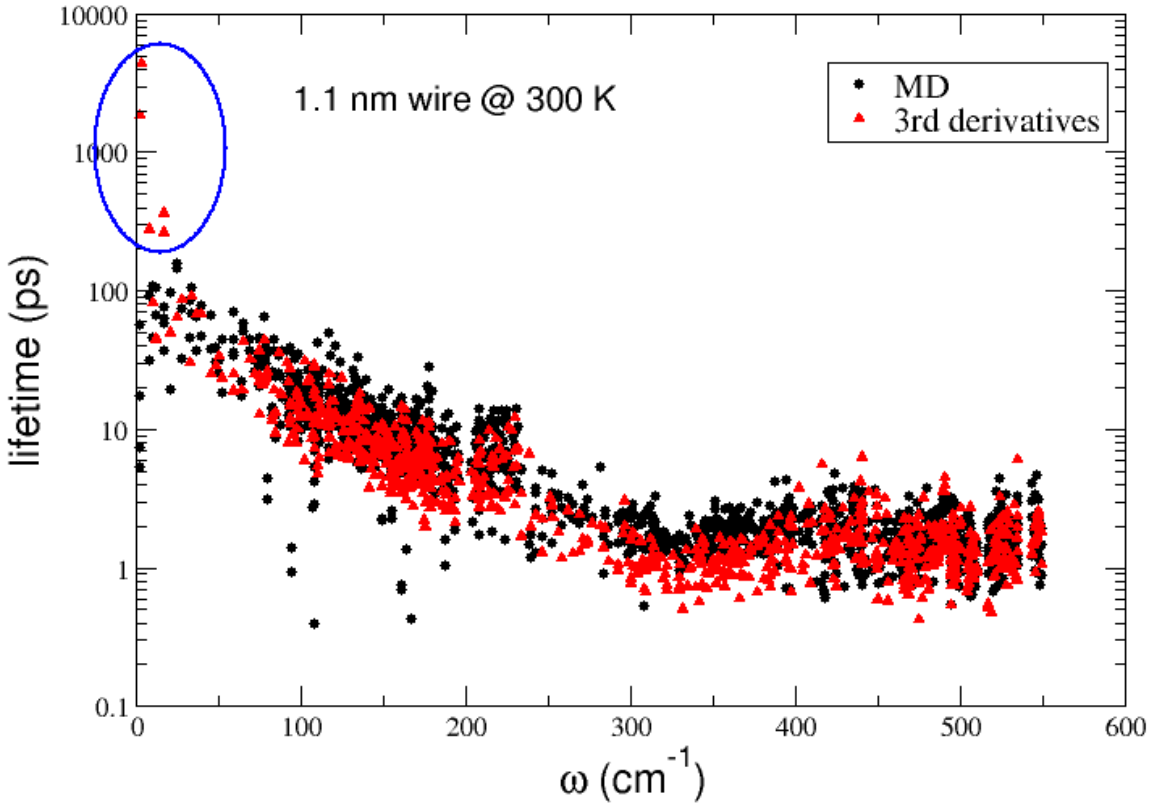
- The integral of the normalized eigenmode energy autocorrelation function gives the relaxation time:

$$\tau_i = \int_0^\infty dt \left\langle E_i(0) E_i(t) \right\rangle$$

W.Hoover PRB 1984 (applied to Argon crystal)

No calculations of lifetimes at all orders using *ab-initio* Hamiltonians

Calculations of lifetime may be tricky



Self-consistent solution of the Boltzman transport equation (BTE)

If one considers three-phonon scattering processes only, the BTE can be written without resorting to the SMRT approximation. Solution must be obtained self-consistently→ often referred to as "the" self-consistent solution of the BTE.

$$F_{\lambda\alpha} = F^0_{\lambda\alpha} + \Delta F_{\lambda\alpha}$$

$$n^1_\lambda = n^0_\lambda (n^0_\lambda + 1)\beta \vec{F}_\lambda \cdot \nabla T$$

$$F^0_{\lambda\alpha} = \frac{\hbar\omega_\lambda n^0_\lambda (n^0_\lambda + 1) v_{\lambda\alpha}}{T Q_\lambda}$$

$$\Delta F_{\lambda\alpha} = \frac{1}{Q_\lambda}\left\{ \sum_{\lambda'\lambda''} \left[W^+_{\lambda\lambda'\lambda''}(F_{\lambda''\alpha} - F_{\lambda'\alpha}) + \frac{1}{2} W^-_{\lambda\lambda'\lambda''}(F_{\lambda''\alpha} + F_{\lambda'\alpha}) \right] \right\}$$

$$Q_\lambda = \sum_{\lambda'\lambda''} \left(W^+_{\lambda\lambda'\lambda''} + \frac{1}{2} W^-_{\lambda\lambda'\lambda''} \right) + \sum_{\lambda'} W^{imp}_{\lambda\lambda'}.$$

Ab-initio self-consistent calculations for C-diamond: Ward et al. Phys Rev B 80, 125203 (2009)

Several techniques are available to compute k_l

- Green-Kubo formulation and calculation of heat current from equilibrium Molecular Dynamics (MD)

- Non-equilibrium MD to compute heat flux (or temperature gradient) from applied temperature gradient (or heat flux)

- Boltzman Transport Equation (BTE) to compute deviation of phonon occupation distribution from equilibrium distribution

- Green's functions approach: Landauer-Buttiker transmission function formalism

Carbon Nanotubes and Si Nanowires

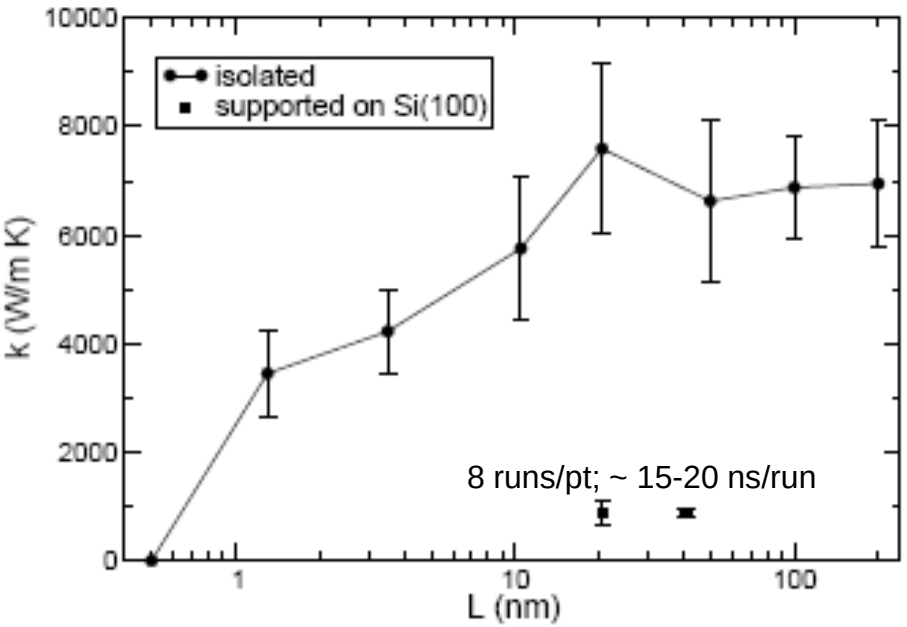
Carbon nanotubes

- Consistent results are obtained from equilibrium MD and BTE in the single relaxation time approximation
  - Many technical issues have been solved
- Use of MD to study influence of external media

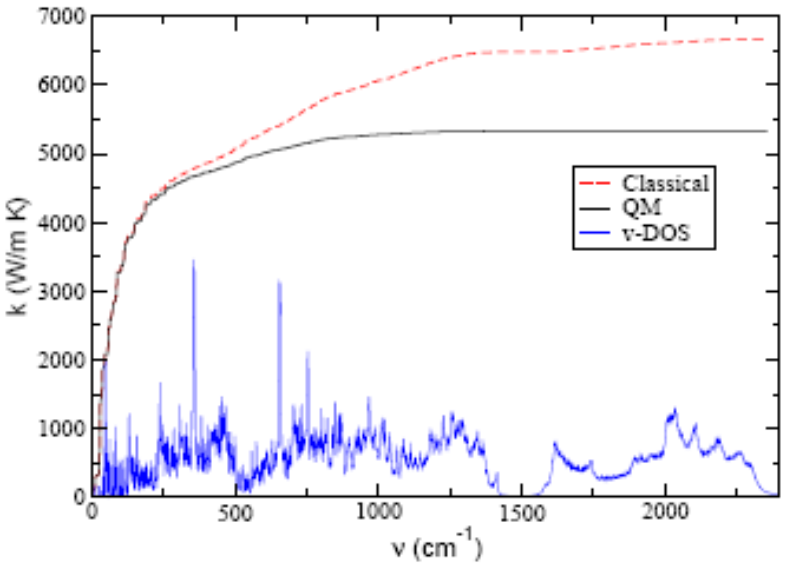
Tersoff potential

Consistent picture obtained from classical MD and Boltzman Transport equation

Classical MD results for (10,0)



We find convergence of MD results for L > ~ 20 nm

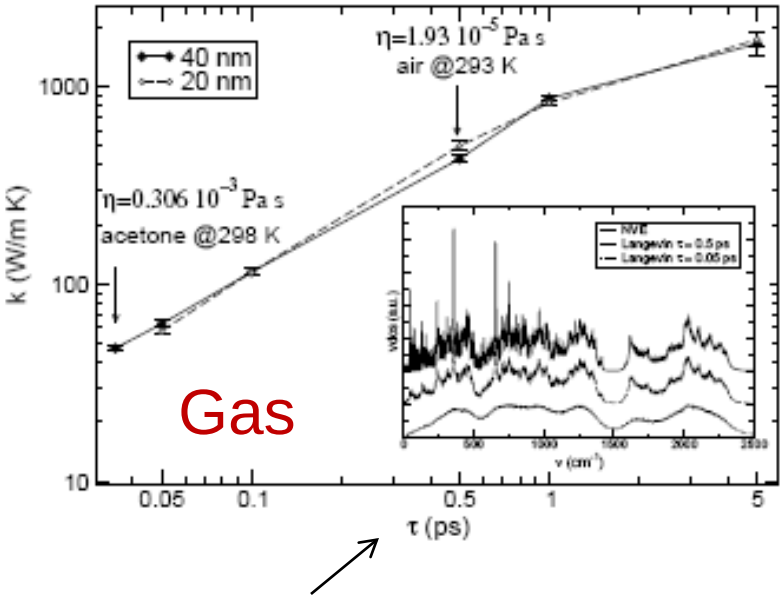


BTE and MD give the same result, within statistical error bars, for classical mode distribution

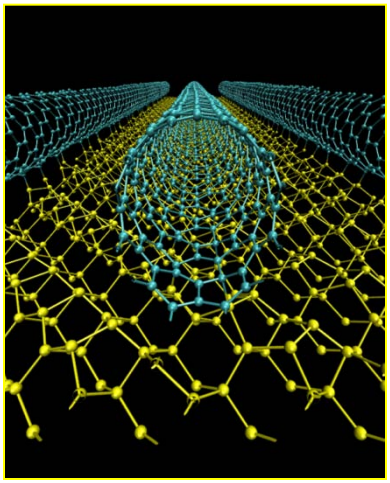
Interaction with an external medium may reduce the thermal conductivity of CNTs by up to 2 orders of magnitude

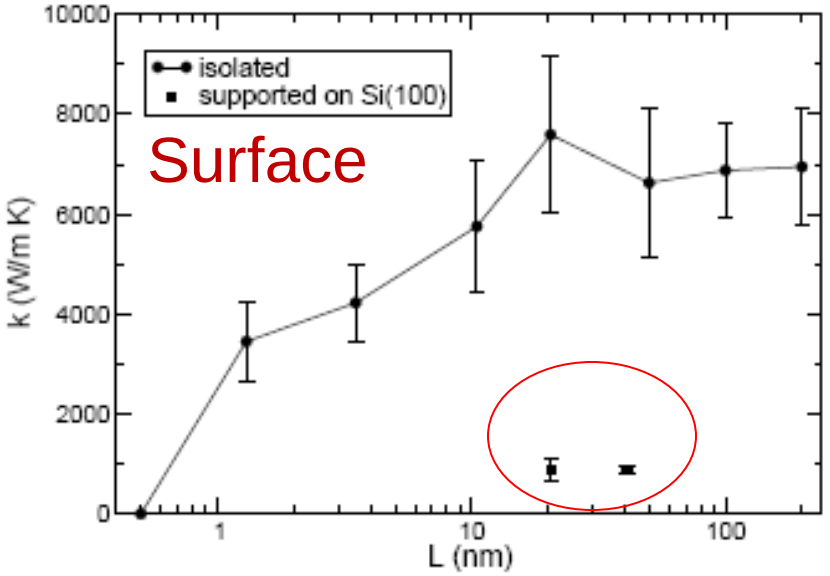
D.Donadio, G.G. Phys. Rev. Lett. 2007

Interaction with an external medium may reduce the thermal conductivity of CNTs by up to 2 orders of magnitude



Relaxation time of Langevin thermostat

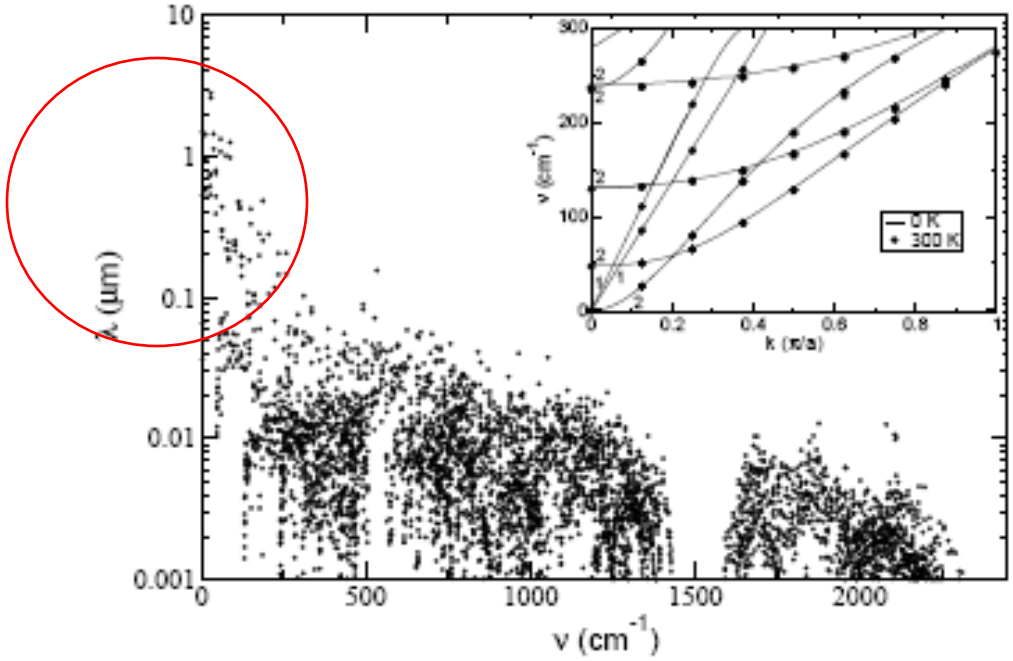




D.Donadio, G.G. Phys. Rev. Lett. 2007

Acoustic and flexure modes with mean free path of ~ few μ are major contributors to thermal conductivity

Phonon lifetimes from correlation functions of dynamical matrix eigenmodes



D.Donadio, G.G. PRL 2007

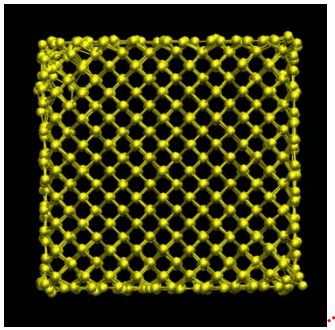
Silicon nanowires with ‘realistic’ surfaces

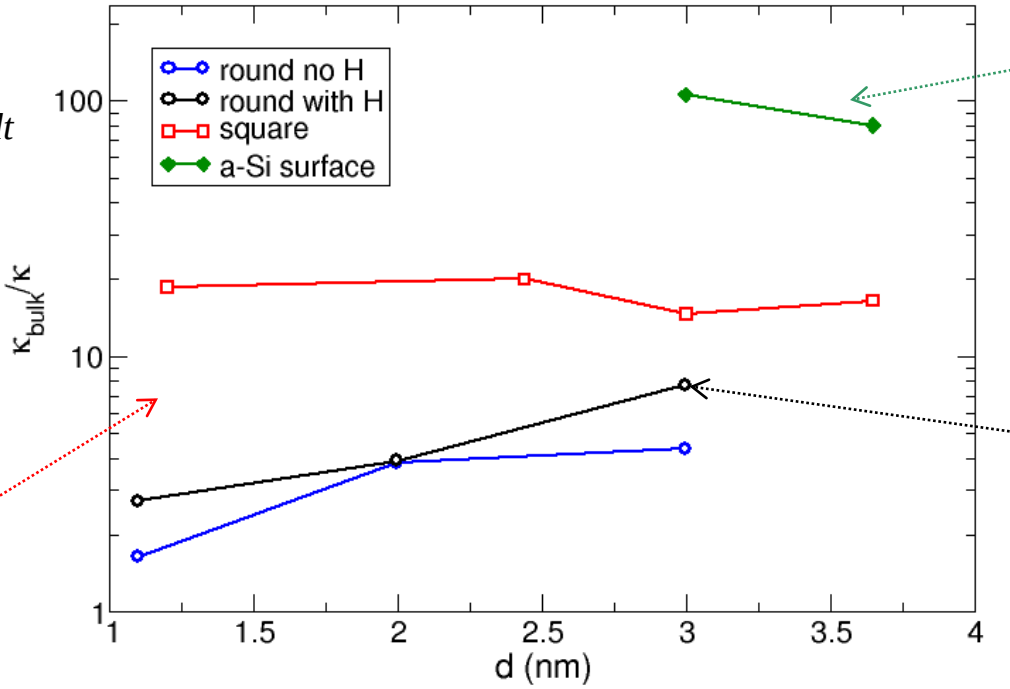
- Propagating (phonons) and non propagating vibrations contribute to heat transport → BTE insufficient to compute thermal conductivity
- MD results analyzed using BTE for phonons and approximate heat current evaluation for “diffusive” modes
- No localized modes giving substantial contributions to heat transport have been found
- *Yet unable to find consistent results from equilibrium and non equilibrium MD, possibly due to technical issues (consistency achieved for bulk systems)*

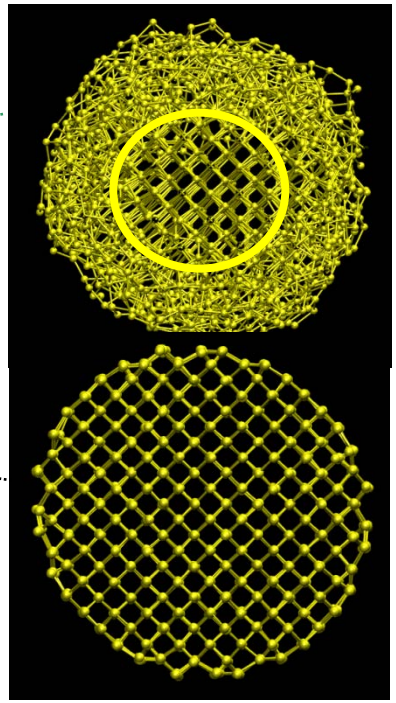
Shape and surface structure strongly affect values of thermal conductivity of Si NWs

Classical MD

$$k = \frac{1}{Vk_bT^2}\int_0^\infty \langle J(t)J(0)\rangle dt$$





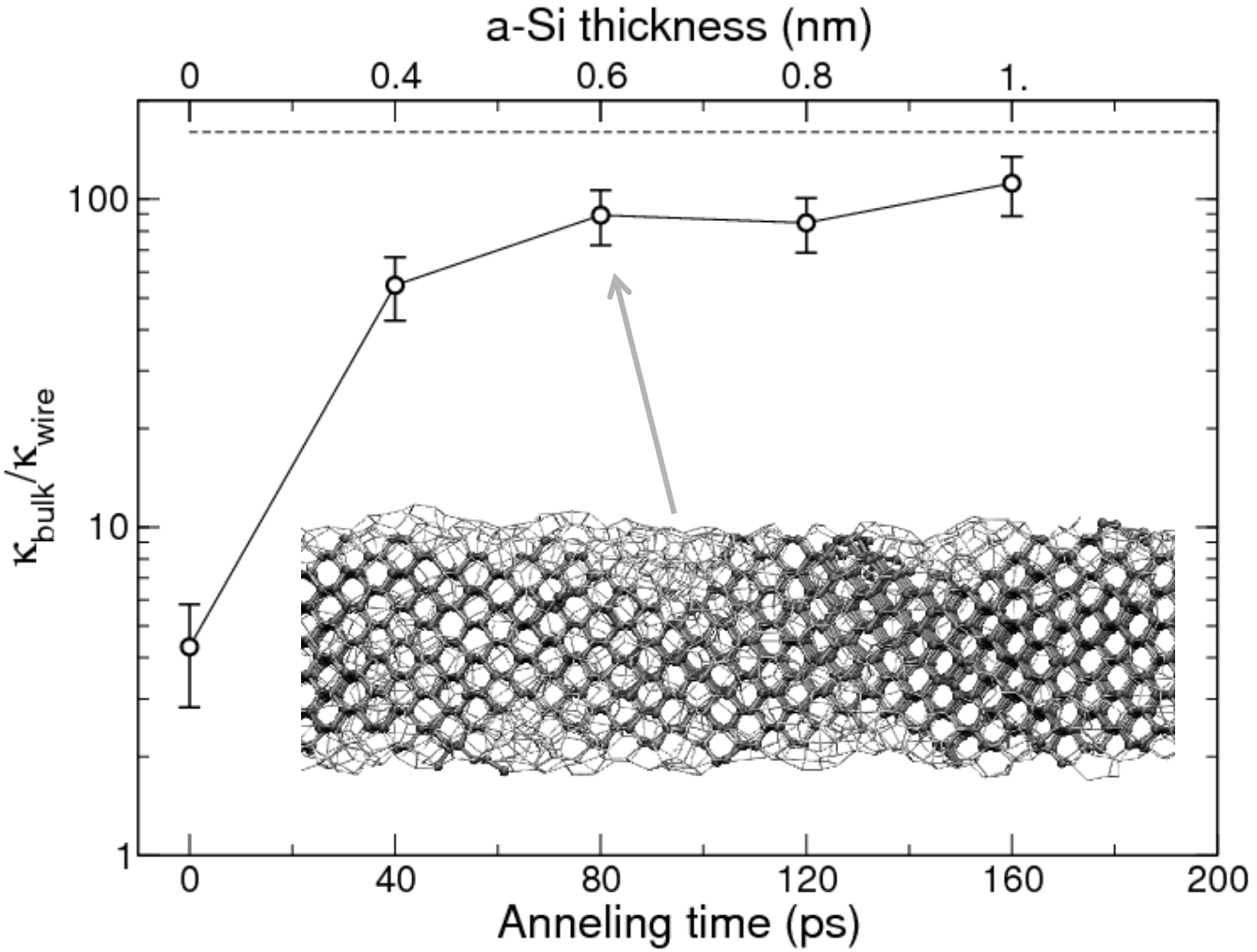


Size reduction may not substantially decrease thermal conductivity below bulk values

Surface structure play a key role in heat transport at the nanoscale

D.Donadio and G.G. PRL 2009

Core-shell wires: effect of disorder



Shape and surface structure strongly affect values of thermal conductivity of Si NWs

Why?

Surface amorphization decreases vibrational lifetimes (τ) by about one order of magnitude. However differences in τ of wires with different surfaces are not large enough to account for the observed differences in κ.

Group velocities of most modes vanish in wires with disordered surfaces => **non propagating modes, diffusive**; these cannot be treated using the Boltzman Transport Equation

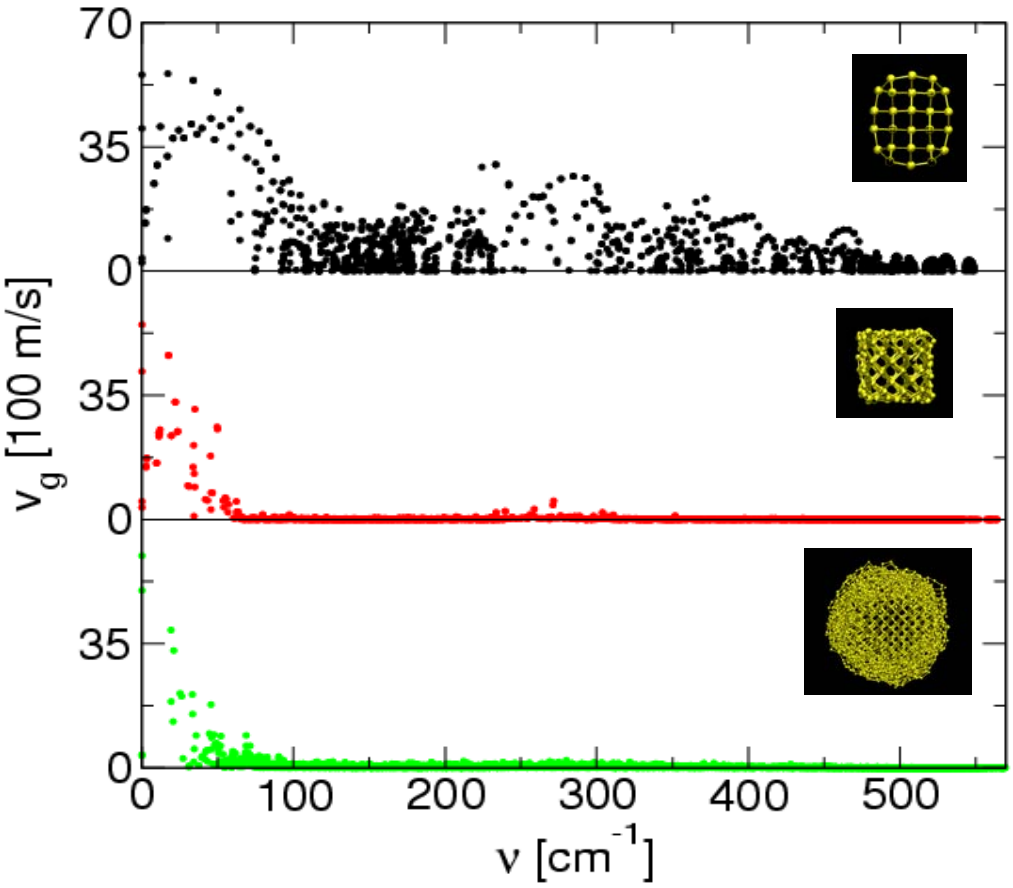
Diffusive modes are heat carriers: treated using the formulation proposed by Allen and Feldman (PRL and PRB 1993) for a-Si.

$$k_i = C_i D_i;$$

$$D_i = \frac{\pi V^2}{\hbar^2 \omega^2} \sum_{j \neq i} \left| \langle i | J_z | j \rangle \right|^2 \delta(\omega_i - \omega_j)$$

P.B. Allen & J.L. Feldman PRB 48, 12581 (1993)

Group velocities in wires with different surface structure

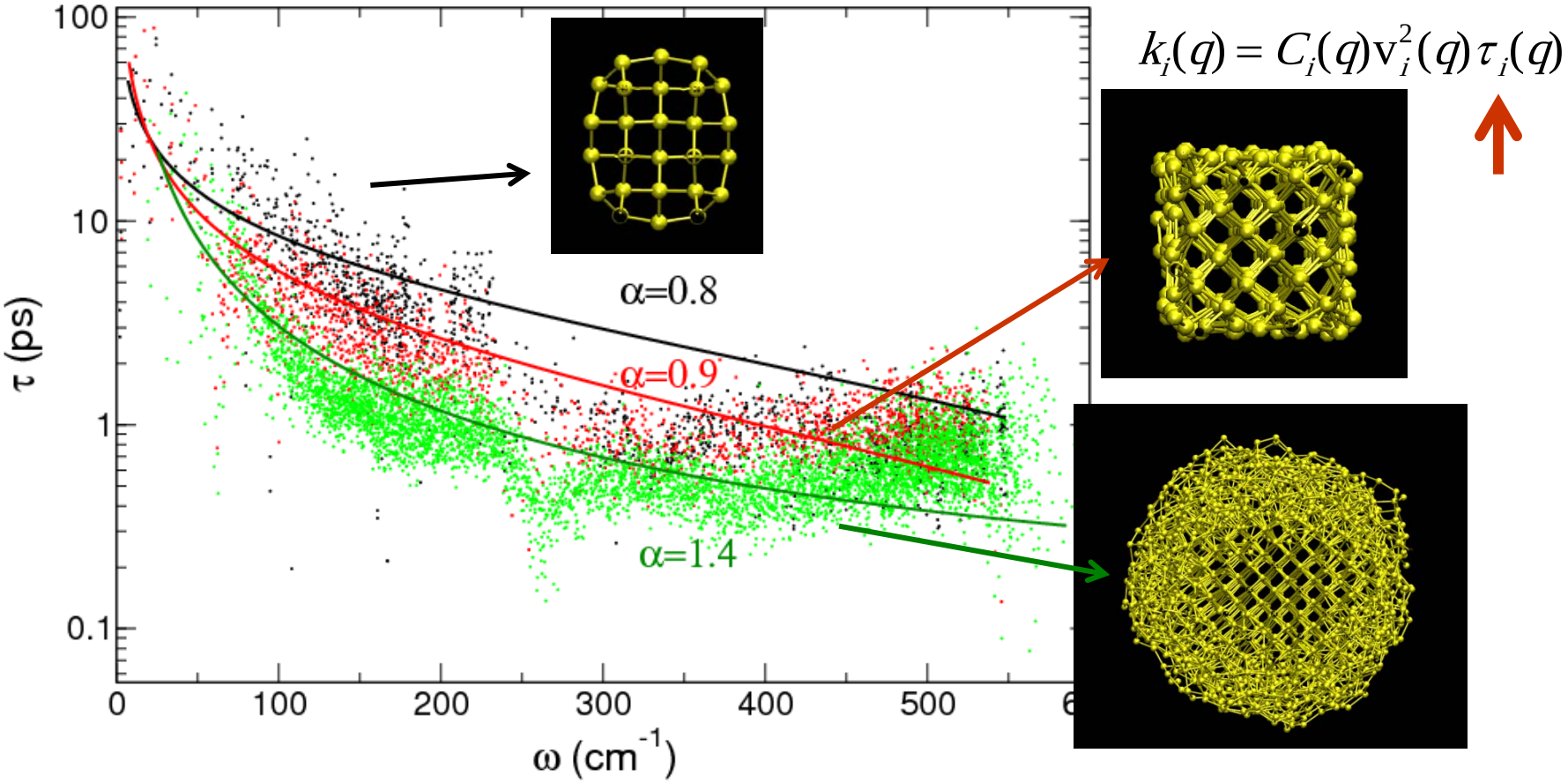


$$k_i(q) = C_i(q)\mathrm{v}_i^2(q)\tau_i(q)$$

Group velocities are computed by diagonalizing the dynamical matrix at different q points, at zero K and using finite differencs.

Group velocities of most modes vanish in wires with disordered surfaces ➔ non propagating modes, they cannot be treated using the Boltzman Transport Equation

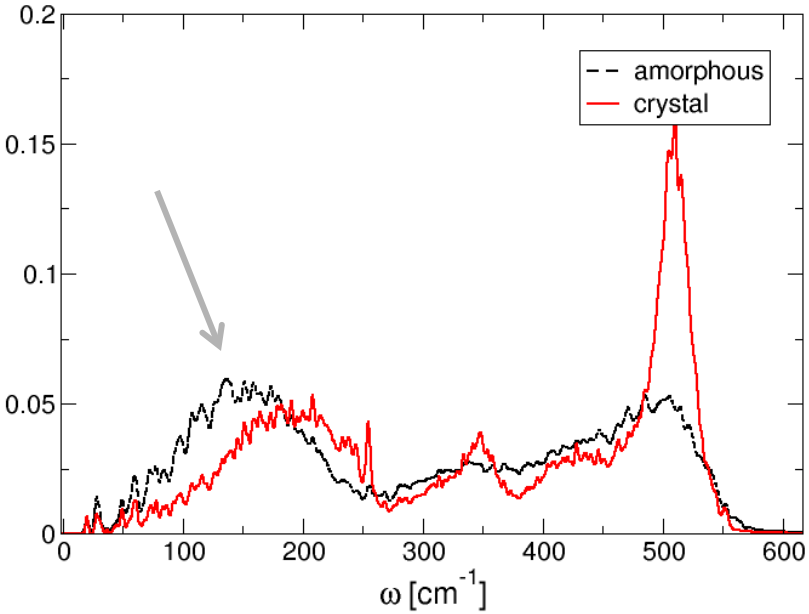
Phonon lifetimes of wires as a function of morphology

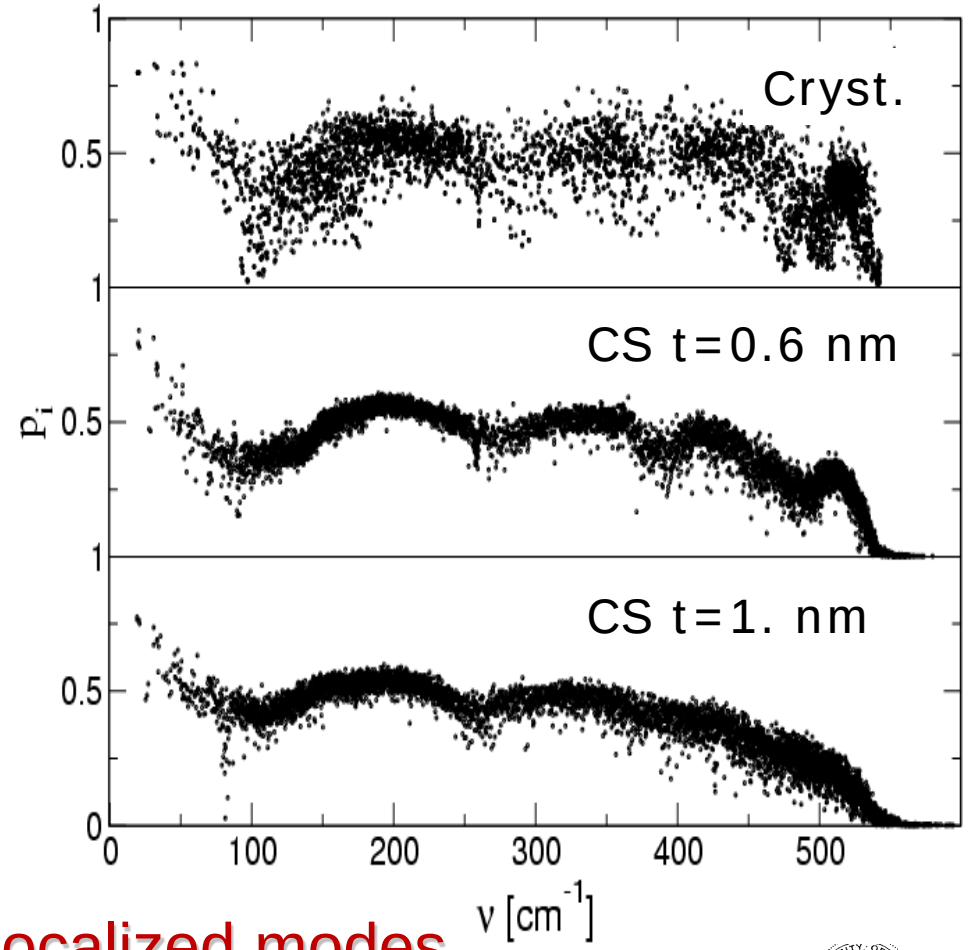


Surface amorphization decreases vibrational lifetimes (τ) by about one order of magnitude. However differences in τ of wires with different surfaces are not large enough to account for the observed differences in thermal conductivity.

Localization of vibrational modes

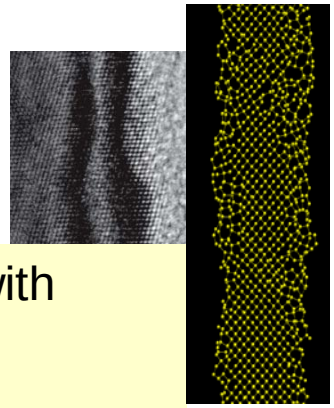
3 nm SiNW with different amorphous layers





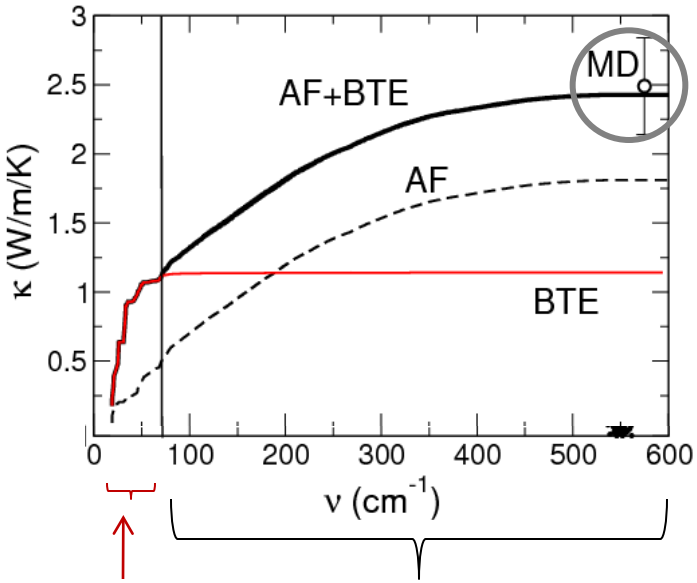
No evidence of localized modes

Key interplay between order and disorder in thermal conductivity of Si NWs



Non propagating, diffusive modes are major heat carriers in wires with disordered surfaces

Small contributions of low frequency phonons to the thermal conductivity



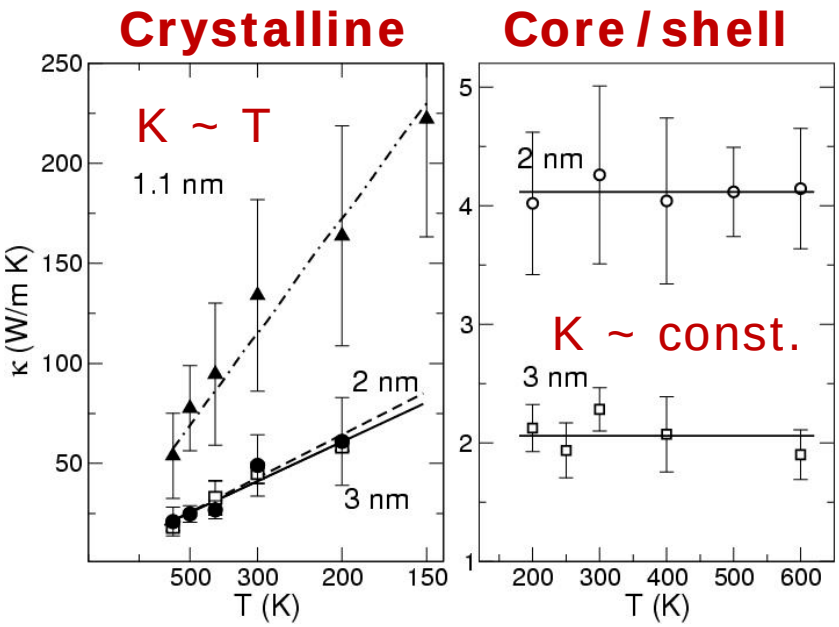
Some localized modes are present at **high frequency** (similar to a-Si) and their contribution to heat transport is negligible

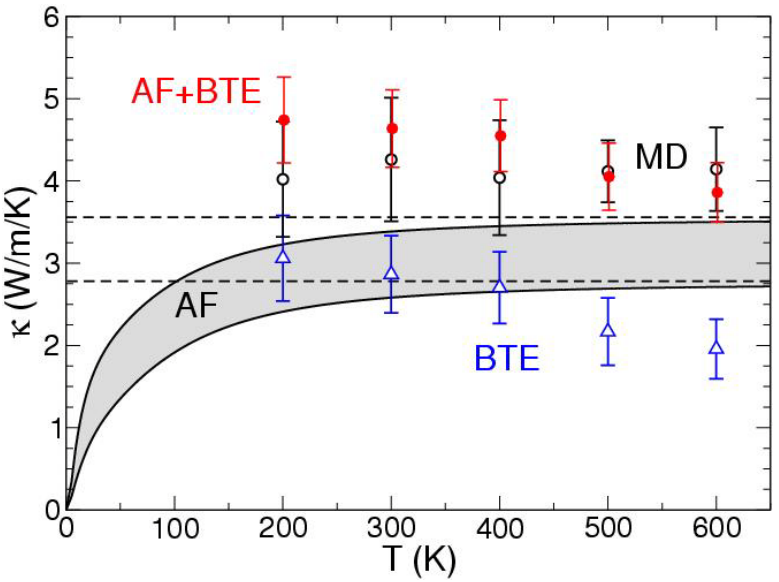
Contribution from non propagating modes or diffusons (described by Allen-Feldman Theory –AF)

Contribution from low frequency phonons (described by Boltzman Transport Equation-BTE; SC does not appear to be very important)

AF: P.B. Allen & J.L. Feldman PRB 48, 12581 (1993); BTE: Boltzman Transport Equation; MD: Molecular Dynamics D.Donadio and G.G. PRL 2009

Temperature dependence of thermal conductivity of core-shell wires





- A parameter free model built upon atomistic simulations explains temperature dependence of thermal conductivity of crystalline and core-shell (CS) wires
- **Combination of dimensionality reduction* and presence of disorder is responsible for 'peculiar' T dependence in CS wires.**
- Qualitative agreement with recent experimental findings+

*T. Thonhauser and G. D. Mahan, Phys. Rev. B 69,075213 (2004).
+R. Chen et al. PRL 101, 105501 (2009)

Reducing thermal conductivity of semiconductors by alloying

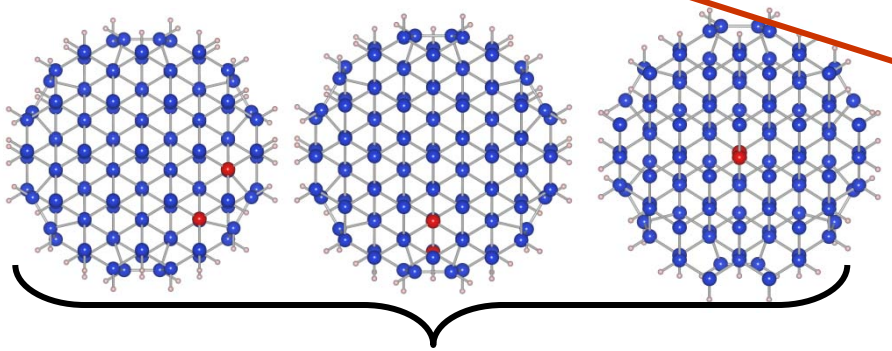
- How to compute thermal conductivity of alloys?
  - —Unexplained discrepancy between GF results and MD results
- Need for sensible structural models of alloys

We used Cluster Expansion (CE) techniques to investigate alloying effects

How to alloy Si and Ge
for optimal thermal conductivity?

$$\hat{\kappa}_j = \sum_\alpha V_\alpha \Phi_\alpha(\vec{\sigma}_j), \qquad \Phi_\alpha(\vec{\sigma}_j) = \left\langle \prod_{i \in \alpha_k} \vec{\sigma}_j(i) \right\rangle_k$$

Calculate κ for many structures (from molecular dynamics)



Evaluate correlations for each structure

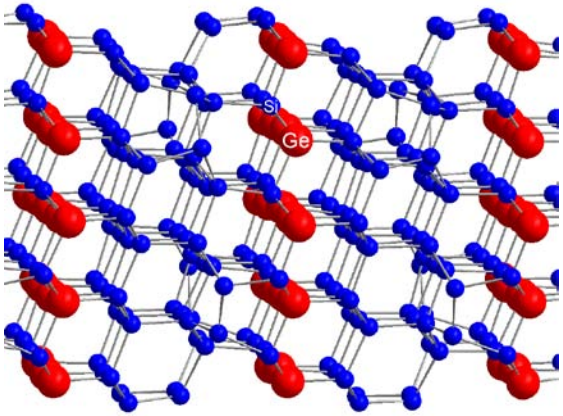
Example of clusters

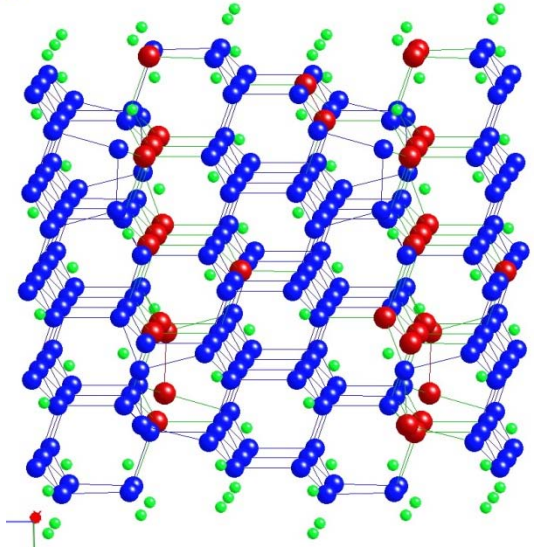
Determine expansions coefficients V:

- Use least-squares fitting to find the parameters
- Minimize cross-validation error while avoiding over-fitting

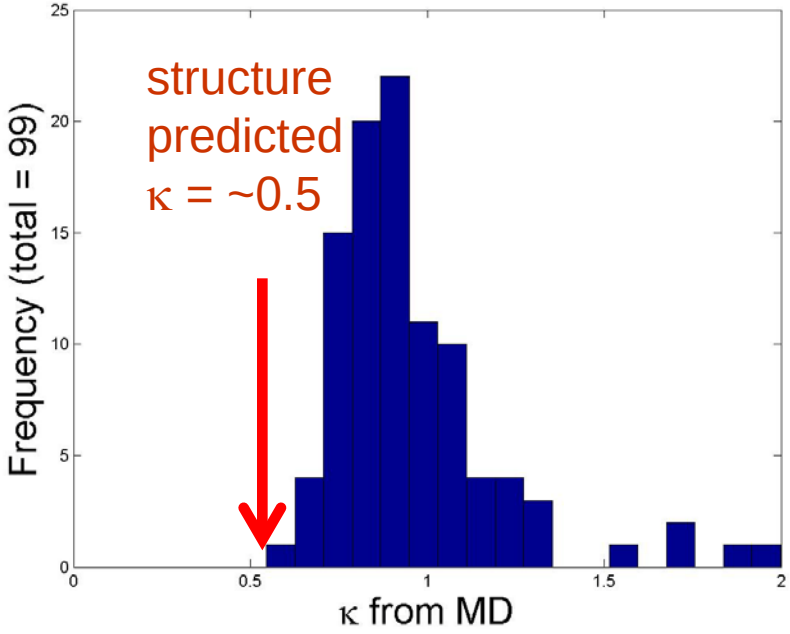
M.Chang, J.Reed, S. Meng, G.Ceder, G.G. (submitted)

New lowest κ structure predicted





side view



Coarse-grained cluster expansion predicts new wire with κ lower than any calculated.

M.Chang, J.Reed, S. Meng, G.Ceder, G.G.

Thermal conductivity of $Si_{0.5}Ge_{0.5}$

$$\kappa = \frac{L}{S}\int_0^\infty \frac{\hbar\omega}{2\pi}\sum_{\mathbf{k}_{xy}} w(\omega,\mathbf{k}_{xy})\overline{\mathcal{T}'}(\omega,\mathbf{k}_{xy})\frac{df_{BE}(\omega,T)}{dT}d\omega.$$

$$\sum_{\mathbf{k}_{xy}} w(\omega,\mathbf{k}_{xy})\overline{\mathcal{T}'}(\omega,\mathbf{k}_{xy}) = \sum_{\mathbf{k}_{xy}} w(\omega,\mathbf{k}_{xy})N(\omega,\mathbf{k}_{xy})l_e(\omega)/L.$$

- Experimental values: $\kappa \approx 7$ W/m K.
- Atomistic Green's function approach:
  - No anharmonicity: $\kappa = 10.9$ W/m K.
  - With anharmonicity: $\kappa = 7.6$ W/m K.
- Molecular dynamics predictions: $\kappa = 1.1$ W/m K.

Ref. A. Skye and P. K. Schelling, JAP **103**, 113524 (2008)

→ ?

I.Savic and N.Mingo, 2009

Atomistic Green's function approach to phonon transport II

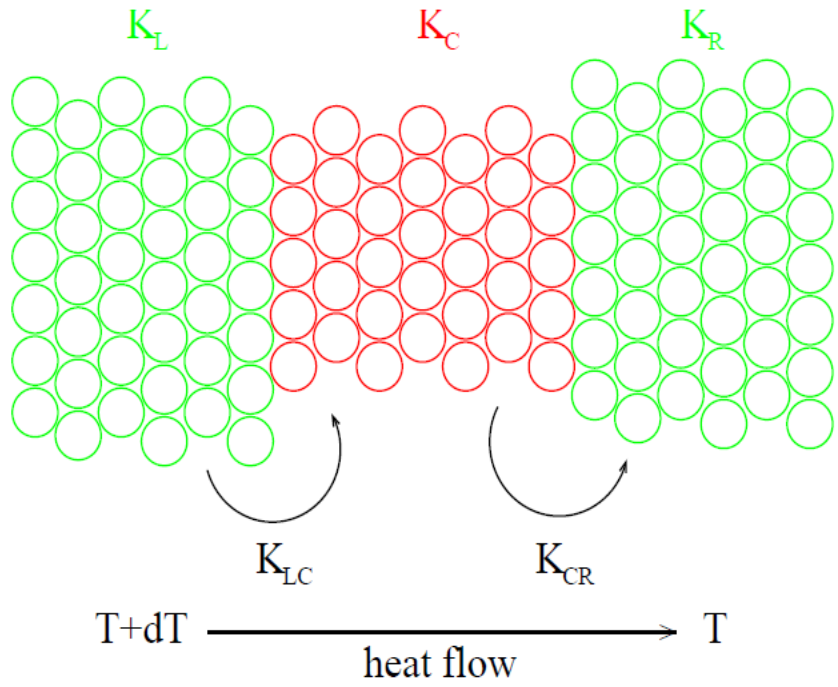
- Central region:

$$G_C(\omega) = [\omega^2 I - K_C - \Sigma_L(\omega) - \Sigma_R(\omega)]^{-1}$$

$$\Sigma_{L,R}(\omega) = K_{C(L,R)} g_{L,R}(\omega) K_{(L,R)C}.$$

- Contacts:

$$g_{L,R}(\omega) = [(\omega^2 + i\delta)I - K_{L,R}]^{-1},\ \delta \to 0.$$



- Landauer-Buttiker transmission function formalism:

$$\mathcal{T}(\omega) = \mathrm{Tr}[\Gamma_L(\omega) G_C(\omega) \Gamma_R(\omega) G_C^{\dagger}(\omega)],\ \Gamma_{L,R}(\omega) = -2\mathrm{Im}[\Sigma_{L,R}(\omega)].$$

- Thermal conductance:

$$\sigma = \int_0^{\infty} \frac{\hbar\omega}{2\pi} \mathcal{T}(\omega) \frac{df_{BE}(\omega)}{dT} d\omega.$$

Ref.: N. Mingo and L. Yang, PRB **68**, 245406 (2003).

I.Savic and N.Mingo, 2009

Outlook

- Thermal transport calculations using empirical potentials are becoming rather robust
- *Ab-initio* calculations are still very challenging but *ab-initio* simulations may be feasible for (partially) disordered systems
- Unsolved issues in the case of alloys
- Inclusion of electron-phonon interaction may be crucial in many instances

Some other work of possible interest to this workshop

- "Ab initio calculation of **van der Waals** bonded molecular crystals", D. Lu, Y. Li, D. Rocca and G. Galli, *Phys. Rev. Lett.* 102, 206411 (2009)
- "Van der Waals Interactions in Molecular Assemblies from First-Principles Calculations", Y.Li, D. Lu, H.-V. Nguyen, and G. Galli (submitted)
- "The nature and strength of inter-layer binding in graphite", L.Spanu, S.Sorella, G. Galli, *Phys. Rev. Lett.* (accepted)
- "Solution of the **Bethe-Salpeter equation** within density matrix perturbation theory: Ab-initio calculations of optical absorption spectra", D.Rocca, D.Lu, and G.Galli (submitted)

http://angstrom.ucdavis.edu/

Ab-initio Nanoscience Group
for Simulations and Theoretical Research On Materials

Davide Donadio (UCD)

Yuping He (UCD)

J.-H. Lee and Jeff Grossman (MIT)

Maria Chan and Gerd Ceder (MIT)

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