High-Precision yet Efficient Search for Thermal Insulators

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Introduction

Thermal Conductivity is an import material property in many applications, for example:

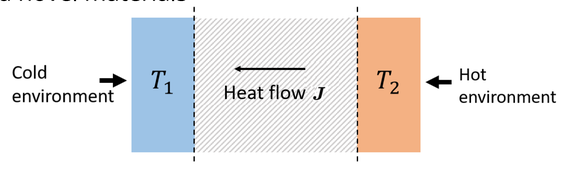
- **Thermoelectrics**: figure of merit zT increased by low thermal conductivity κ
- **Thermal Barrier Coatings**: increase efficiency of heat engines
- **Thermal Management**: High thermal conductivity increases lifetime of devices

→ Fundamental understanding open routes to find novel materials

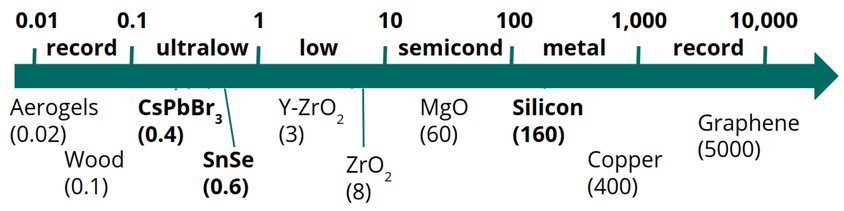
Thermal Conductivity κ

Fourier's Law

$$\boldsymbol{J} = -\kappa \boldsymbol{\nabla} T$$



Scale [W / mK]



Goals

- Compute thermal conductivities for hundreds of compounds
- Use data to derive mechanisms behind (ultra-)low thermal conductivity
- Extract simple descriptors to guide future seach for thermal insulators

ab initio Green-Kubo Method [Carbogno17]

Fluctuation-Dissipation Theorem

Relates transport coefficient to fluctuations of the corresponding flux [Kubo57]

$$\kappa_{\alpha\beta}(T,p) = \frac{V}{k_B T^2} \lim_{\tau\to\infty} \int_0^\tau \langle G[J]_{\alpha\beta}(\tau') \rangle_{(T,p)} \, \mathrm{d}\tau'$$

Heat-Flux Autocorrelation Function

$$G[\boldsymbol{J}]_{\alpha\beta}(\tau) = \lim_{t_0\to\infty} \frac{1}{t_0} \int_0^{t_0-\tau} J_\alpha(t) J_\beta(t+\tau) \, \mathrm{d}t$$

Heat-Flux Definition

Starting from the continuity equation, integration by parts on open boundaries yields flux

$$\boldsymbol{J}(t) = \frac{\mathrm{d}}{\mathrm{d}t} \sum_I \boldsymbol{R}_I E_I = \sum_I \boldsymbol{R}_I \dot{E}_I + \cancel{\dot{\boldsymbol{R}}_I E_I}$$

Convective term vanishes in absence of diffusion [Ladd86, Ercole16]

ab initio: Virial Stress

Non-convective flux obtained from virials, i.e., **atomic contributions to stress tensor** [Carbogno17]

$$\boldsymbol{J}(t) = \sum_I \sigma_I \dot{\boldsymbol{R}}_I(t)$$

implemented in FHI-aims [Knuth15]

Time and Size Convergence

For materials with slowly decaying heat flux autocorrelation function, project dynamics onto effective harmonic model for extrapolating in time and size [Carbogno17]

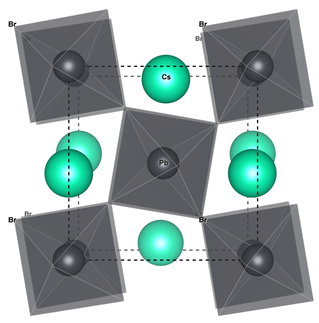
$$\boldsymbol{J}(t) = \sum_I \boldsymbol{J}_I(t) \quad \equiv \quad \sum_q \boldsymbol{J}(\boldsymbol{q},t) \quad \rightleftharpoons \quad \int_{\text{Brillouin Zone}} \boldsymbol{J}(\boldsymbol{q},t) \, \mathrm{d}q$$

aiGK Application: Cesium Lead Bromide ($CsPbBr_3$, $\sigma^A = 0.53$)

$CsPbBr_3$ has one of the lowest thermal conductivities of any inorganic crystal and possesses a **non 1/T dependence of κ** – a clear deviation from traditional phononic heat transport. We model by ab initio Green Kubo method (300K, 3x50ps, PBEsol, 160atoms).

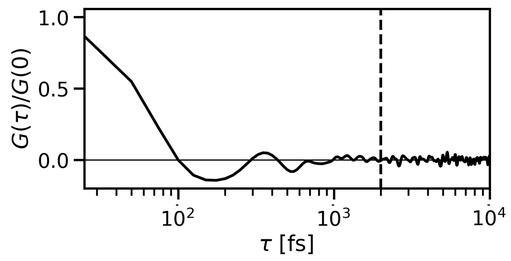
Structure

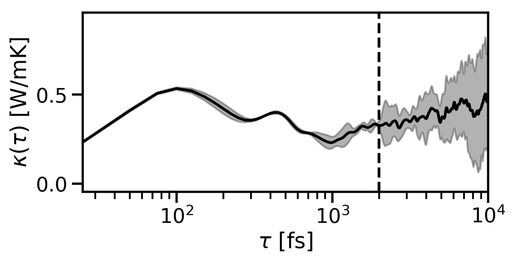
- orthormbic space group (*Pnma*, 62)
- 20 atoms in primitive unit cell
- 360K: phase transition to tetragonal (*P4/mbm*)
- 400K: phase transition to cubic (*Pm-3m*)



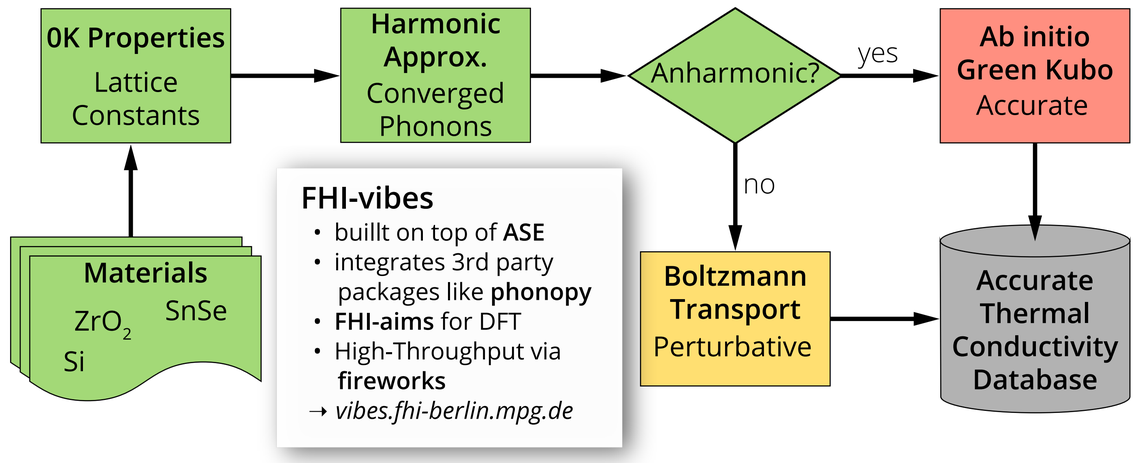
Results

Confirm ultralow conductivity: κ = **0.32 ± 0.06 W/mK**
(exp : 0.42 ± 0.04 W/mK [Lee17])





Workflow: Screen materials to single out candidates for aiGK



Direct Assessment of Anharmonicity

We estimate the anharmonic contribution to the potential energy of nuclei by inspecting atomic forces and removing the harmonic part:

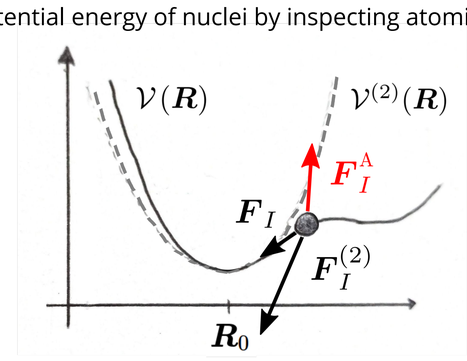
$$\mathcal{H}(\boldsymbol{P},\boldsymbol{R}) = \mathcal{K}(\boldsymbol{P}) + \mathcal{V}^{(2)}(\boldsymbol{R}) + \mathcal{V}^{\mathrm{A}}(\boldsymbol{R})$$

$$\boldsymbol{F}_I = \boldsymbol{F}_I^{(2)} + \boldsymbol{F}_I^{\mathrm{A}}$$

ab initio force — **anharmonic** contribution

Harmonic Approximation:

$$\mathcal{V}^{(2)}(\boldsymbol{R}) = \tfrac{1}{2} \sum_{\substack{I,J \\ \alpha,\beta}} \Phi_{\alpha,\beta}^{I,J} \Delta R_I^\alpha \Delta R_J^\beta$$



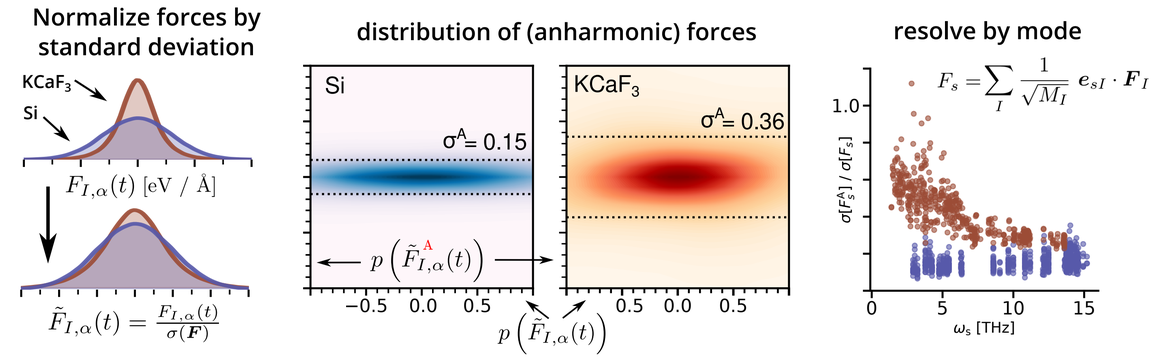
Quantify Anharmonicity

Use standard deviation of normalized anharmonic force contribution to quantify anharmonicity:

$$\sigma\left[\tilde{\boldsymbol{F}}^{\mathrm{A}}\right] = \sqrt{\frac{\sum_{I,t}\left(\boldsymbol{F}_I(t) - \boldsymbol{F}_I^{(2)}(t)\right)^2}{\sum_{I,t} \boldsymbol{F}_I^2(t)}} \equiv \sigma^{\mathrm{A}}$$

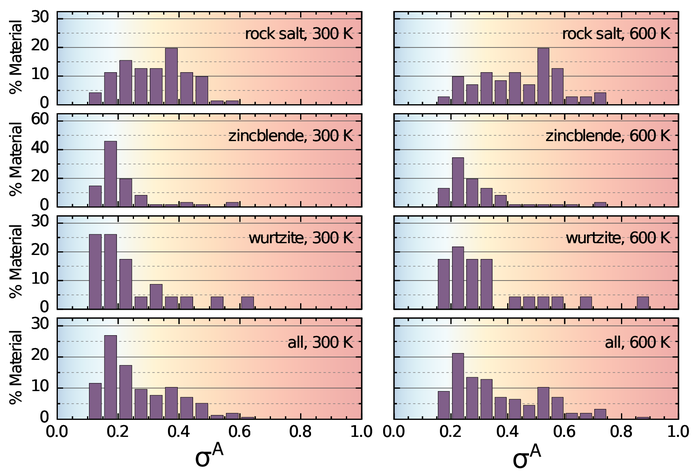
Visualize Anharmonicity in Normalized Forces

We compare normalized forces $\tilde{F}_{I,\alpha}(t)$ observed during *ab initio* molecular dynamics at 300K for Silicon and the complex perovskite $KCaF_3$ to their anharmonic contribution $\tilde{F}^{\mathrm{A}}_{I,\alpha}(t)$ (xc: PBEsol)



How Common is Anharmonicity in Material Space?

We investigate 156 simple zincblende, wurtzite, and rocksalt elemental and binary materials. We use a **Monte Carlo sampling technique [West06, Zacharias17]** so that screening can be performed with **less than 10 *ab initio* supercell force evaluations** per material. (xc: PBEsol)



Observations

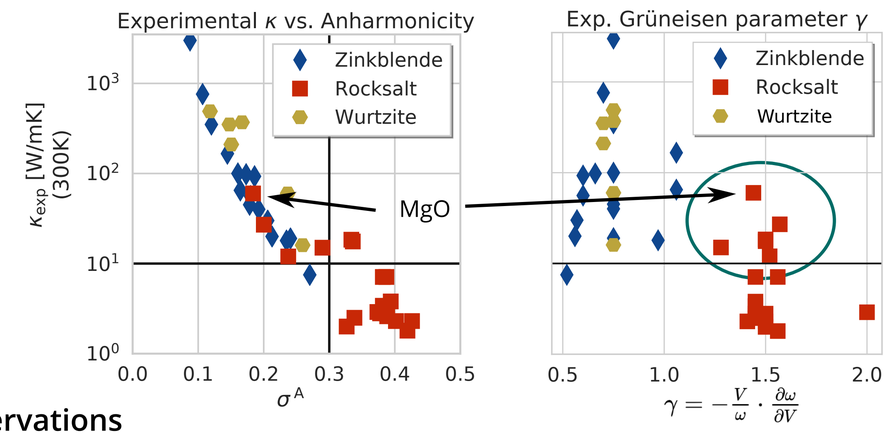
- majority of the materials are harmonic with $\sigma^A < 0.3$ at room temperature
- some of the simple materials show more significant anharmonicity already at 300K
- especially rocksalts are more anharmonic than zincblende and wurtzite
- σ^A increases systematically with temperature

→ Anharmonicity not uncommon, **already in simple materials**

Relevance of σ^A for physical properties?

Anharmonicity and Thermal Conductivity

We investigate 41 compounds from the above set for which experimental thermal conductivities are available [Morelli06] and plot vs. estimated anharmonicity



Observations

- σ^A correlates strongly with κ
  - especially for harmonic materials $\sigma^A < 0.3$
- γ groups materials, but correlates less with κ
- rocksalts are less conductive and more anharmonic on average
- γ fails to discern harmonic rocksalts like MgO

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