THERMAL CONDUCTIVITY AT HIGH TEMPERATURES FROM FIRST PRINCIPLES

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HEAT TRANSPORT

**Macroscopic Effect:**

\[ \kappa = \kappa_{\text{photon}} + \kappa_{\text{elec.}} + \kappa_{\text{nucl.}} \]

Fourier’s Law:

\[ \mathbf{J} = -\kappa \nabla T = -\alpha \rho c_V \nabla T \]
HEAT TRANSPORT

Macroscopic Effect:

Fourier's Law:

\[ J = -\kappa \nabla T = -\alpha \rho c_V \nabla T \]

Microscopic Mechanisms:

\[ \kappa = \kappa_{\text{photon}} + \kappa_{\text{elec.}} + \kappa_{\text{nucl.}} \]
Heat Transport Mechanisms

Semi-empirical potentials

+ vast experience
+ established methodologies
– inaccurate interactions
Heat Transport Mechanisms

**Semi-empirical potentials:**
- + vast experience
- + established methodologies
- – inaccurate interactions

**First-principles approaches:**
- + more accurate interactions
- – limited time and length scales
TIME AND LENGTH SCALES

This talk:
How to adapt heat transport simulation techniques developed for semi-empirical potentials to first-principles calculations.

First-principles approaches:
+ more accurate interactions
– limited time and length scales
## FIRST-PRINCIPLES APPROACHES

<table>
<thead>
<tr>
<th></th>
<th>Order of interaction</th>
<th>Thermal Equilibrium</th>
<th>Finite Size Effects</th>
<th>Disorder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boltzmann-Transport Eq.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
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<td></td>
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BOLTZMANN TRANSPORT EQUATION


\[ \kappa \sim \sum_s C_s^2 \omega_s^2 n_s (n_s + 1) \tau_s \]

- Group velocity
- Frequency
- Equilibrium population
- Phonon lifetime
- Harmonic phonon theory
Phonon Lifetimes from First Principles

Primitive ("perfect") 0K - unit cell:

• from Density Functional Perturbation Theory $\mathcal{O}(r^3)$

• from fitting the forces in ab initio MD $\mathcal{O}(r^3)$-$\mathcal{O}(r^4)$

• from fitting the AIMD phonon spectrum $\mathcal{O}(r^3)$

"Disorder": Defects, Alloying, ...

• Density Functional Theory based Modeling
## First-Principles Approaches

<table>
<thead>
<tr>
<th>Method</th>
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<th>Disorder</th>
</tr>
</thead>
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Boltzmann-Transport-Eq. gives very accurate results for perfect crystals at low temperatures.
Thermal conductivity can be calculated by applying Fourier’s Law.

\[ J = -\kappa \nabla T \]
FINITE SIZE EFFECTS

Finite Size Corrections

\[ \frac{1}{\kappa} \sim \left( \frac{1}{l_\infty} + \frac{4}{L_z} \right) \]

mean free path

supercell length

Non-equilibrium MD exhibits strong finite-size artifacts in supercells typically accessible within DFT/AIMD.

Non-equilibrium MD can suffer from non-linear artifacts in supercells typically accessible within DFT/AIMD.

Finite Size Effects


unphysically large $\nabla T \gg 10^9 \text{K/m}$

$1/k (\text{W/mK})^{-1}$

$1/L_z (\text{nm}^{-1})$

$1/\kappa (\text{W/mK})^{-1}$

$1/L_z (\text{nm}^{-1})$

Si $T=1000K$

Si $T=500K$

Diamond $T=1000K$
Non-Equilibrium MD approaches are in principle exact, in DFT however prohibitively costly to converge accurately.

<table>
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Heat

\[ T = T_{\text{hot}} \]

\[ T = T_{\text{cold}} \]

“LASER FLASH” MEASUREMENTS

Heat Diffusion Equation:

\[
\frac{\partial T(x, t)}{\partial t} + \alpha \frac{\partial^2 T(x, t)}{\partial x^2} = 0
\]
Mimic the "Laser-Flash Measurements" in *ab initio* MD simulations:

(A) Prepare two supercells: a **small hot** one and a **large cold** one.
In the quasi-harmonic approximation, the positions $r_i$ and the velocities $v_i$ are related to the vibrational eigenfrequencies $\omega_s$ and -vectors $e_s$. 

\[ r_{0i} + \Delta r_i = \sum_s A_s(T) \cos (\Phi_s + \omega_s t) \sqrt{M_i} e_s \]

\[ v_i = -\sum_s A_s(T) \sin (\Phi_s + \omega_s t) \sqrt{M_i} \cdot e_s \]
SUPERCELL PREPARATION

SUPERCELL PREPARATION


Temperature

$T_{\text{hot}}$

$T_{\text{cold}}$

$T > 0$

Interface Mismatch

heat diffusion axis
The cartesian displacements $\mathbf{r}_i$ are related to the eigenfrequencies $\omega_s$ and -vectors $\mathbf{e}_s$ of the dynamical matrix.

$$\Delta \mathbf{r}_i = \frac{1}{\sqrt{M_i}} \sum_s A_s(T) \cos(\Phi_s - \omega_s t) \cdot \mathbf{e}_s$$

Maxwell-Boltzmann distributed amplitudes  
random phase  
harmonic approximation

Enforce consistent boundary conditions at the interface!
PHASE MATCHING


\[ T = T_1 = T_2 \]

Random Phases

Phase Matching

\( T = 700 \text{ K} \)
\( T = 500 \text{ K} \)
\( T = 300 \text{ K} \)
\( T = 100 \text{ K} \)

„Phase matching“ reduces the artifacts by two orders of magnitude.
Mimic the “Laser-Flash Measurements” in \textit{ab initio} MD simulations:

(A) Prepare two supercells: a \textbf{small hot} one and a \textbf{large cold} one.

(B) Let the \textbf{heat diffuse} via \textit{ab initio} MD and \textbf{monitor} the \textbf{temperature profile} $T(x,t)$. 
Monitor temperature of the central cell

The finite number of atoms leads to large temperature fluctuations.
Fit to

\[ T(x, t) = T_{\text{cold}} + (T_{\text{final}} - T_{\text{cold}}) \sum_{n} (-1)^n \exp \left( -n^2 \pi^2 \alpha t \right) \]
How do the properties of the impurities affect the thermal conductivity of the system?

\( \text{Si}_{192} \) supercell containing \(~5.2\%\) impurities
Vacancies

Thermal conductivity can be controlled via the impurities' mass!

APPLICATION TO IMPURITIES IN SI

APPLICATION TO IMPURITIES IN SI


Not all impurities are created equal!

- Carbon
- Iron
- Germanium

- $^{12}$C
- $^{55}$Fe
- $^{74}$Ge
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Laser-flash MD yields accurate qualitative results at low temperatures within moderate computational costs. Quantitative predictions require finite size corrections, though.
GREEN-KUBO METHOD


**Fluctuation-Dissipation Theorem**

\[ \kappa \sim \int_0^\infty d\tau \langle J(0) \ J(\tau) \rangle_{eq} \]

The thermal conductivity is related to the autocorrelation function of the heat flux.

Simulations of the thermodynamic equilibrium

\[ \Downarrow \]

Information about non-equilibrium processes
THE ATOMICHE HEAT FLUX

E. Helfand, Phys. Rev. 119, 1 (1960)

\[ J(t) = \frac{d}{dt} \left( \sum_i r_i(t) \varepsilon_i(t) \right) \]

- \( r_i \) \( i \ldots \) Position of atom \( i \)
- \( \varepsilon_i \) \( i \ldots \) Energy of atom \( i \)

Energy contribution \( \varepsilon_i \) of the individual atoms required!

\( \Rightarrow \) Green-Kubo Method hitherto only used with classical potentials!
THE AB INITIO HEAT FLUX

\[ \mathbf{J}(t) = \frac{d}{dt} \int \mathbf{r} \cdot \mathbf{\varepsilon}(\mathbf{r}, t) \, d\mathbf{r} \]

**Energy Density** in Density Functional Theory:


\[ \int \mathbf{\varepsilon}(\mathbf{r}, \{\mathbf{R}\}) \, d\mathbf{r} \Leftrightarrow \text{Harris-Foulkes Total Energy Functional} \]

\[ \mathbf{\varepsilon}(\mathbf{r}, \{\mathbf{R}\}) = \sum_i T_i + \sum_l \varepsilon_l f_{l\text{occ}}^{\text{occ}} |\Psi_l(\mathbf{r})|^2 - n(\mathbf{r}) v_{xc}[n(\mathbf{r})] \]

\[ + E_{xc}[n(\mathbf{r})] - \frac{1}{2} n(\mathbf{r}) v_{es}(\mathbf{r}) + \frac{1}{2} \sum_{ij} \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} \delta(\mathbf{r} - \mathbf{R}_i) \]
ASSESSING THE THERMAL CONDUCTIVITY

\[ \kappa = \frac{V}{3k_B T^2} \int_0^\infty d\tau \langle J(0) J(\tau) \rangle_{eq} \]

Finite Size Artifacts artificially reduce the thermal conductivity at low frequencies!

PERIODIC BOUNDARY CONDITIONS

\[ J(t) = \frac{d}{dt} \int \mathbf{r} \cdot \varepsilon(\mathbf{r}, t) \, d\mathbf{r} \]

Small heat flux through boundaries leads to huge change in energy barycenter.
CORRECTING FOR FINITE SIZE EFFECTS


\[ \kappa_{FS}(\omega) = \kappa(\omega) - \Theta_{FS}(\omega) = \sum_n \frac{\kappa_n}{1 + \alpha_n \omega^2} - \frac{\kappa_{art}}{1 + \alpha_{art} \omega^2} \]

Finite Size \( \kappa_{FS}(\omega) \) is superposition of bulk conductivity \( \kappa(\omega) \) and finite size effects \( \Theta_{FS}(\omega) \)!

Finite Size corrected \( \kappa(\omega) \)!
Green-Kubo Simulations with Hardy’s Heat Flux exhibit only small finite size effects.
APPLICATION TO ZIRCONIA

Experiment:

Classical MD:

Image Description:
- Temperature (K) range from 500 to 2000 K.
- Conductivity (κ) range from 0 to 10 W/mK.
- Graph showing data points and curves for Classical MD, Experiment, and DFT-LDA-V(0K).
- 2x2x2 Supercell, > 30ps AIMD / data point.
APPLICATION TO ZIRCONIA

Experiment:

Classical MD:
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*Ab initio* Green-Kubo approach allows the **accurate** and **predictive** computation of lattice thermal conductivities $\kappa$ at **arbitrarily high temperatures**!
Fourier's Law:

\[ \mathbf{J} = -\kappa \nabla T = -\alpha \rho c_v \nabla T \]

Macroscopic Effect:

\[ \kappa = \kappa_{\text{photon}} + \kappa_{\text{elec.}} + \kappa_{\text{nucl.}} \]
**CHALLENGES**

**Macroscopic Effect:**

\[ \mathbf{J} = -\kappa \nabla T = -\alpha \rho c_V \nabla T \]

\[ \kappa = \kappa_{\text{photon}} + \kappa_{\text{elec.}} + \kappa_{\text{nucl.}} \]

Is the separation into *electronic* and *nuclear* thermal conductivities still valid at high temperatures?