multiscale aspects of thermal transport

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Top-down approach: from Fourier ...

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

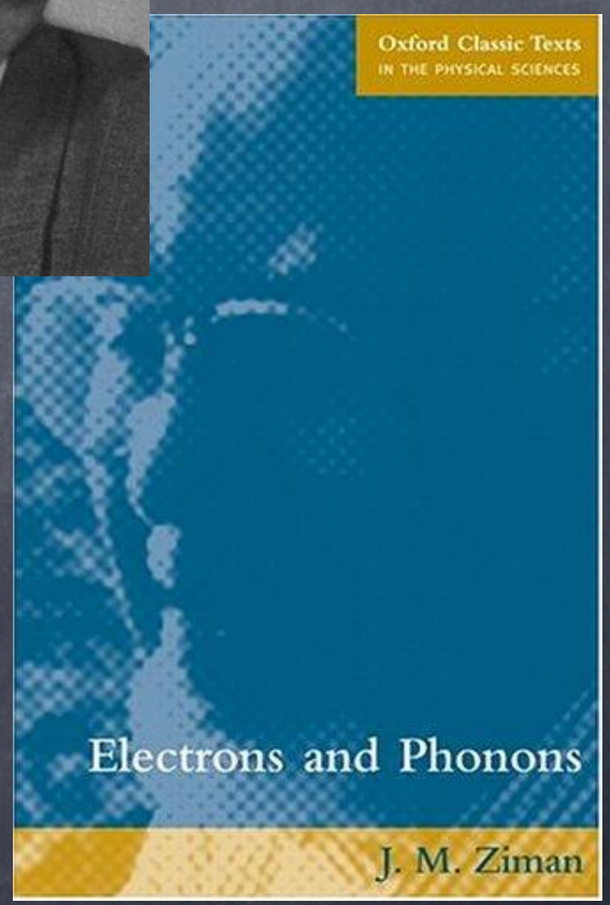
Steady-state condition: $\vec{J} = \kappa \vec{\nabla} T$

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



Boltzmann-Peierls equation for phonons

Transport equation

$$\frac{\partial n}{\partial t} + v\frac{\partial n}{\partial r} + \frac{F}{m}\frac{\partial n}{\partial t} = \left(\frac{\partial n}{\partial t}\right)_{collision}$$

Relaxation time approx.

$$\left(\frac{\partial n}{\partial t}\right)_{collision} = -\frac{n - n^0}{\tau}$$

stationary conditions

$$\vec{v}\cdot\vec{\nabla}n = -\frac{n - n^0}{\tau}$$

linearize

$$n = n^0 + \delta n \longrightarrow \delta n = -\tau\frac{\partial n^0}{\partial T}\vec{v}\cdot\vec{\nabla}T$$

Solution of the linearized Boltzmann-Peierls equation

the heat flux (power/area) is linked to δn:

$$\vec{J} = \sum_s \int_{BZ} d^3q \frac{\hbar\omega_s(q)}{8\pi^3} \delta n_s(q) \vec{v}_s(q)$$

using Fourier's law and $\delta n = -\tau \frac{\partial n^0}{\partial T} \vec{v} \cdot \vec{\nabla} T$

$$J_\alpha = \sum_s \int_{BZ} d^3q \frac{\hbar\omega_s(q)}{8\pi^3} \frac{\partial n_s^0(q)}{\partial T} \tau v_{s,\alpha}(q) v_{s,\beta}(q) \nabla_\beta T$$

$$\kappa_{\alpha\beta}$$

here we assumed that normal modes populations can be treated separately!

Solution of the Boltzmann-Peierls equation

- In a more human-readable and computer-practicable way:

$$\kappa_{\alpha\beta} = \sum_{s,q} C(s,q) v_\alpha v_\beta \tau$$

phonon mean free path λ

- more approximations on top:
  - single relaxation time
  - v: speed of sound

Collisions: where does λ (or τ) come from?

- Anharmonicity: phonon-phonon scattering (3-phonon processes are the lowest order)
- Defects
- Isotopic mass disorder
- Boundaries

$$\tau_b^{-1} = (\langle 1/c \rangle_b l F)^{-1},$$

$$\tau_a^{-1} = B T \omega^2 e^{-C/T},$$

$$\tau_i^{-1} = A \omega^4.$$

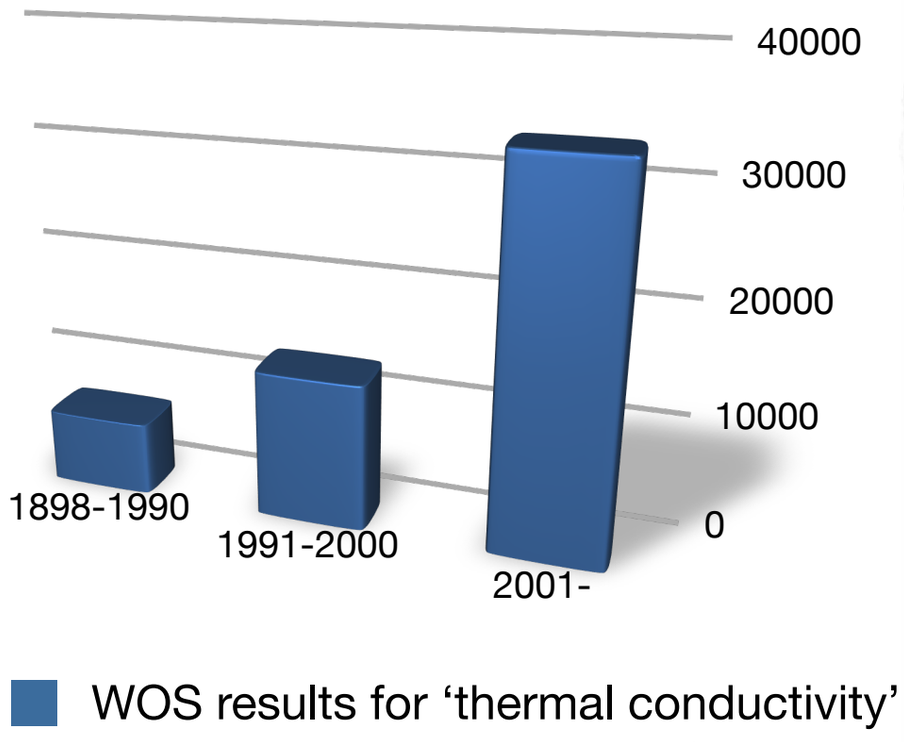
Simple models from BP: Callaway's model (1959)

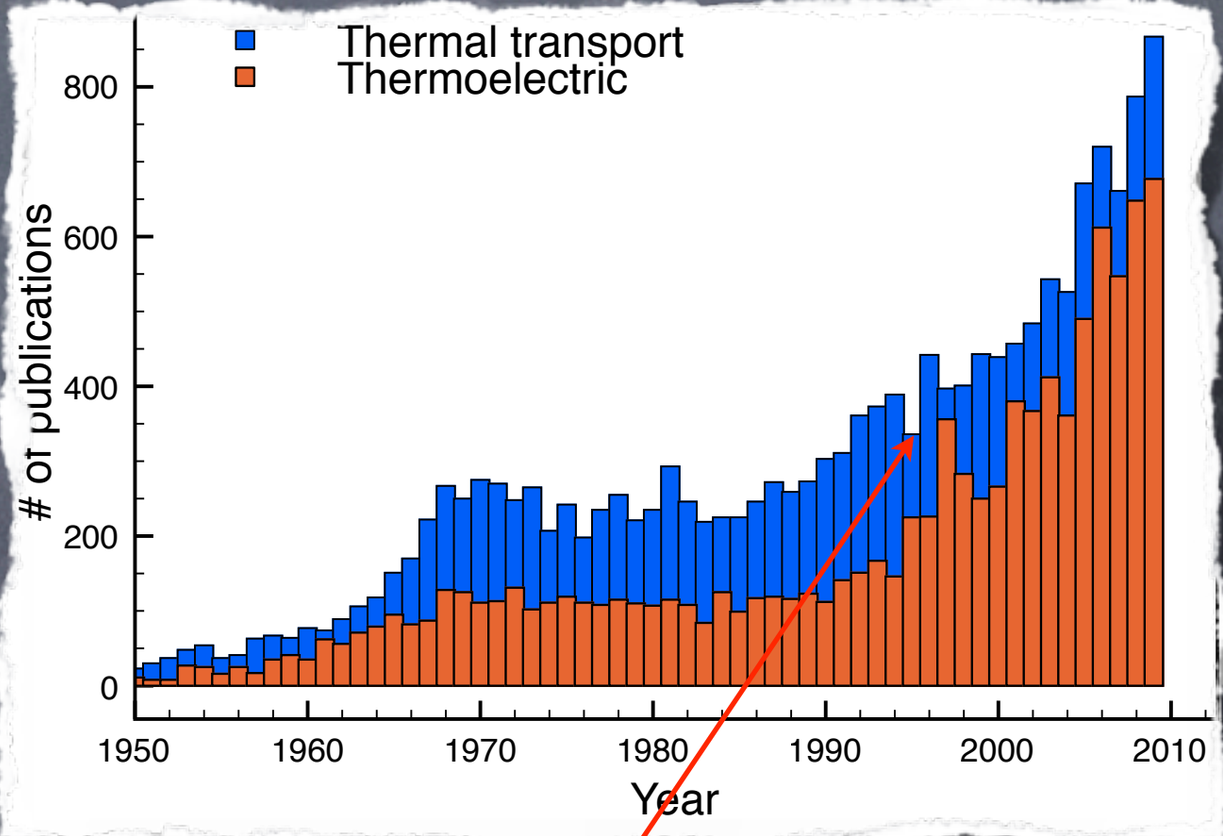
- Disregard distinct phonon branches
- Assume linear dispersion: $\omega = \bar{v}_g q$
- Effective lifetime τ^* and λ^*

$$\kappa(T) = \rho^{-2/3} \int_0^{\omega_D} d\omega \lambda^* \frac{\hbar\omega}{2\pi} \frac{\partial n}{\partial T}$$

- Refinements followed, but do not work for nanostructures (more parameters)

Thriving research activity in thermal transport





new (and nanostructured) thermoelectric materials

Atomistic methods: equilibrium MD

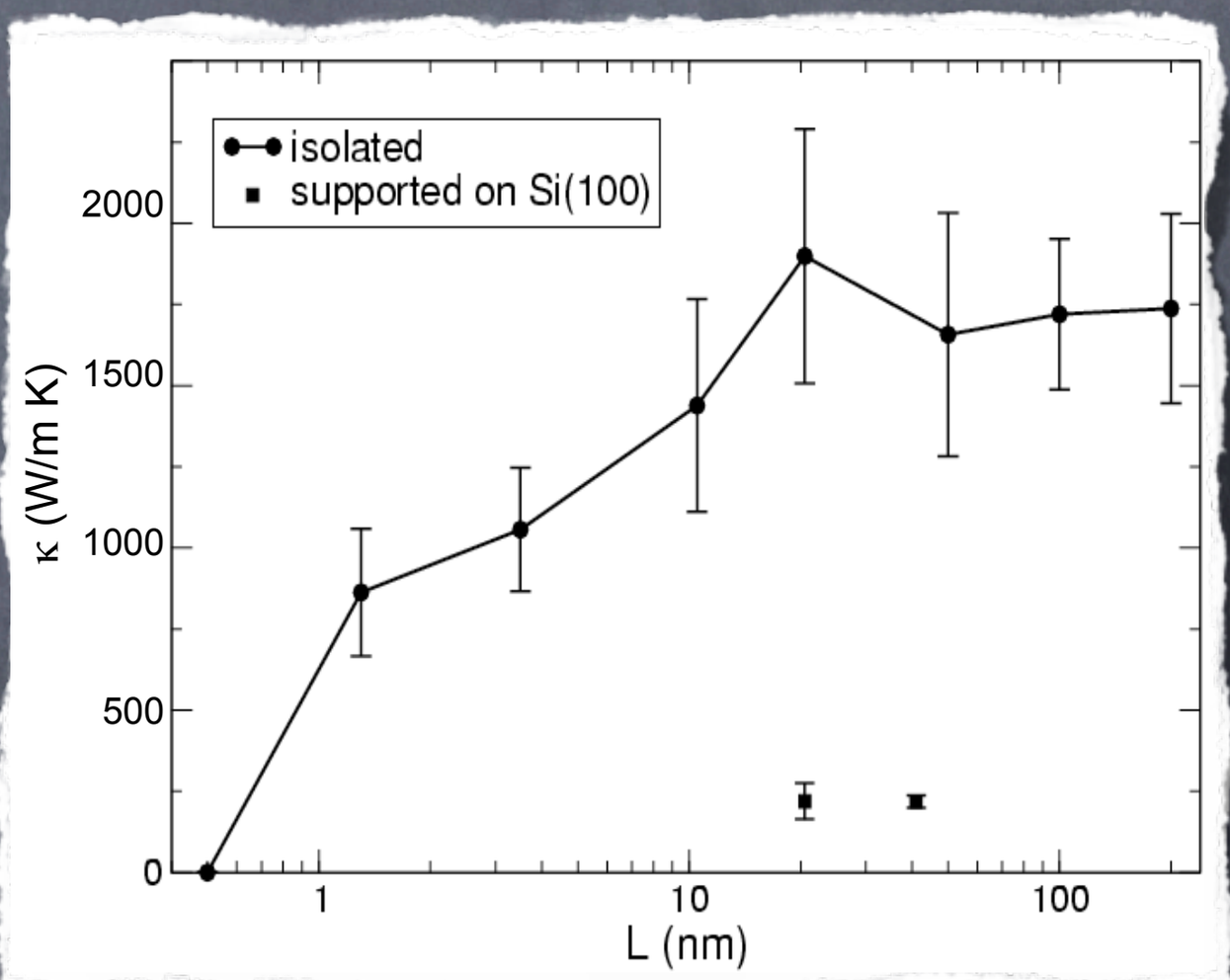
- The thermal conductivity is just another response function.
- Green-Kubo theory: $\kappa = \frac{1}{kT^2V}\int_0^\infty dt\langle J(o)J(t)\rangle$
- or Einstein relation:

$$\kappa_{\alpha\beta} = \frac{1}{k_B T^2}\lim_{t\to\infty}\lim_{V\to\infty}\frac{1}{2V}\frac{d}{dt}\langle[R_\alpha(t) - R_\beta(0)]^2\rangle$$

Size and time convergence require special care

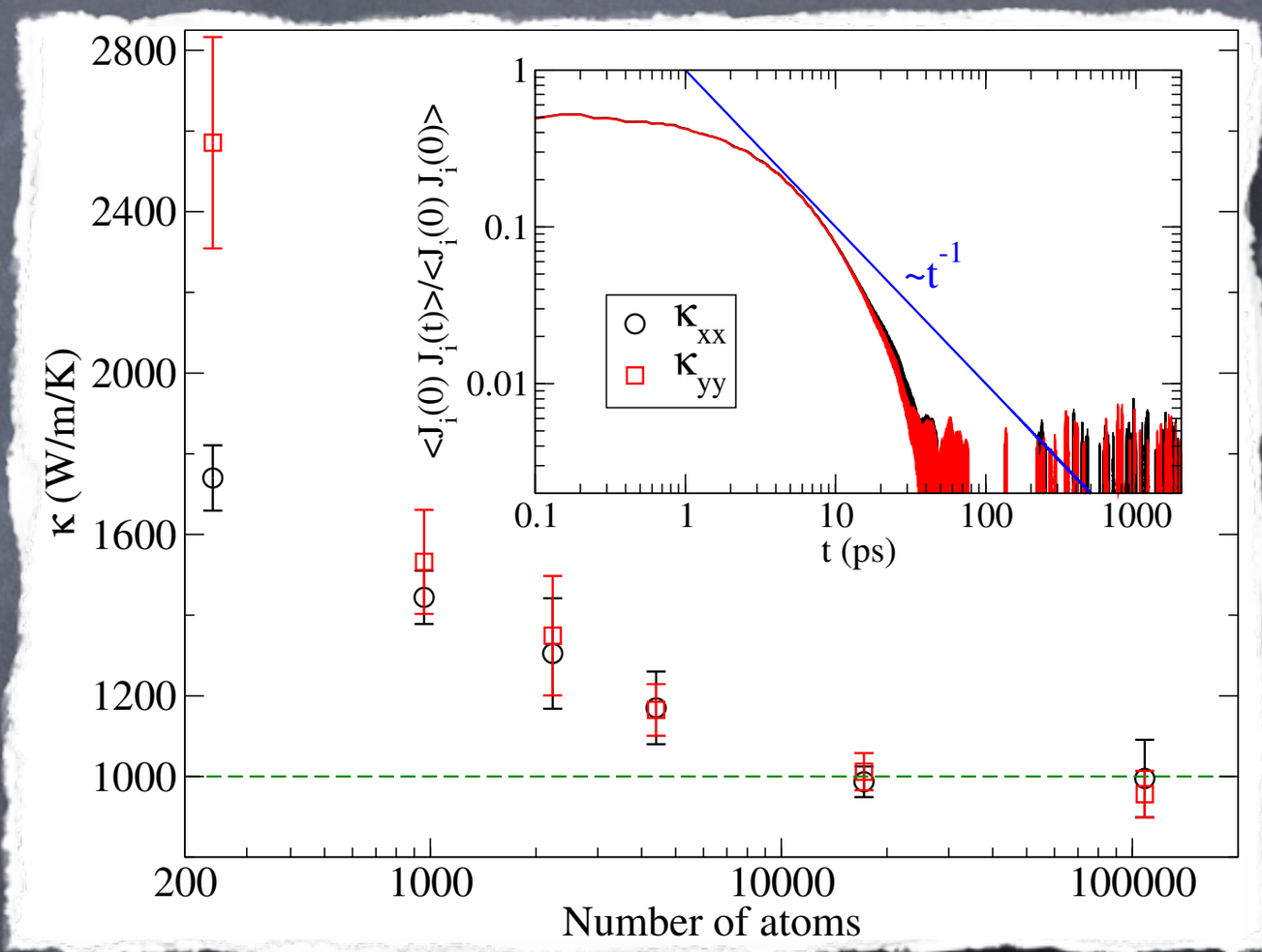
Size and time convergence: carbon nanotubes

- Several long (100 ns) runs are needed
- need to sample well low frequency modes, which contribute a lot



Size and time convergence: graphene

- k converges, unlike purely 2D and 1D models: flexural modes
- Convergence occurs from above: in general convergence is non-monotonic
- phonons are heat carriers but also scatterers



L.F. Pereira, DD (in preparation)

MD, lattice dynamics and the Boltzmann-Peierls equation

$$\kappa_{\alpha\beta} = \sum_{s,q} C(s,q) v_\alpha v_\beta \tau$$

Shopping list:

- Normal modes $\mathbf{e}_i$: diagonalization of the force constant matrix
- Group velocities: dispersion curves
- Phonon lifetimes: projection of a MD trajectory on the normal modes (all orders of anharmonicity)

Phonon lifetimes from MD

Green-Kubo formula for τ:

Energy of mode *i*:

Projection of the atomic displacements over the eigenmode e_i of the dynamical matrix

$$\lambda_i = v_i \tau_i \qquad v\text{: from dispersion curves}$$

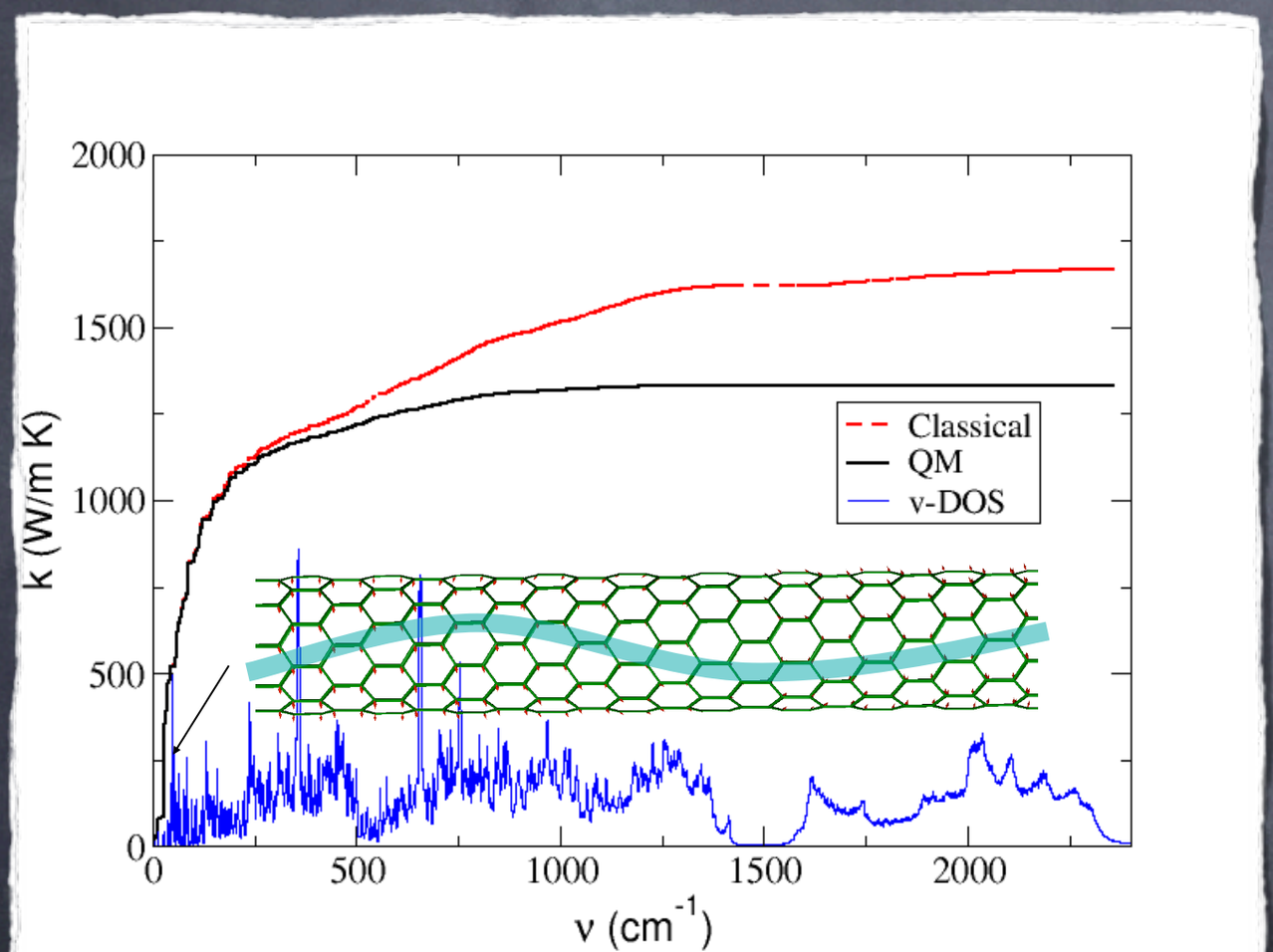
$$\tau_i = 2\int_0^\infty dt \left\langle E_i(0) E_i(t) \right\rangle$$

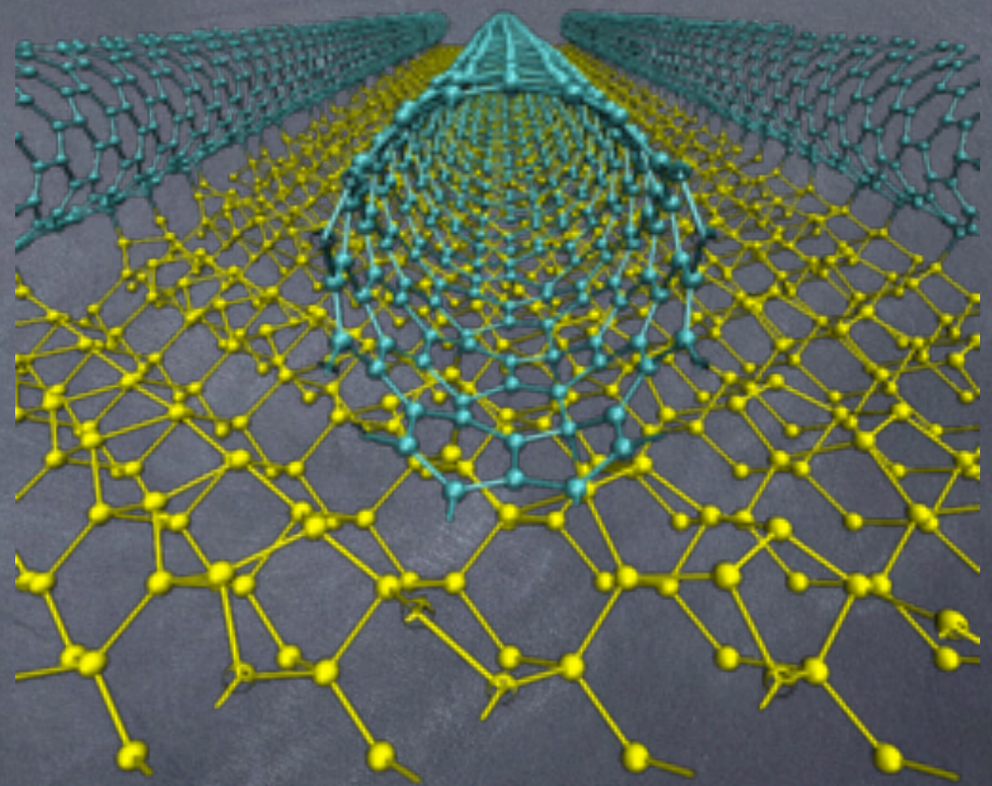
$$E_i = \frac{\omega_i^2 S_i^* S_i}{2} + \frac{\dot{S}^* \dot{S}}{2}$$

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

Ladd, Moran, Hoover Phys. Rev. B 34, 5058 (1986)
P. Chantrenne et al. J. Appl. Phys. 97, 104318 (2005)
A.J.H McGaughey et al. Phys. Rev. B 69, 094303 (2004)

Resolving contributions to k
-> customize heat transport





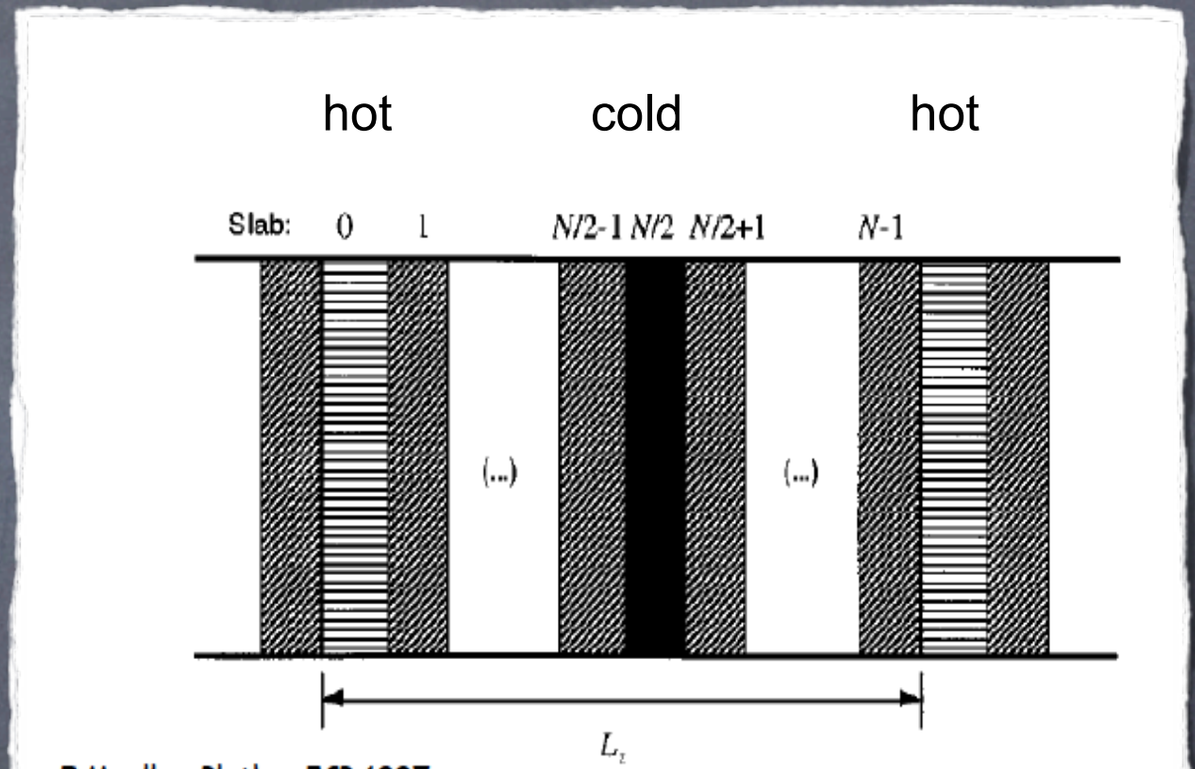
Suspended CNT: ~1600 W/m K
On a Si substrate: ~250 W/m K

DD & G. Galli PRL 99, 255502 (2007)

Non-Equilibrium MD

- Use Fourier's law
- Thermostats are applied to hot/cold temperature reservoirs
- Temperature gradients are computed at stationary non-equilibrium conditions
- Size scaling. Usually:

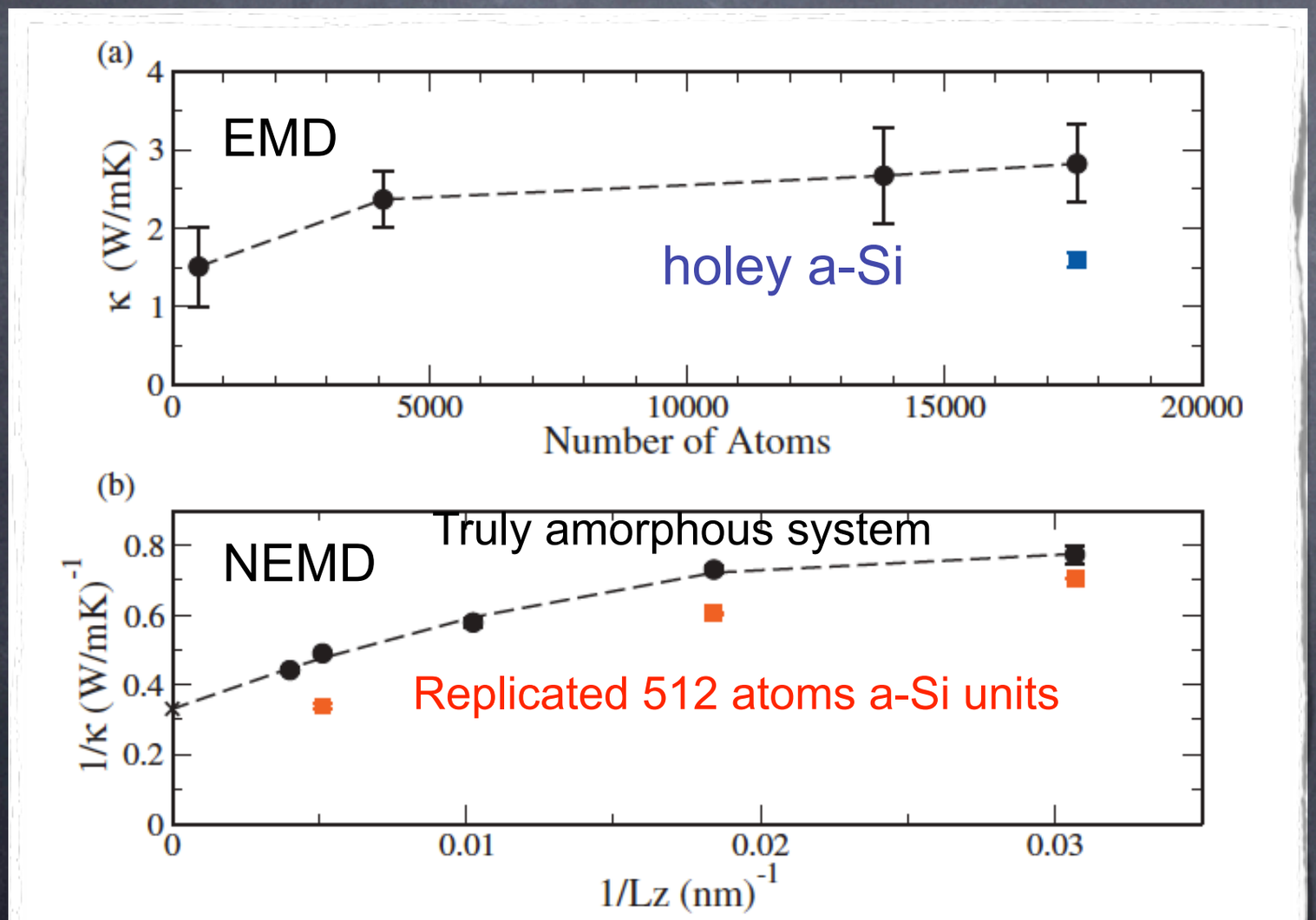
$$\frac{1}{\kappa_L} = \frac{1}{k} + \frac{A}{L}$$



F.Mueller-Plathe, JCP 1997

Comparing EMD and NEMD

Good news: sometimes they give the same result



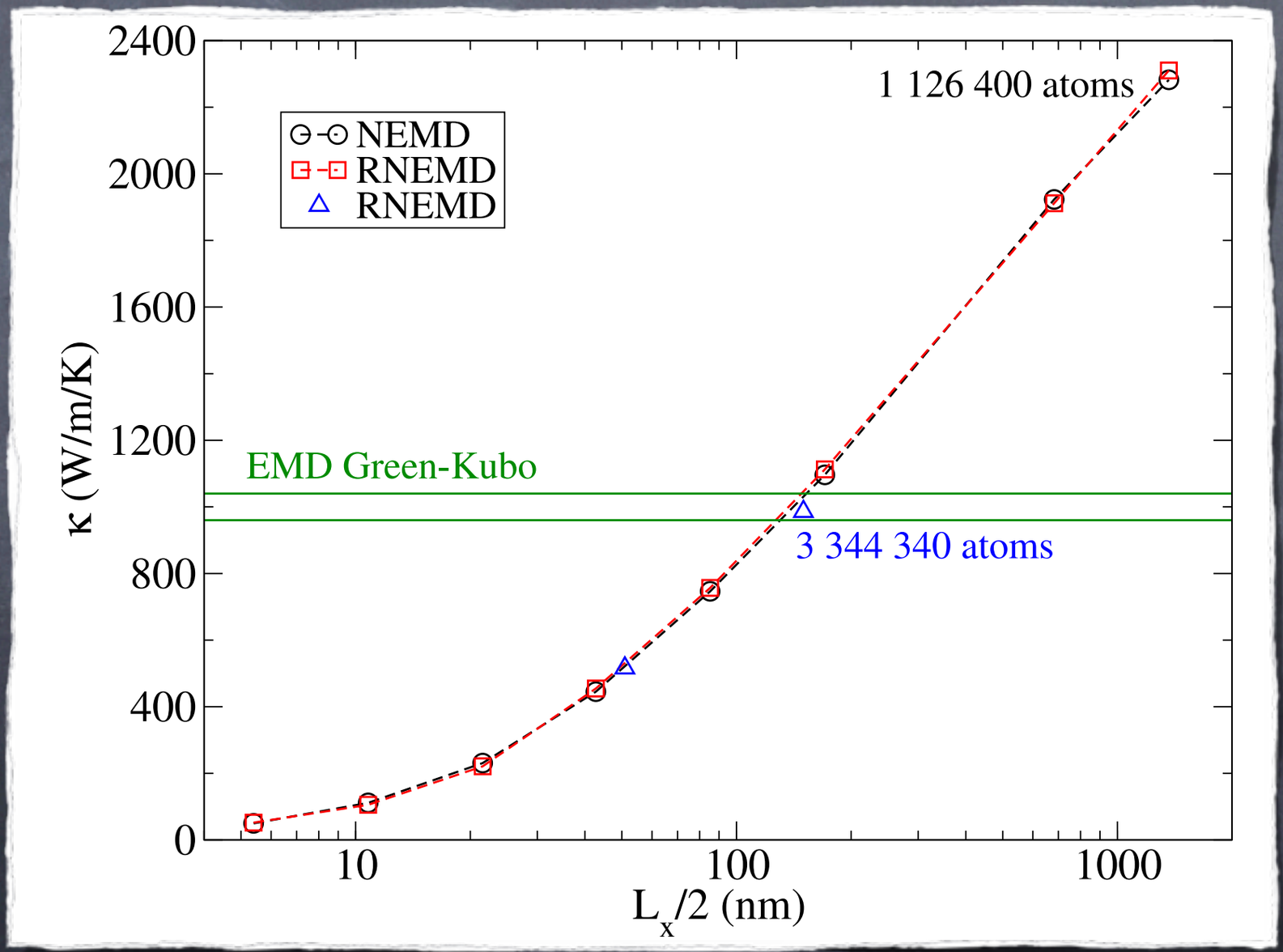
amorphous silicon

1/k is not linear with 1/L

Y. He, DD, G. Galli, APL (2011)

Comparing EMD and NEMD

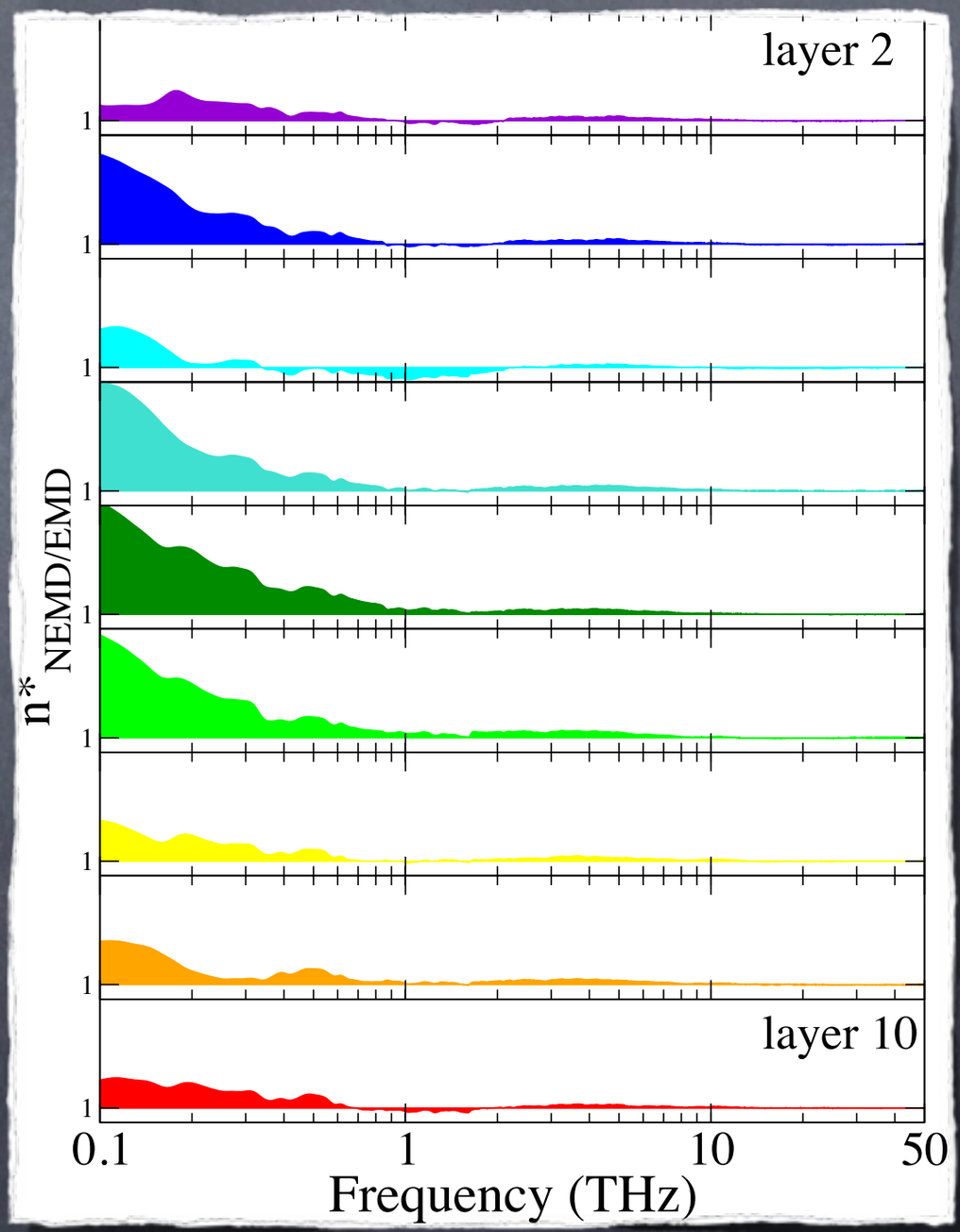
... but some other times they don't! (graphene)



L.F. Pereira, DD (in preparation)

(non)-Equilibrium phonon populations

- non-equilibrium phonon populations must be explicitly considered
- this would imply failure of the single-mode relaxation time approximation



(Dis)advantages of MD

- ✓ Full details, atomistic treatment
- ✓ Relatively large scales (million-atom systems)
- ✓ No truncation of anharmonicity
- ✓ Possibility to simulate systems out of equilibrium
- * No quantum effects (important at room temperature for Si, crucial for C)
- * Need for very accurate forcefields: so far the method cannot be implemented in a DFT framework

Other atomistic approaches

- ballistic transport by non-equilibrium Green's function or scattering theory (elastic scattering)
  - very good at low T, but no anharmonicity
- self-consistent solution of the Boltzmann-Peierls equation (limited to 3-phonon scattering)
  - extremely expensive, and fails at high T

Recent and future developments

- neural network approximation of DFT potentials
  - ✓ recently applied to phase-changing materials
- pushing the limit of the scattering matrix approach to million atom simulations
- hard-matter/soft-matter interfaces: model systems and realistic composite materials

Chances for multiscale modeling?

- Systematic application of DFT-quality neural network potentials
- How much can we learn from model systems?
- Energy transfer in biological systems (cell membranes)
- Quantum dynamics

Systems and references

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Amoprhous GeTe	G. Sosso et al. submitted (2012)

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