Modeling thermal conductivity: a Green-Kubo approach

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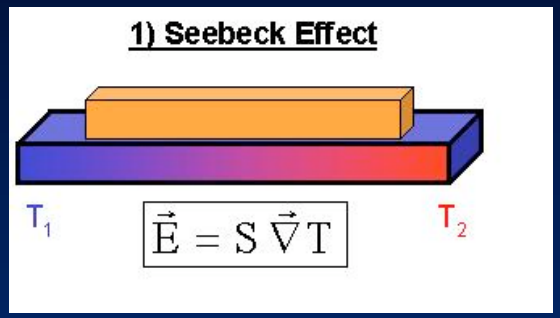
Outline

- Motivation -- thermoelectrics
- Theory
- Implementation
- Preliminary results

Motivation: Thermoelectrics

- **Goal: Optimize ZT (efficiency)**
  - **engineering of phonon & electronic energy dispersions**

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



Focus of this work is on lattice contribution, κ_{ph}

Motivation: Optimization of ZT

Parameter fitting (Genetic Algorithm)

First principles electronic structure

Tight binding calculation

Boltzmann Transport Equation
Green Kubo formalism

Electronic contribution:
- Seebeck coefficient
- Electrical conductivity
- Thermal conductivity

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

Lattice contribution:
- Thermal conductivity

Boltzmann Transport Equation
Green Kubo formalism

First principles Force Fields

JPL Lattice Contribution to Thermal Conductivity

Goals / General Approach:

Principal goal is the optimization of thermoelectric figure of merit ZT.

- Validate code by computing λ for C, Si, Ge
- Compute λ for various bulk materials (e.g. Bi_2Te_3)
- Generalize to simple nanostructures.

Technical Approach:

- Can compute λ by MD or BTE
- One option is NEMD (non-equilibrium), but …
  - NEMD requires large temperature gradients
  - boundary condition issues at interfaces
- Instead pursue Green-Kubo approach:
  - Fluctuation-Dissipation theorem:

$$\lambda_{\alpha\beta}(\omega) = \frac{1}{Vk_B T^2}\int_0^\infty dt < j_\alpha(0) j_\beta(t) > e^{i\omega t}$$

$$j = \frac{d}{dt}\sum_i E_i r_i$$

Status:

- Derived analytic expression for heat flux for Tersoff potential.
- Implemented heat flux calculation in IMD (ITAP) code and integrated output thereof into separate code to compute thermal conductivity.
- Computed λ for diamond structures (C,Si,Ge).

Implementation:

- Modified pre-existing software, ITAP: *www.itap.physik.uni-stuttgart.de/~imd*
- Two options: numerical/analytic differentiation compute heat flux.

Modified IMD code
- compute j(t) and save to binary file

→

Postprocessing Module
- compute heat auto correlation function
- integrate to compute thermal conductivity

Evaluation of heat current

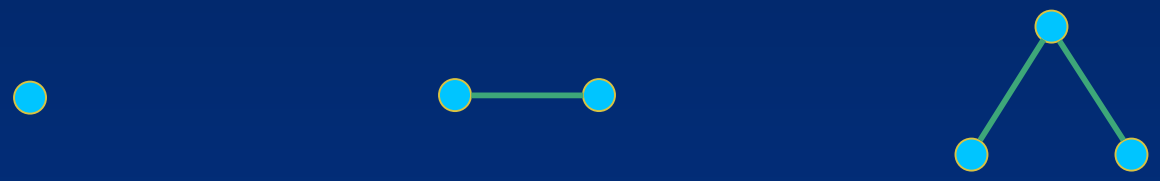
$$j = \frac{d}{dt}\sum_i E_i r_i$$

$$= \sum_i E_i v_i + \sum_{ij} r_{ji} v_i \cdot \frac{\partial E_j}{\partial r_i}$$

$$= \sum_i E_i v_i + \frac{1}{2}\sum_{i\neq j} r_{ji}\left(v_i \cdot \frac{\partial V_{ij}}{\partial r_i} - v_j \cdot \frac{\partial V_{ij}}{\partial r_j}\right) + \frac{1}{2}\sum_{i\neq j\neq k}\left(r_{ji} - 2r_{ki}\right)v_k \cdot \frac{\partial V_{ij}}{\partial r_k}$$

Symmetrized Tersoff:

$$V_j \equiv \tfrac{1}{2}\sum_k V_{jk} + V_{kj}$$

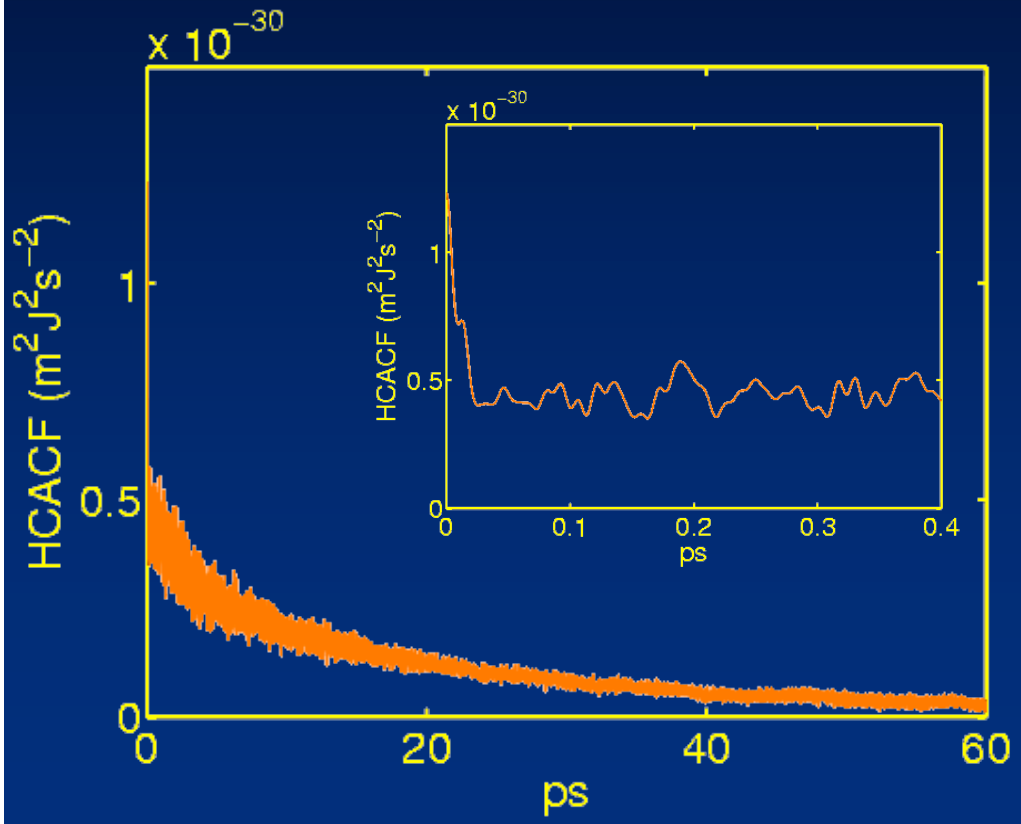


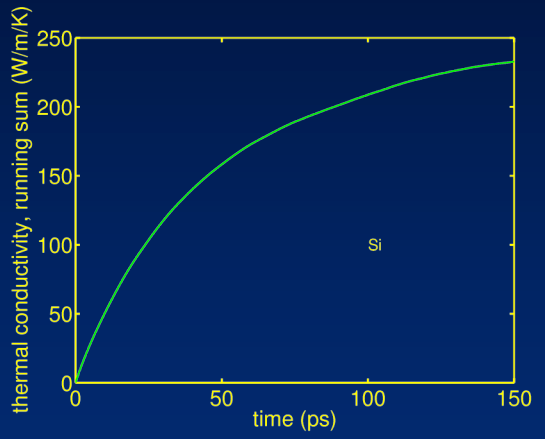
Convergence of auto-correlation function

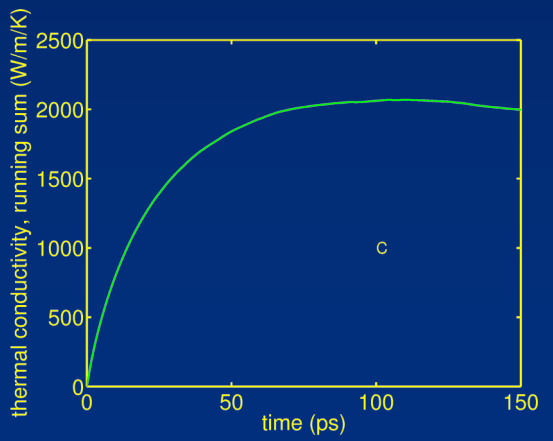
$$\lambda_{\alpha\beta}(\omega) = \frac{1}{Vk_BT^2}\int_0^\infty dt < j_\alpha(0) j_\beta(t) > e^{i\omega t}$$

Convergence requires a large number of ensembles: tens of ns required…

Nevertheless, convergence of integral may still be slow or worse, not well behaved:

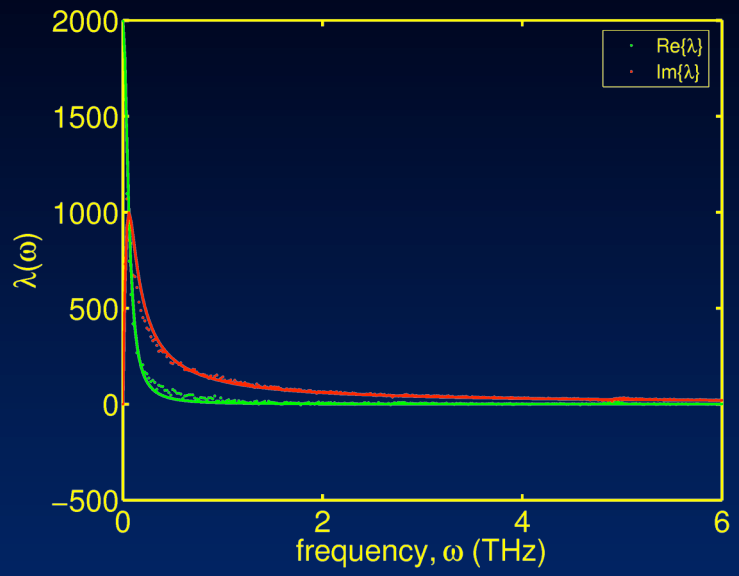






Conductivity calculation: three approaches

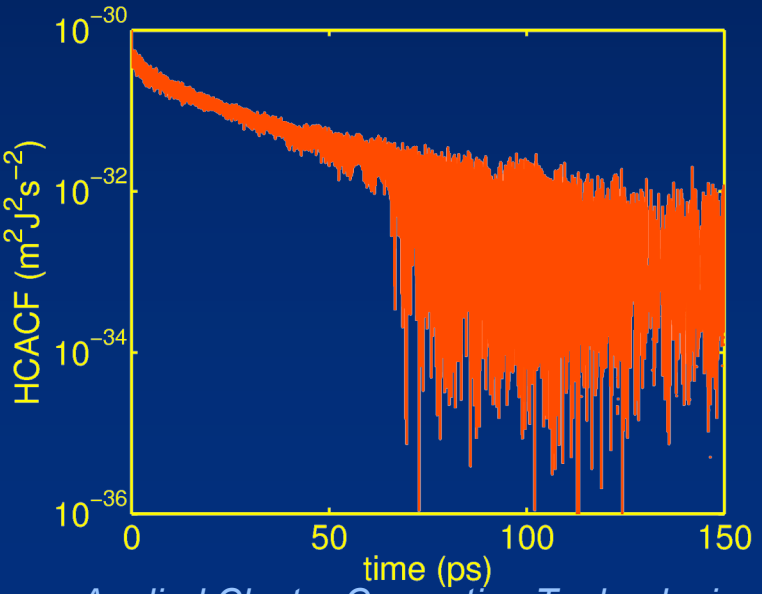
- **Three approaches:**
  - **Direct integration**
  - **Fit frequency dependent thermal conductivity to single relaxation time approximation (Volz/Chen).**
  - **Fit autocorrelation function directly to a small set of relaxation times (Che et al.)**



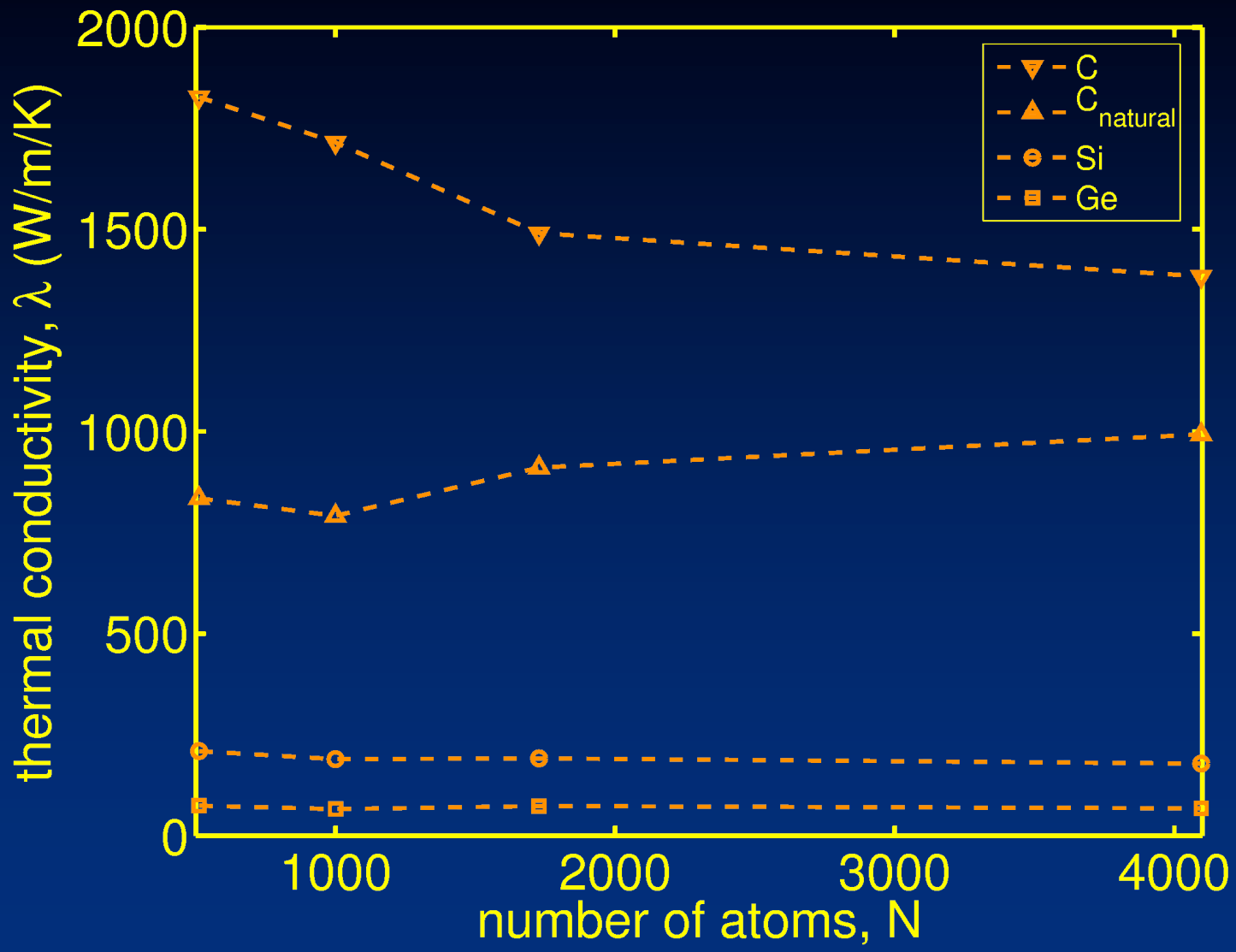
Ansatz:

$$< j(0)\,j(t) >= Ae^{-it/\tau}$$

$$\lambda(\omega) = \frac{\lambda(0)}{1 - i\omega\tau}$$



Results: λ(N)


2000
1500
1000
500
0
thermal conductivity, λ (W/m/K)
1000
2000
3000
4000
number of atoms, N
C
C natural
Si
Ge

Results: C, Si, Ge

Material	λ (calc)	λ (calc)	λ (exp)
C	1390	1200 *(Brenner)* *Che/Cagin/Deng/Goddard*	
C, natural	990	840 *(Brenner)* *Che/Cagin/Deng/Goddard*	2190 *Anthony et al.*
Si	180	230 *(Stillinger-Weber)* *Volz/Chen*	130 *(natural)* *Capinski/Maris/ et al*
Ge	80	114 *(Tersoff)* *Dong/Sankey/Myles*	62 *(natural)* *Slack/Glassbrenner*

** λ: units of W/m/K*

- Good agreement with previous theoretical calculations.
- Reasonable agreement with experiment -- trends are correct.
- Ratio $\lambda(^{12}C) / \lambda(C_{natural}) = 1.4$ in agreement with experiment.

Summary

- Demonstrated modification of existing software to compute thermal conductivities using a Green-Kubo approach.
- Evaluated several convergence schemes.
- Obtained preliminary results for diamond-like materials in agreement with previous theoretical models and experiment.