Introduction to phonon transport

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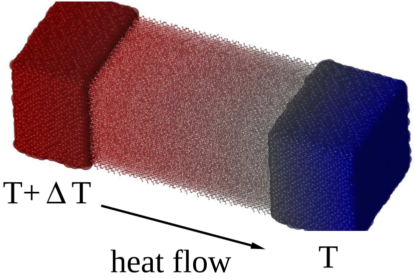
Outline

- Thermal transport and sustainable energy.
- Overview of atomistic approaches to study thermal transport in materials:
  - Boltzmann transport equation.
  - Non-equilibrium molecular dynamics.
  - Equilibrium molecular dynamics.
- Critical assessment of these approaches, recent developments and future challenges.
- Examples of their applications and insights gained from them.

Basic problem

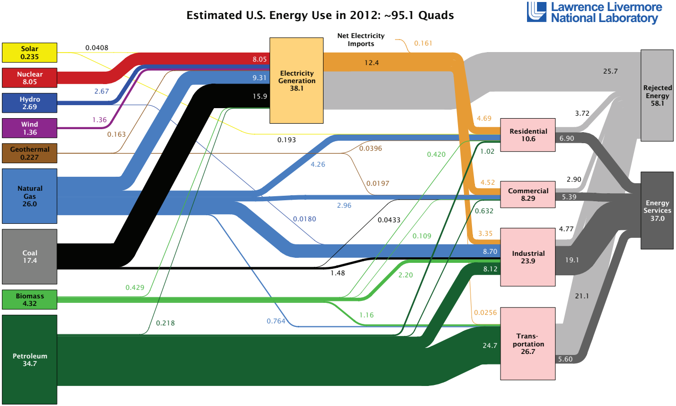
- How is energy (heat) transported in a semiconducting material due to the temperature gradient?



- Fourier law: $\mathbf{J} = -\kappa \nabla T$; $\mathbf{J}$ - heat current, κ - thermal conductivity.
- $\kappa = \kappa_{\text{lattice}} + \kappa_{\text{electronic}} + \kappa_{\text{radiative}}$.
- $\kappa \approx \kappa_{\text{lattice}}$ in semiconductors.

Why do we study thermal transport in semiconductors?

- Sustainable energy: convert waste heat into electricity.

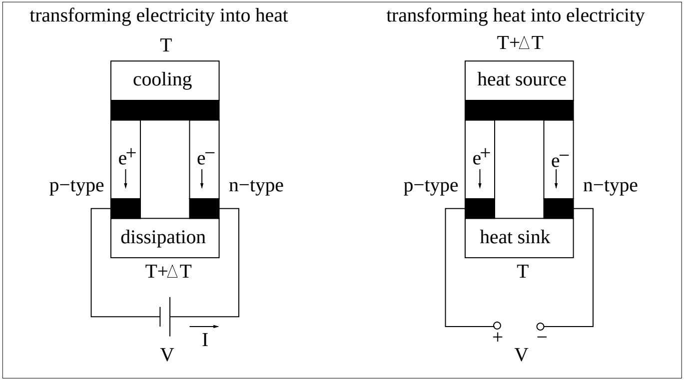


Source: LLNL 2013. Data is based on DOE/EIA-0035(2013-05), May, 2013. If this information or a reproduction of it is used, credit must be given to the Lawrence Livermore National Laboratory and the Department of Energy, under whose auspices the work was performed. Distributed electricity represents only retail electricity sales and does not include self-generation. EIA reports consumption of renewable resources (i.e., hydro, wind, geothermal and solar) for electricity in BTU-equivalent values by assuming a typical fossil fuel plant "heat rate." The efficiency of electricity production is calculated as the total retail electricity delivered divided by the primary energy input into electricity generation. End use efficiency is estimated as 65% for the residential and commercial sectors 80% for the industrial sector, and 21% for the transportation sector. Totals may not equal sum of components due to independent rounding. LLNL-MI-410527

Thermoelectric energy conversion

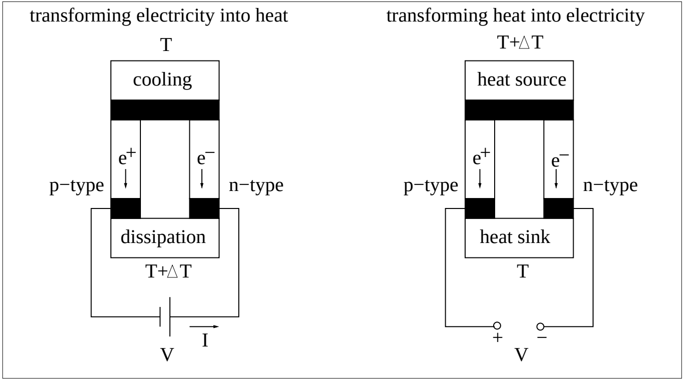
- Maximum efficiency of the thermoelectric couple:

$$\eta_{\max} = \frac{\Delta T}{T + \Delta T} \frac{\sqrt{1 + Z\overline{\overline{T}}} - 1}{\sqrt{1 + Z\overline{\overline{T}}} + T/(T + \Delta T)}.$$



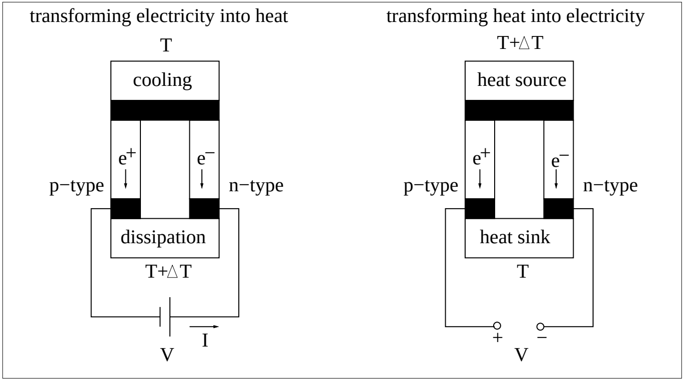
Thermoelectric energy conversion

- Thermoelectric figure of merit: $ZT = \sigma\alpha^2 T/\kappa$
  - σ - electrical conductivity.
  - α - Seebeck coefficient ($\alpha = V/\Delta T$).
  - κ - thermal conductivity.



Thermoelectric energy conversion

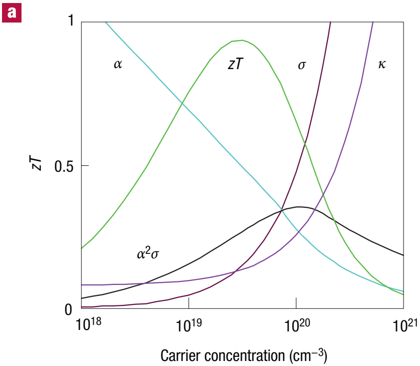
- If $ZT \to \infty$, Carnot limit: $\eta_{\text{max}} \to \Delta T/(T + \Delta T)$.
- State-of-the-art bulk thermoelectric materials: $ZT \sim 1$, $\eta_{\text{max}} \sim 0.17 \times \eta_{\text{Carnot}}$.



Why is it difficult to increase ZT in bulk materials?

$$ZT = \sigma\alpha^2 T/(\kappa_{\rm el} + \kappa_{\rm latt})$$

Conflicting effects on ZT: $\alpha \sim 1/\sigma \sim m^*$, $\kappa_{\rm el} \sim \sigma$, $\kappa_{\rm latt} \sim \sigma$.



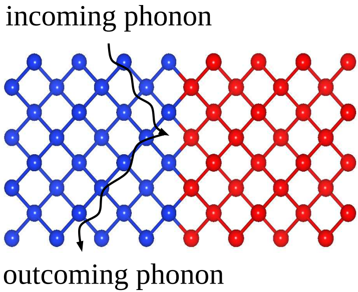
C. J. Snyder and E. Toberer, Nature Mater. **7**, 105 (2008)

Nanostructured thermoelectric materials

- $ZT = \sigma\alpha^2 T/\kappa$.
- Nanostructuring can improve ZT of bulk materials:

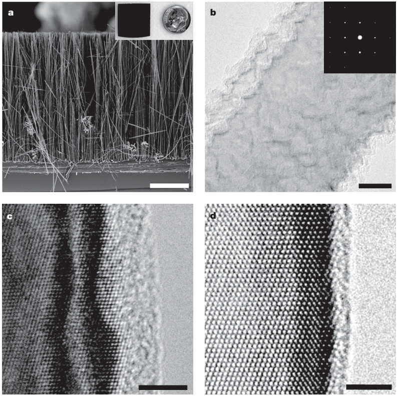
  M. S. Dresselhaus *et al.*, Adv. Mater. **19**, 1043 (2007)

  - Reduce the thermal conductivity κ.
  - The power factor $\sigma\alpha^2$ is reduced less than κ.



High *ZT* nanostructured materials: Si nanowires with rough surface

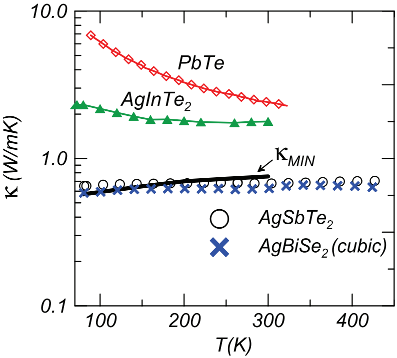
$ZT \sim 0.6$, 60 times larger than that of bulk Si due to the κ reduction.



A. I. Hochbaum *et al.*, Nature **451**, 163 (2008)

Extremely anharmonic bulk materials

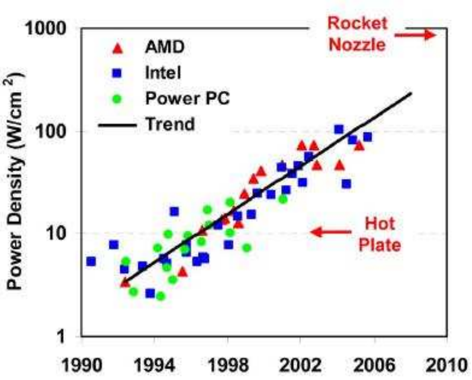
- Low ω optical branches and strong phonon-phonon interaction $\Rightarrow$ very low κ.



D. T. Morelli *et al.*, PRL **101**, 035901 (2008)

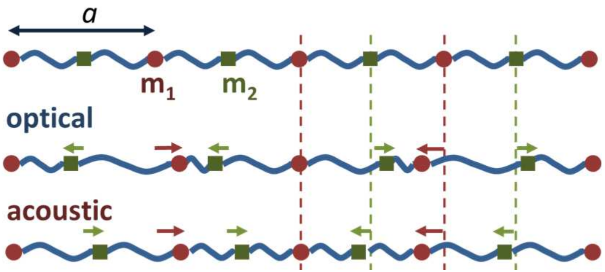
Thermal management in nano- and opto-electronics

- Solid state cooling via thermoelectric materials.



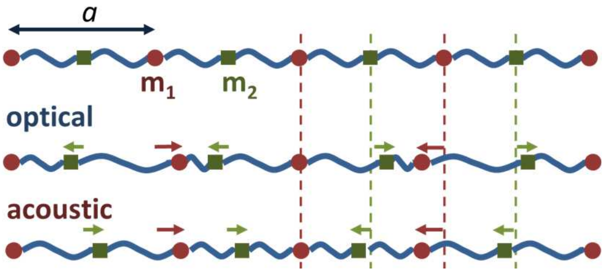
E. Pop and K. E. Goodson, J. Electron. Packag. **128**, 102 (2006)

Lattice vibrations in solids



- Atom = ion cores + valence electrons.
- Ion cores move in a potential field generated by the average motion of valence electrons.

Lattice vibrations in solids



- Displacements from equilibrium positions can be described as a linear combination of normal modes.
- Energy of a normal mode is quantized: $(n + 1/2)\hbar\omega$, $n = 0, 1, ...$
- Phonons are quanta of energy of normal modes.

Lattice Hamiltonian of crystalline solids

- Total potential energy of the crystal in the harmonic approximation:

$$V = V_0 + \sum_{\mathbf{lb},\alpha} \frac{\partial V}{\partial u_\alpha(\mathbf{lb})}\bigg|_0 u_\alpha(\mathbf{lb}) +$$

$$+\frac{1}{2!}\sum_{\mathbf{lb},\mathbf{l'b'},\alpha,\alpha'} \frac{\partial^2 V}{\partial u_\alpha(\mathbf{lb})\partial u_{\alpha'}(\mathbf{l'b'})}\bigg|_0 u_\alpha(\mathbf{lb})u_{\alpha'}(\mathbf{l'b'}) + \ldots$$

$u_\alpha(\mathbf{lb})$ - deviation of atom **lb** from its equilibrium position in the α direction.

- Equations of motion:

$$m_b \frac{d^2 u_\alpha(\mathbf{lb})}{dt^2} = -\sum_{\mathbf{b'},\alpha'} \frac{\partial^2 V}{\partial u_\alpha(\mathbf{lb})\partial u_{\alpha'}(\mathbf{l'b'})} u_{\alpha'}(\mathbf{l'b'}).$$

Lattice Hamiltonian of crystalline solids

- Reciprocal space:

$$u_\alpha(\mathbf{lb}) = \frac{1}{m_b} \sum_{\mathbf{q}} U_\alpha(\mathbf{q};\mathbf{b}) \exp[i(\mathbf{q}\cdot\mathbf{x}(\mathbf{l}) - \omega t)].$$

- Equations of motion become

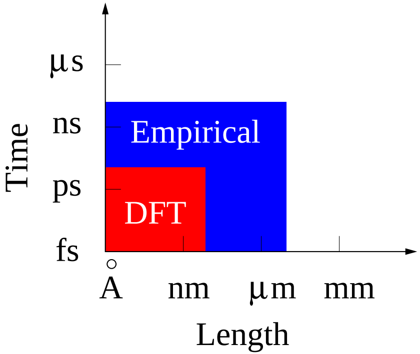
$$\omega^2 U_\alpha(\mathbf{q};\mathbf{b}) = \sum_{\mathbf{b}'\alpha'} D_{\alpha\alpha'}(\mathbf{bb}'|\mathbf{q}) U_{\alpha'}(\mathbf{q};\mathbf{b}').$$

- Dynamical matrix is defined as

$$D_{\alpha\alpha'}(\mathbf{bb}'|\mathbf{q}) = \frac{1}{\sqrt{m_{\mathbf{b}} m_{\mathbf{b}'}}} \sum_{\mathbf{l}'} \frac{\partial^2 V}{\partial u_\alpha(\mathbf{0b}) \partial u_{\alpha'}(\mathbf{l}'\mathbf{b}')} \exp(i\mathbf{q}\mathbf{l}').$$

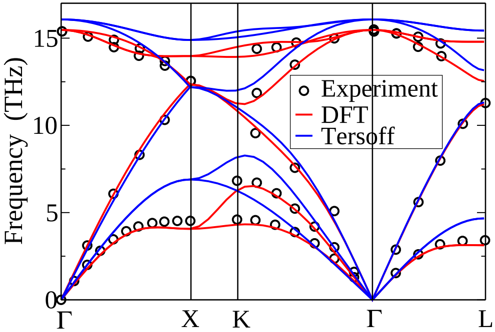
G. P. Srivastava, "The physics of phonons"

How do we obtain the interatomic potential?



- Density functional theory (DFT):
  - No fitting parameters.
  - Computationally expensive.
  - Short length and time scales.
- Empirical potentials:
  - Fitted to experimental data.
  - Computationally less expensive.
  - Longer length and time scales.

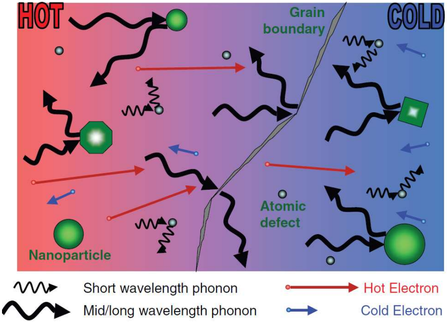
Phonon band structure: Example of Si



- DFT reproduces well experimental phonon frequencies.
- Empirical potentials do not describe phonon frequencies as accurately as DFT.

Lattice dynamics: beyond the harmonic approximation

- Harmonic approximation $\Rightarrow$ infinite phonon lifetimes and κ.
- Finite phonon lifetimes (but still infinite κ) due to boundaries, defects, impurities, alloying...



C. J. Vineis *et al.*, Adv. Mater. **22**, 3970 (2010)

Lattice dynamics: beyond the harmonic approximation

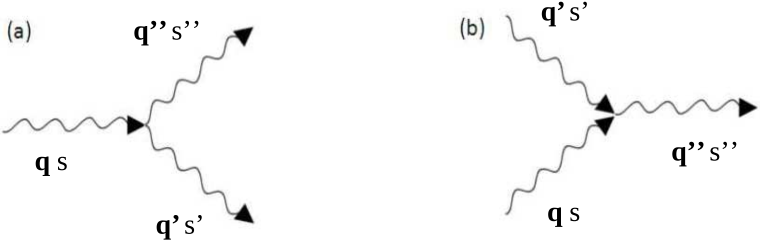
- Finite phonon lifetimes and finite κ due to anharmonicity:

$$V = V_0 + \sum_{\mathbf{lb},\alpha} \frac{\partial V}{\partial u_\alpha(\mathbf{lb})}\bigg|_0 u_\alpha(\mathbf{lb}) +$$

$$\frac{1}{2!} \sum_{\mathbf{b},\mathbf{b}',\alpha,\alpha'} \frac{\partial^2 V}{\partial u_\alpha(\mathbf{b})\partial u_{\alpha'}(\mathbf{b}')}\bigg|_0 u_\alpha(\mathbf{b}) u_{\alpha'}(\mathbf{b}') + \frac{1}{3!} \times$$

$$\sum_{\mathbf{b},\mathbf{b}',\mathbf{b}'',\alpha,\alpha',\alpha''} \frac{\partial^3 V}{\partial u_\alpha(\mathbf{b})\partial u_{\alpha'}(\mathbf{b}')\partial u_{\alpha''}(\mathbf{b}'')}\bigg|_0 u_\alpha(\mathbf{b}) u_{\alpha'}(\mathbf{b}') u_{\alpha''}(\mathbf{b}'') + \ldots$$

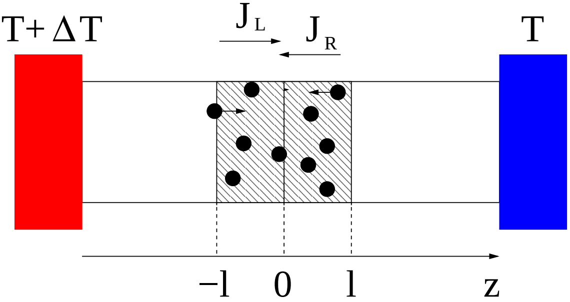
Three-phonon scattering



(a) Annihilation of one phonon and creation of two phonons:
$\omega(\mathbf{q}, s) = \omega(\mathbf{q}', s') + \omega(\mathbf{q}'', s'')$, $\mathbf{q} + \mathbf{G} = \mathbf{q}' + \mathbf{q}''$.

(b) Annihilation of two phonons and creation of a third phonon:
$\omega(\mathbf{q}, s) + \omega(\mathbf{q}', s') = \omega(\mathbf{q}'', s'')$, $\mathbf{q} + \mathbf{q}' = \mathbf{q}'' + \mathbf{G}$.

Thermal conductivity in the kinetic theory of gases



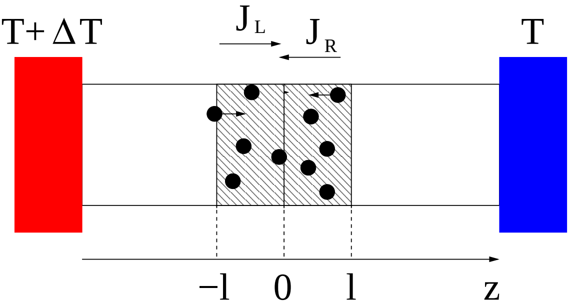
- Heat current: $J_z = n v_z \epsilon$,

  n - concentration, v_z - speed of gas atoms, ϵ - energy.

- $J_z = J_L - J_R \sim n v_z k_B \left[\left(T - l\frac{dT}{dz}\right) - \left(T + l\frac{dT}{dz}\right)\right]$,

  l - mean free path.

Thermal conductivity in the kinetic theory of gases



- Thermal conductivity: $\kappa_z = c_v v_z l = c_v v_z^2 \tau$,

  c_v - heat capacity, $\tau = l/v_z$ - average collision time.

More advanced theory: Boltzmann transport equation

- Time evolution of the distribution function n(**r**,**v**,t):

$$n(\mathbf{r} + d\mathbf{r}, \mathbf{v} + d\mathbf{v}, t + dt) - n(\mathbf{r}, \mathbf{v}, t) = dt \left.\frac{\partial n}{\partial t}\right|_{\text{scattering}}$$

$$\mathbf{r} - \text{position}, \quad \mathbf{v} - \text{velocity}, \quad t - \text{time}.$$

- Boltzmann transport equation (BTE):

$$\frac{\partial n}{\partial t} + \mathbf{v}\nabla_{\mathbf{r}} n + \frac{\mathbf{F}}{m}\nabla_{\mathbf{v}} n = \left.\frac{dn}{dt}\right|_{\text{scattering}}$$

$$\mathbf{F} - \text{driving force}.$$

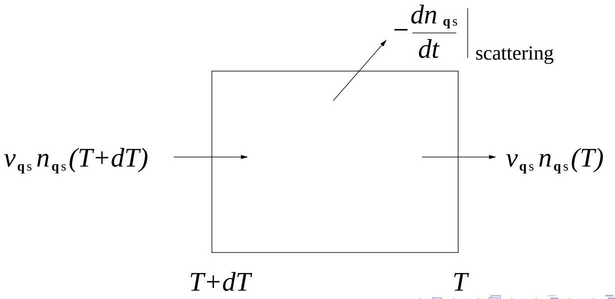
More advanced theory: Boltzmann transport equation

- Phonon Boltzmann transport equation in the steady state:

$$v_{\mathbf{q},s} \nabla T \frac{dn_{\mathbf{q},s}}{dT} = \left.\frac{dn_{\mathbf{q},s}}{dt}\right|_{\text{scattering}}$$

$n_{\mathbf{q},s}$ – occupation (= Bose-Einstein distribution in equilibrium),

$v_{\mathbf{q},s} = d\omega_{\mathbf{q},s}/d\mathbf{q}$ – group velocity.



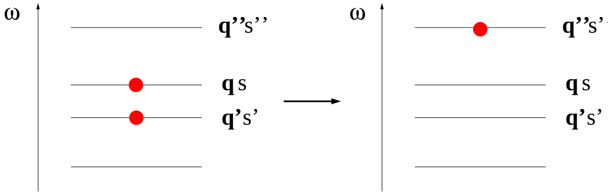
Scattering rates due to three-phonon processes

- Fermi's golden rule:

$$P_i^f(3ph) = \frac{2\pi}{\hbar}|\langle f|V_3|i\rangle|^2\delta(\omega_f - \omega_i),$$

- Scattering term in BTE:

$$\left.\frac{dn_{\mathbf{q},s}}{dt}\right|_{\text{3ph}} = \sum_{\mathbf{q}',s'}\sum_{\mathbf{q}'',s''}\left(-P_{\mathbf{q}s,\mathbf{q}'s'}^{\mathbf{q}''s''} - \frac{1}{2}P_{\mathbf{q}s}^{\mathbf{q}'s',\mathbf{q}''s''} + P_{\mathbf{q}''s''}^{\mathbf{q}s,\mathbf{q}''s''} + \frac{1}{2}P_{\mathbf{q}'s',\mathbf{q}''s''}^{\mathbf{q}s}\right)$$



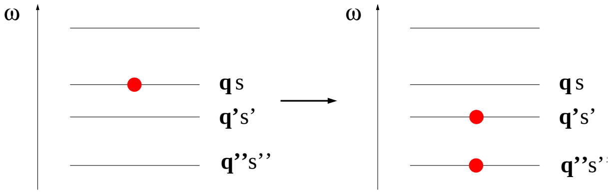
Scattering rates due to three-phonon processes

- Fermi's golden rule:

$$P_i^f(3ph) = \frac{2\pi}{\hbar} |\langle f|V_3|i\rangle|^2 \delta(\omega_f - \omega_i),$$

- Scattering term in BTE:

$$\left.\frac{dn_{\mathbf{q},s}}{dt}\right|_{3\text{ph}} = \sum_{\mathbf{q}',s'} \sum_{\mathbf{q}'',s''} \left(-P_{\mathbf{q}s,\mathbf{q}'s'}^{\mathbf{q}''s''} - \frac{1}{2} P_{\mathbf{q}s}^{\mathbf{q}'s',\mathbf{q}''s''} + P_{\mathbf{q}''s''}^{\mathbf{q}s,\mathbf{q}''s''} + \frac{1}{2} P_{\mathbf{q}'s',\mathbf{q}''s''}^{\mathbf{q}s} \right)$$



Thermal conductivity in the BTE framework

- Solve linearized BTE self-consistently to determine occupations.
- Heat current:

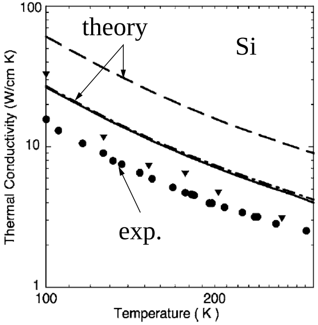
$$\mathbf{J} = \frac{1}{N_{\mathbf{q}} V} \sum_{\mathbf{q},s} \hbar\omega_{\mathbf{q},s} n_{\mathbf{q},s} \mathbf{v}_{\mathbf{q},s}.$$

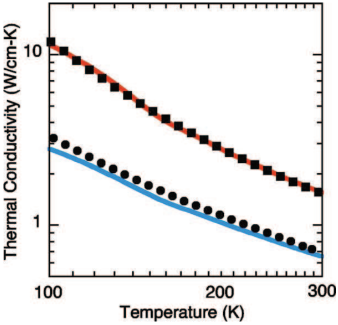
- Thermal conductivity from Fourier law:

$$\kappa_{\alpha\beta} = -\frac{\mathbf{J}_\alpha \cdot \nabla T_\beta}{|\nabla T|^2} = -\frac{1}{N_{\mathbf{q}} V |\nabla T|^2} \sum_{\mathbf{q},s} \hbar\omega_{\mathbf{q},s} n_{\mathbf{q},s} \mathbf{v}_{\mathbf{q},s} \cdot \nabla T_\beta.$$

G. P. Srivastava, "The physics of phonons"

Thermal conductivity from linearized BTE: Example of Si and Ge





Empirical potentials: D. A. Broido *et al.*, PRB **72**, 014308 (2005)

First principles (DFT): D. A. Broido *et al.*, APL **91**, 231922 (2007)

- Very good agreement between first principles results and experiment.
- Empirical potentials give good trends, but are not very accurate.

BTE in the relaxation time approximation approach (BTE-RTA) for thermal transport

- Relaxation time ($\tau_{\mathbf{q},s}$) approximation:
  - Assume equilibrium phonon distribution in all states except ($\mathbf{q}$,s):

$$\tau^{-1}_{\mathbf{q},s} = \frac{1}{\bar{n}_{\mathbf{q},s}(\bar{n}_{\mathbf{q},s}+1)} \sum_{\mathbf{q}',s'} \sum_{\mathbf{q}'',s''} \left(\bar{P}^{\mathbf{q}''s''}_{\mathbf{q}s,\mathbf{q}'s'} + \frac{1}{2}\bar{P}^{\mathbf{q}'s',\mathbf{q}''s''}_{\mathbf{q}s}\right),$$

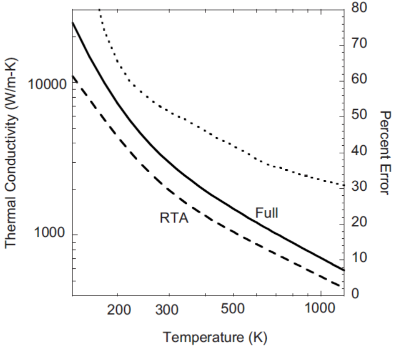
$$\left.\frac{dn_{\mathbf{q},s}}{dt}\right|_{\text{scattering}} = -\frac{n_{\mathbf{q},s}-\bar{n}_{\mathbf{q},s}}{\tau_{\mathbf{q},s}}.$$

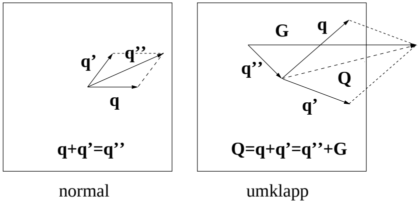
- Thermal conductivity:

$$\kappa = \frac{1}{N_{\mathbf{q}}V}\sum_{\mathbf{q},s} c_{\mathbf{q},s} v^2_{\mathbf{q},s}\tau_{\mathbf{q},s}, \quad c_{\mathbf{q},s} - \text{heat capacity.}$$

G. P. Srivastava, "The physics of phonons"

Self-consistent BTE or BTE-RTA? Example of carbon diamond



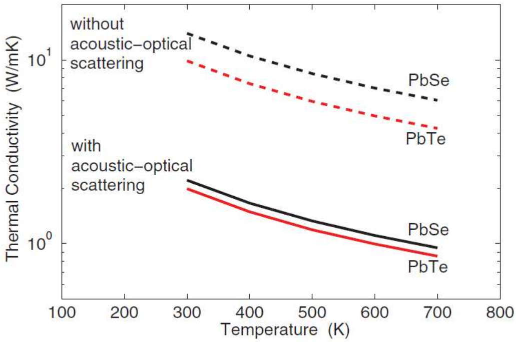


A. Ward *et al.*, PRB **80**, 125203 (2009)

- If umklapp scattering is weak, self-consistent BTE solution differs from BTE-RTA.

Insights gained from BTE simulations of κ

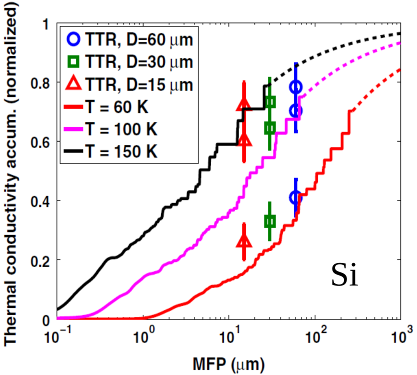
- Mechanisms for low κ in bulk materials can be uncovered.
- Provide guidance in the search for more efficient materials.



Z. Tian *et al.*, PRB **85**, 184303 (2012)

Insights gained from BTE simulations of κ

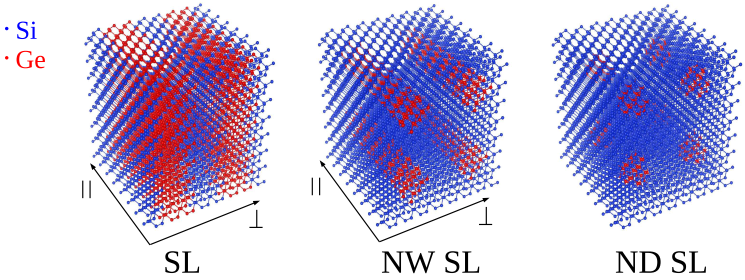
- κ vs mean free path in bulk materials.
- Estimate nanostructure dimensions to achieve a desired κ reduction.



A. J. Minich *et al.*, PRL **107**, 095901 (2009)

Challenges for BTE approach applied to nanostructured and disordered materials

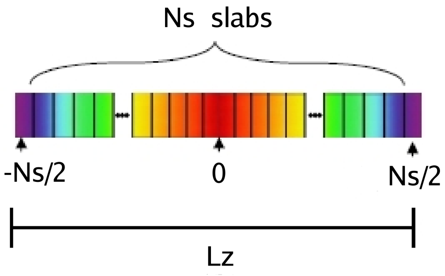
- How to solve BTE for large scale systems?



- How to calculate the first principles input to BTE for large scale systems?
- How to extend BTE to treat disordered materials without resorting to the virtual crystal + effective lifetimes approximation?

Non-equilibrium MD (NEMD) approach to thermal transport

- Impose ∇T in MD simulation by exchanging the energy of the atoms in the central and end slabs.

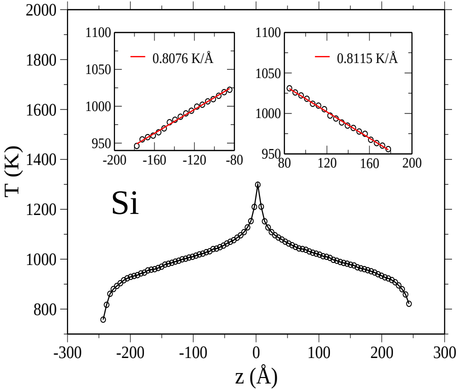


- Critical feature: existence of boundaries at the edges of the heat source and sink.

F. Muller-Plathe, JCP **106**, 6082 (1997)

Extracting κ from the temperature profile

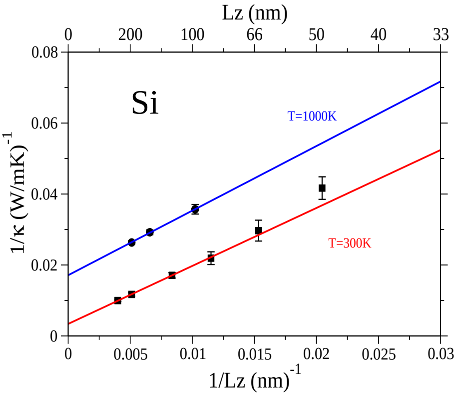
- Instantaneous local temperature in slab k: $T_k \sim \sum_{i \in k} m_i v_i^2$.



- Heat flux J_z determined from the transferred kinetic energy.
- $\kappa = \langle J_z(t) \rangle / (\partial T / \partial z)$.

Y. He, I. Savić, D. Donadio, and G. Galli, PCCP **14**, 16209 (2012)

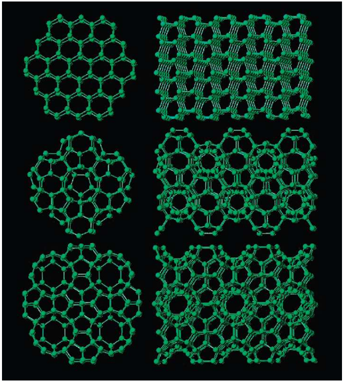
Size effects in NEMD simulations of κ



- Boundary scattering: $l_L^{-1} = l_\infty^{-1} + 4L_z^{-1} \Rightarrow \kappa_L^{-1} = \kappa_\infty^{-1} + CL^{-1}$.
- Difficult to ensure both the cross-section and length convergence: Is NEMD good enough for disordered materials?

Insights gained from NEMD simulations of κ

- Complex materials can be straightforwardly simulated.

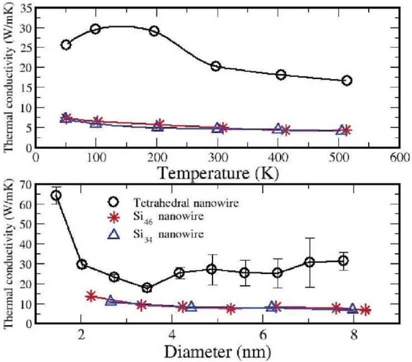


Si nanowires

I. Ponomareva *at al.*, Nano Lett. **7**, 1155 (2007)

Insights gained from NEMD simulations of κ

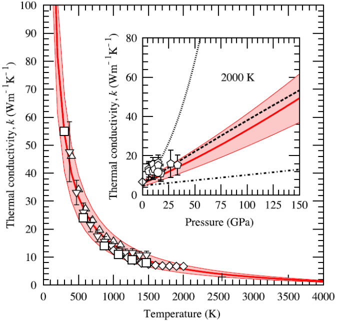
- Predict κ trends for complex materials.



Si nanowires

I. Ponomareva *at al.*, Nano Lett. **7**, 1155 (2007)

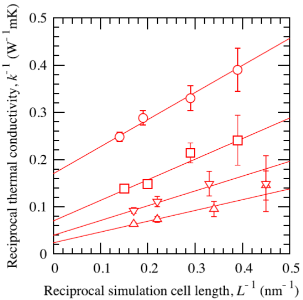
NEMD approach to calculate κ from first principles



- Straightforward coupling of *ab-initio* and NEMD heat transport methods.
- Good agreement with experiments for MgO, predictions for temperatures and pressures in the Earth mantle.

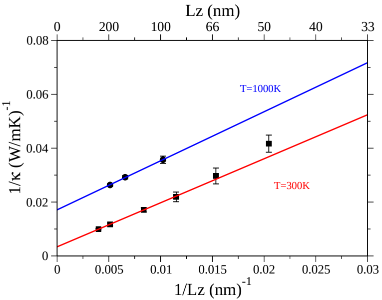
S. Stackhouse *at al.*, PRL **104**, 2085012 (2010)

Size effects in NEMD approach from first principles



First principles:

S. Stackhouse *at al.*, PRL **104**, 2085012 (2010)



Empirical potentials:

Y. He *et al.*, PCCP **14**, 16209 (2012)

- Much smaller sizes accessible than with empirical potentials.
- Much shorter simulation time than with empirical potentials: $\sim$ 10 ps versus $\sim$ 1 ns.

Equilibrium MD (EMD) approach to thermal transport

- Green-Kubo formalism (fluctuation-dissipation theorem):

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

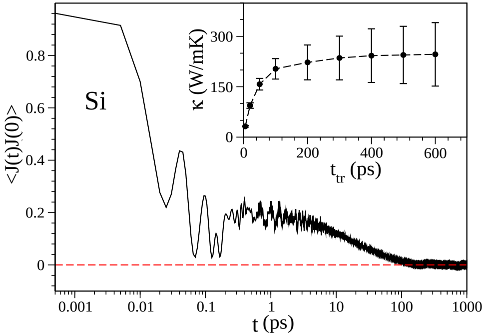
- Heat current obtained from EMD:

$$\mathbf{J} = \frac{d}{dt} \sum_i \mathbf{r}_i(t)\epsilon_i(t); \text{ i - atomic site, } \mathbf{r}_i \text{ - coordinate, } \epsilon_i \text{ - energy.}$$

- ϵ_i can be defined for empirical potentials, but not in a unique way.
- Open problem: how to define the local energy from first principles?

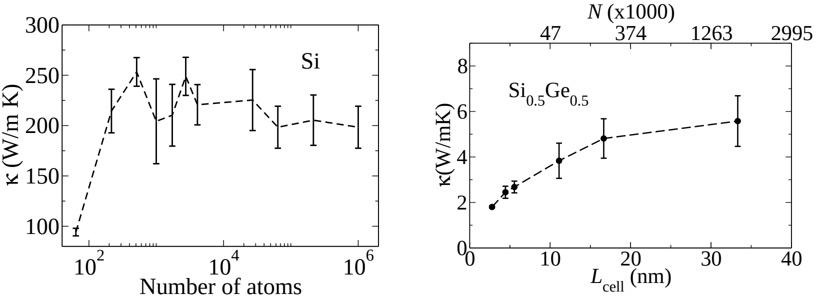
Time scale for EMD simulations of κ

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



- $\langle J(t)J(0)\rangle$ indirect measure of longest phonon lifetimes ($\sim$ 100 ps).
- Total simulation time $\sim$ 10 ns.

Size effects in EMD simulations of κ

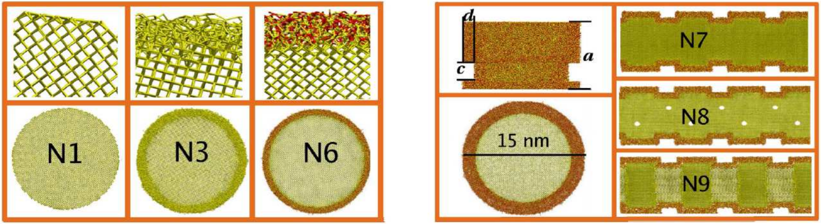


- Convergence for large samples ($\sim 10^5 - 10^6$ atoms).
- Samples with $10^5 - 10^6$ atoms can be simulated with EMD.
- Disordered samples can be simulated with EMD.

Y. He, I. Savić, D. Donadio, and G. Galli, PCCP **14**, 16209 (2012)

Insights gained from EMD simulations of κ

- Materials with very complex morphologies can be simulated.
- Closest to mimicking realistic materials so far!

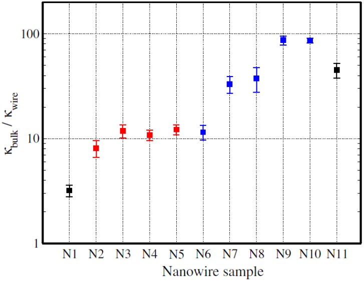


Si nanowires with surface roughness

Y. He and G. Galli, PRL **108**, 215901 (2012)

Insights gained from EMD simulations of κ

- Powerful probe to determine which types of disorder cause strong scattering and κ reduction.

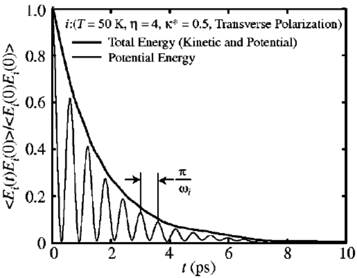


Si nanowires with surface roughness

Y. He and G. Galli, PRL **108**, 215901 (2012)

Calculating κ with lifetimes obtained from EMD

- EMD lifetimes from the exponential decay of the normal mode potential energy autocorrelation function.

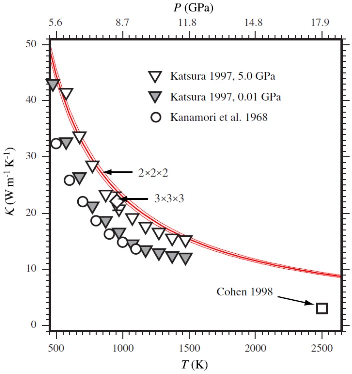


- Use EMD lifetimes for κ: $\kappa_{\tau_{\text{EMD}}} = \frac{1}{N_{\mathbf{q}} V} \sum_{\mathbf{q},s} c_{\mathbf{q},s} v^2_{\mathbf{q},s} \tau^{\text{EMD}}_{\mathbf{q},s}$.
- Typically $\kappa_{\text{EMD}} \approx \kappa_{\tau_{\text{EMD}}}$ for small system sizes ($\sim$ 1000 atoms).

A. J. H. McGaughey and M. Kaviani, PRB **69**, 094303 (2004)

κ with EMD lifetimes from first principles

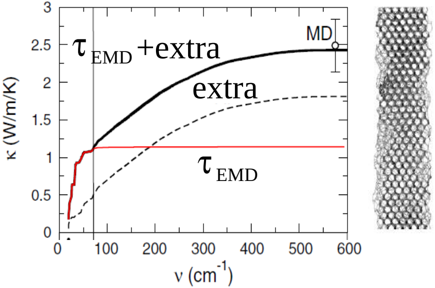
- Can be calculated for small system sizes ($\sim$ 100 atoms) and short simulation times ($\sim$ 40 ps).
- Good agreement with experiments for MgO.



N. de Koker, PRL **103**, 125902 (2009)

Can we use EMD lifetimes to study heat transport in disordered materials? Example of rough Si nanowires

- $\kappa_{\text{EMD}} \neq \frac{1}{N_{\mathbf{q}} V} \sum_{\mathbf{q},s} c_{\mathbf{q},s} v_{\mathbf{q},s}^2 \tau_{\mathbf{q},s}^{\text{EMD}}$.
- Non-propagating and non-localized vibrations give additional contribution to κ.



D. Donadio and G. Galli, PRL **102**, 195901 (2009)

Summary of atomistic approaches to heat transport

Method	EMD	NEMD	BTE
Disorder	Yes	Yes	Approximate
Anharmonicity	Yes	Yes	Approximate
Transport regimes	Any	Any	Propagating
f_{BE}	?	?	Yes
Ab-initio	?	Yes	Yes

f_{BE} - the Bose-Einstein distribution.

No perfect approach, they complement each other.

Summary

- We need to understand the thermal conductivity to design new thermoelectric materials.
- Atomistic methods to calculate the thermal conductivity could be helpful.
- Lots of recent methodological developments in the field, especially in the domain of first principles calculations.
- Lots of insight gained from applications of these methods, but more insight is needed.
- Quite a few challenges ahead for these methods, especially to model disordered and nanostructured materials.

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