Thermal transport from first-principles DFT calculations

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Classical MD simulations …

- … use an empirical potential fitted to reproduce lattice constant, cohesive energy, elastic properties, some phonons…
- But are not supposed to produce correct third derivatives of the potential energy, determining phonon lifetimes
- They can be used to explain trends in thermal transport, but can not predict quantitatively the thermal conductivity.

Goal

- To develop a general methodology to get accurate estimates of thermal properties using available density functional theory (DFT) tools.

- To make accurate / reliable predictions without fitting any parameters to experimental data.

Outline

- New force field based on FP-DFT
- Approaches for thermal conductivity calculation + illustrations
  - Lattice dynamics model
  - MD
  - Green's functions for coherent transport
- Conclusions

Force field model

Force displacements

$$-F_i^\alpha = \nabla_i^\alpha E = \Pi_i^\alpha + \sum_{j,\beta} \Phi_{ij}^{\alpha\beta} u_j^\beta + \frac{1}{2!}\sum_{jk,\beta\gamma} \Psi_{ijk}^{\alpha\beta\gamma} u_j^\beta u_k^\gamma$$

$$+\frac{1}{3!}\sum_{jkl,\beta\gamma\delta} X_{ijkl}^{\alpha\beta\gamma\delta} u_j^\beta u_k^\gamma u_l^\delta$$

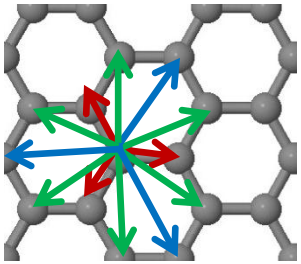
$$\Pi_i^\alpha = \frac{\partial E}{\partial u_i^\alpha};\ \Phi_{ij}^{\alpha\beta} = \frac{\partial^2 E}{\partial u_i^\alpha \partial u_j^\beta};\ \Psi_{ijk}^{\alpha\beta\gamma} = \frac{\partial^3 E}{\partial u_i^\alpha \partial u_j^\beta \partial u_k^\gamma};$$

$$X_{ijkl}^{\alpha\beta\gamma\delta} = \frac{\partial^4 E}{\partial u_i^\alpha \partial u_j^\beta \partial u_k^\gamma \partial u_l^\delta}$$

Derivatives are calculated at or near equilibrium

Exact for small displacements!

As the FCs are 2nd or higher rank tensors, there are a huge number of terms in the Taylor expansion!



9 for each pair * number of pairs

27 for each triplet * number of triplets

81 for each quadruplet * number of quadruplets

They need to be reduced

Method to extract anharmonic force constants from first principles calculations
Keivan Esfarjani and Harold T. Stokes
Phys. Rev. B **77**, 144112 (2008)

Symmetry constraints

The FCs are related by the following symmetry constraints:

- Permutation of the order of derivatives

$$\Phi_{ij}^{\alpha\beta} = \Phi_{ji}^{\beta\alpha}$$

- Global Translational invariance

$$0 = \sum_{\mathrm{j}} \Phi_{\mathrm{ij}}^{\alpha\beta} \; ; \; 0 = \sum_{\mathrm{j}} \Psi_{\mathrm{ijk}}^{\alpha\beta\gamma}$$

Method to extract anharmonic force constants from first principles calculations

Keivan Esfarjani and Harold T. Stokes, Phys. Rev. B **77**, 144112 (2008)

Symmetry constraints

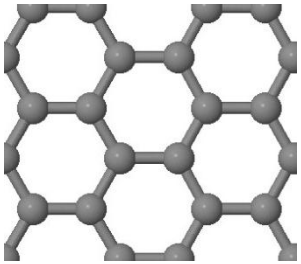
- Global Rotational invariance

Links FCs to higher-order ones

$$\sum_{R} \Psi \times R = \Phi \;\; ; \;\; \sum_{R} X \times R = \Psi$$

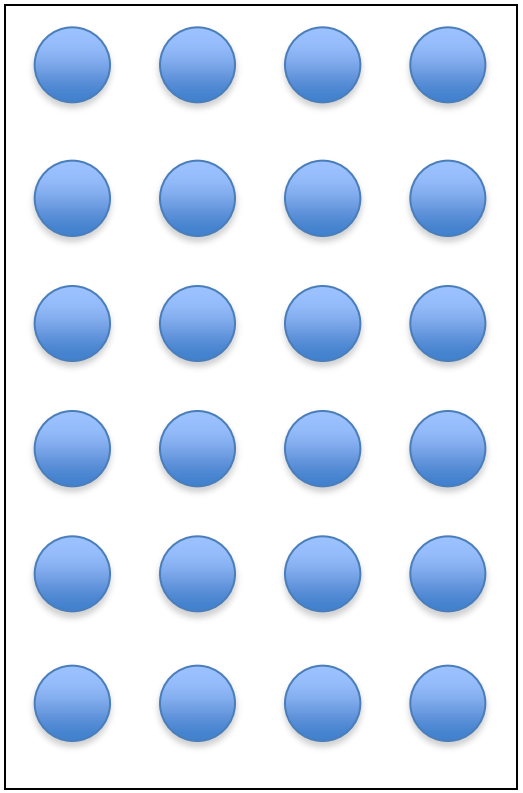
- Group symmetry operation invariance

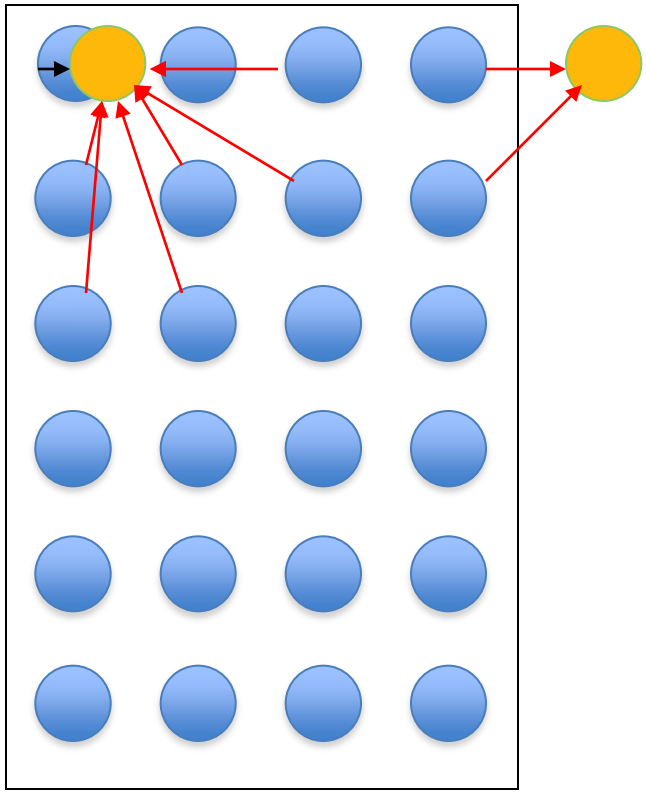
$$\Phi_{ij}^{\alpha\beta} = \sum_{\alpha'\beta'} S_{\alpha\alpha'} \; S_{\beta\beta'} \; \Phi_{S(i)S(j)}^{\alpha'\beta'} \quad \cdots$$



These symmetries must be enforced for any FC model to be physically correct

Methodology : FP-DFT calculations in a supercell (real space)





Supercell size should ideally be larger than the range of the force constants

$$-F_i^\alpha = \Pi_i^\alpha + \sum_{j,\beta} \Phi_{ij}^{\alpha\beta} u_j^\beta + \frac{1}{2!} \sum_{jk,\beta\gamma} \Psi_{ijk}^{\alpha\beta\gamma} u_j^\beta u_k^\gamma + \ldots$$

Extraction of FCs:

- Constraints are **linear** in FCs
- Force-displacement relations also **linear** in FCs

$$\begin{bmatrix} \text{Invariance constraints} \\ U \\ \text{FP-DFT Force-displacement data} \end{bmatrix} \begin{bmatrix} \\ \Phi \\ \\ \end{bmatrix} = \begin{bmatrix} 0 \\ F \\ \\ \end{bmatrix}$$

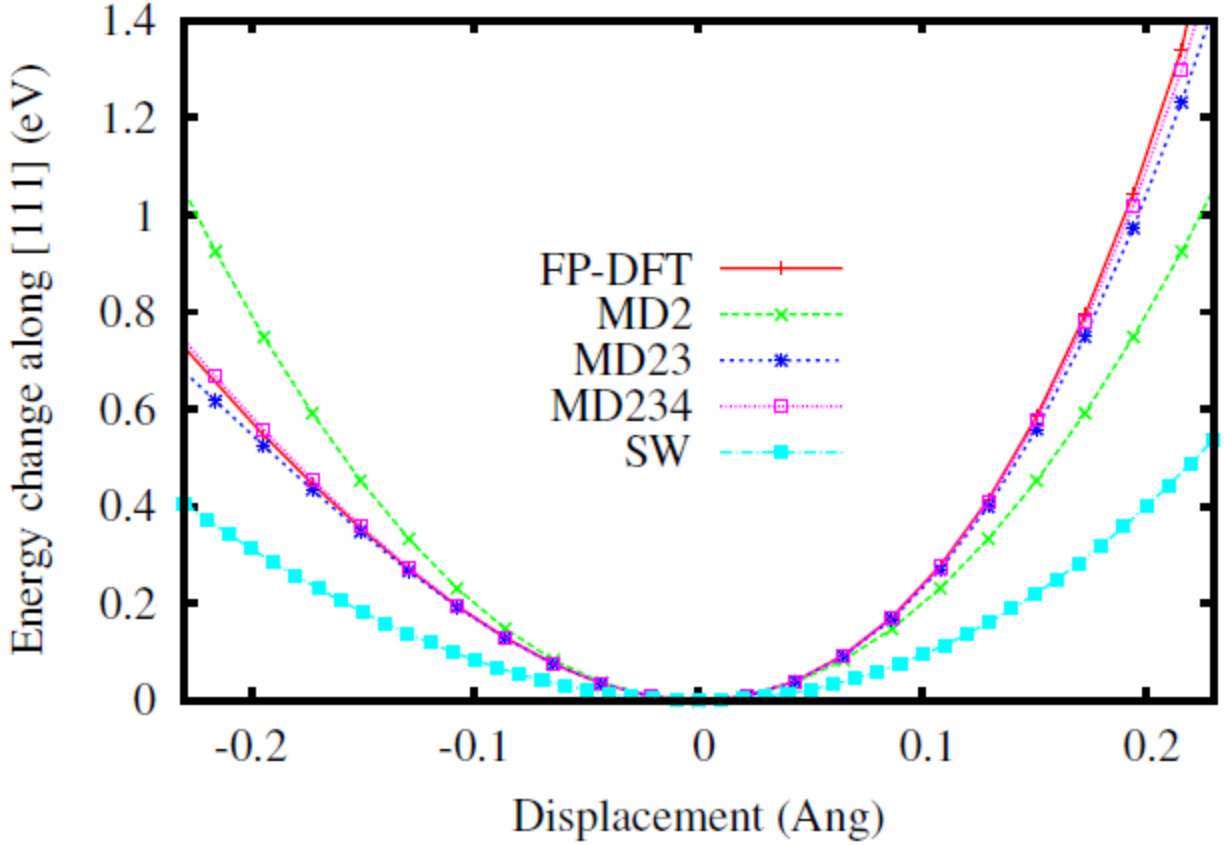
- Over-complete system of linear equations
- FCs are deduced from a SVD algorithm

Method to extract anharmonic force constants from first principles calculations

Keivan Esfarjani and Harold T. Stokes, Phys. Rev. B **77**, 144112 (2008)

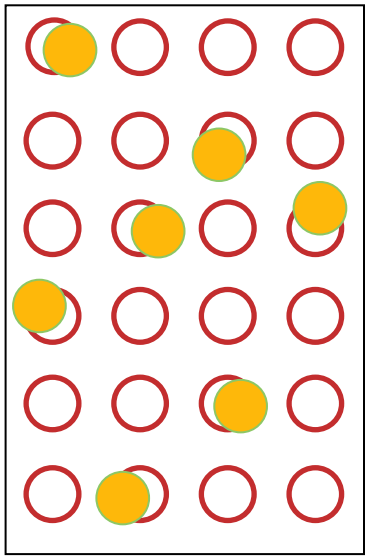
How accurate are the obtained FCs?

- Move one Si atom along [111]



More validation

- Use the FCs to calculate forces for arbitrary atomic displacements



	Denominator	σ(Poly)	σ(SW)
DISP=0.1 Ang	205.67	0.046941	0.34490
DISP=0.2 Ang	1166.9	0.082234	0.28324

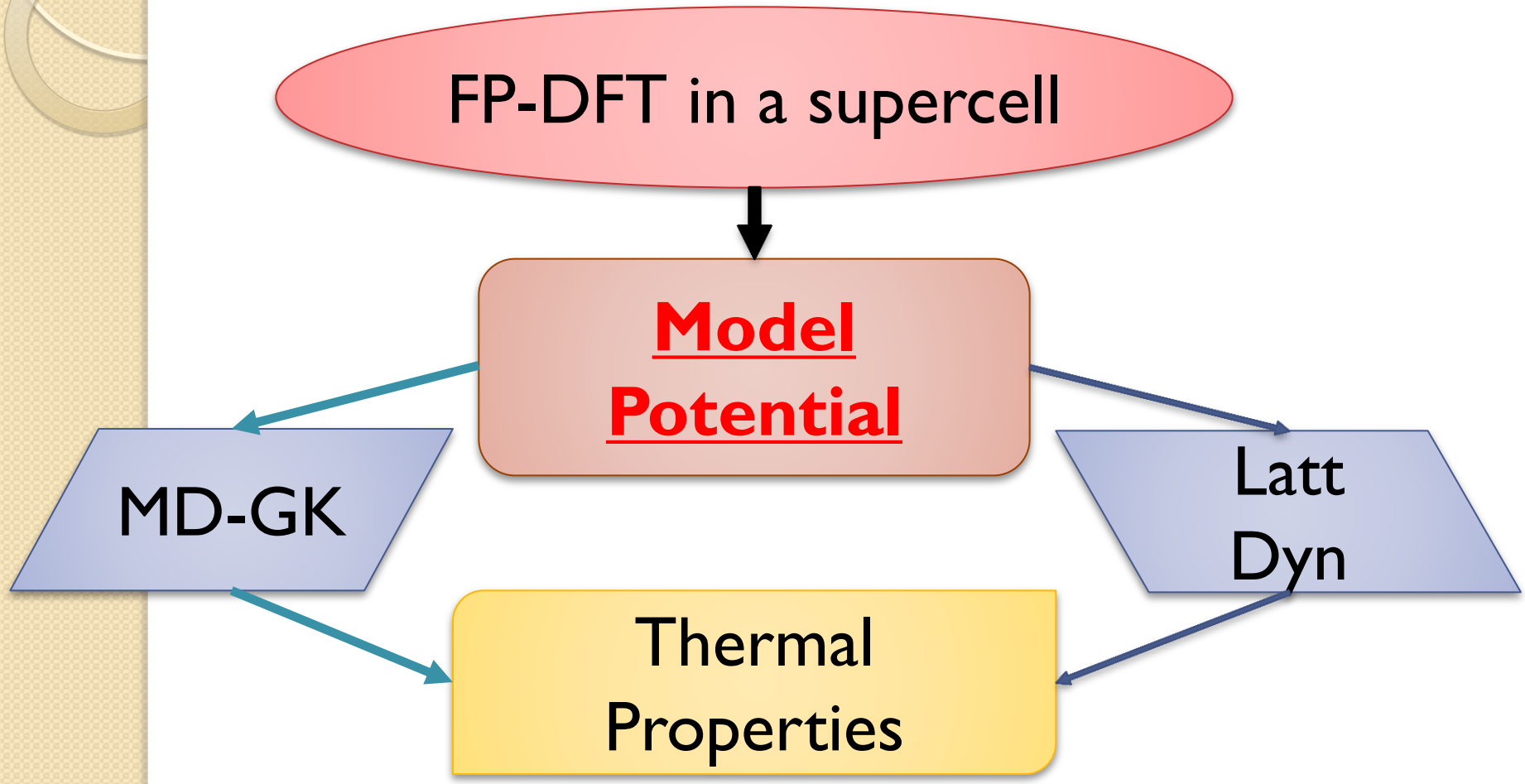
Error is due to choosing (5,1,1) neighbors in the model

Now what ?

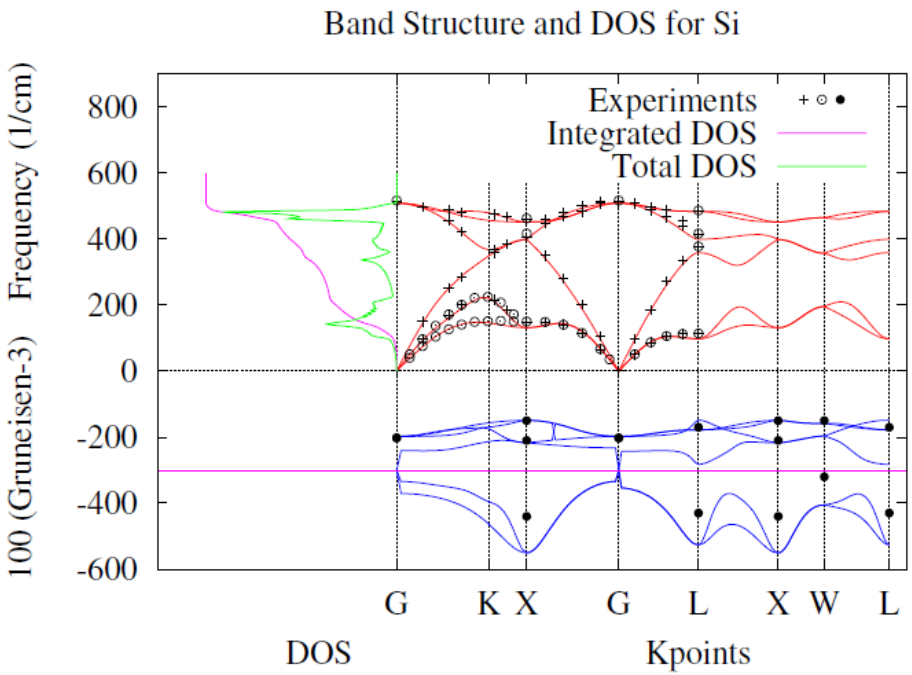
- Use second derivatives to get phonon dispersion
- Use the third derivatives to get phonon lifetimes
- Use all to do MD

Alternative approach to determining FCs uses DFPT
(See talk by Derek Stewart)

Summary of the approach

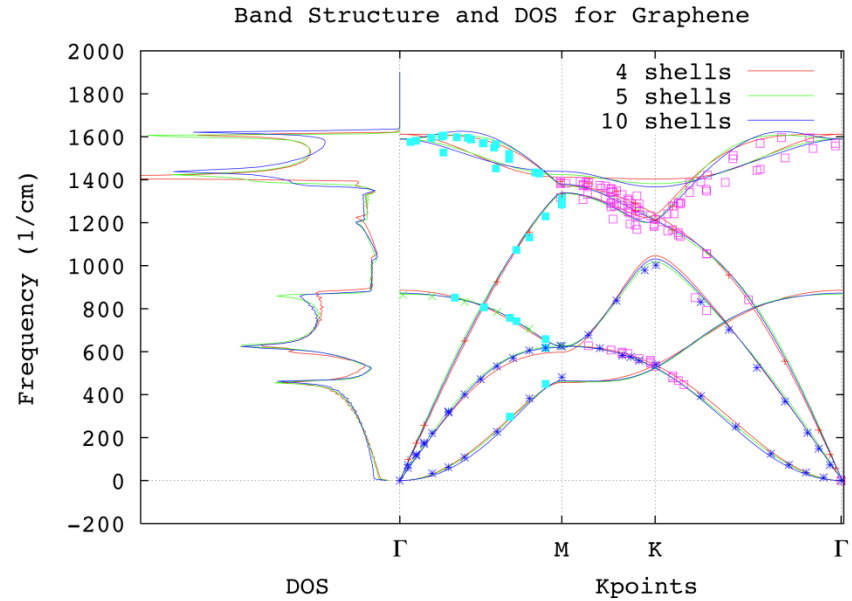


Phonon Dispersion For Si, Graphene, ZrCoSb

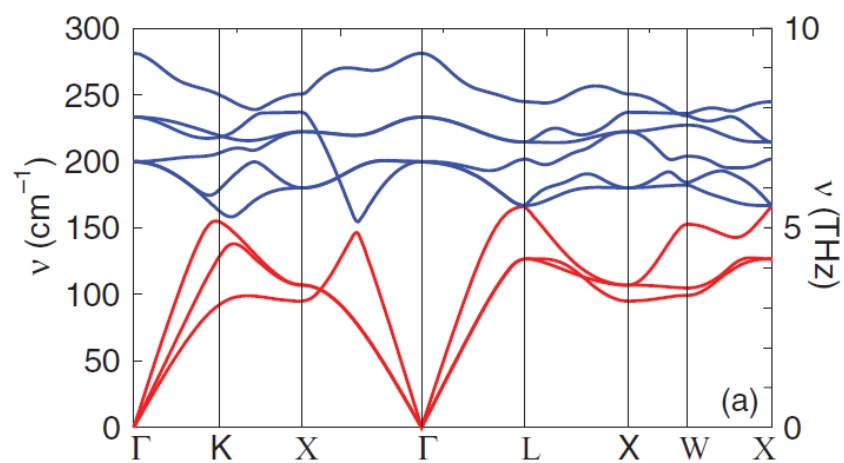


K. Esfarjani, G. Chen, and H.T. Stokes
Phys. Rev. B **84**, 085204 (2011)

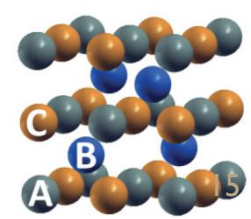
$$\gamma_{k\lambda} = -\frac{d\ln\omega_{k\lambda}}{d\ln V}$$



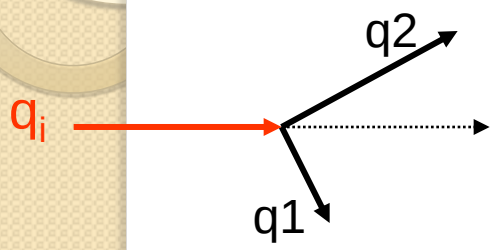
N. Mingo, K. Esfarjani, D.A. Broido, and D.A. Stewart
Phys. Rev. B **81**, 045408 (2010)



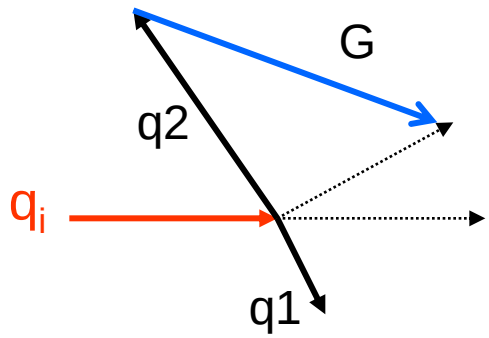
ZrCoSb Half-heusler; By J. Shiomi, KE, G. Chen, PRB 84 (2011)



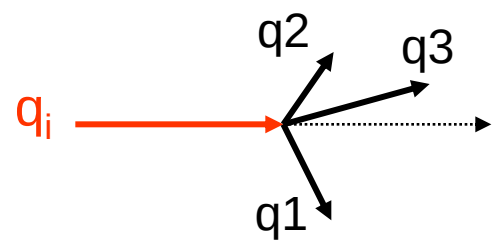
Lifetimes due to 3-phonon processes



Normal process



Umklapp process



a 4−phonon process

$$V = \frac{1}{3!}\sum_{ijk,\alpha\beta\gamma}\Psi_{ijk}^{\alpha\beta\gamma}\, u_i^{\alpha}\, u_j^{\beta}\, u_k^{\gamma} + \frac{1}{4!}\sum_{ijkl,\alpha\beta\gamma\delta} X_{ijkl}^{\alpha\beta\gamma\delta}\, u_i^{\alpha}\, u_j^{\beta}\, u_k^{\gamma}\, u_l^{\delta} + \ldots$$

Phonon creation and annihilation operators

$$W(i,f) = \frac{2\pi}{\hbar}|<i|V|f>|^2\,\delta(E_i - E_f)$$ Fermi Golden Rule

Thermal conductivity

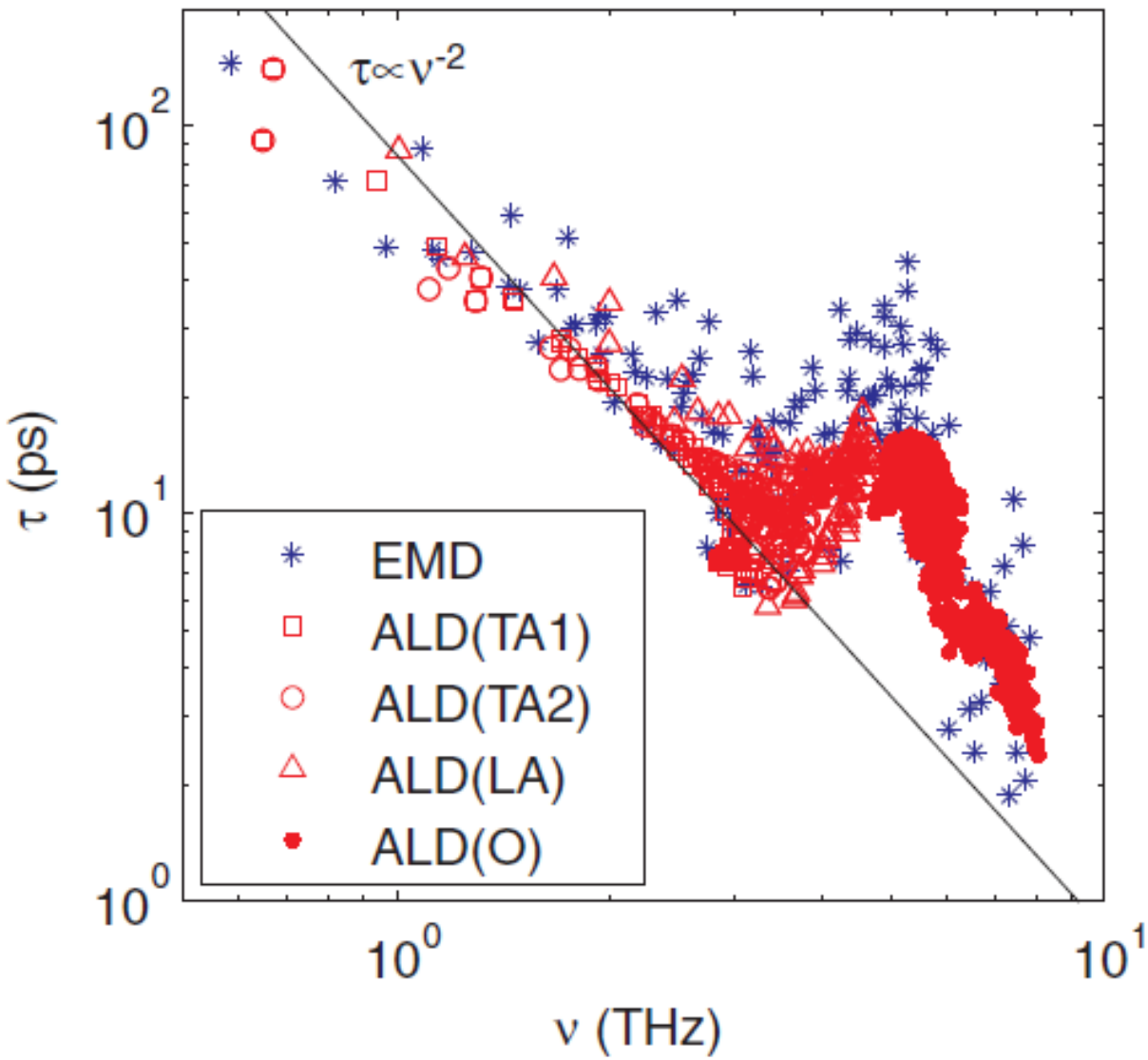
- Use of the relaxation time approximation

$$\kappa = \frac{1}{3}\sum_{k\lambda} v_{k\lambda}^2 \tau_{k\lambda} \hbar\omega_{k\lambda}\, \partial n_{k\lambda}/\partial T$$

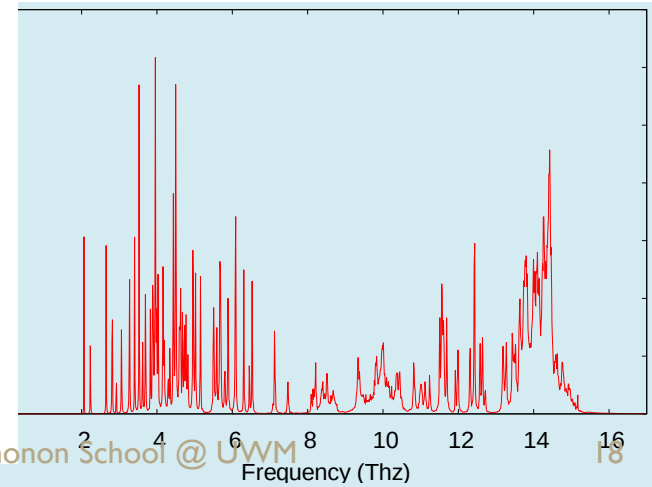
Relaxation time

C_v per mode

ZrCoSb lifetimes: LD-FGR versus MD



$$E(\nu) = \left\langle \sum_{\alpha\eta l} M_\eta \left| \int v^\alpha_{\eta l}(t) e^{-2\pi i \nu} dt \right|^2 \right\rangle,$$

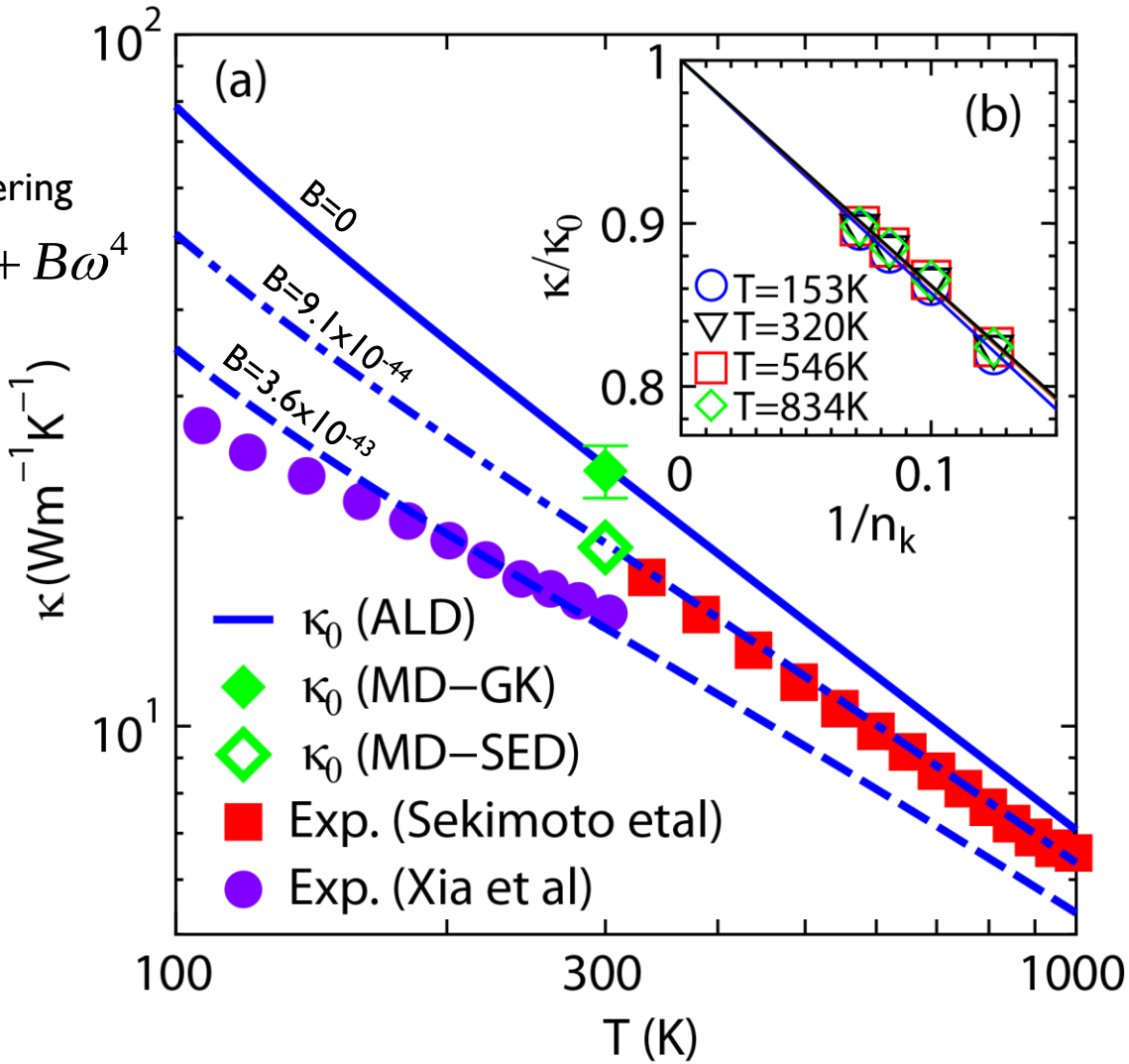


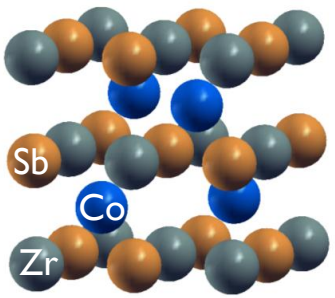
Shiomi, Esfarjani, Chen, Phys. Rev. B 84, 104302 (2011)

Thermal conductivity of ZrCoSb
Simulations vs Experiments

Impurity scattering

$$1/\tau = 1/\tau_0 + B\omega^4$$





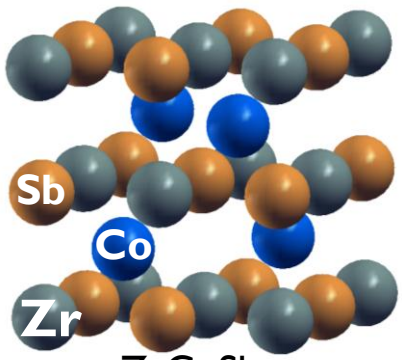
Y. Xia et al., J. Appl. Phys. 88, 1952 (2000).
T. Sekimoto et al., Jpn. J. Appl. Phys. 46, L673 (2007).

Shiomi, Esfarjani, Chen, Phys. Rev. B 84, 104302 (2011)

Alloying effect on half-Heusler thermal conductivity

Transferability of force constants

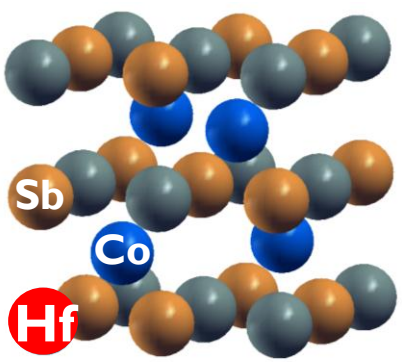
22 $Wm^{-1}K^{-1}$



ZrCoSb

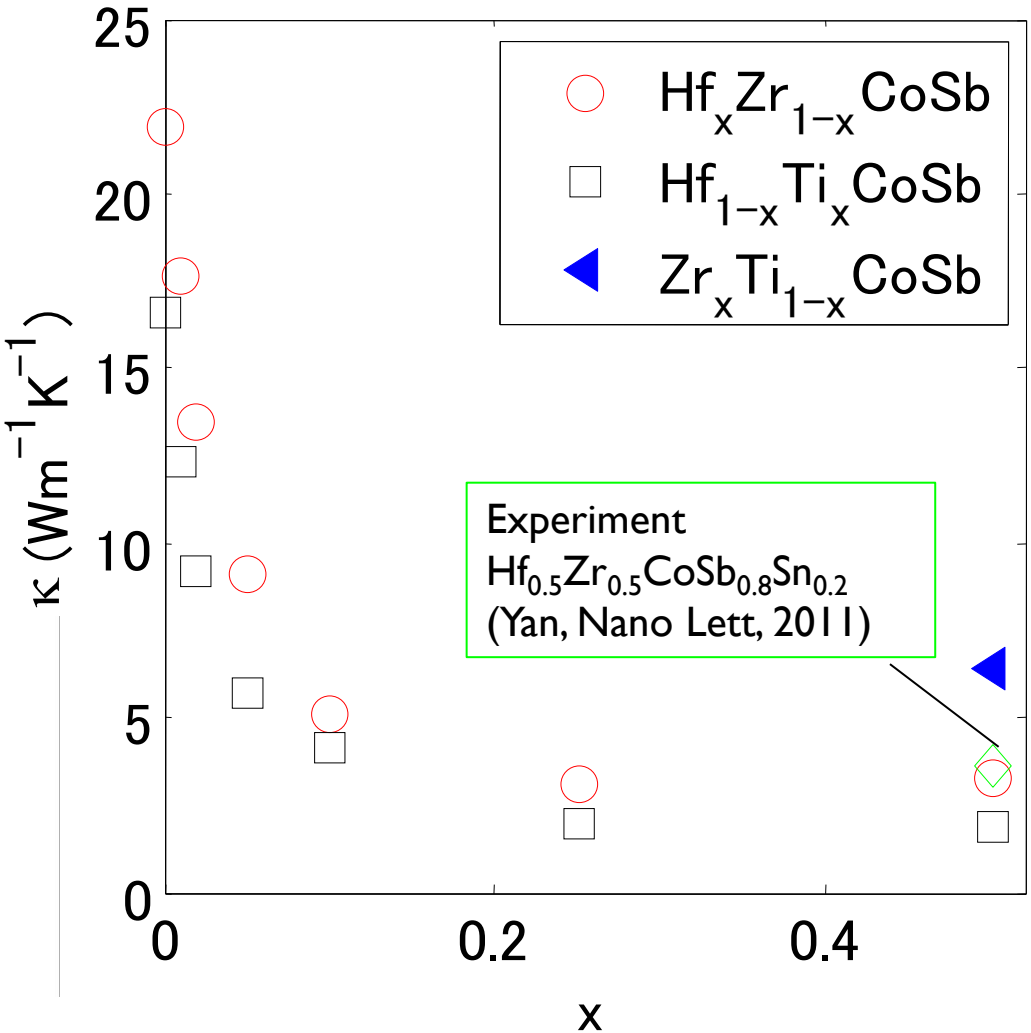
Only changing mass

16 $Wm^{-1}K^{-1}$



HfCoSb

Green Kubo Calculation (300 K)

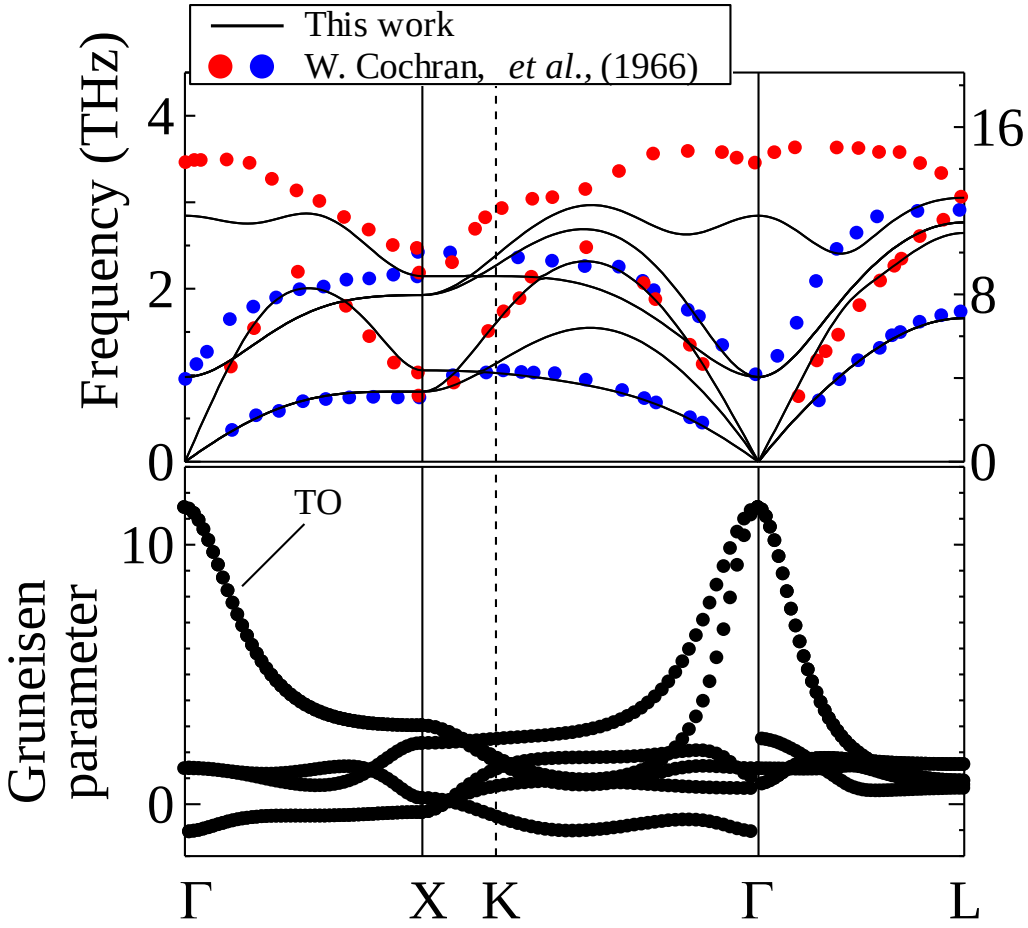


Shiomi, Esfarjani, Chen, Phys. Rev. B 84, 104302 (2011)

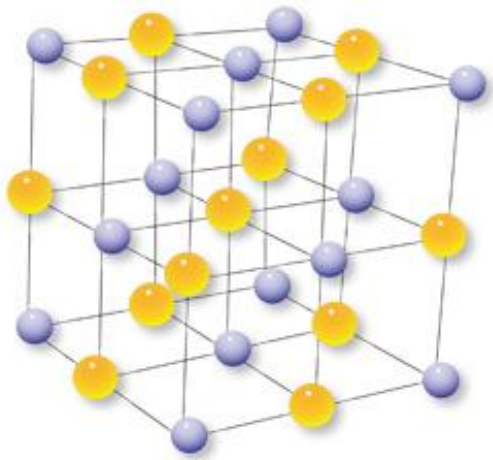
Thermal conductivity of PbTe

Microscopic mechanism of low thermal conductivity in lead telluride
T Shiga, J Shiomi, J Ma, O Delaire, T Radzynski, A Lusakowski, K E, and G Chen
Phys. Rev. B **85**, 155203 (2012)

Takuma Shiga



Why is thermal conductivity of PbTe so low (~2 $Wm^{-1}K^{-1}$ @300K)?



Rocksalt PbTe

Phonons in lead telluride

Takuma Shiga

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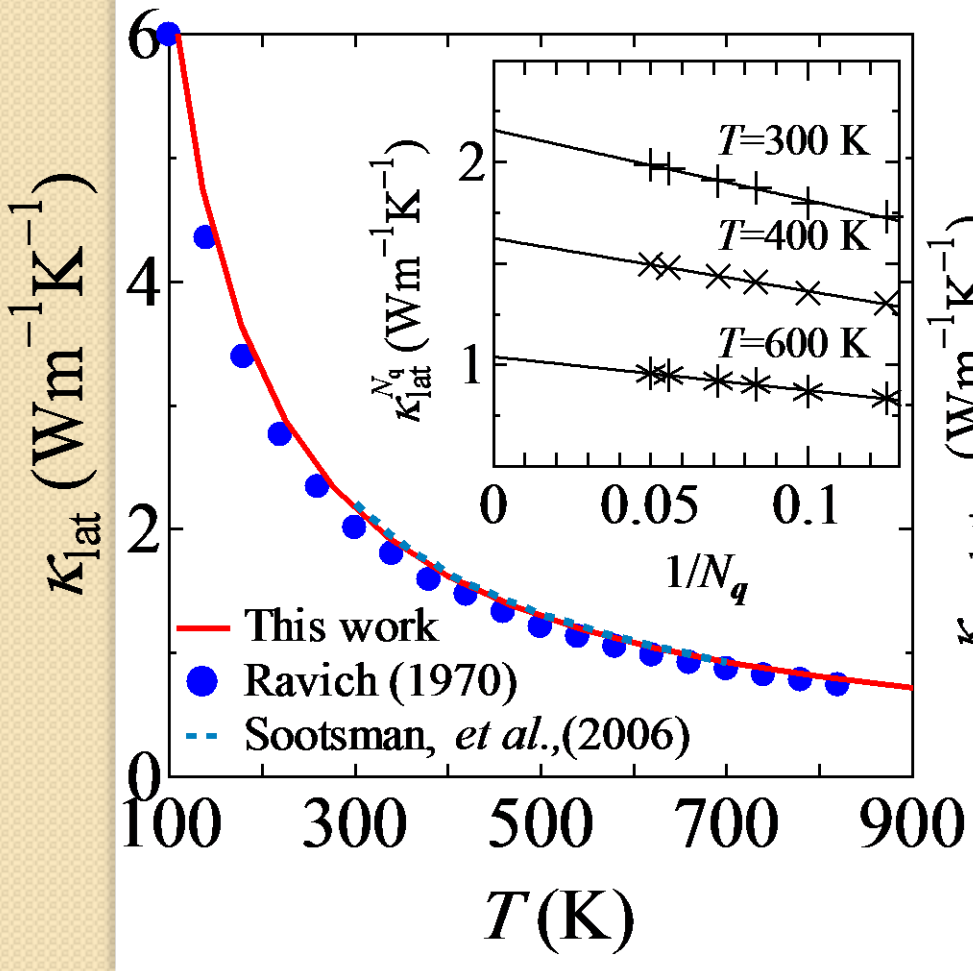
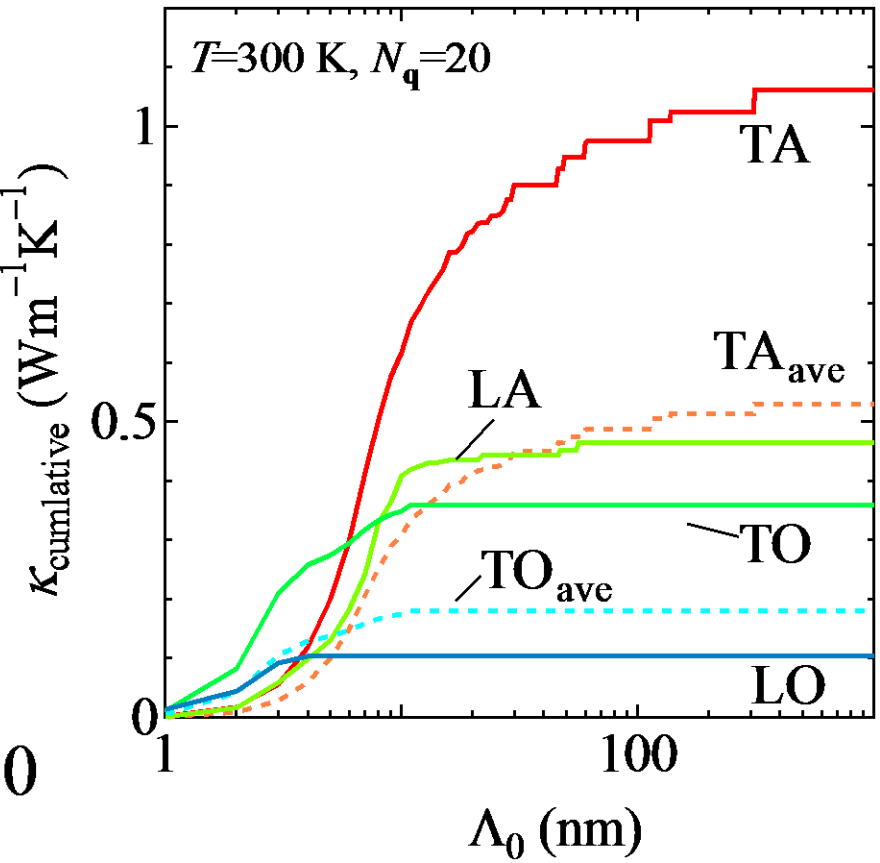
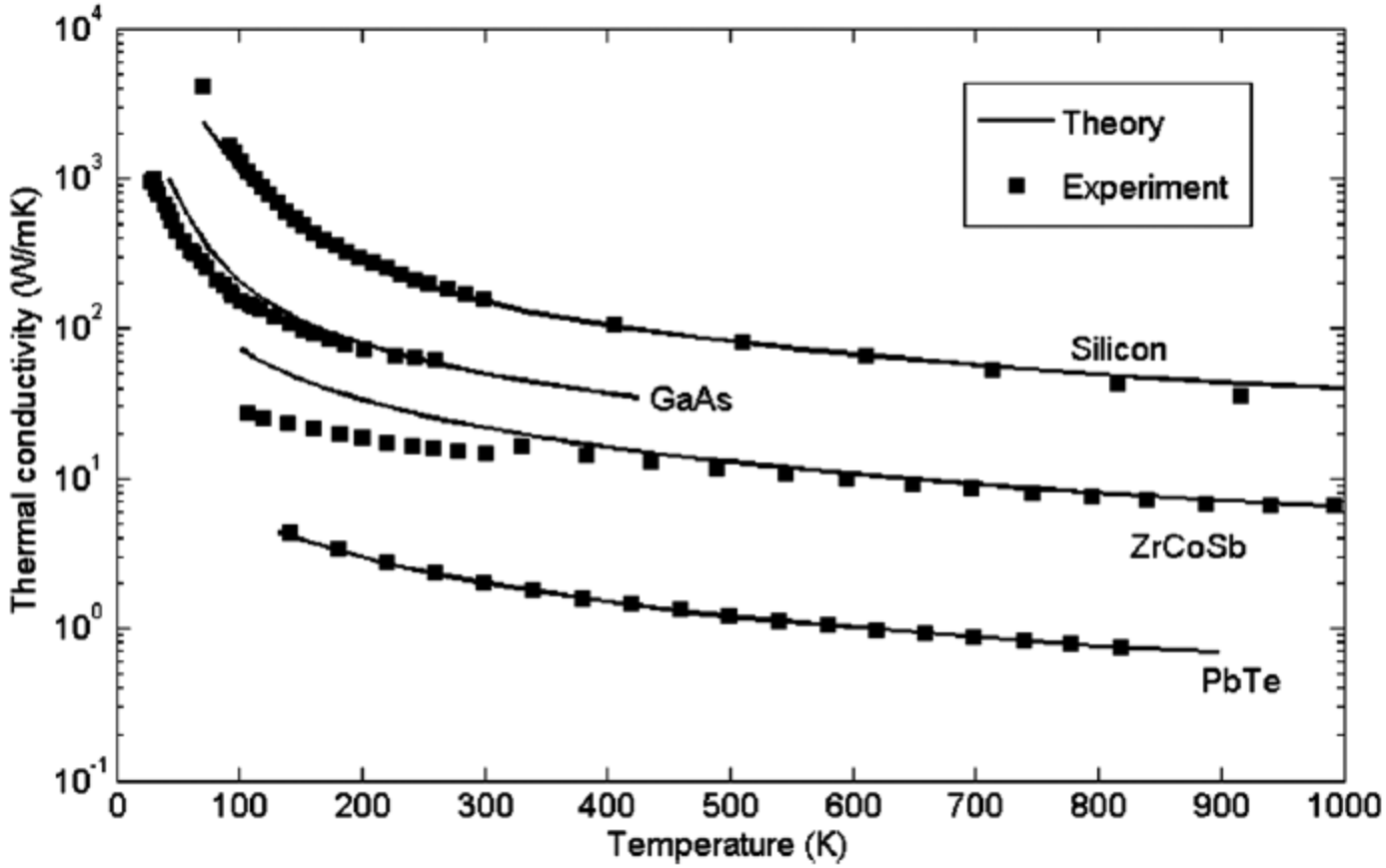




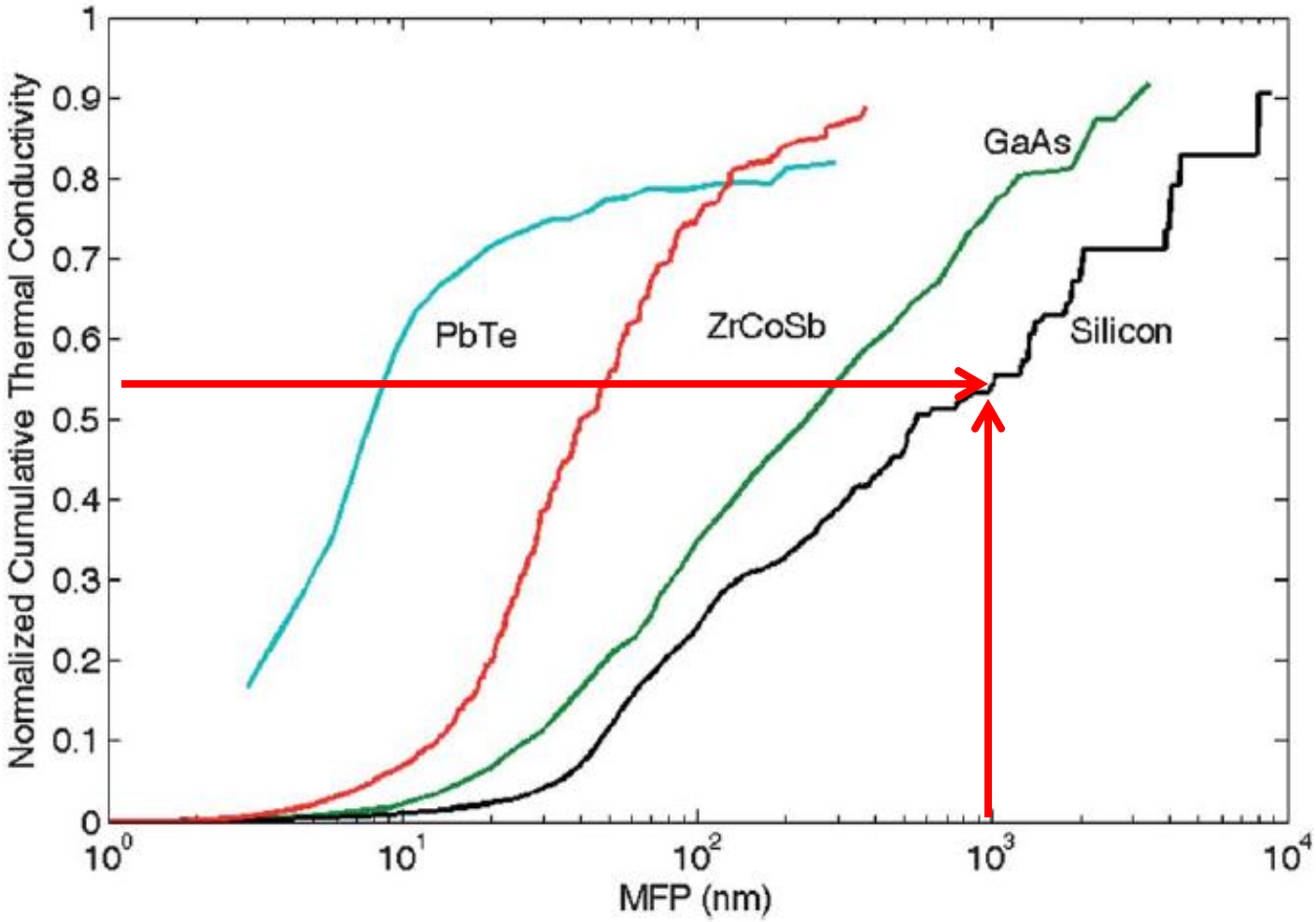
Perspectives on thermoelectrics: from fundamentals to device applications

M. Zebarjadi,[a] K. Esfarjani,[a] M. S. Dresselhaus,[b] Z. F. Ren*[c] and G. Chen*[a]

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



Summary of LD: MFP distribution



Perspectives on thermoelectrics: from fundamentals to device applications

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MD using the polynomial force field

- PROS:
  - Of accuracy similar to DFT
  - Includes anharmonic effects to higher order
- CONS:
  - Can not describe structural changes
  - Hard to include surfaces and defects
- Ideal for thermal conductivity using GK

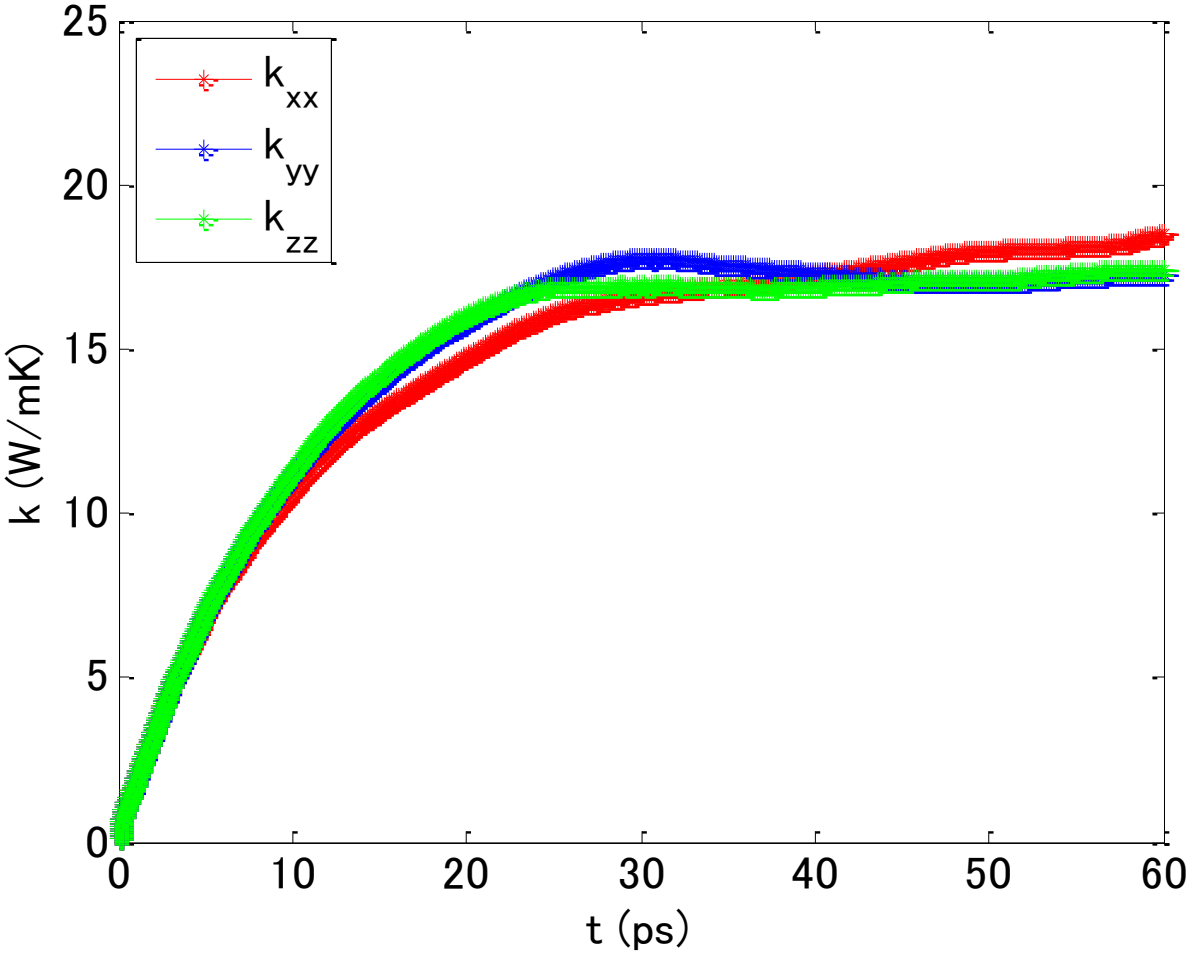
Equilibrium Green-Kubo (GK)

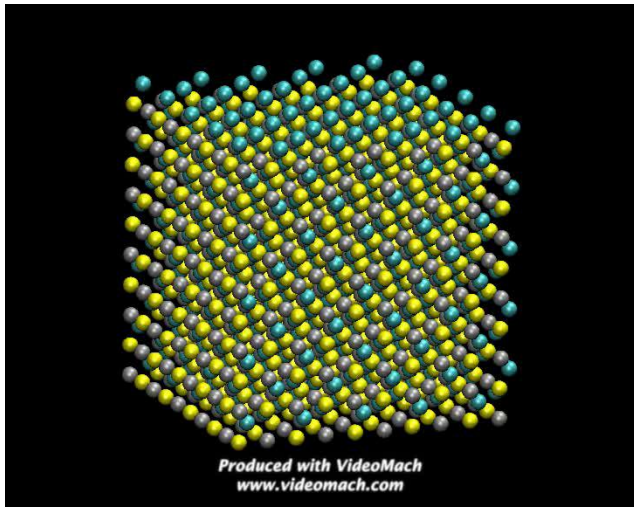
$$\kappa_{\alpha\beta} = \frac{1}{V k_B T^2} \int_0^\infty < J^\alpha(0) J^\beta(t) > \, dt$$

$$J^\alpha = \sum_i J_i^\alpha = \sum_i \frac{d(e_i r_i^\alpha)}{dt} = \sum_{ij} (R_i^\alpha - R_j^\alpha)(v_j \cdot \frac{\partial e_i}{\partial u_j})$$

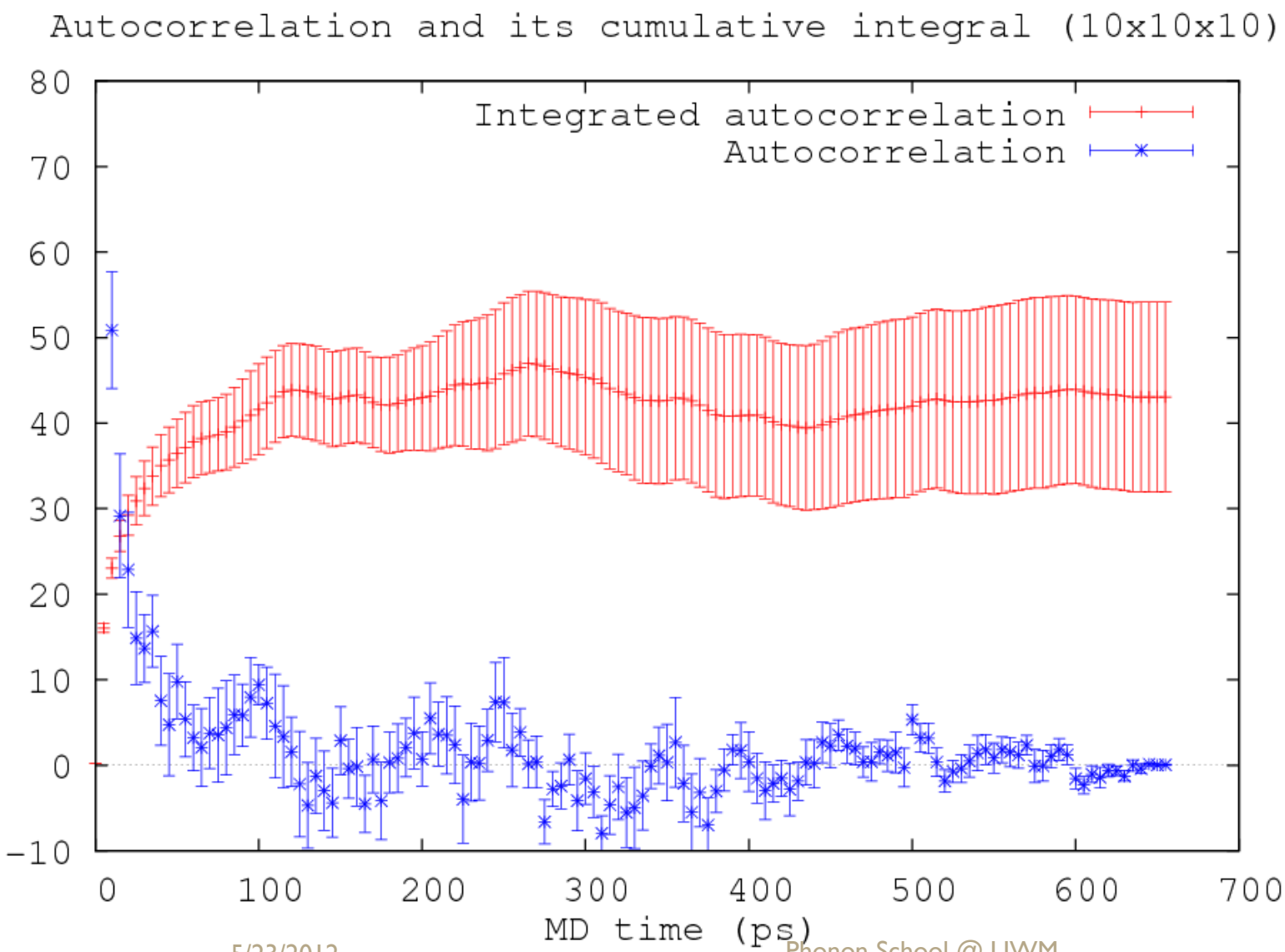
$$\begin{aligned} e_i &= \frac{1}{2} m_i v_i^2 + \frac{u_i}{2} \sum_j [\Phi_{ij}\, u_j + \frac{1}{3} \sum_k \Psi_{ijk}\, u_j u_k \\ &+ \frac{1}{12} \sum_{ijkl} \chi_{ijkl}\, u_j u_k u_l] \end{aligned}$$

Half-Heuslers





Silicon


Autocorrelation and its cumulative integral (10x10x10)
Integrated autocorrelation
Autocorrelation
80
70
60
50
40
30
20
10
0
-10
0
100
200
300
400
500
600
700
MD time (ps)

Wave effects in thermal transport

- Quantization of thermal conductance
- Coherent (ballistic) phonon contribution

Coherent phonon transport

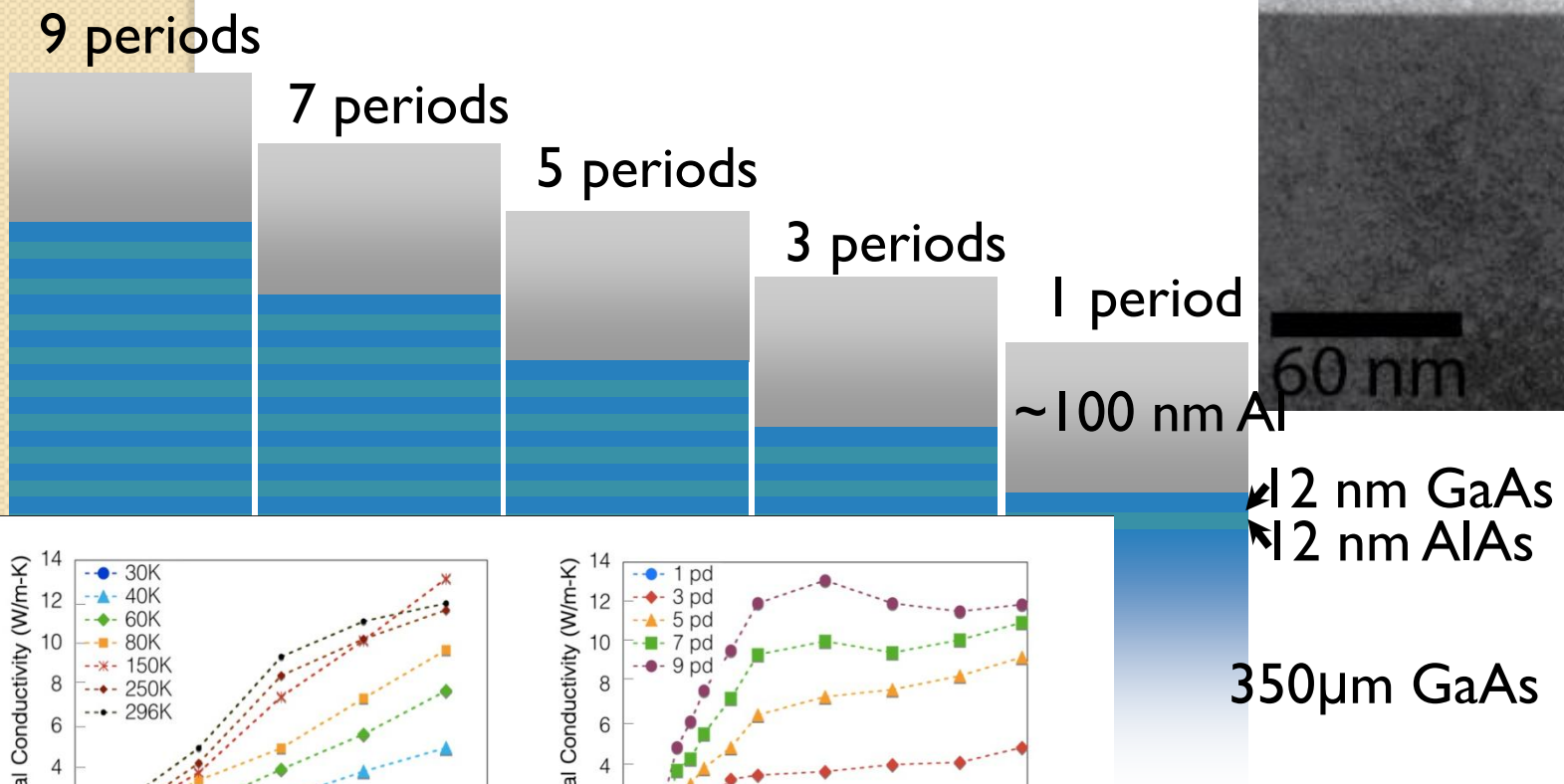
- Landauer formula

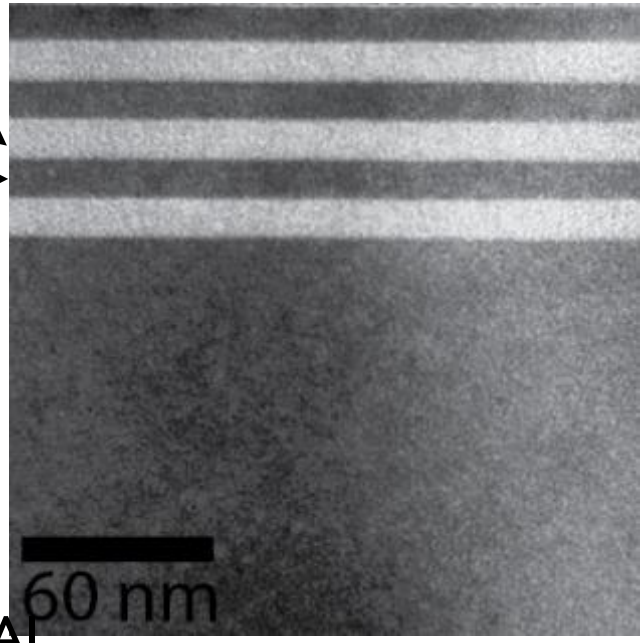
$$G = \sum_{m} \int_{0}^{\infty} \frac{d\omega}{2\pi} \boxed{D_m(\omega)\, v_{gm}} \hbar\omega \frac{\partial n(T,\omega)}{\partial T} \Xi(\omega)$$

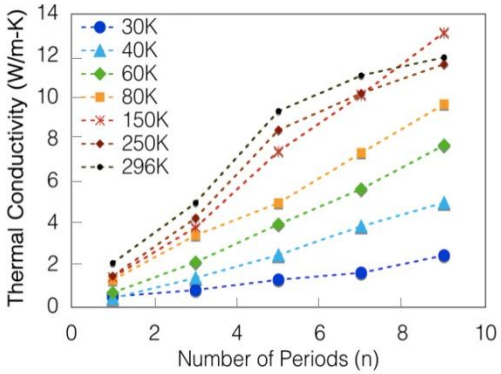
$= 1$

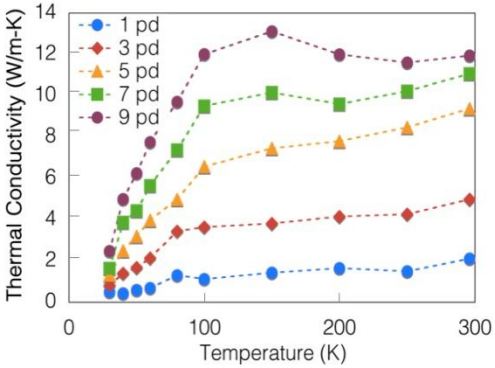
- Transmission formula

Experimental samples



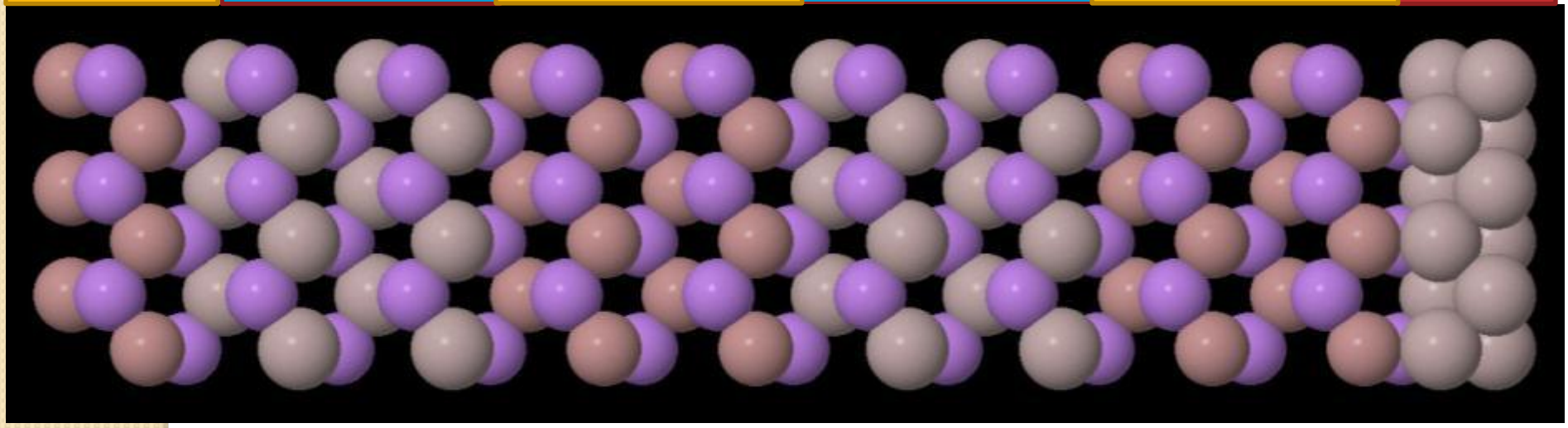






$GaAs\text{-}[(AlAS)_{22}/(GaAs)_{22}]_{N=1,\ldots,9}\text{-}Al$

GaAs	AlAs	GaAs	AlAs	GaAs	Al

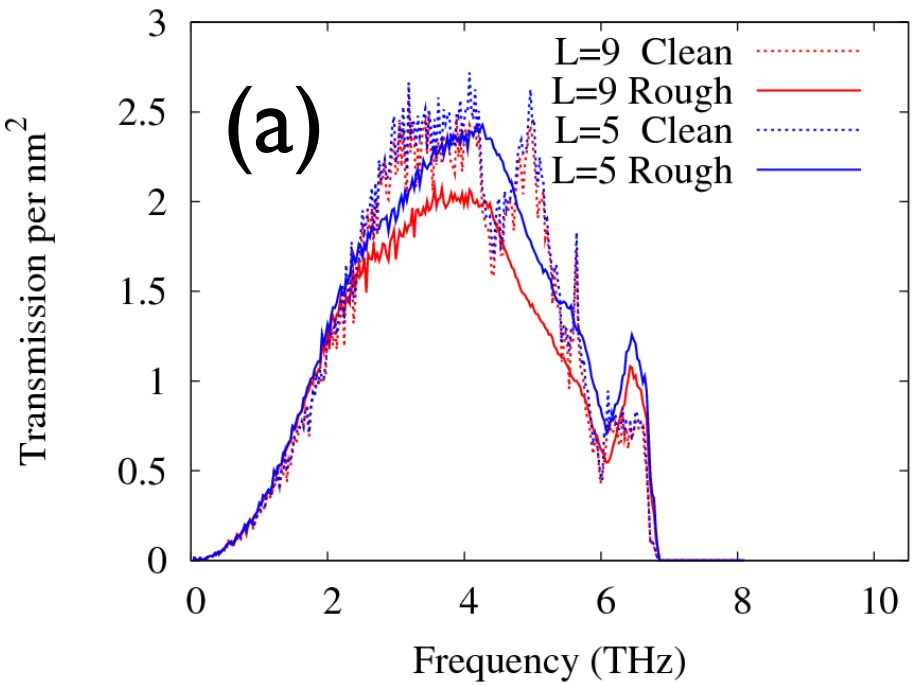


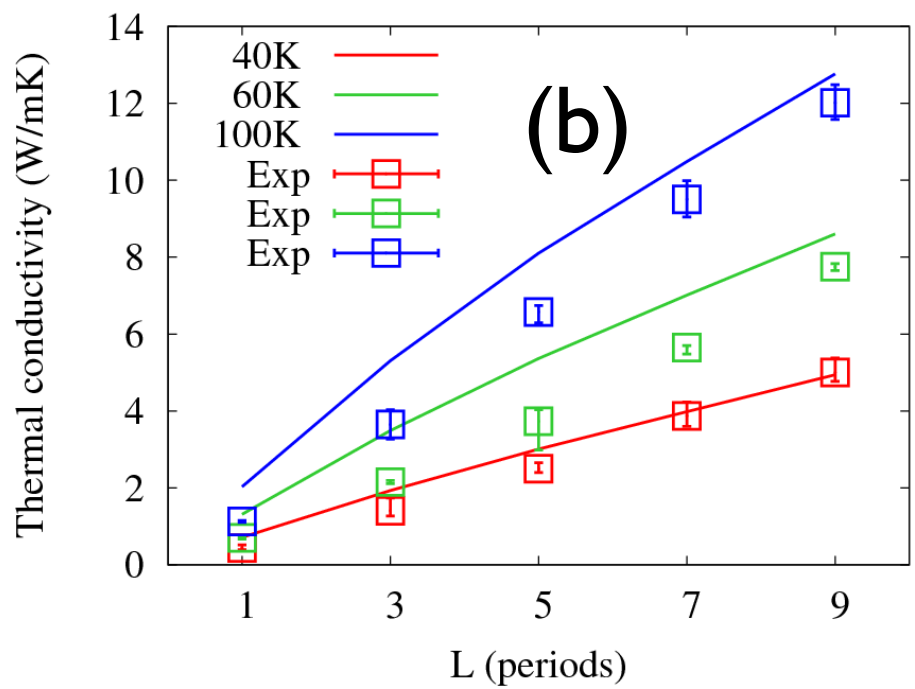
1 unit= 22 layers AlAs+22 layers GaAs

Period length=2*(22*5.4 Ang)=23.76 nm

N-periods (**N=1,3,5,7,9**); 3x3 cross section for a total of 1584,…,up to 14256 atoms

Transmission and Conductivity





Conclusions

- The developed force field can be calculated for an arbitrary crystal structure
- It can be used to:
  - Do LD, get phonon spectra, lifetimes, κ (fast)
  - Do MD, get lifetimes and κ including alloy scattering and anharmonic effects nonperturbatively
  - Set up the GFs to calculate transmission & conductance
- LD faster and more accurate than GK-MD, but valid at low T
- In nanostructured materials:
  - Wave effects are important,
  - Heat transport can have a large ballistic component
  - Boundary scattering can be dominant
  - Optical modes contribution is increased

Acknowledgements

- Gang Chen (MIT)
- Junichiro Shiomi (U Tokyo) ZrCoSb, PbTe
- Takuma Shiga (U Tokyo) PbTe
- Maria Luckyanova (MIT) GaAs/AlAs SLs
- J. Garg (MIT) GaAs/AlAs phonon lifetimes
- TF Luo (Notre Dame) GaAs