Physics of Heat Transport

at the Nanoscale

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Outline

Heat at the atomic scale, New physics appear at the nanoscale!

Thermal conductivity relations

- Linear response formula MD: Green-Kubo (Equilibrium, crystals and amorphous materials)
- Boltzmann Transport equation (Lattice dynamics + Fermi Golden rule)
- Landauer formula (Green's function method, AMM, DMM)
- NEMD

Interface effects: Thermal boundary conductance

Coherent transport in superlattices

Near-field

What is heat and how does it move?

First law: $\Delta U=W+Q$

- Change in internal energy in the absence of work; $Q=C\Delta T$

Microscopic: $U=\Sigma\ ni\ Ei \Rightarrow dU=\Sigma\ (ni\ dEi + dni\ Ei)$

- Changes in internal energy associated with changes in populations

Transfer through: **conduction**, convection and radiation(from hot to cold by 2nd law)

- i.e. in solids with no net (advective) motion of atoms

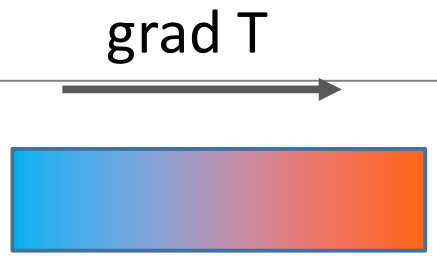
Heat carriers: electrons, phonons, photons, magnons… all quasiparticles having energy are **heat carriers**

Semiconducting solids

Crystals: phonons

Amorphous solids: “vibrons”…

Conduction law



Fourier: J = - κ grad T

- Local relation
- Experimentally validated
- defines the thermal conductivity **in the linear regime** (grad T "not too large")
- κ supposedly intrinsic property of the material (but temperature dependent)

Counter examples?

- Yes! At the nanoscale
- It is strictly-speaking non-local: $J(x,t) = -\int dx'dt'\,\kappa(x,t;x',t')\,\nabla T(x',t')$

  But the kernel $\kappa(x,x')$ decays quickly to zero as the distance x-x' becomes "large"

  More convenient to represent in Fourier space as convolution becomes a simple product: $J(q,\omega) = -\kappa(q,\omega) \times iqT(q,\omega)$

Orders of magnitude

From: Bergman, Lavine, Incropera&DeWitt

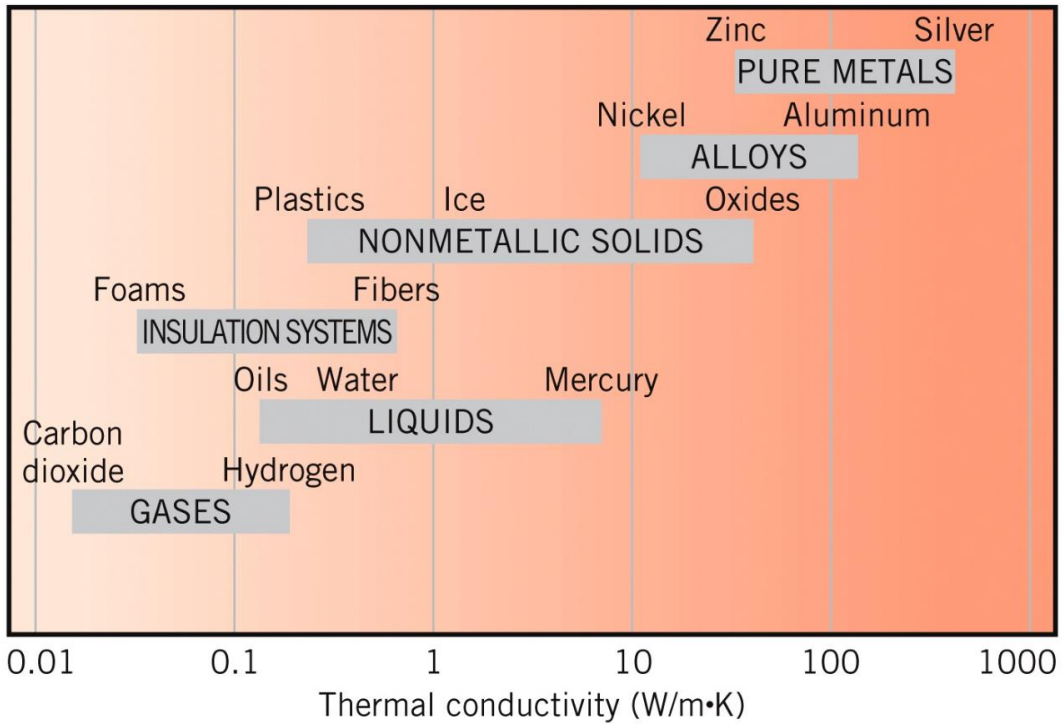
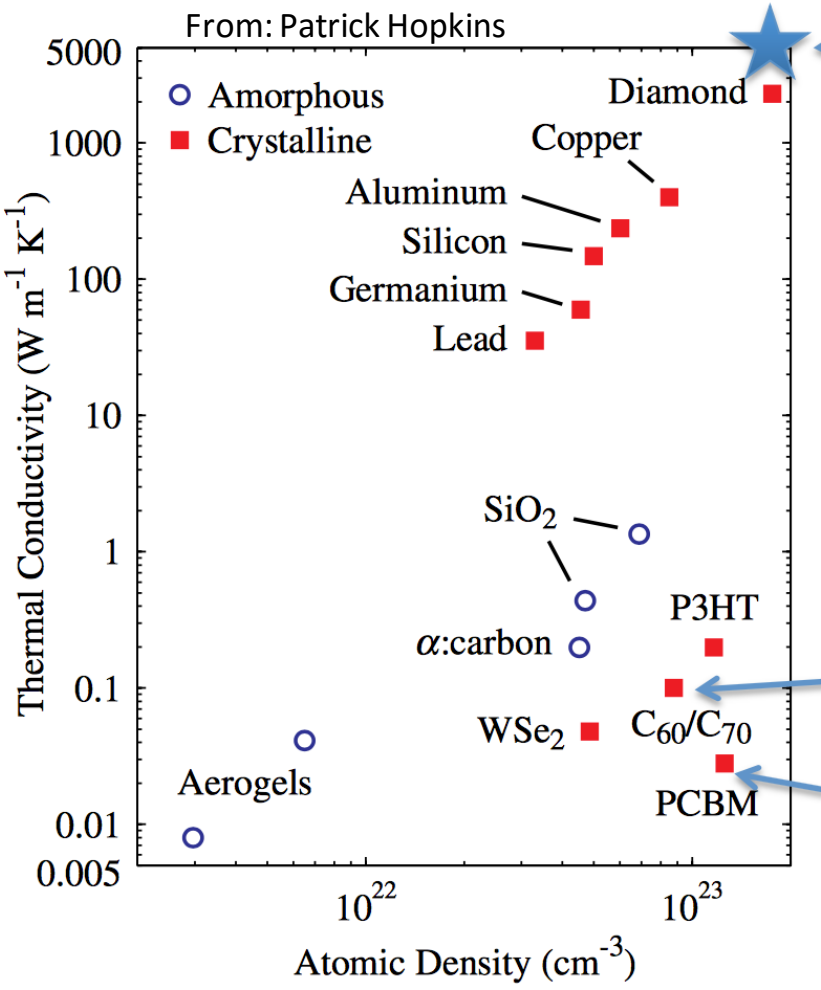


Figure 2.4

From: Patrick Hopkins



What does the thermal conductivity depend on?

Heat carriers:

- their statistics (Fermions or Bosons or classical),
- their collisions
- Their energy and velocity

What theories can describe it?

- **Linear response theory** developed by Green and Kubo (very general)
- **Boltzmann transport theory** (statistics come in, used for crystals: phonon language)
- **Landauer formula** (transport theory at the nanoscale where coherence and wave effects dominate)

How is the heat current density defined?

J(r,t) = heat current density (w/m^2)

- No need to differentiate between heat and energy currents if no work involved
- Use heat-balance (or energy continuity) equation: $\frac{\partial H}{\partial t} + \nabla . J = S$

2nd law: Due to local differences in temperature, heat will diffuse to make it uniform:

$dU = \Sigma_i \, E_i \frac{dn_i}{dT} \, dT$ => J=… => -J/grad T=…

How much energy will move per unit time, given ΔT? It is ultimately a counting problem!

Green-Kubo general formula
from linear response theory

Two flavors:

- Kubo: $\kappa = \frac{1}{3k_B T^2 V} \int_0^\infty dt < \vec{J}(t).\vec{J}(0) >$
- Einstein: $\kappa = \frac{1}{3k_B T^2 V} \lim_{t\to\infty} \frac{1}{2t} < |\vec{G}(t) - \vec{G}(0)|^2 >$

Where $\vec{G}(t) = \Sigma_i \vec{r}_i(t)\, e_i(t)$ and $\vec{J}(t) = \frac{d\vec{G}(t)}{dt}$ (in Wm)

Can be applied to crystals or amorphous

Uses a supercell with PBC: check convergence vs size and time

Based on Statistical Mechanics (equilibrium distribution) => requires ensemble averaging

Extension by A. Henry to separate mode contribution (useful for **amorphous** materials and **interface** studies):

Heat current density definition

Recall enery conservation: $\frac{\partial H}{\partial t} + \nabla . J = 0$

Define energy displacement density by: $h + \nabla . g = 0$ so that $\int h(r,t)\, dr = H(t)$; $\int g(r,t)\, dr = G(t)$ and $J = \frac{\partial g}{\partial t}$

$h(r,t) = < \sum_i \delta\big(r - r_i(t)\big)\, e_i(t) >$ with $e_i(t) = \frac{p_i^2}{2m_i} + \frac{1}{2}\sum_j' V_{ij}$

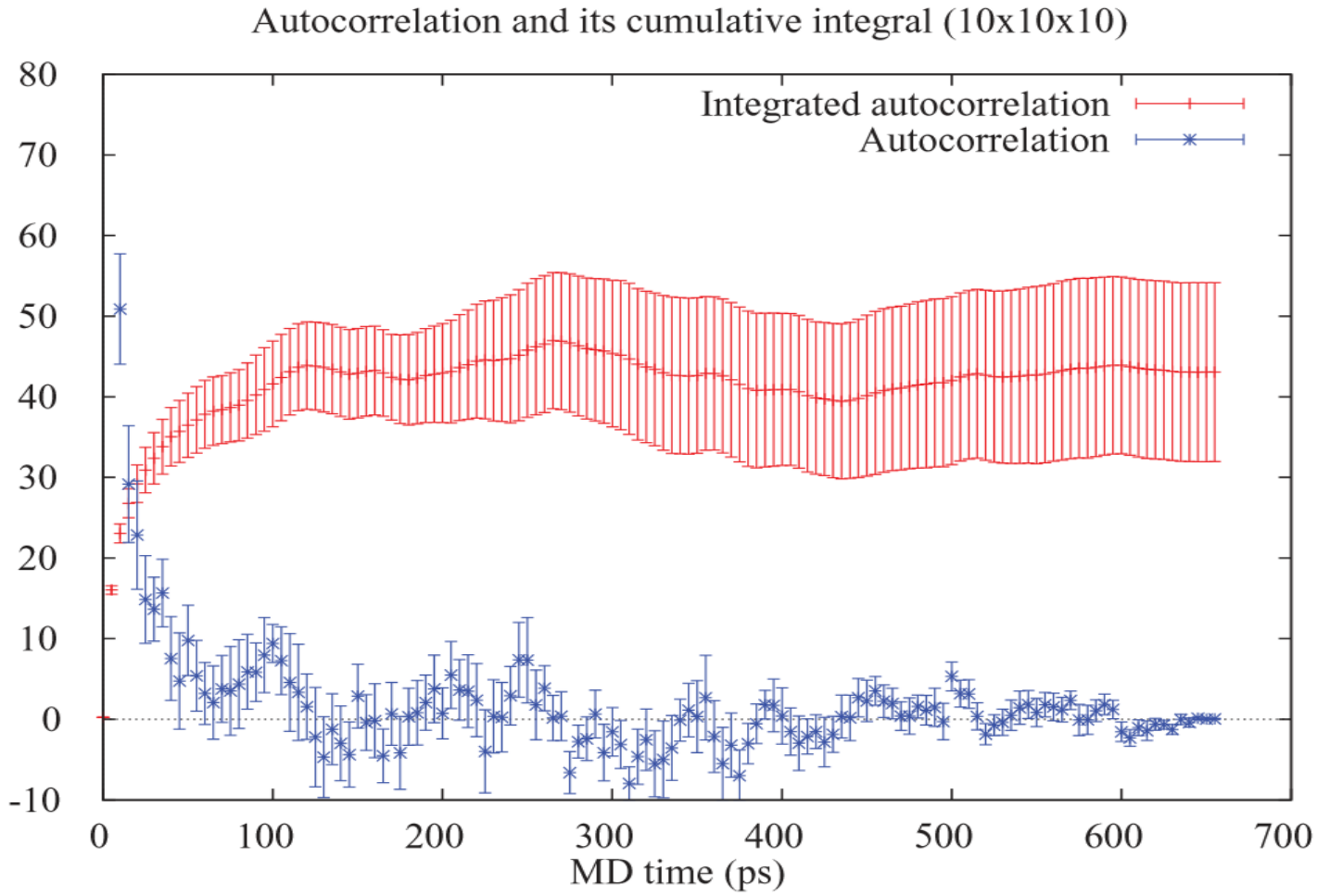
Work in Fourier space: $h(q,t) + iq.\, g(q,t) = 0 \Rightarrow iq.\, g = < \sum_i e_i\, e^{iqr_i} >$

Take $q \to 0$ limit (Taylor expand) to get $g(q \to 0, t) = G(t) = < \sum_i e_i\, r_i >$

Therefore: $J(t) = < \sum_i e_i\, v_i + \frac{de_i}{dt} r_i >$

$$\mathbf{J}(t) = \sum_i \frac{de_i}{dt}\mathbf{R}_i = \sum_i \mathbf{R}_i.(\mathbf{v}_i.\mathbf{F}_i + \frac{1}{2}\sum_{j\neq i} \mathbf{F}_{ij}.(\mathbf{v}_i - \mathbf{v}_j)) = \frac{1}{4}\sum_{i,j\neq i} \mathbf{R}_{ij}\,(\mathbf{F}_{ij}.(\mathbf{v}_i + \mathbf{v}_j))$$

Application of GK to bulk Si



K.Esfarjani, H. Stokes and G. Chen, PRB 84, 085204 (2011)

Boltzmann Transport Equation (BTE)
Crystalline solid: **Phonon gas model**

$$\frac{\partial f_k}{\partial t} + \vec{v}_k \,.\vec{\nabla} f_k = -\sum_{k'} C_{kk'} f_{k'}$$

Relaxation time approximation (RTA): RHS=$-\frac{f_k - f_k^o}{\tau_k}$

Driving field

For a homogeneous system near equilibrium: $f_k = f_k^o - \frac{df_k^o}{dT} \vec{\nabla} T . \tau_k \vec{v}_k$

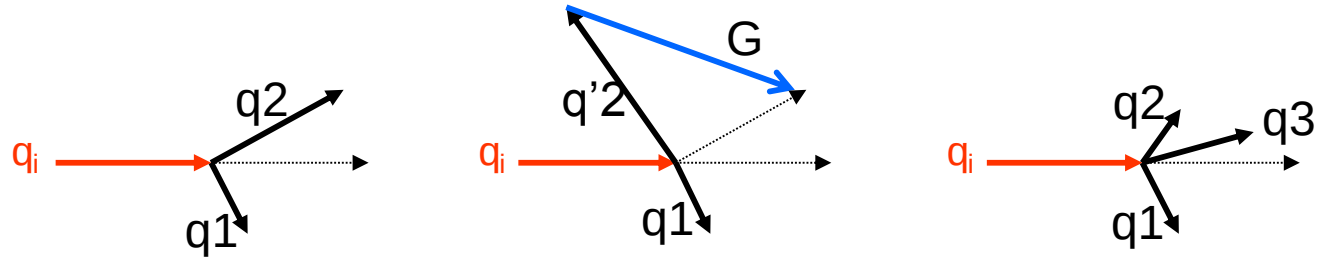
Total heat current: $\vec{J} = \sum_k e_k \vec{v}_k f_k = \sum_k e_k \vec{v}_k \delta f_k = \sum_k e_k \vec{v}_k \frac{df_k^o}{dT} (-\vec{\nabla} T) . \tau_k \vec{v}_k$

Thermal conductivity: $\overleftrightarrow{\kappa} = \frac{1}{V} \sum_k e_k \frac{df_k^o}{dT} \tau_k \vec{v}_k \vec{v}_k = \frac{1}{V} \sum_k C_k \tau_k \vec{v}_k \vec{v}_k$

Mean free path: $\Lambda_k = \tau_k v_k$

Scattering processes

Three-phonon processes (intrinsic);



Normal Umklapp process a 4-phonon process

RTA: $\frac{1}{\tau_{3ph}} \approx \frac{1}{\tau^N} + \frac{1}{\tau^U} \propto \omega^2 T \ (at\ low\ \omega)$

Impurities/point defects $\frac{1}{\tau_{defect}} = A\,\omega^4$

Boundary $\frac{1}{\tau_{boundary}} \approx \frac{v}{L}$

Add the rates since independent processes

$$\frac{\mathbf{1}}{\boldsymbol{\tau}} = \frac{\mathbf{1}}{\boldsymbol{\tau_{3ph}}} + \frac{\mathbf{1}}{\boldsymbol{\tau_{defect}}} + \frac{\mathbf{1}}{\boldsymbol{\tau_{boundary}}} \approx 1/\tau_{boundary} (at\ low\ \omega\ or\ low\ T)$$

First-principles methods
MD+Lattice Dynamics

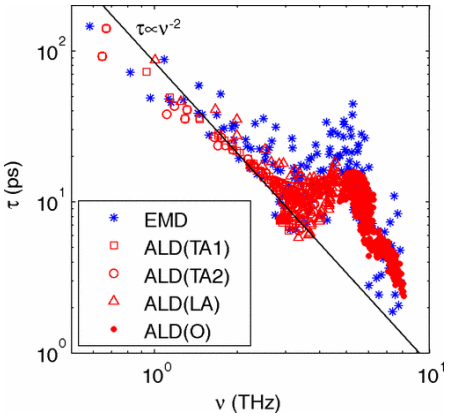
$$-F_i^a = \nabla_i^a E = P_i^a + \sum_{j,b} F_{ij}^{ab} u_j^b + \frac{1}{2!}\sum_{jk,bg} Y_{ijk}^{abg} u_j^b u_k^g + \frac{1}{3!}\sum_{jkl,bgd} C_{ijkl}^{abgd} u_j^b u_k^g u_l^d$$

$$P_i^a = \frac{\partial E}{\partial u_i^a};\ F_{ij}^{ab} = \frac{\partial^2 E}{\partial u_i^a \partial u_j^b};\ Y_{ijk}^{abg} = \frac{\partial^3 E}{\partial u_i^a \partial u_j^b \partial u_k^g};\ C_{ijkl}^{abgd} = \frac{\partial^4 E}{\partial u_i^a \partial u_j^b \partial u_k^g \partial u_l^d}$$

Based on BTE with RTA

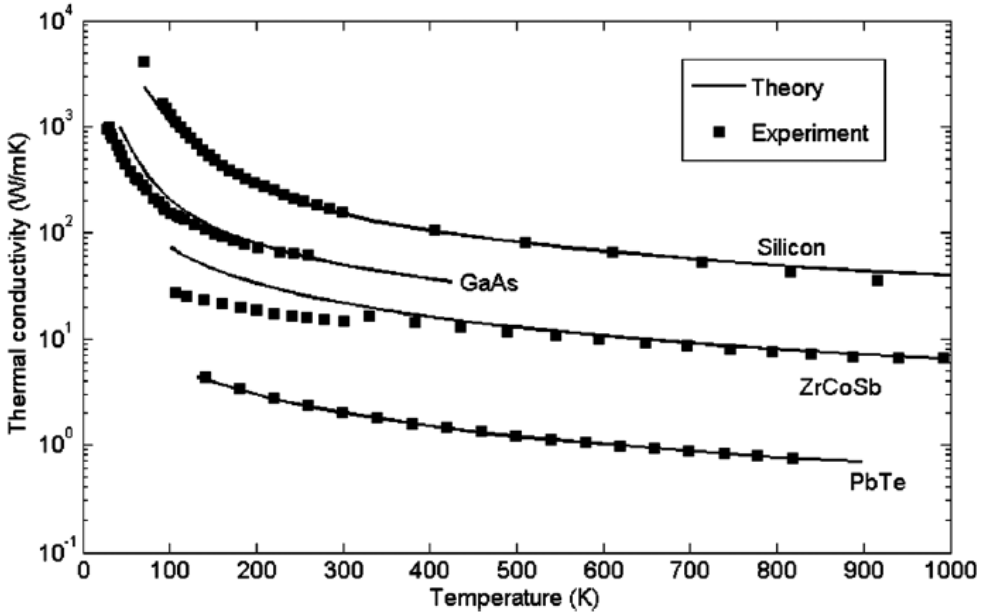
LD used to get phonon dispersion

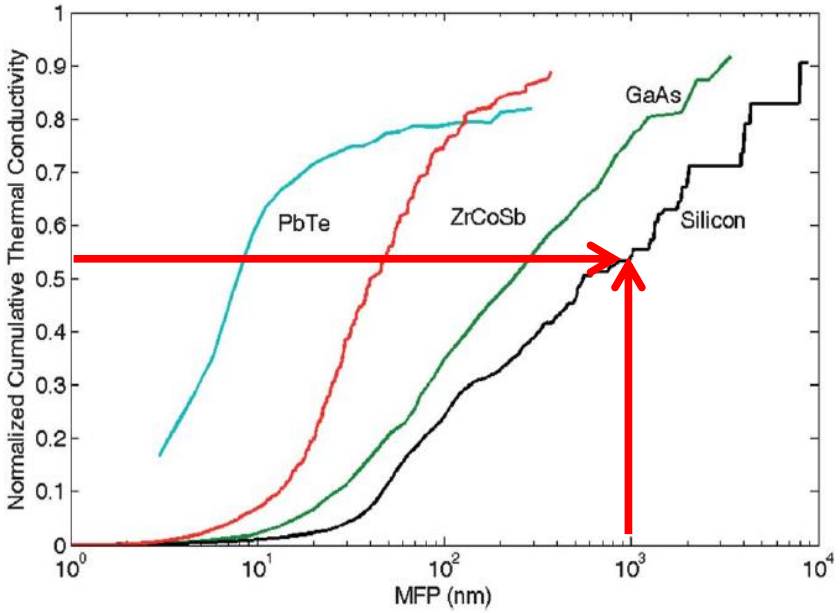
MD or FGR used to calculate phonon lifetimes



Thermal conductivity of half-Heusler compounds from first-principles calculations
Junichiro Shiomi, Keivan Esfarjani, and Gang Chen
Phys. Rev. B 84, 104302 –2011

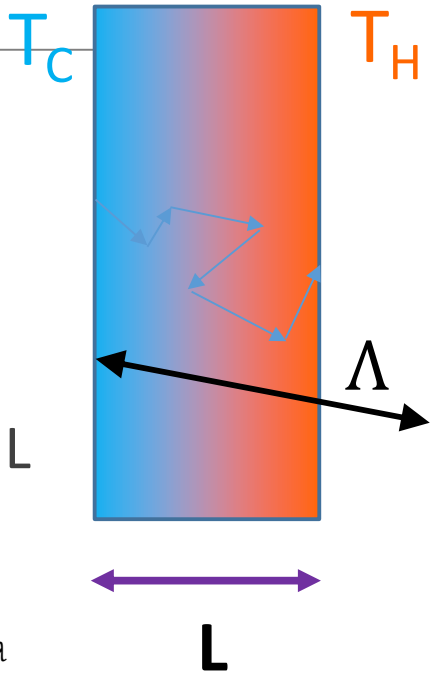
Mean free paths distribution: Size effect on κ





Perspectives on thermoelectrics; M. Zebarjadi, K Esfarjani, MS Dresselhaus, ZF Ren, G Chen Energy Environ. Sci. **5**, 5147 (2012).

Size effects



What happens when L becomes small?

Until 10-20 atomic layers thick phonon dispersion does not change

But MFPs become limited to L

- Phonons with Λ<L are not affected
- Phonons with Λ>L have their MFP cutoff to L
  - Reduction in their contribution to thermal conductivity

$$\kappa = \frac{1}{3V}\sum_{k\lambda} \Lambda_{k\lambda}\, v_{k\lambda}\, C_{k\lambda}$$

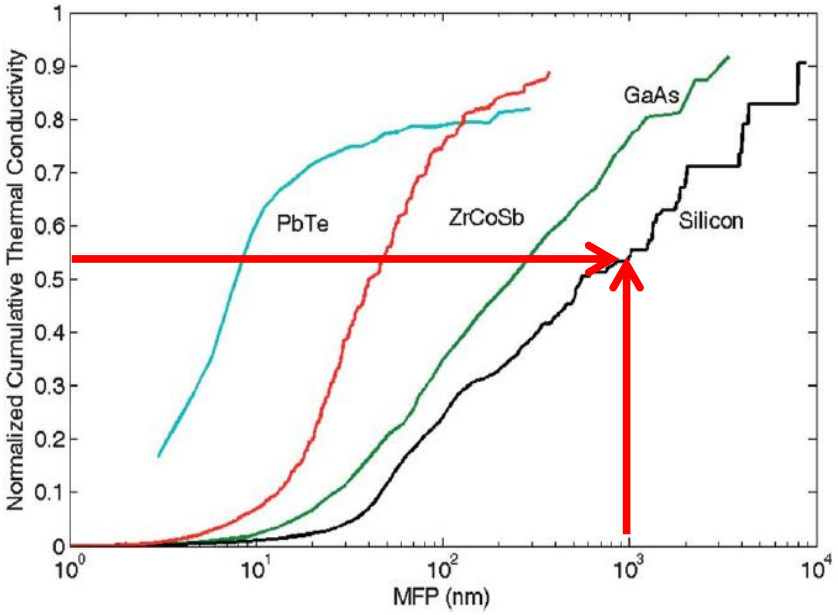
They become **ballistic**

$\Rightarrow$ Ballistic phonons "carry less heat"

because they become **smaller in number** $\delta f = \Lambda \frac{\partial f}{\partial T} \nabla T$ when Λ is reduced to L

(net carried heat is: $\sum_{modes} v\ \hbar\omega\ \delta f$) with reduced δf for ballistic phonons

Size effects



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Energy Environ. Sci. **5**, 5147 (2012).

The TDTR or FDTR experiments

Interpretation still based on Fourier law $D\frac{\partial^2 T}{\partial x^2} = \frac{\partial \mathrm{T}}{\partial t}$

$$D = \frac{\Lambda_{grey}^2}{\tau_{grey}};\ \frac{D}{L_C^2} = \frac{1}{t_c} = \omega$$

Define the thermal penetration depth $\mathrm{L_{th}} = \frac{<\Lambda_{\mathrm{grey}}>}{\sqrt{\omega<\tau>}}$

$\mathrm{L_{th}} \approx 1000 < \Lambda_{\mathrm{grey}} >$ if $\omega \approx MHz; \tau \approx ps$

- If $\Lambda > \mathrm{L_{th}}$ "ballistic" transport
- These phonons carry less heat (MFP will be limited to $\mathrm{L_{th}}$), leading to lower κ; see also the MFP distribution

Monte Carlo method

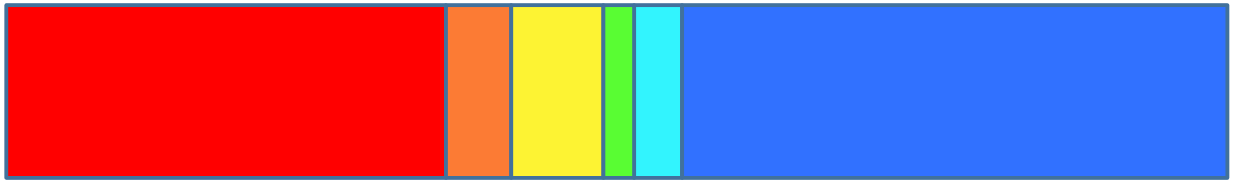
Can solve BTE for inhomogeneous and out of equilibrium systems

Requires dispersions, group velocities and scattering rates as input

Treats boundary scattering properly

Can also treat higly non-linear out of equilibrium cases

Non-Equilibrium Green's Function or the Landauer formula



Left lead Device Right Lead

$Conductance =$ heat flux per 1K temperature difference (in W/m²K)

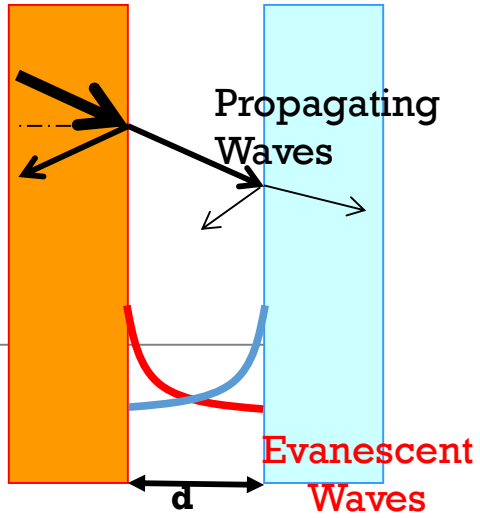
$$J = \frac{1}{V}\sum_k \ \Xi_{\mathrm{L-R}}(k) v_k^z \ e_k \ (f(\omega_k, T_L) - f(\omega_k, T_R))$$

$$G = \frac{1}{V}\sum_k \ \Xi_{\mathrm{L-R}}(k) v_k^z \ e_k \ \frac{df_k^o}{dT}$$ (in the linear regime)

$\Xi_{\mathrm{L-R}}(k)$= Transmission probability function=L × Tr $[G\Gamma_L G^+ \Gamma_R]/(DOS_L v_L)$

$$G = \frac{1}{V}\int_0^\infty d\omega \, D_L(\omega) \, \Xi_{\mathrm{L-R}}(\omega) \, v_L^z(\omega) \, C_L(\omega, T) \ = \frac{1}{A}\int_0^\infty d\omega \ \mathrm{Tr}\,[G\Gamma_L G^+ \Gamma_R] C(\omega)$$

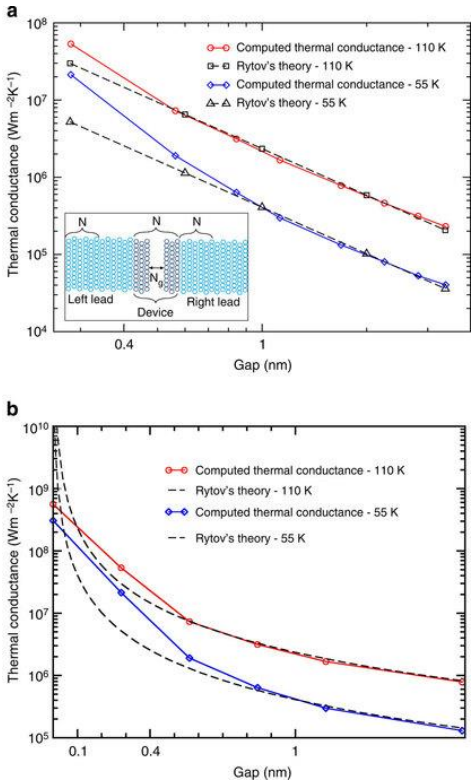
Application 1: near-field



At large distances, EM fields propagate like sine waves (far-field)

At distances small compared to the thermal wavelength, Plank's law of black-body radiation is not valid

- Evanescent modes which exist at the surface can "tunnel" and carry their energy to the other material. This can be orders of magnitude larger than the far-field black (or grey)-body radiation
- Long wavelength acoustic phonon "tunneling" contributes in this regime.
- **No distinction between Conduction and Radiation! They become the same!**



Application 2: Coherence effects in superlattices

Meaning of "Coherence"

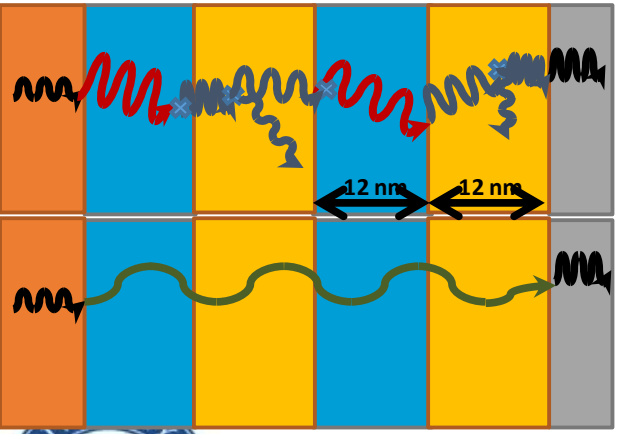
Long MFP phonons (Λ>5-10 a) "see" the superlattice and their constructive interference leads to a superlattice mode, which we call "coherent"

If Λ<a, then motion is diffusive and we call it "incoherent"

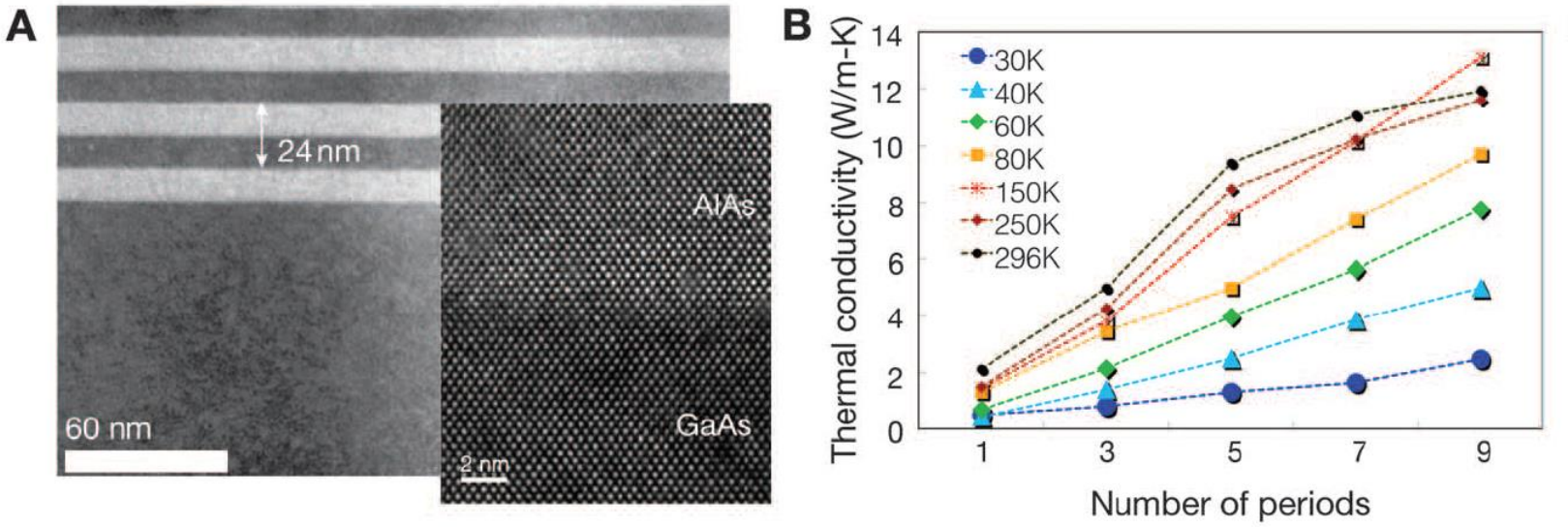
- Optical modes are usually incoherent, while long wavelength acoustic modes are coherent

How coherence can be observed?

- For small length samples, coherent modes usually travel ballistically (G=conductance=constant): size effect (κ increases with T: boundary scattering dominant, and with L)
- If Resistance increases with length (ohm's law) meaning $\kappa = constant$, diffusive incoherent

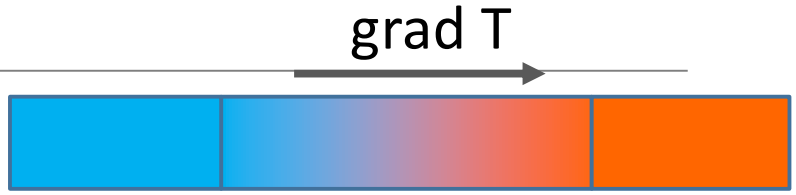


Coherence observed in GaAs/AlAs



Coherent Phonon Heat Conduction in Superlattices
Maria N. Luckyanova, Jivtesh Garg, Keivan Esfarjani et al. *Science* 16 Nov 2012: Vol. 338, Issue 6109, pp. 936-939

Non-Equilibrium Molecular Dynamics (NEMD)



Attach the two ends to two thermostats

Or attach one thermostat at one end and one thermostat to the middle atoms

Calculate the temperature profile and needed heat input at the two thermostats: $m\frac{d^2u}{dt^2} = F - m\xi\frac{du}{dt}$

Use Fourier Law to interpret data

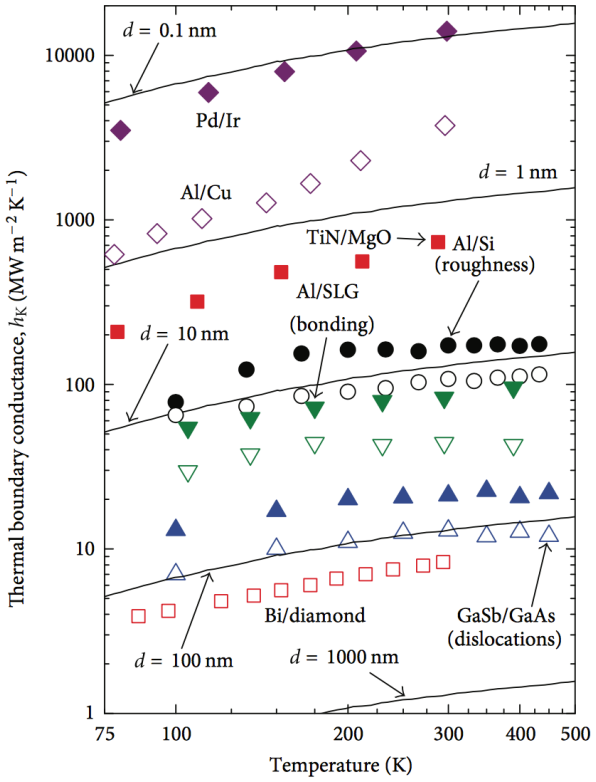
Classical MD good for studying trends and **gaining insights**, not very quantitative

Can treat both ordered and disordered systems

Problem: Size scaling for bulk materials; requires extrapolation of results to infinite size.

Thermal boundary resistance

From P. E. Hopkins



Discontinuity of the temperature profile at the interface between 2 materials

Due to partial reflection of some of the phonons

Non-equilibrium distribution of the phonons near the interface

Accounting for partial transmission and partial reflection leads to a thermal resistance

Models for transmission: (all harmonic)

- AMM for clean interfaces (similar to snell's law of refraction)
- DMM for rough interfaces (equal probability of reflection and transmission of a mode)
- Landauer formula (Transmission calculated using Green's function method or transfer matrix)
- NEMD is the other alternative

Summary

Many ways to compute/model thermal conductivity

Standard model (LD-BTE) works well for many materials

However new phenomena need better theories:

- Hydrodynamic phonon transport as in graphene
- Coherence in short superlattices
- Superdiffusive transport in some alloys
- Localization in some disordered systems

Acknowledgement

ICTP-ECAR sponsorship

Izmir Institute of Technology

Their Staff