The Abdus Salam International Centre for Theoretical Physics

2371-2

Advanced Workshop on Energy Transport in Low-Dimensional Systems: Achievements and Mysteries

15 - 24 October 2012

Atomistic Simulations of Thermal Transport in Nanostructured Semiconductors (Thermal Transport in Nanostructured and Amorphous Materials

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Thermal transport in nanostructured and amorphous materials

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People and funding

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- **Jeff Grossman and Joo-Young Lee (MIT)**
- **G. Sosso, M. Bernasconi (Uni Milano Bicocca)**
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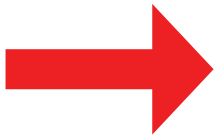
NIC-Julich Computer center (JUGENE)

Why heat?

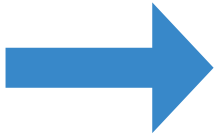
- Thermal management
  - e.g. passive cooling devices



High thermal conductivity

  - thermal barrier coating

- Renewable energy
  - thermoelectric materials



Low thermal conductivity

Much less studied than electronic transport

From Fourier ... macroscopic theory

Joseph Fourier
1768-1830
"Analytic theory of Heat"
continuum theory, partial differential equations

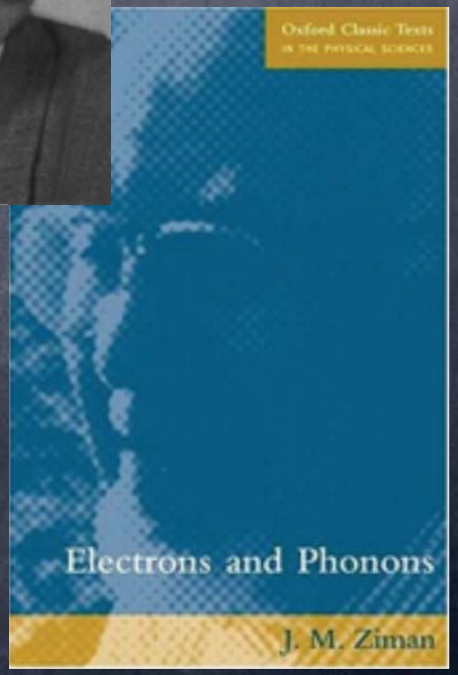
Steady-state condition: $\vec{J} = \kappa \vec{\nabla} T$

thermal conductivity

...to Peierls kinetic theory of heat transport

- Heat carriers: **electrons** and lattice vibrations (**phonons**)
- **Electrons**: Wiedman-Franz law: $\frac{\kappa}{\sigma} = LT$
- **Phonons:** obey a transport equation analogous to the Boltzmann transport equation, but with quantum statistics.

Rudolf Peierls 1907-1995



Equilibrium Molecular Dynamics

- Green-Kubo formula (fluctuation dissipation theorem):

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

- J is the heat flux, to be calculated as the time derivative of the energy density R
- Equivalently κ can be obtained by fitting an Einstein-like relation for Brownian motion (Helfand):

$$\left\langle \left(R(t)-R(0)\right)^2 \right\rangle \approx 2\kappa\left[t+\tau(e^{-t/\tau}-1)\right] \text{ with } R(t)=\int_0^t dt' J(t')$$

- Special care must be taken when calculating R with **periodic boundary conditions.**
- Time and size **convergence issues.**
- MD details: DLPOLY code - Tersoff interatomic potential.
- Data collected in NVE runs.

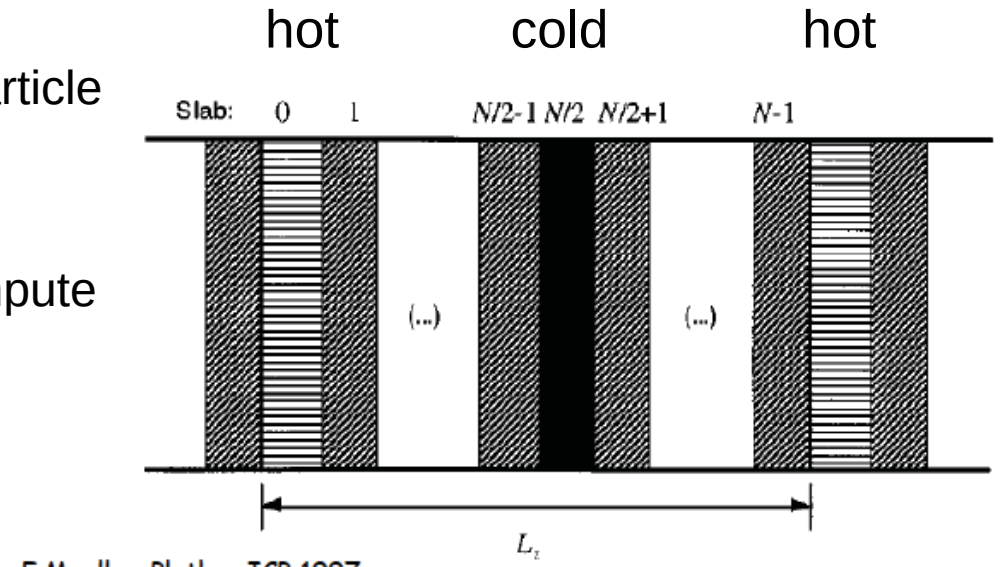
Non equilibrium MD

- Use Fourier's relation: $J = -\kappa \nabla T$

- Exchange heat by exchanging particle velocities every τ

- At stationary non-equilibrium compute the gradient of T

$$\kappa = \frac{\sum \frac{1}{2} m\left(v_{hot}^2 - v_{cold}^2\right)}{2\tau A \nabla T}$$



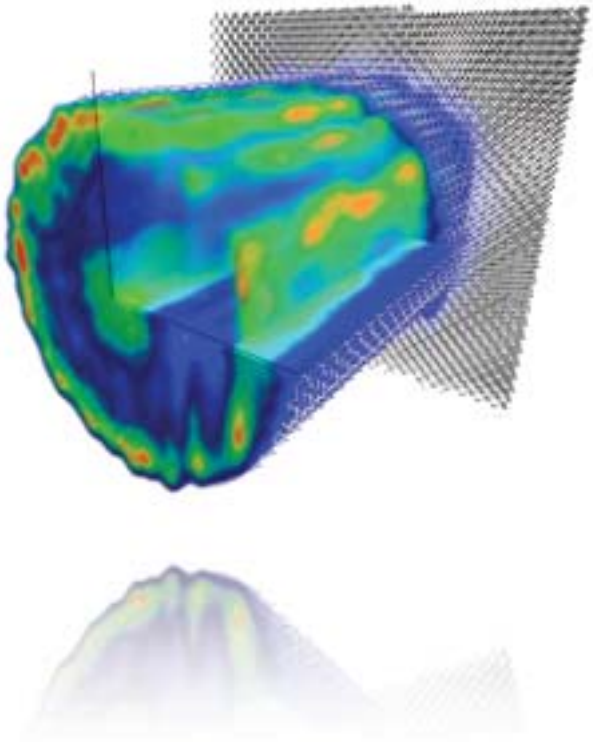
F.Mueller-Plathe, JCP 1997

- Results are strongly size dependent.
  The standard approach is to scale k as:

$$\frac{1}{\kappa_{Lz}} = \frac{1}{\kappa} + \frac{A}{L_z}$$

Outline

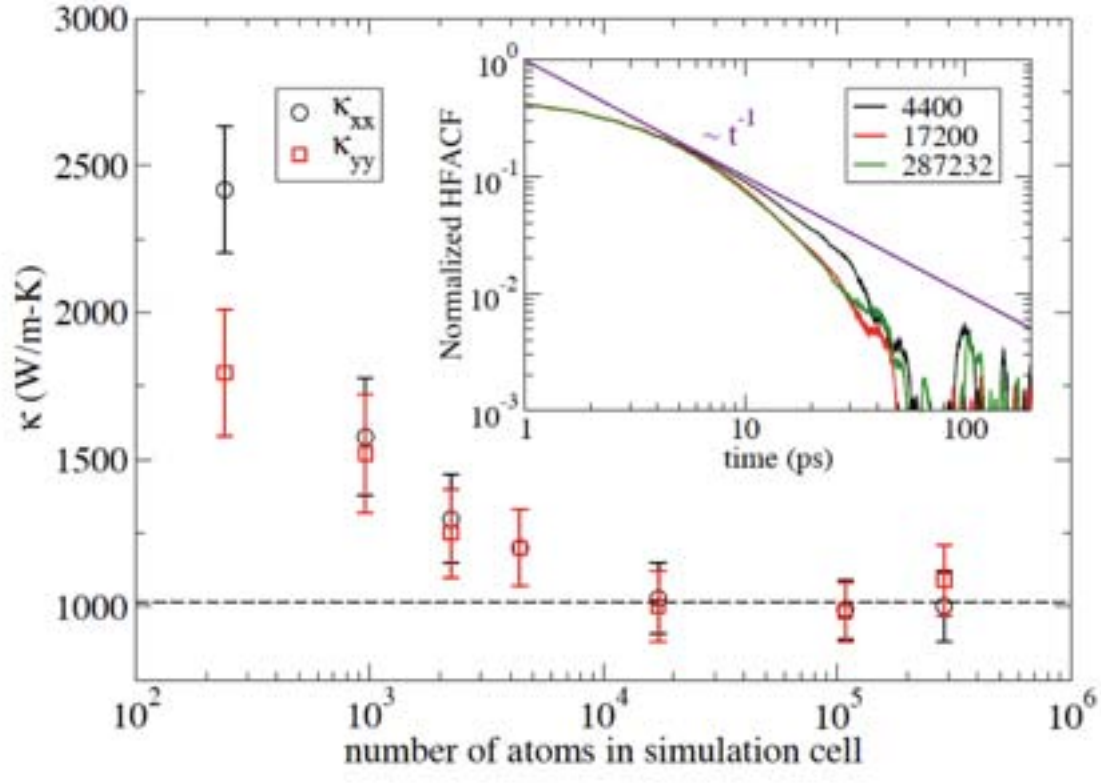
- Suspended graphene
- Silicon nanostructures:
  - Thin wires
  - Nanoporous Si and SiGe
  - Contact conductance: SiNW/crystalline Si interface
  - Finite size wires
- Phase-change materials



Suspended graphene

Suspended Graphene

- Transport coeff. in 2D systems normally diverge
- This is not the case for graphene, due to out-of-plane (ZA) modes*

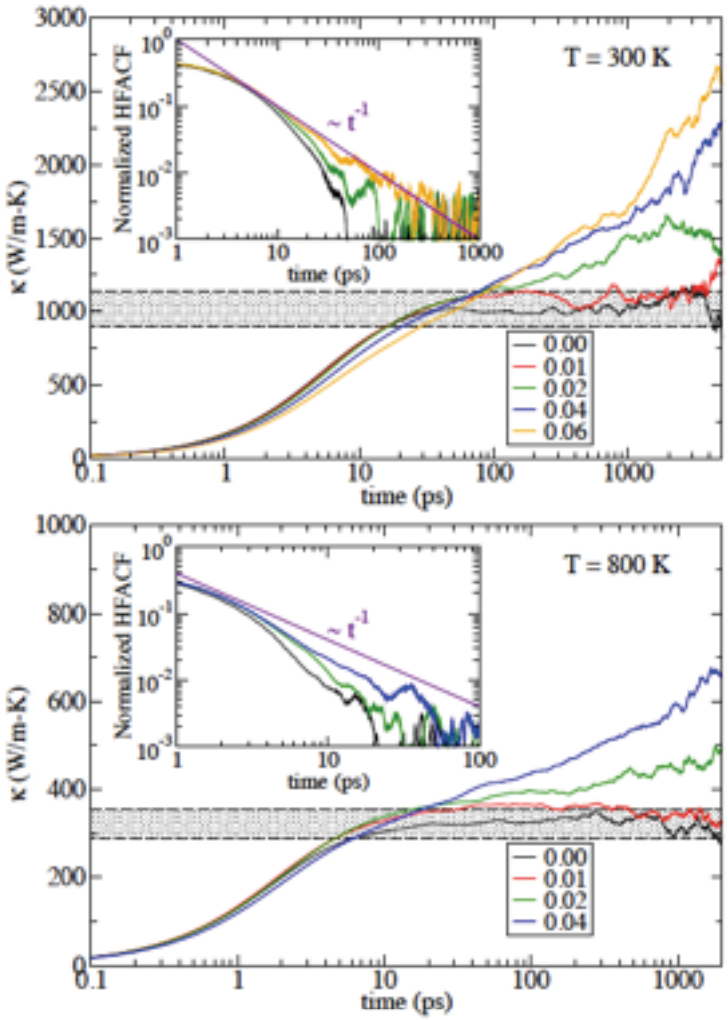


*Ab initio anharmonic lattice dynamics (up to 3-phonon scattering):

N. Bonini, J. Garg, N. Marzari, Nano Lett. 12, 2673 (2012)

Uniaxially Strained Graphene

- Ab initio LD predicts divergence of κ for any strain
- k diverges for tensile strain larger than 2% at finite temperature
- raising the temperature to 800 K does not change the crossover value of strain



Boltzmann transport equation (made easy)

- Boltzmann-Peierls equation: $$\frac{\partial n_\lambda}{\partial t} + \mathbf{v}_\lambda \cdot \nabla n_\lambda = \left(\frac{dn_\lambda}{dt}\right)_{scat}$$
- **single mode relaxation time** approximation,

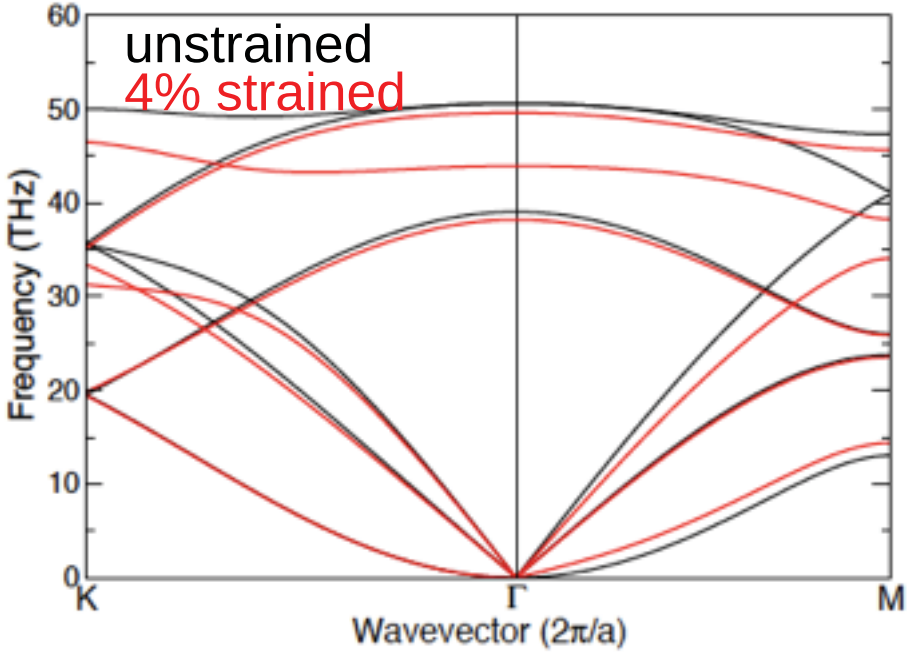
$$\kappa_i(q) = C_i(q)\mathrm{v}_i^2(q)\tau_i(q)$$

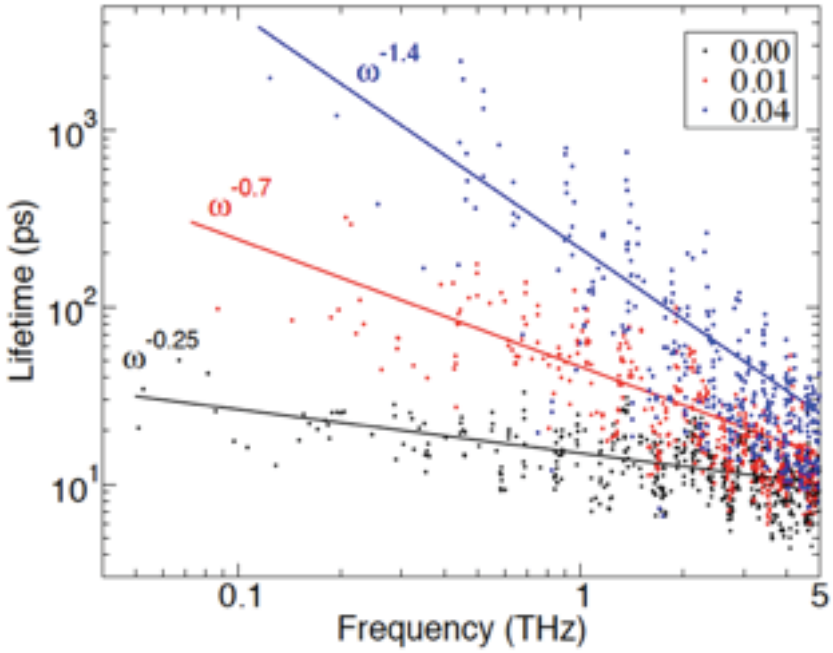
τ from MD

- τ contains all orders of anharmonicities
- Calculation of the single contribution from each phonon mode
- Evaluation of the importance of quantum effects

- This approach reproduces MD results for Carbon Nanotubes (see DD, G. Galli PRL 2007)

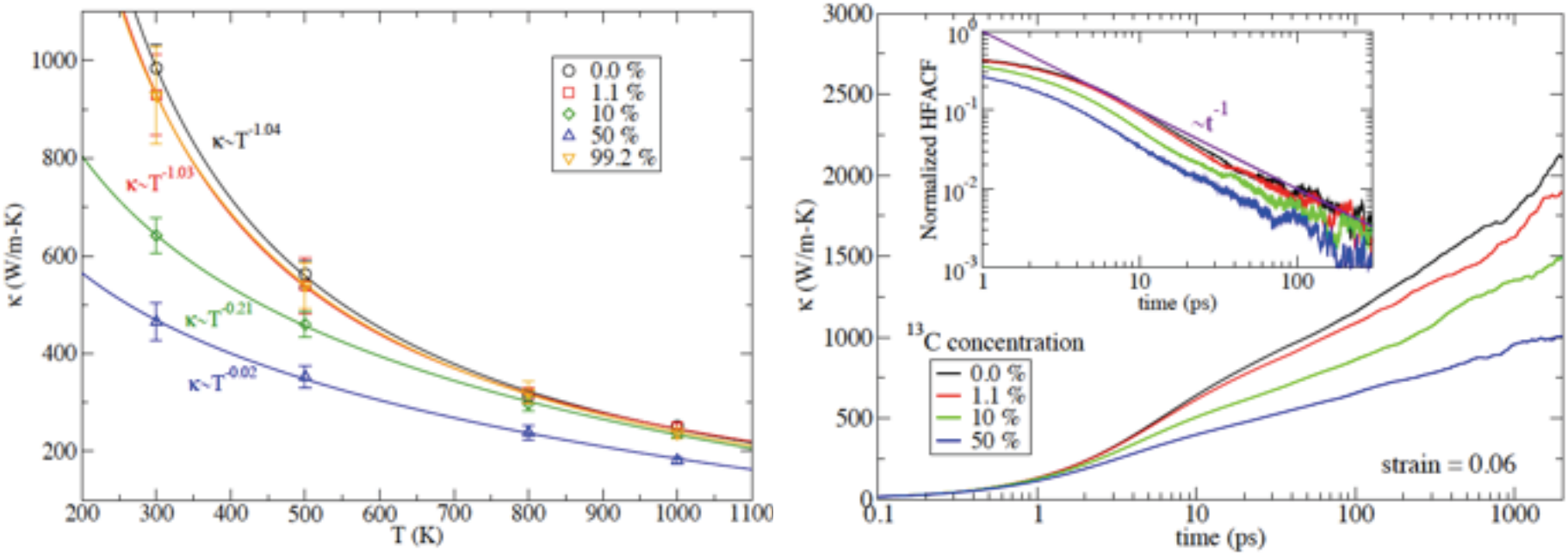
Phonon dispersions and lifetimes





- Linearization of ZA modes near the Γ point along the strain axis
- assume: that each phonon contributes as $\kappa_i(q) = C_i(q)\mathrm{v}_i^2(q)\tau_i(q)$
  - for $\omega \to 0$ $\tau \sim \omega^{-\alpha}$, κ diverges for exponents larger than 1

Can isotopic (C^{12}-C^{13}) disorder suppress divergence?



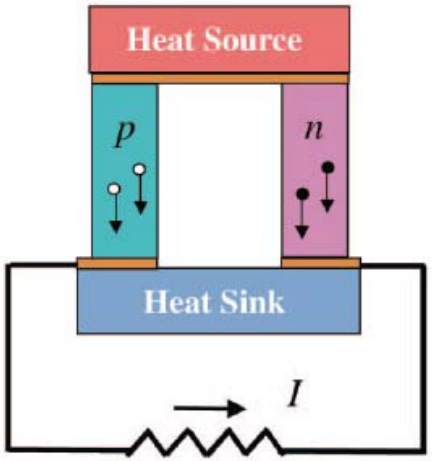
- 50% reduction of κ in unstrained graphene by isotopic doping, as seen in experiments*
- divergence of κ persists even at 50% C^{12}/C^{13} ratio

*Chen et al. Nat. Mater. 11, 203 (2012)

Silicon nanostructures for thermoelectric applications

Thermoelectric efficiency: $\eta = \frac{\Delta T}{T_H} \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+T_C/T_H}$

- Figure of merit ZT:



Seebeck coefficient

Electrical conductivity

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

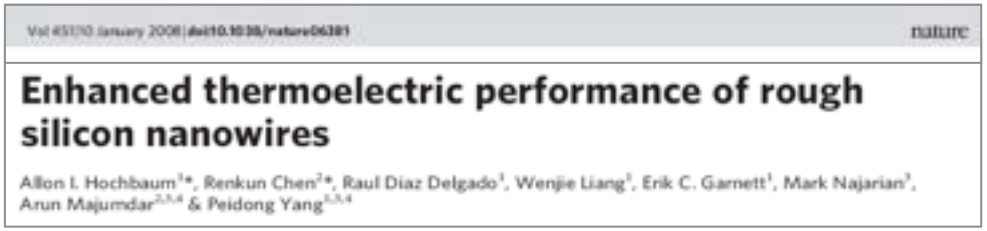
Electronic thermal conductivity

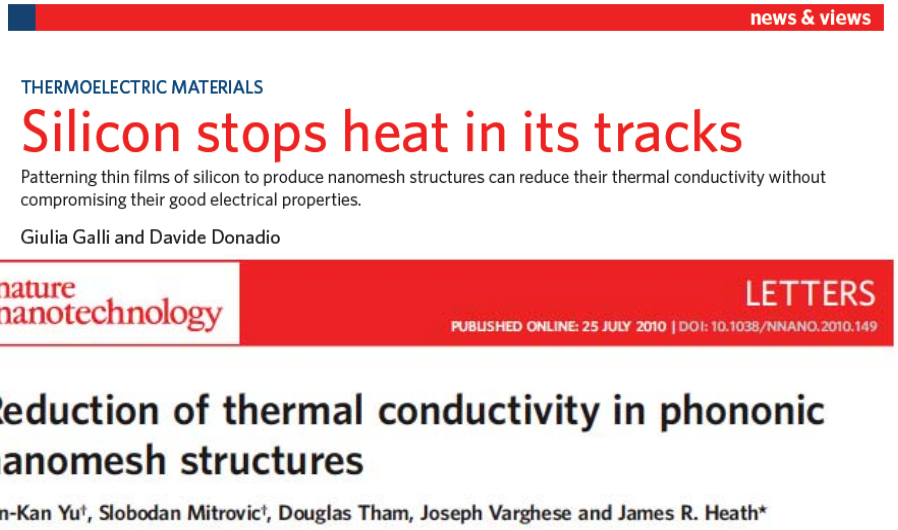
Ionic thermal conductivity

- Electronic properties are strongly intertwined, but the ionic thermal conductivity may be decoupled
- ZT>1 for thermoelectric applications

Silicon Nanostructures

Bulk silicon has a very low ZT (0.01 @ RT) but nano-Silicon may reach ZT~1 + are compatible with Si-based technology





High ZT is mostly due to a drop of κ_i :

κ_i bulk @ room temperature ~ 160 W/m K

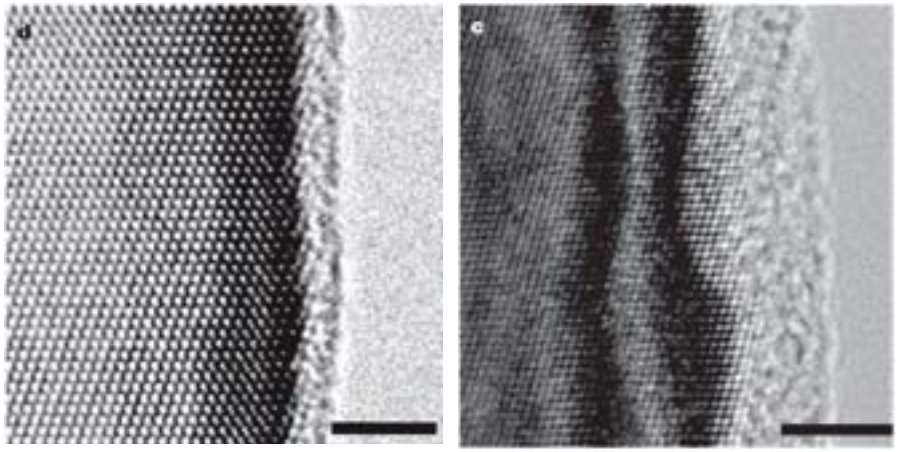
κ_i nano-Si @ room temperature < 4 W/m K

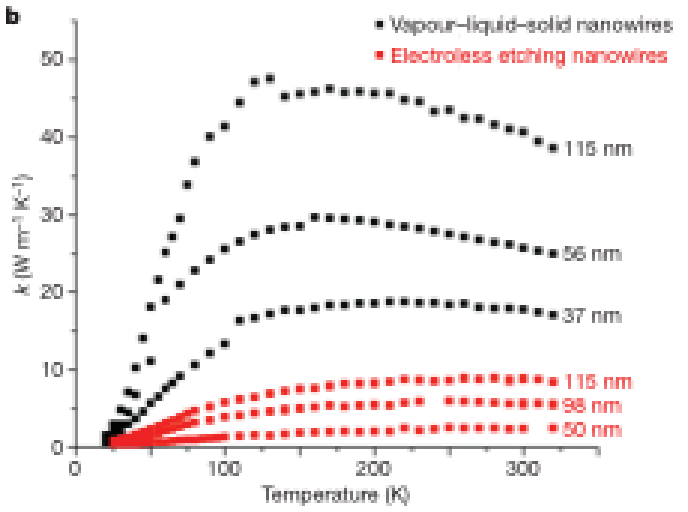
Nanostructures and disorder

Different growth processes:

- VLS:
  - Growth in a preferential direction only (<110>)
  - Wires with smooth surfaces and thin a-SiO_2 layers
- Electro-less Etching
  - The orientation of the wires is the same as the substrate
  - Thicker oxide layer with rough core-shell interface

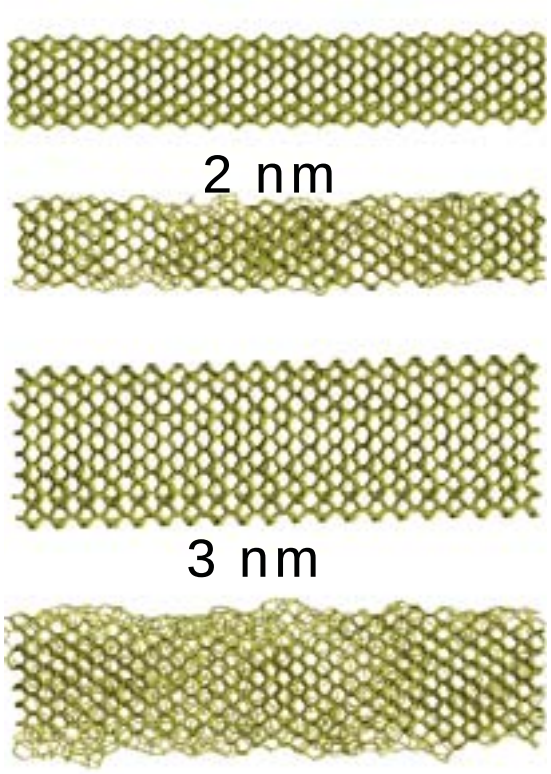
- **Dimensionality reduction**
- **Surface scattering**



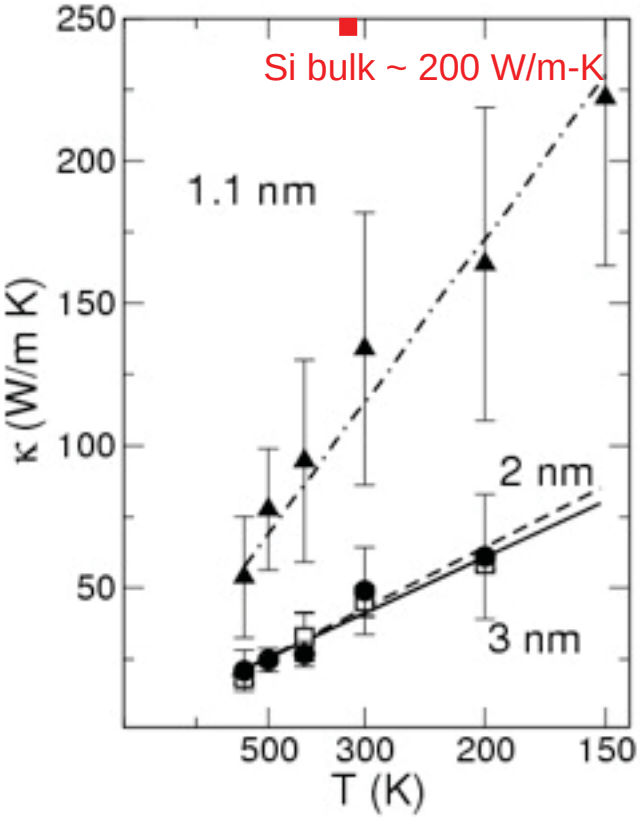


Hochbaum et al. Nature 451, (2008)

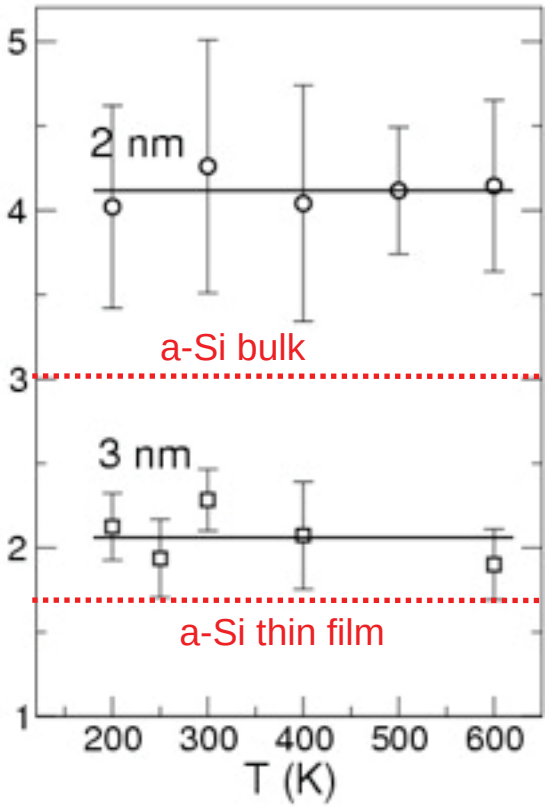
MD results: thin Si nanowires



crystalline

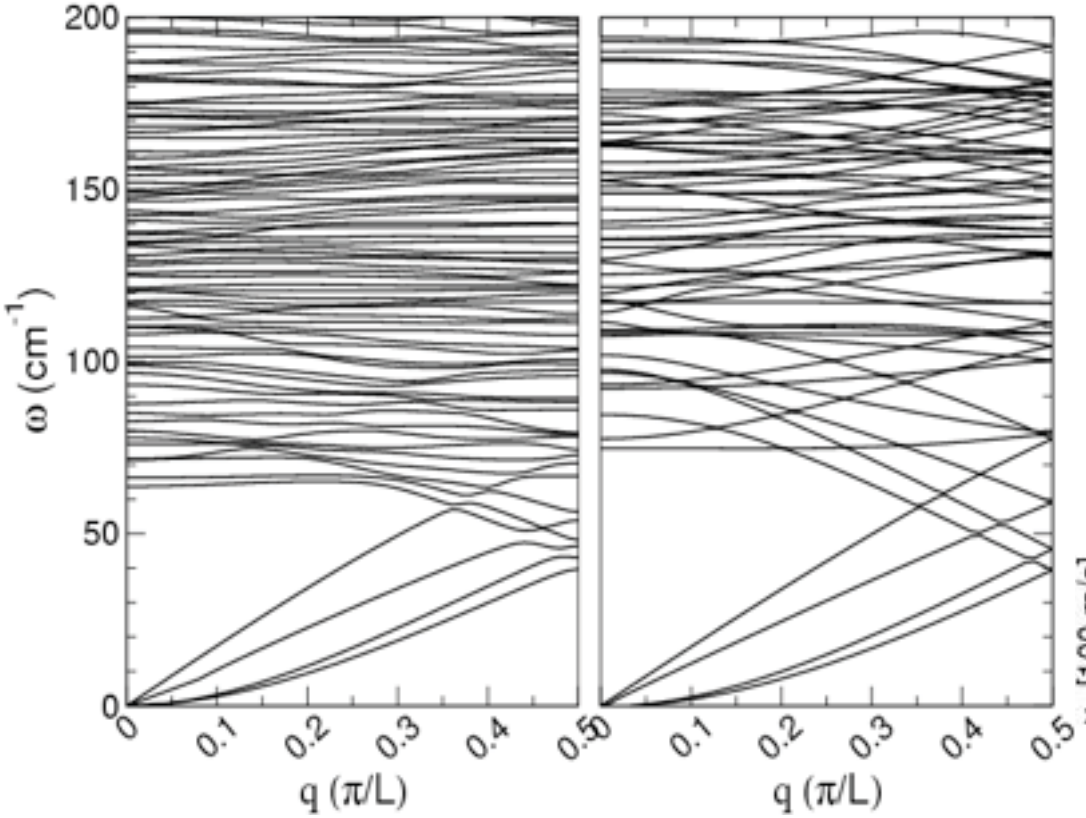


core/shell

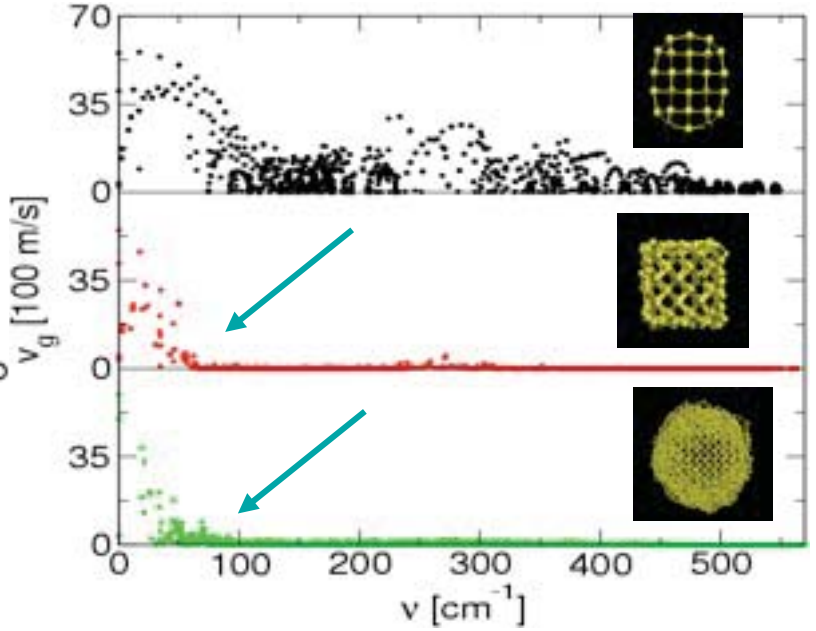


Phonon-phonon scattering Lattice disorder scattering

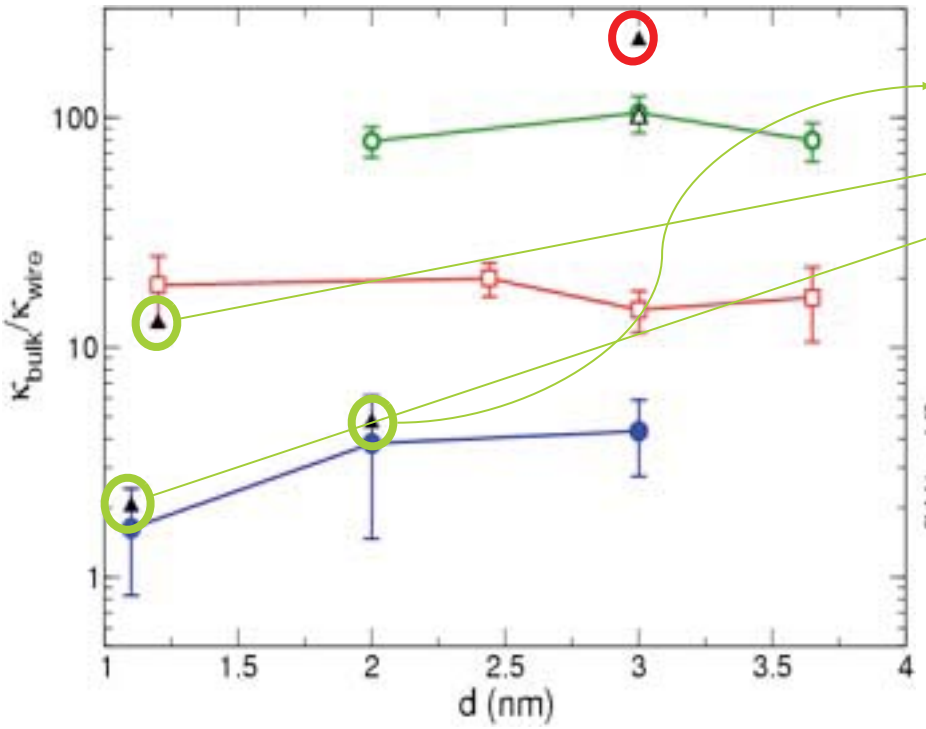
Dispersion curves and group velocities



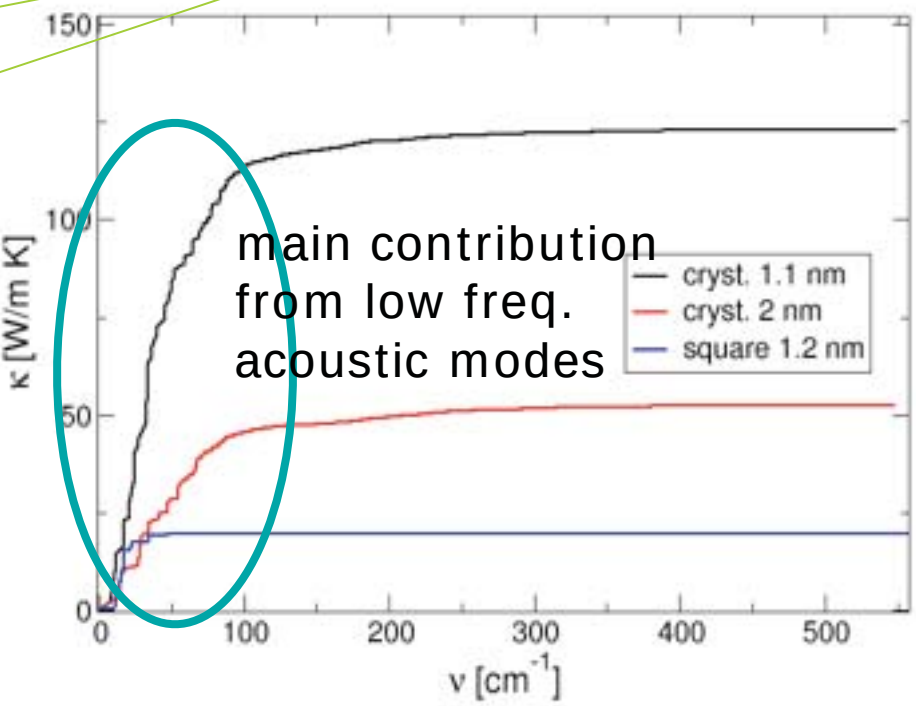
Group velocities vanish in the systems with surface disorder



Boltzmann Transport Equation: results



BTE reproduces MD results for crystalline systems



Allen-Feldman theory for heat transport in disordered systems

- Group velocities are ill-defined in amorphous systems
- Vibrational modes may be **propagating** (like phonons), **diffusive** or **localized**.
- Diffusive modes are heat carriers: they contribute to κ as:

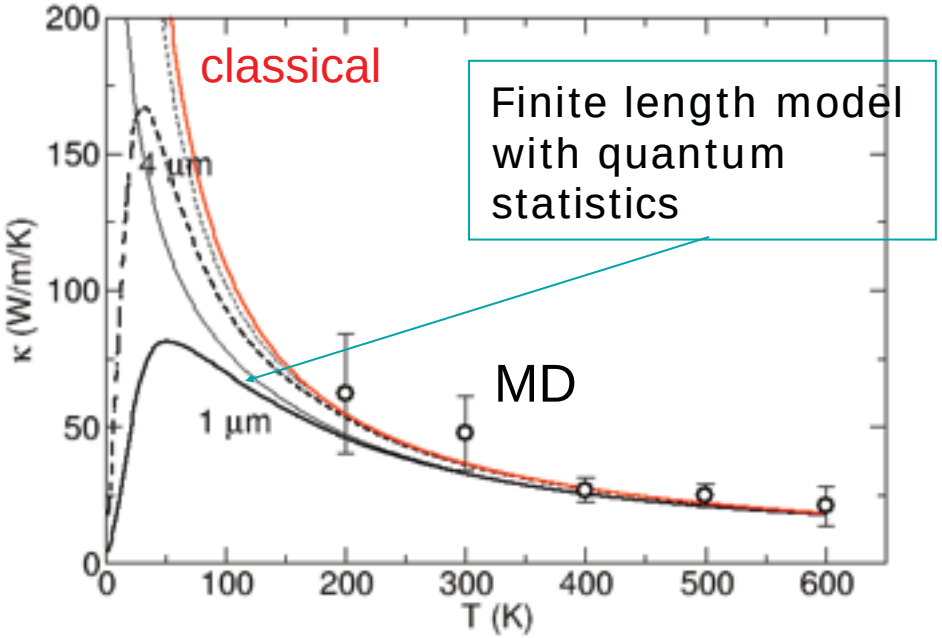
$$k_i = C_i D_i;$$

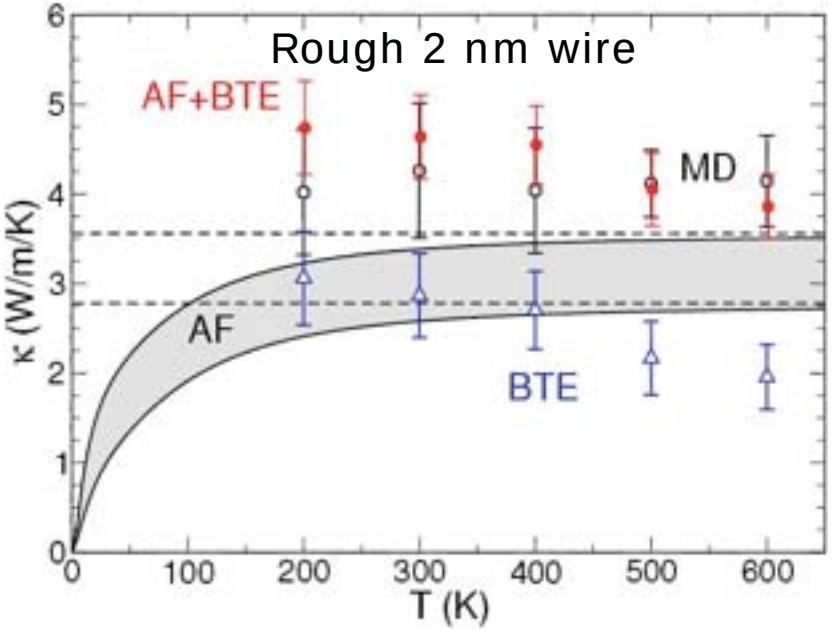
$$D_i = \frac{\pi V^2}{\hbar^2 \omega^2} \sum_{j \neq i} \left| \langle i | J_z | j \rangle \right|^2 \delta\left(\omega_i - \omega_j\right)$$

- Diffusive modes are treated within the harmonic approximation

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

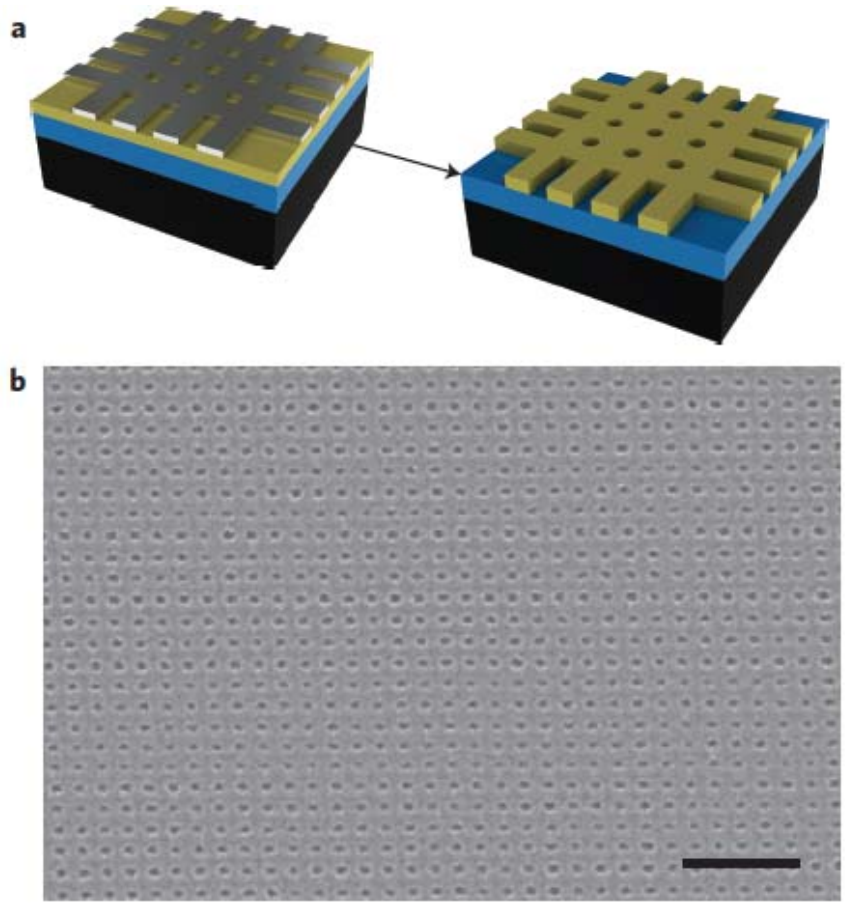
Comparison with transport equation





- Single phonon contribution to thermal conductivity: $\kappa_i(q) = C_i(q)\mathrm{v}_i^2(q)\tau_i(q)$
- The Boltzmann transport equation result has to be supplemented by extra terms accounting for “non-propagating” modes in core-shell wires
- “non-propagating” modes have zero group velocity but still contribute to heat transport by hopping mechanism

Nanomeshes & Nanoporous Silicon



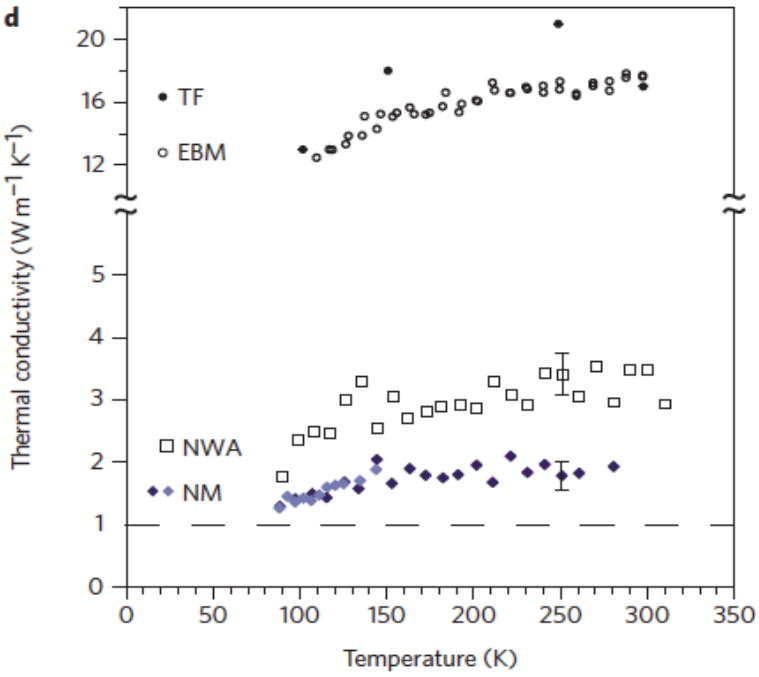
First theoretical predictions of low κ:

J-H. Lee, et al. APL (2007)

Fabrication and measurements:

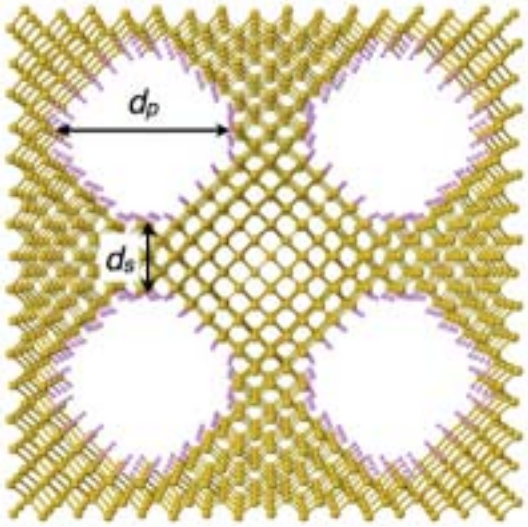
J.-K. Yu et al. Nature Nanotech. (2010)

J. Tang Nano Lett. (2010)

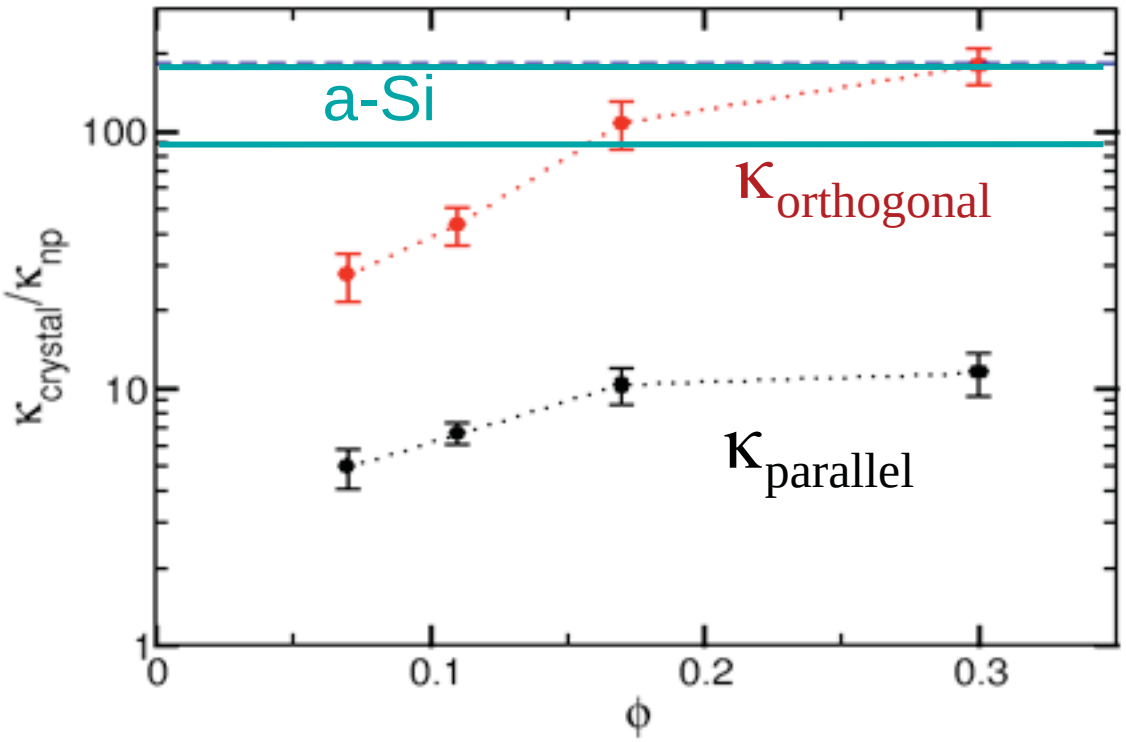


Nanoporous Silicon

A bulk nanostructured material



$$\phi = \frac{\pi d_p^2}{4\left(d_p + d_s\right)^2}$$

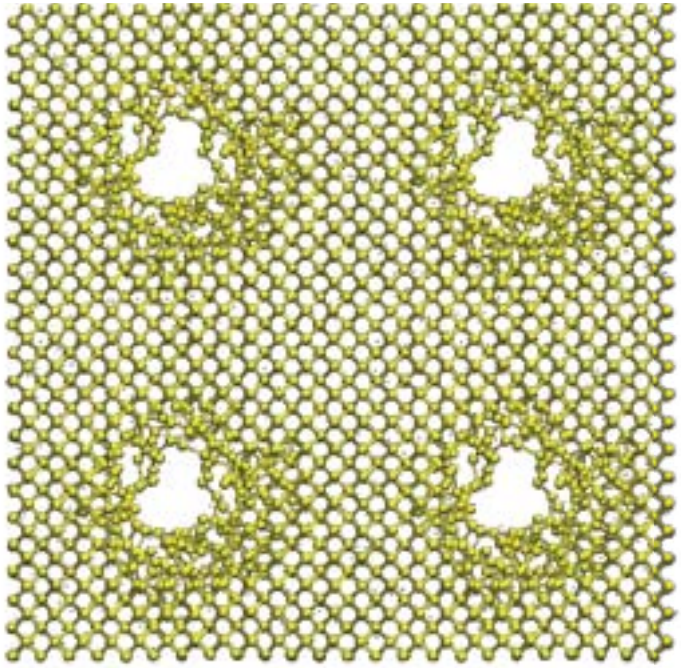


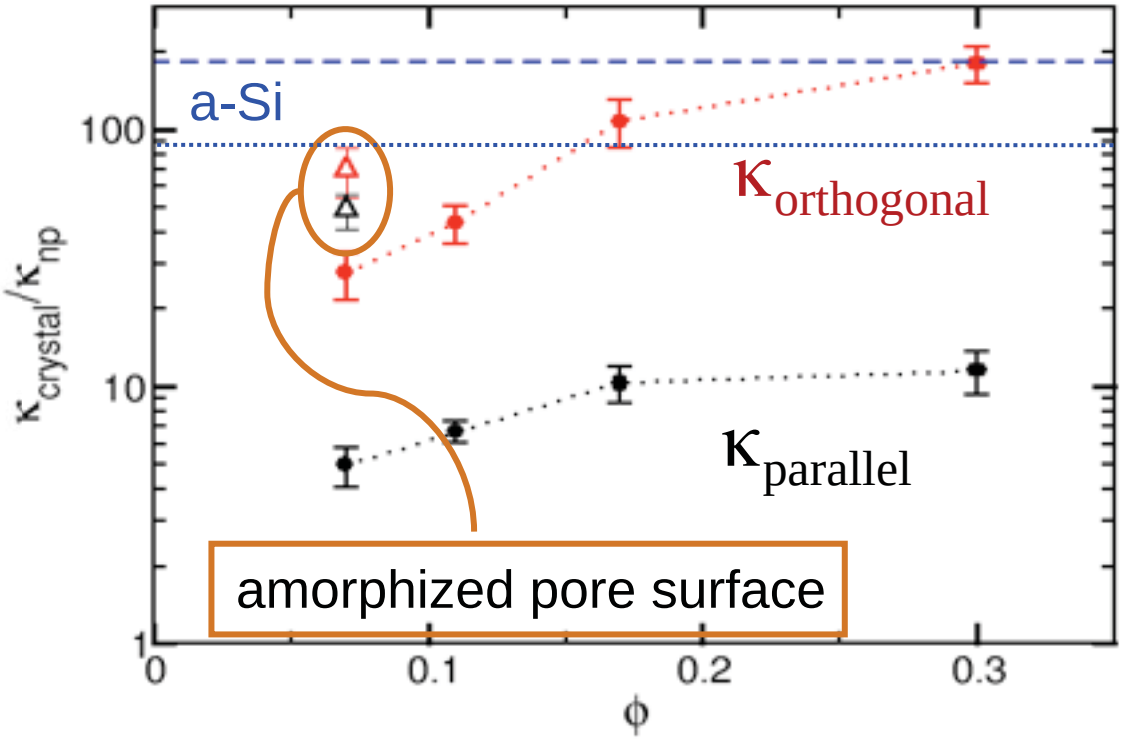
J-H. Lee, et al. APL (2007)
J-H. Lee, et al. NL (2008)
Y. He et al. ACS-Nano (2011)

Effective reduction of κ, well beyond the volume reduction

Nanoporous Silicon

Effect of surface roughening

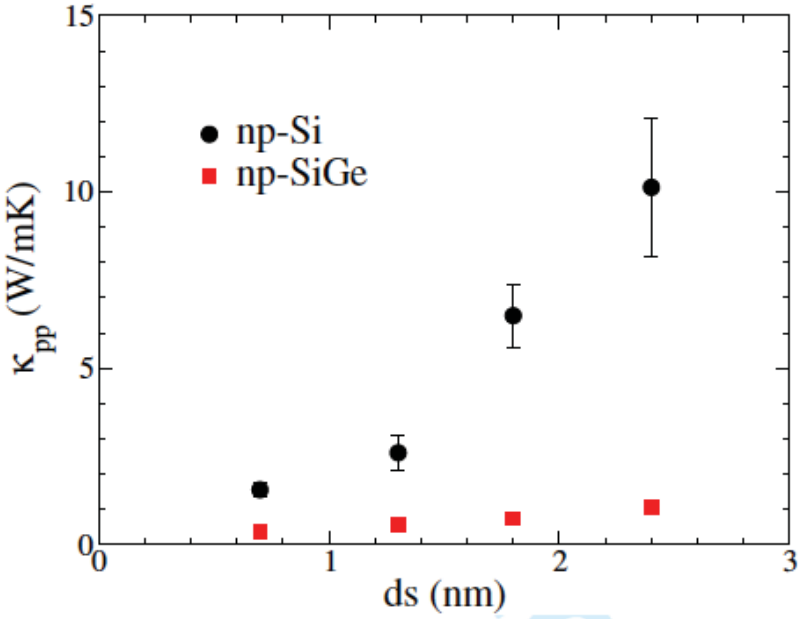




Surface amorphization significantly reduces thermal conductivity along the axis of the pores.

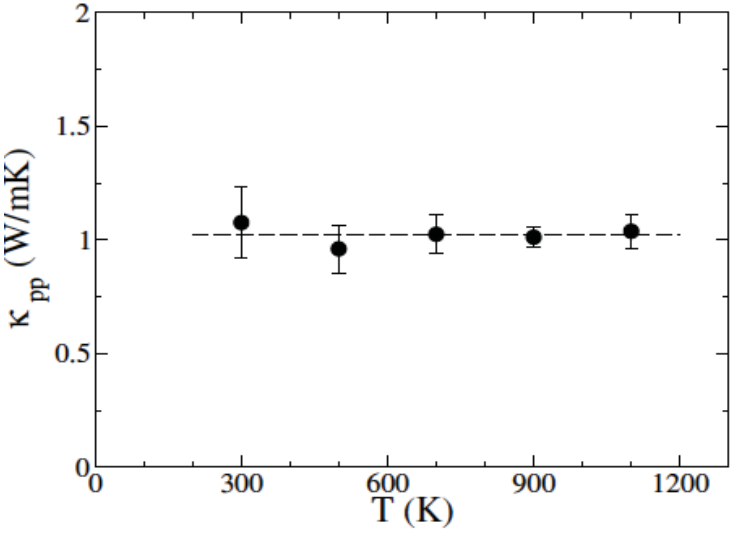
Y. He, DD, J-Y. Lee, J. Grossman, G. Galli ACS-Nano 2011

np-SiGe alloy



ϕ	ρ nm^{-1}	κ_{pp} W/mK	d_s nm	d_p nm
0.27	1.09	0.36±0.03	0.70	1.00
0.15	0.62	0.56±0.04	1.26	1.00
0.10	0.39	0.74±0.05	1.83	1.00
0.07	0.27	1.08±0.16	2.40	1.00
0.07(rough surfaces)	0.27	0.98±0.15	2.40	1.00
0.07	0.07	1.78±0.36	10.00	4.40
0.07(20nm film)	0.07	1.89±0.46	10.00	4.40

- Even lower κ
- Weak dependence on porosity, morphology and pore alignment
- No temperature dependence



Y. He, DD and G. Galli Nano Lett. (2011)

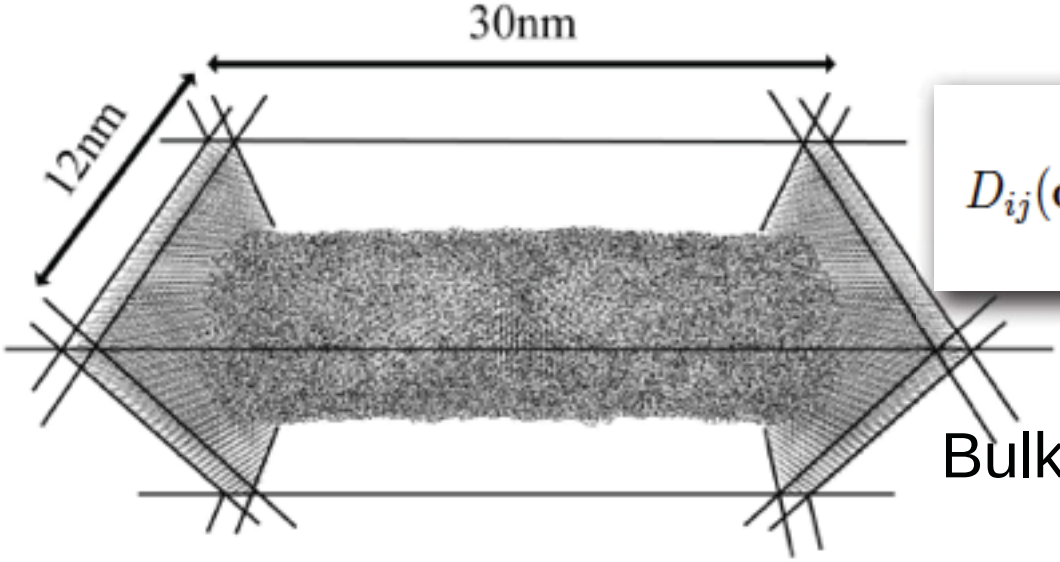
Summary on Si nanostructures

- Main contribution to κ in 1-D systems is provided by low frequency acoustic modes
- Crystalline NW have κ comparable to bulk
- κ can be reduced by 2 decades by surface amorphization
- The main reason for κ reduction is the transformation of propagating phonons into diffuse non-propagating vibrations: group velocities are significantly reduced
- Nanostructuring, alloying and dimensionality reduction (thin films) lead to extremely low k in nanoporous Si and SiGe

- DD and G. Galli, Phys. Rev. Lett. 102, 195801 (2009) SiNW
- DD and G. Galli Nano Lett 10, 847 (2010) SiNW
- MYK Chan et al. Phys. Rev. B 81, 174303 (2010) SiGe heterostructures
- Y. He, et al. ACS Nano 5, 1839 (2011) np-Si
- Y. He, DD, G. Galli Nano Lett. (2011) np-SiGe

Simulations of open systems
Silicon Nanowire-based devices

Open systems: scattering matrix approach



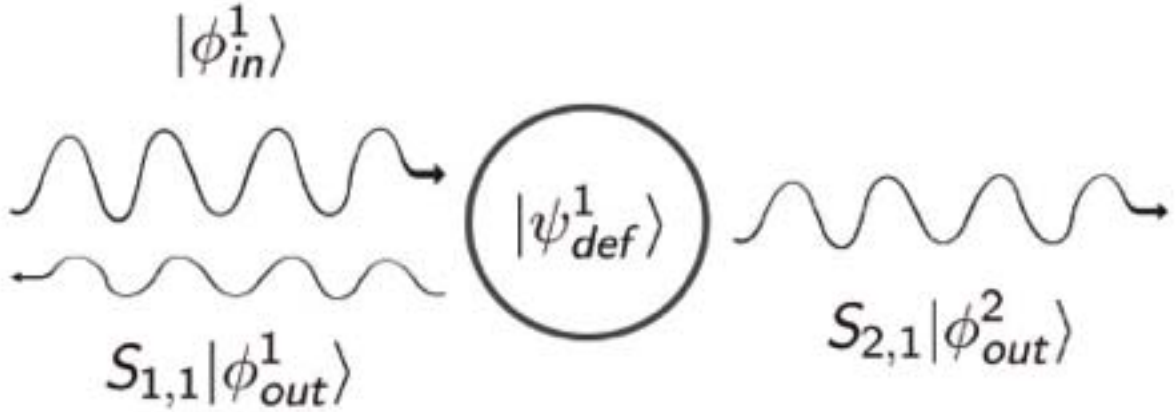
Bulk Si

$$D_{ij}(\mathbf{q}) = \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 V}{\partial x_i \partial x_j} \exp(i\mathbf{r}_{ij} \cdot \mathbf{q})$$

The energy flux between two parts A and B is expressed in terms of the scattering matrix: S

$$\Phi_{A\to B} = \int d\omega \frac{\hbar\omega}{2\pi} \sum_{i\in A} \sum_{j\in B} \left|S_{ij}(\omega)\right|^2 \left[f(\omega,T_A) - f(\omega,T_B)\right]$$

Scalable scattering approach: theory



- S is obtained by decomposing the eigenmodes of the system into the incoming and outgoing reservoir states:

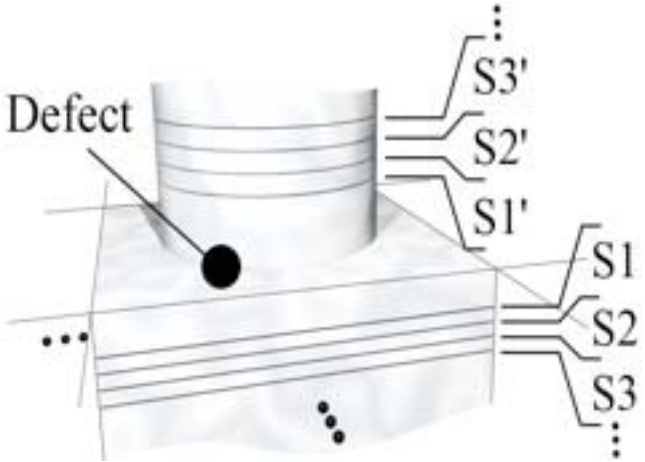
$$v_i(\omega) = |\phi^i_{in}(\omega)\rangle + \sum_j S_{j,i}|\phi^j_{out}(\omega)\rangle + |\psi^i_{def}(\omega)\rangle$$

- The transmission function is given by $\mathcal{T}(\omega)=\Sigma_i\Sigma_j S_{ij}(\omega)^2$

Scalable scattering approach: implementation

- The eigenvalue problem is equivalent to a kernel equation*

$$\mathbf{D}v = \omega^2 v \quad \Leftrightarrow \quad v \in \ker(\mathbf{D} - \omega^2)$$



- Partitioning and knitting algorithm:

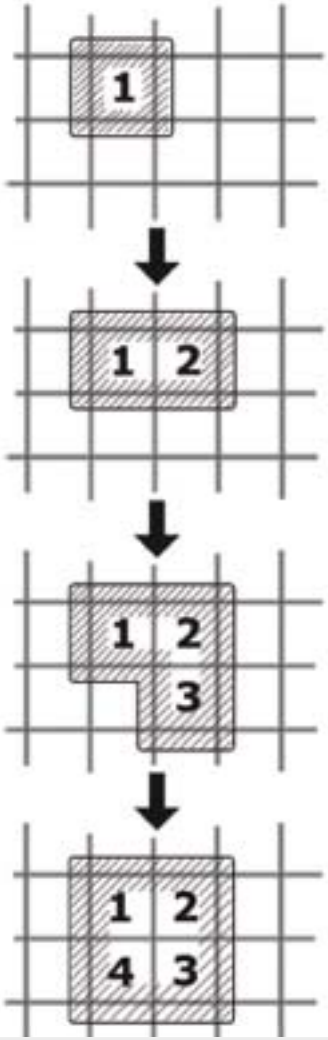
$$\{\mathbf{P}_i\} / \sum \mathbf{P}_i = \mathbb{I} \quad , \quad v \in \ker(\mathbf{D} - \omega^2) \Leftrightarrow v \in \bigcap \ker(\mathbf{P}(\mathbf{D} - \omega^2))$$

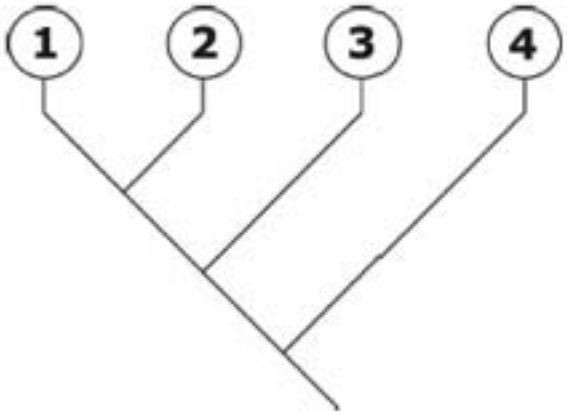
- The approach is equivalent to Green's Function
- The final outcome are transmission spectrum $\mathscr{T}(\omega)$ and conductance:

$$\sigma = \frac{\hbar}{2\pi} \int d\omega \mathscr{T}(\omega) \omega \frac{\partial f_{BE}}{\partial T}$$

* Note that frequencies are not quantized in an open system!

Knitting algorithm: serial reconstruction

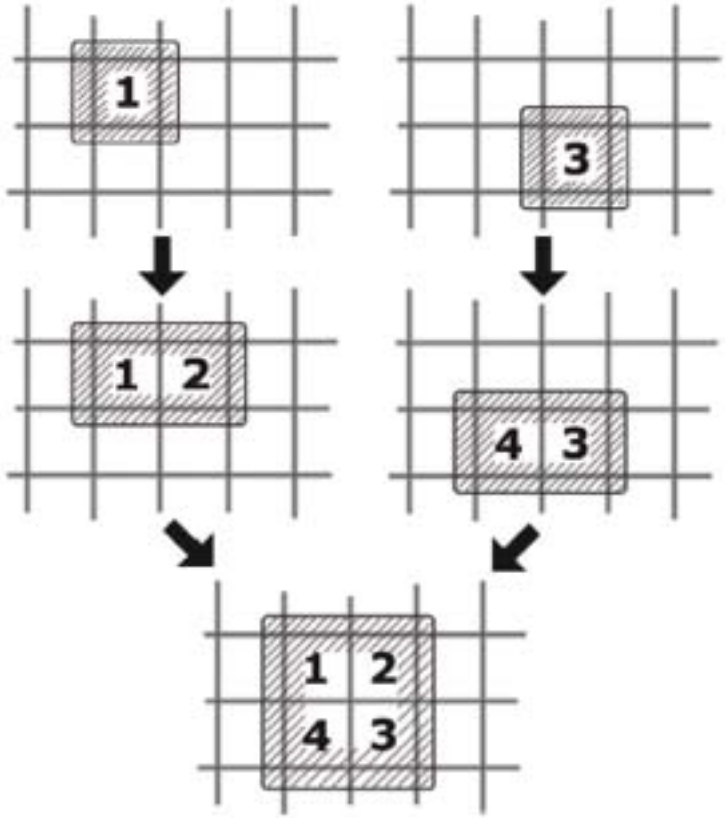


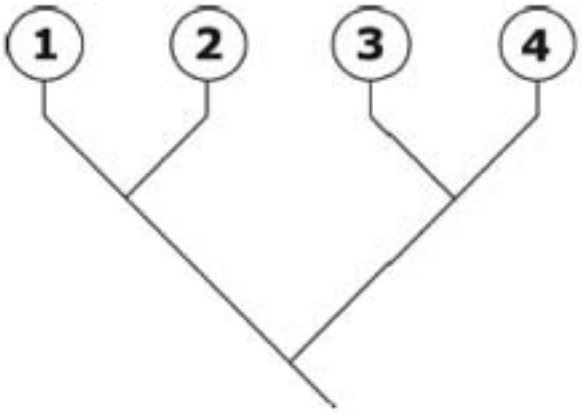


Serial reconstruction

- ▶ Start from a single seed
  - ↷ Solve neighbor kernel
  - ⇝ Intersect with solution
- ✓ Keeps memory needs low
- ⚠ Complexity is R^7

Knitting algorithm: parallel reconstruction

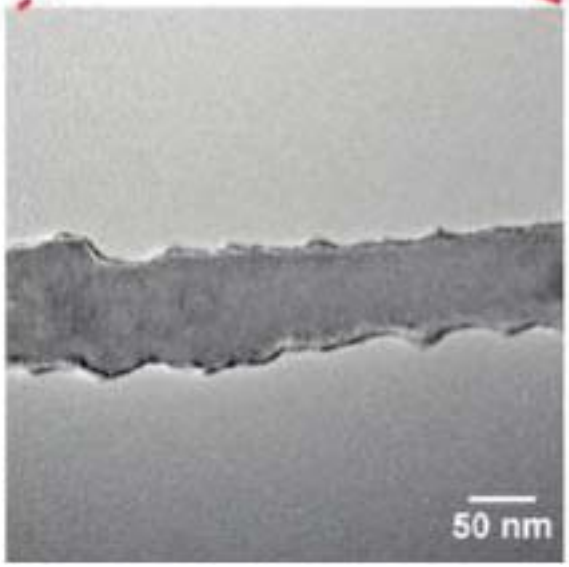




Parallel reconstruction

- ▶ Start with all kernels
  - ↻ Intersect neighboring solutions
- ✓ Complexity is R^6
- ⚠ High memory requirement

Bulk/wire monolithic coherent contacts

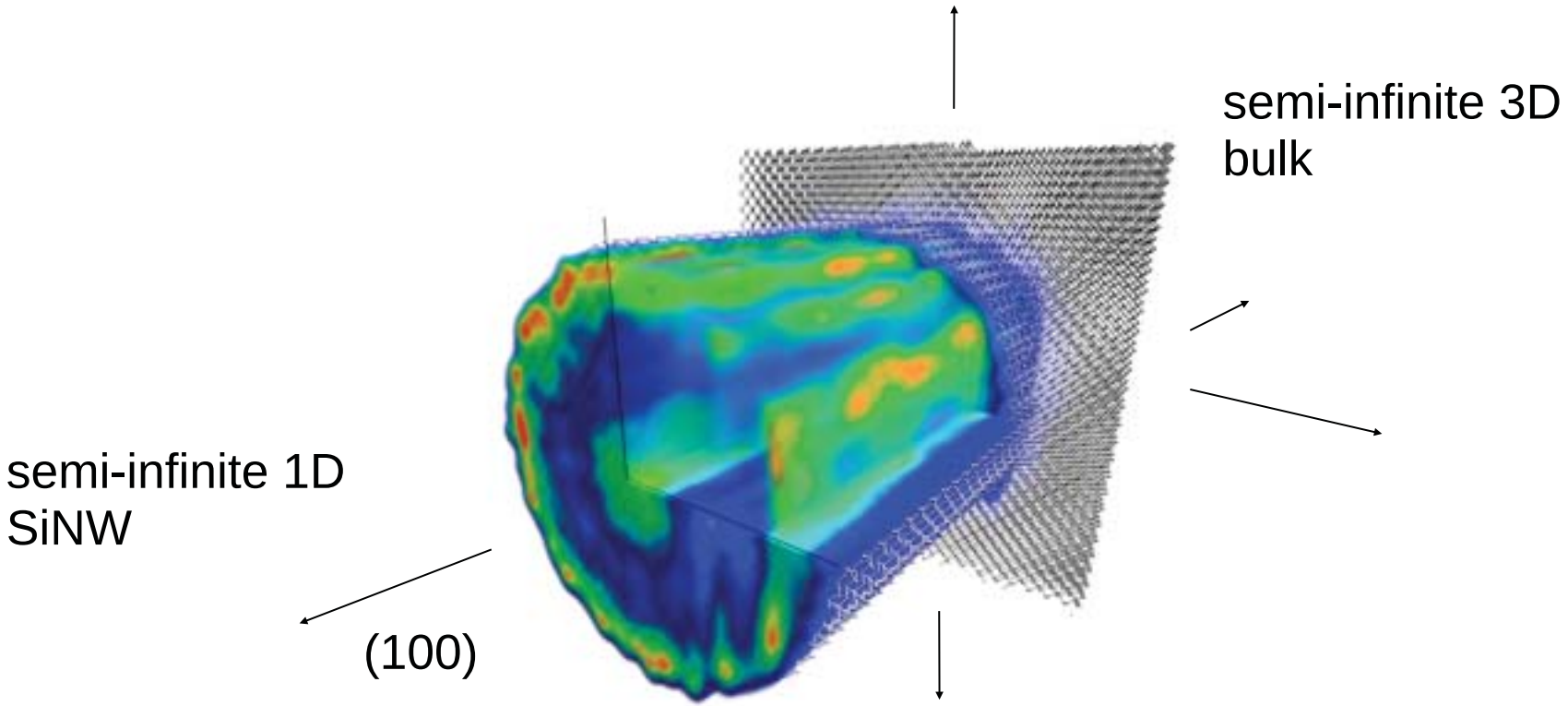


- Coherent contacts achieved by photolitography
- Critical thickness ~ 80 nm
- Length from 5 to 55 μm

- (almost) zero contact thermal resistance
- $\kappa \sim 20\ Wm^{-1}K^{-1}$
- $\kappa(T) \sim T^3$ at low T

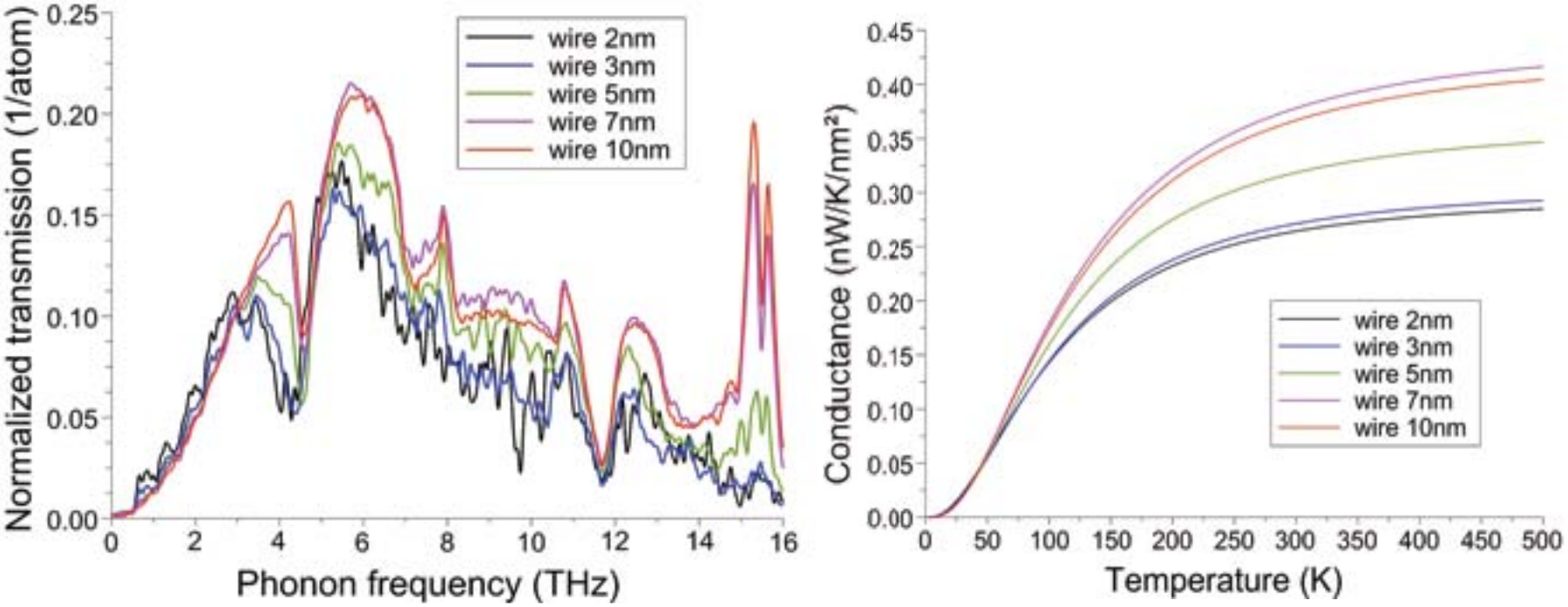
Hippalgaonkar et al. Nano Lett 10, 4341 (2010)

Model: bulk/SiNW contact



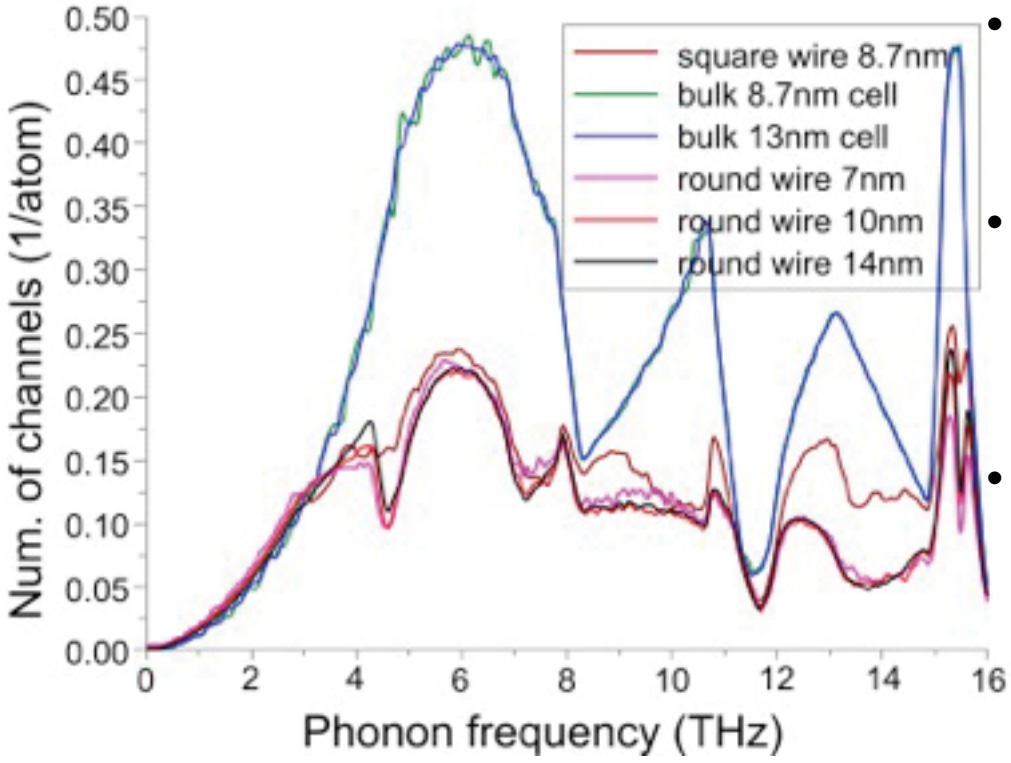
diameter from 2 to 14 nm

Transmission spectra and conductance



- Transmission and conductance scale with the wire section (number of atoms per slice).
- There are deviations from the trend for NWs with d<7 nm

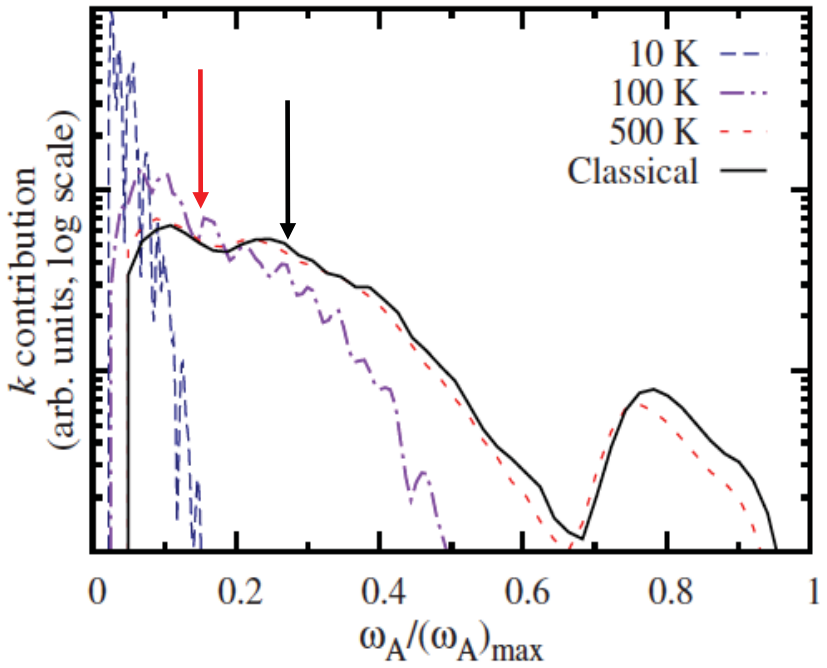
Shape and dimensionality

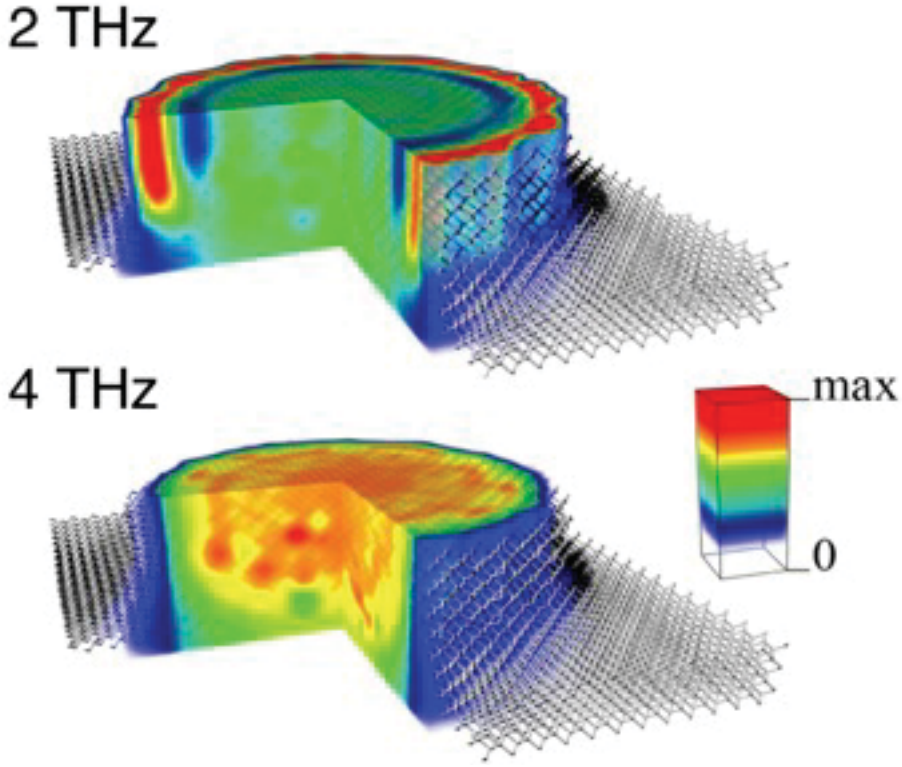


- Bulk convergence is achieved already at 8.7 nm
- The normalized spectrum never approaches the 3D bulk limit (dimensionality/periodicity effect)
- The shape of the normalized spectrum depends also on the shape

Crystal/nanowire interface

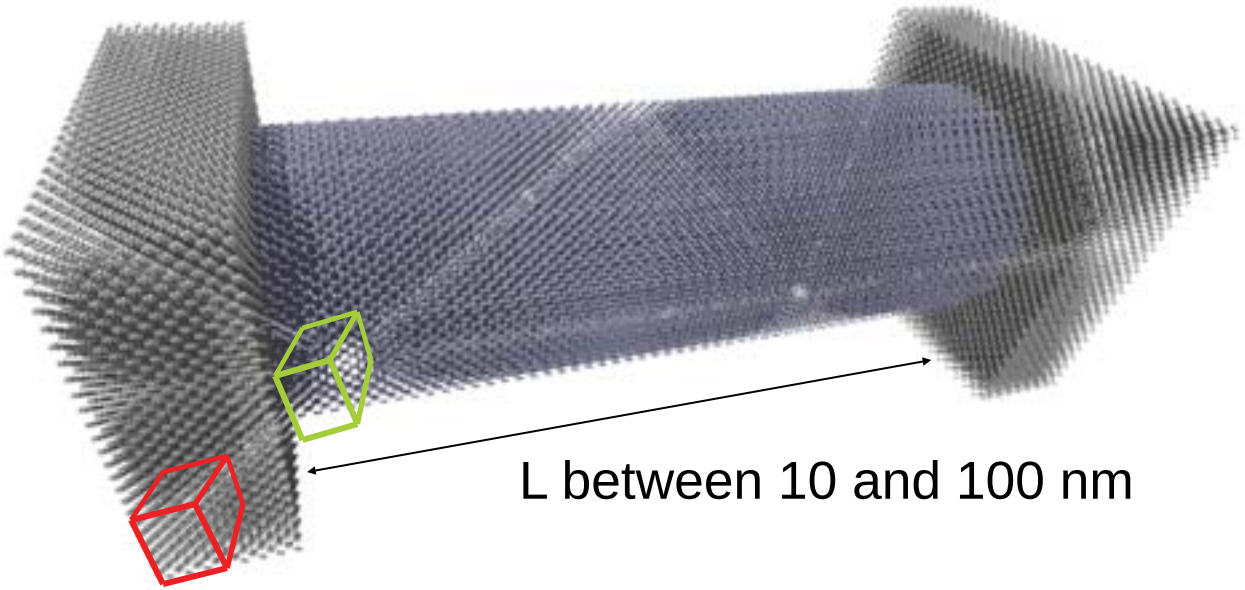
Real space evaluation of the heat flux for each channel





surface trasport vs core transport

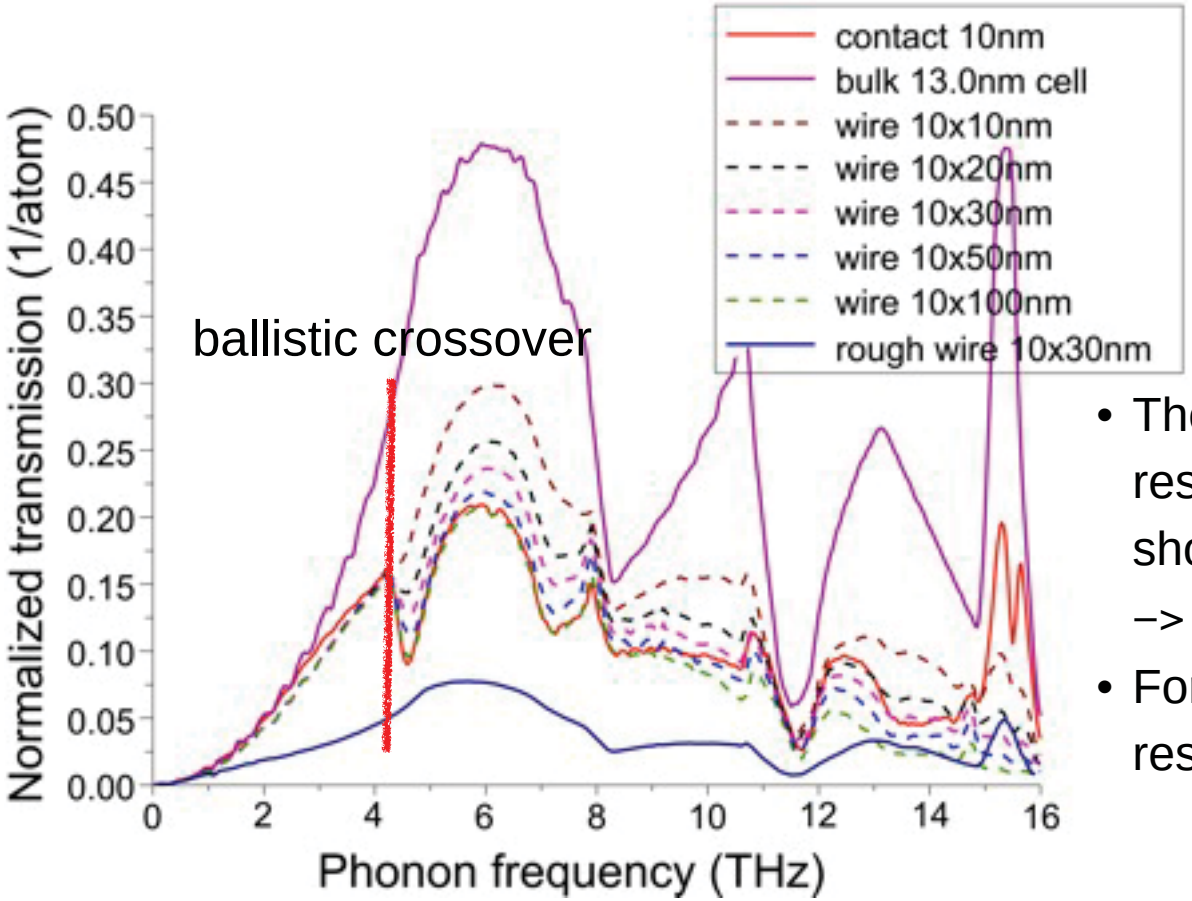
10 nm diameter wires between bulk leads



Very convenient to treat with our implementation:

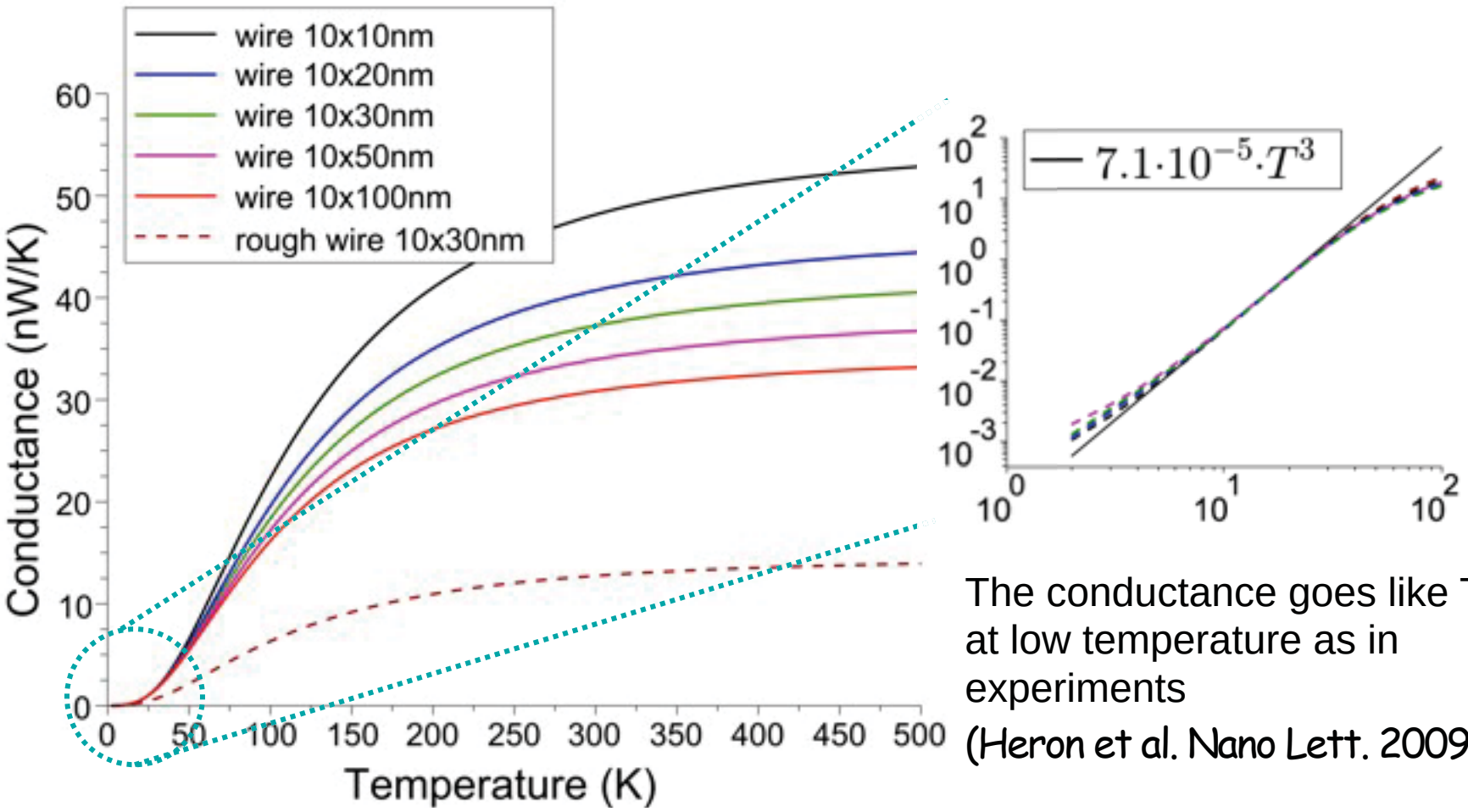
- semi-periodic leads can be represented by replicating unit-cell solutions
- the wire can be divided in boxes, finding the optimal performance between kernel equation and intersection

10 nm wire between bulk reservoirs



- The transmission spectrum resembles the bulk for very short wires
  –> phonon tunneling
- For longer wires contact resistance dominates

10 nm diameter wire between bulk leads

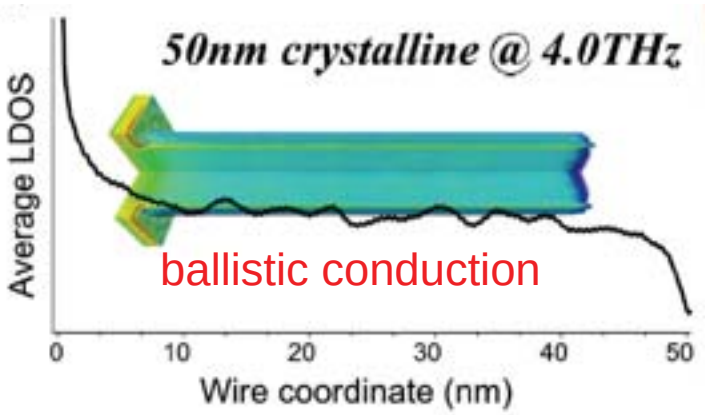


The conductance goes like T^3 at low temperature as in experiments

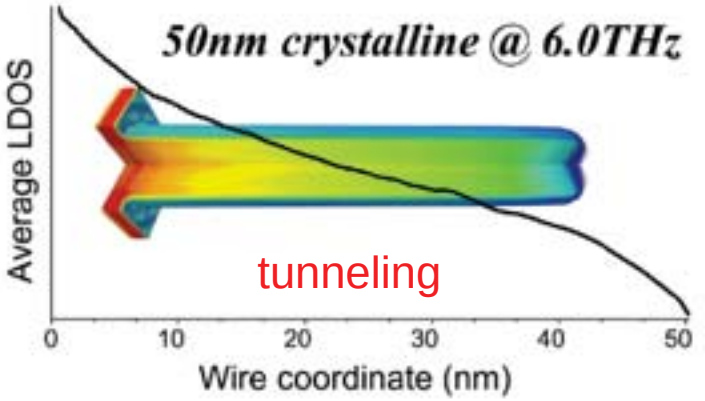
(Heron et al. Nano Lett. 2009)

Transport regime in crystalline wires

Local energy

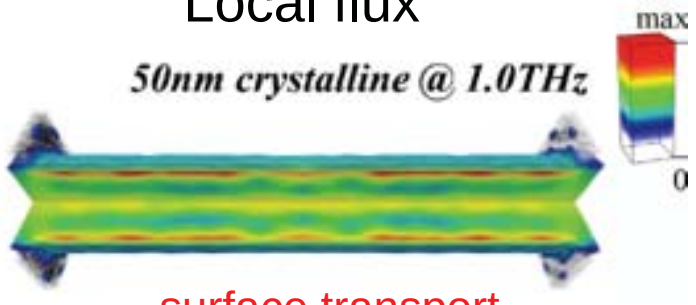


ballistic conduction



tunneling

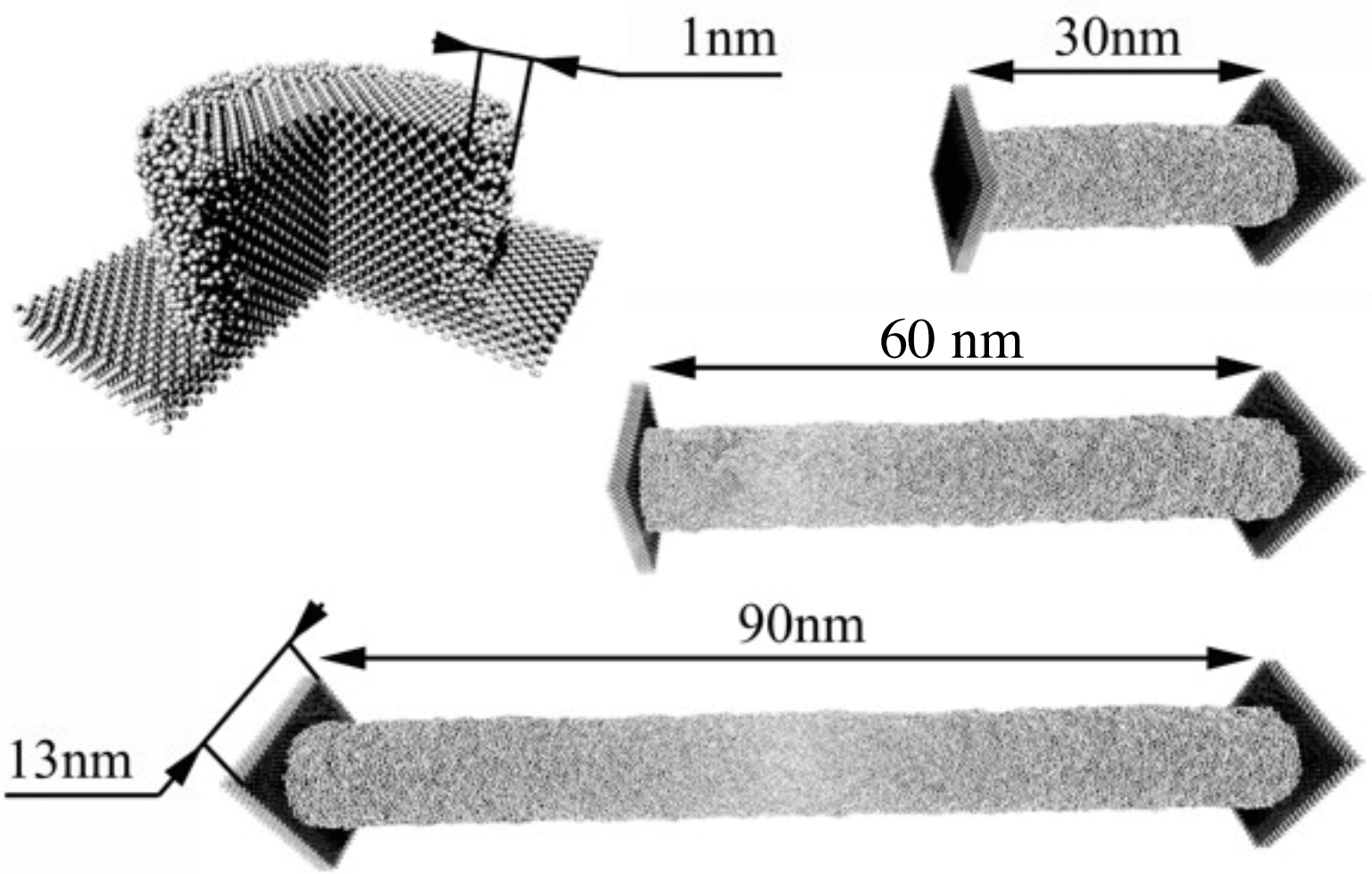
Local flux



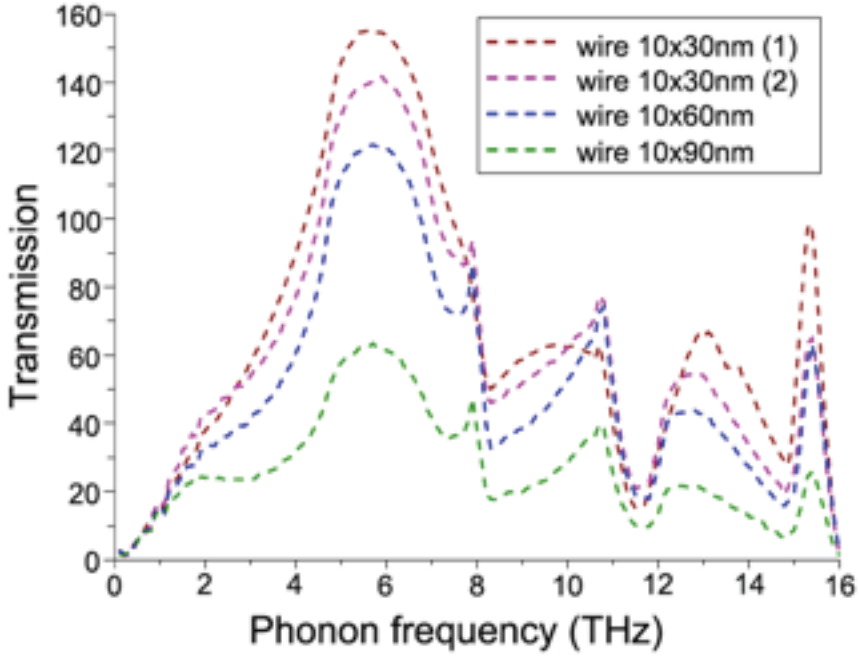
surface transport

bulk transport

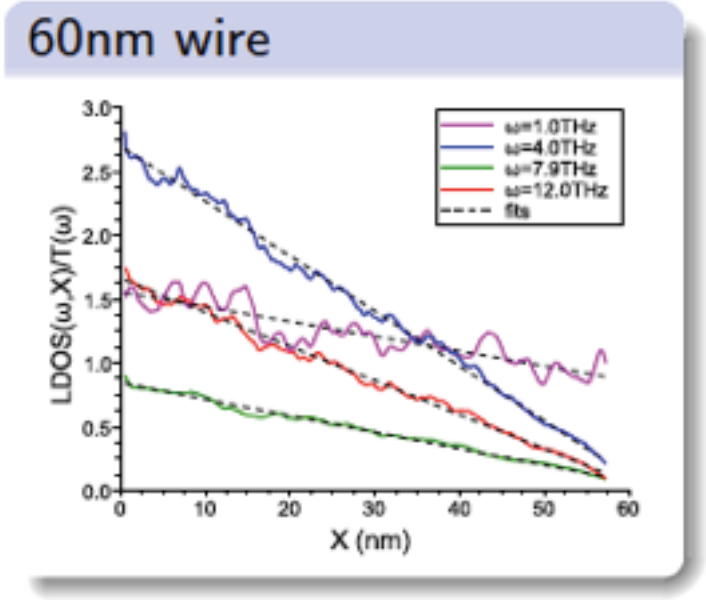
Rough wires

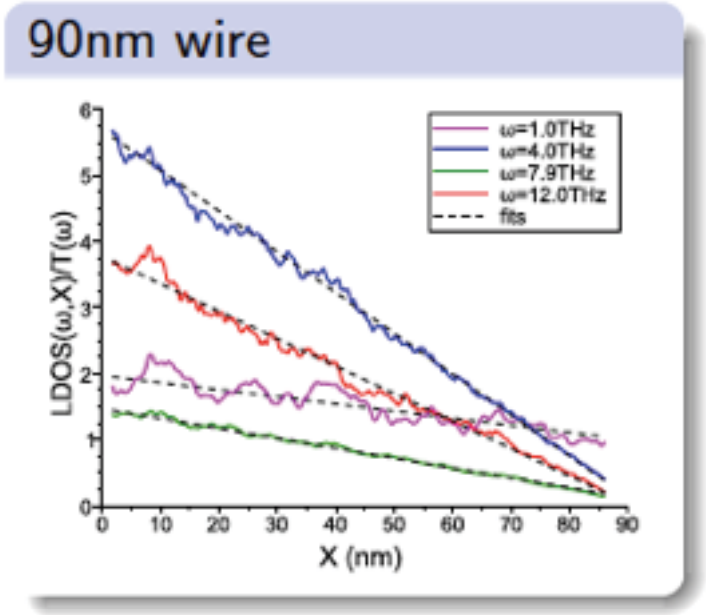


Transmission and attenuation



- The reduction of conductance is not as significant as in the infinite size limit of thin wires
- Rough wires act as a low frequency pass filter

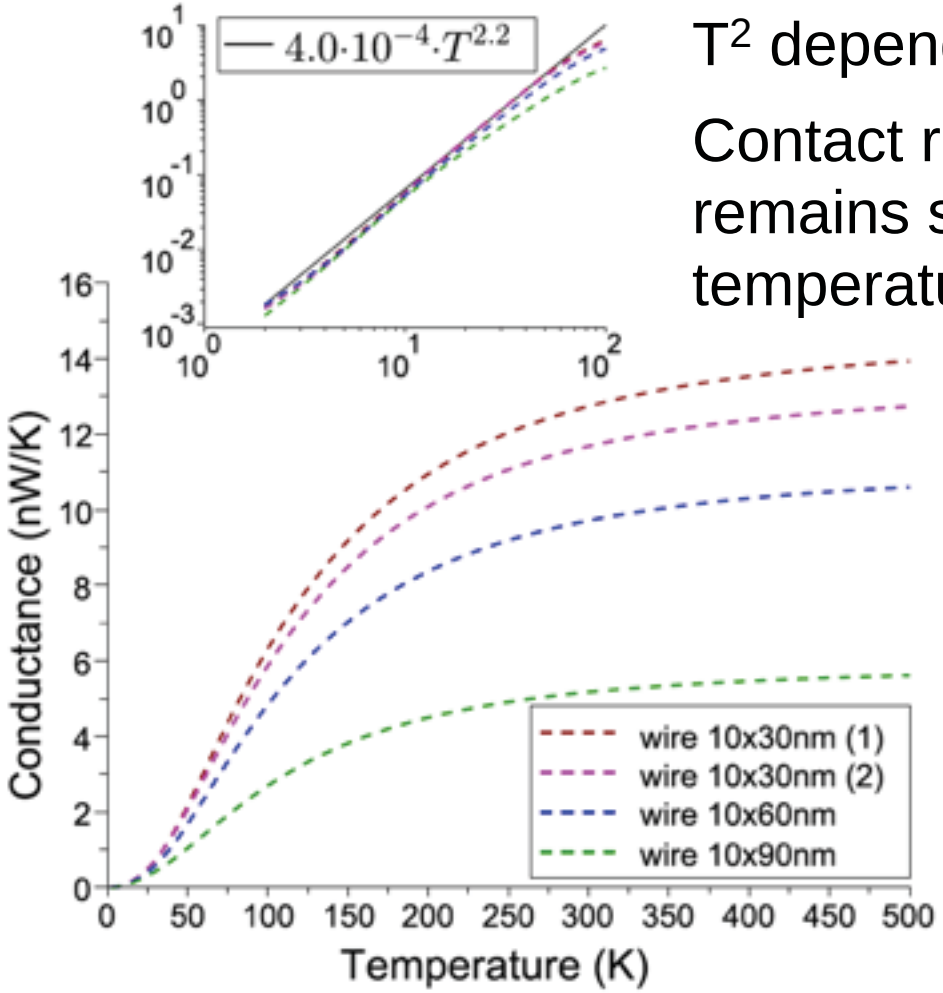


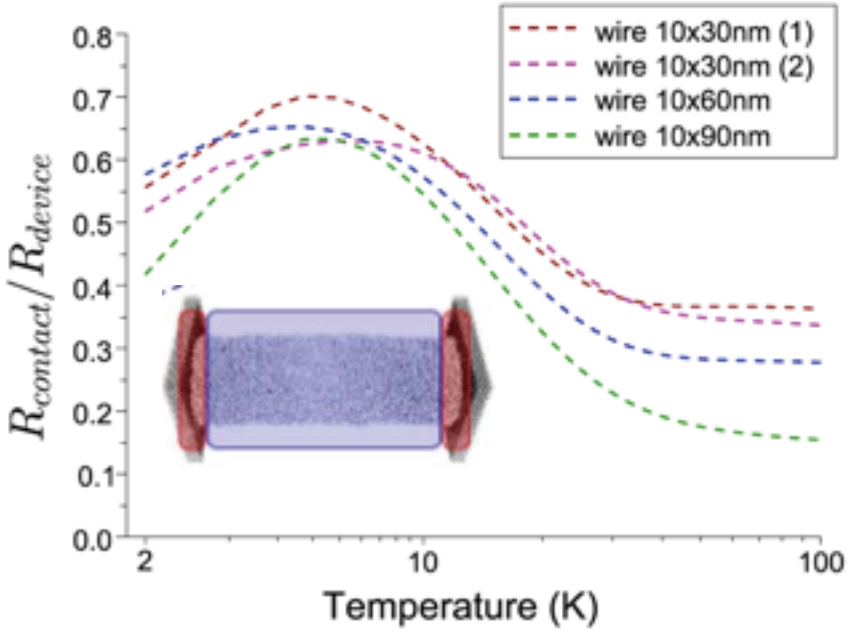


Contact and wire resistance

T^2 dependence at low T

Contact resistance rules at low T and remains significant at room temperature: e.g. ~30% in 90 nm wire





Summary

- Scattering matrix approach
  - numerically stable and scalable (at worst $O(N^{2.3})$)
  - efficient parallel implementation
  - direct space representation of energy and heat flux
  - open source project to be released

- Nanowire devices
  - calculation of the conductance of bulk/SiNW contacts
  - effects of dimensionality reduction and shape
  - phonon tunneling in short SiNW devices
  - Effect of surface roughness much smaller than in infinite thin SiNW

Systems and references

Silicon Nanowires	DD and G. Galli, Phys. Rev. Lett. 102, 195801 (2009) DD and G. Galli Nano Lett 10, 847 (2010)
SiGe alloys and heterostructures	MYK Chan et al. Phys. Rev. B 81, 174303 (2010) Y. He, DD, and G. Galli, Nano Lett. 11, (2011) I. Savic, DD, F. Gygi and G. Galli, submitted (2012)
Amorphous and nanoporous Silicon	Y. He, et al. ACS Nano 5, 1839 (2011) Y. He, DD, and G. Galli, Appl. Phys. Lett. (2011) G. Galli and DD, Nat. Nanotech. 5, 701 (2010)
Carbon nanotubes and graphene	DD and G. Galli, Phys. Rev. Lett. 99, 255502 (2007) L.F.C. Pereira and DD (2012)
Contact interfaces and SiNW devices	I. Duchemin and DD Phys, Rev. B 84, 115423 (2011) I. Duchemin and DD Appl. Phys. Lett. 100, 223107(2012)
Amorphous GeTe	G. Sosso et al. submitted (2012)