Ab initio Green-Kubo simulations for the discovery of thermal insulators

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NOMAD — NOVEL MATERIALS DISCOVERY

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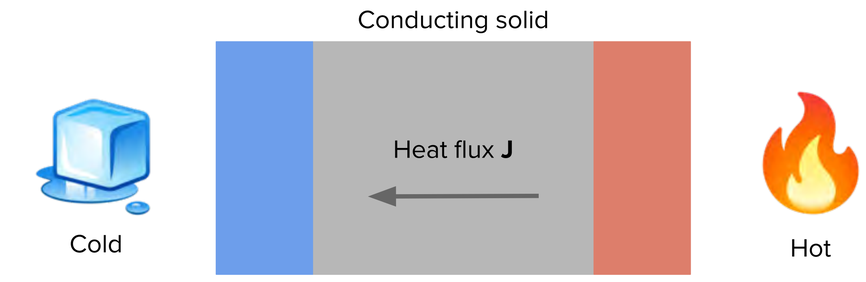
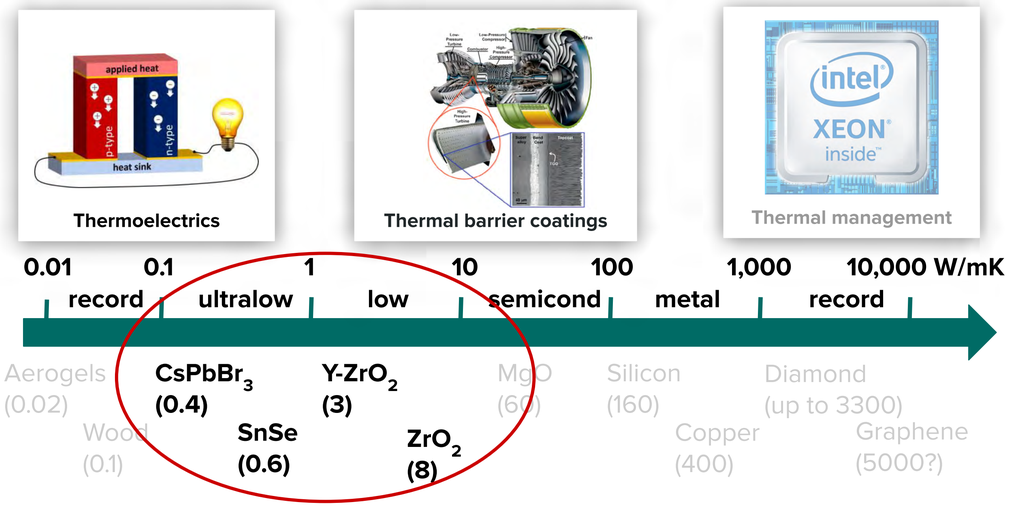
Thermal transport: Intuition



Fourier's law: $\mathbf{J} = -\kappa \nabla T$ Unit: $[\kappa] = \left[\frac{\mathbf{J}}{\nabla T}\right] = \frac{\mathrm{W}}{\mathrm{mK}}$

κ: Thermal conductivity

Our interest: Thermal insulators



Ab initio Green-Kubo [1]

Fluctuation-Dissipation Theorem:

FHI-aims — The ab initio materials simulation package

$$\kappa(T) = \frac{V}{3k_{\mathrm{B}}T^2} \int_0^\infty \langle \boldsymbol{J}(t) \cdot \boldsymbol{J}(0) \rangle \, \mathrm{d}t$$

Non-convective heat flux from ***ab initio* atomic virials**:

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

Atomic velocities from *ab initio* Molecular Dynamics

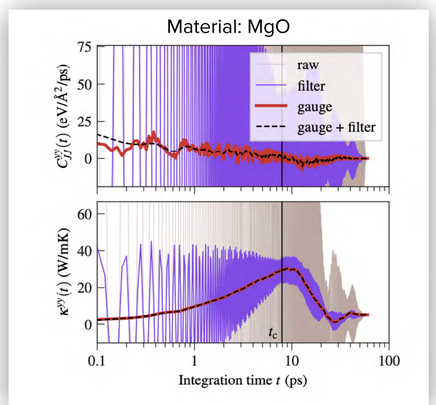
No Approximations to Potential Energy Surface!

[1] C Carbogno, R Ramprasad, M Scheffler, *PRL* **118**, 175901 (2017)

Finite time and ensemble: Reduce noise!

fv

Implementation:
FHI-vibes [1]
flokno.me/vibes
JOSS 10.21105/joss.02671



raw flux from MD

gauge invariance [2, 3]

noise filtering [4]

➡ smooth curves!

➡ first dip criterion.

[1] FK, TAR Purcell, M Scheffler, C Carbogno, *JOSS* **5**, 2671 (2020)
[2] L Ercole et al., *JLTP* **185**, 79 (2016)
[3] A Marcolongo, L Ercole, S Baroni, *JCTC* **16**, 3352 (2020)
[4] FK, Ph.D. thesis, Humboldt University 2022

Finite size: Extrapolate! [1, 4]

Project dynamics on modes [2]:

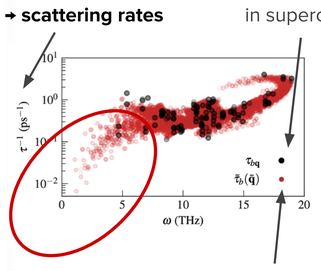
$$\{\mathbf{R}(t), \mathbf{P}(t)\} \rightarrow E_{b\mathbf{q}}(t)$$

Fit analytic expression:

$$G_{b\mathbf{q}}(t) = \frac{\langle E_{b\mathbf{q}}(t) E_{b\mathbf{q}} \rangle}{\langle E^2_{b\mathbf{q}} \rangle} \approx \mathrm{e}^{-2\Gamma_{b\mathbf{q}}t} \equiv \mathrm{e}^{-t/\tau_{b\mathbf{q}}}$$

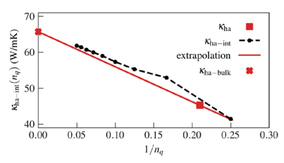
➡ **Extract lifetimes.**

***Inverse* lifetimes ➡ scattering rates** — **extract** in supercell



long-range+lifetime phonons — **interpolate** in Brillouin zone [3]

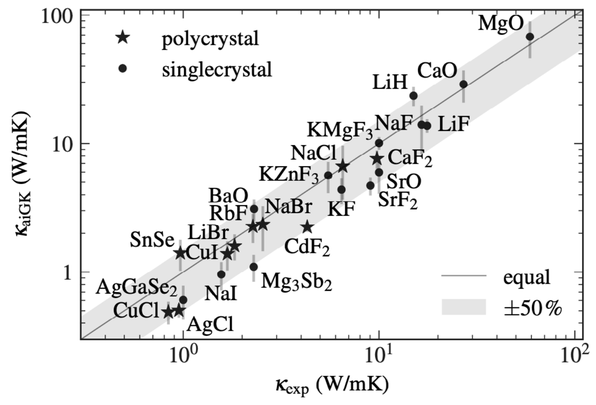
use BTE-like expression to extrapolate κ [1, 4]:



increase no. of q-points n_q ➡ **size extrapolation**

[1] C Carbogno, R Ramprasad, M Scheffler, *PRL* **118**, 175901 (2017)
[2] O Hellman, P Steneteg, IA Abrikosov, SI Simak, *PRB* **87**, 104111 (2013)
[3] C Herring, *PR* **95**, 954 (1954)
[4] FK, Ph.D. thesis, Humboldt University 2022

Quantitative benchmark: Compare to experiment



xc: PBEsol
approx. 200 atoms
30-60ps simulation time
4-5fs time step

Comparison to experiment where available: **Good accuracy for thermal insulators**

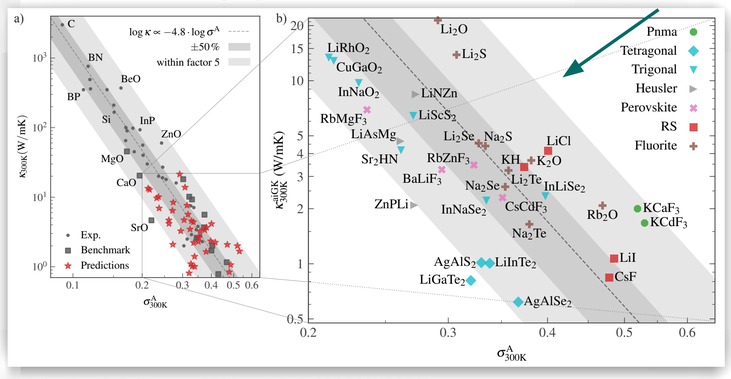
High-throughput search for thermal insulators

Step 1: Screening

Estimate anharmonicity of 454 materials via σ^{A} at room temperature [1, 2]

Step 2: Thermal conductivity

Compute κ for **58 materials** via aiGK [3]: benchmark (w/ exp.) + **33 predictions** (w/o exp.)

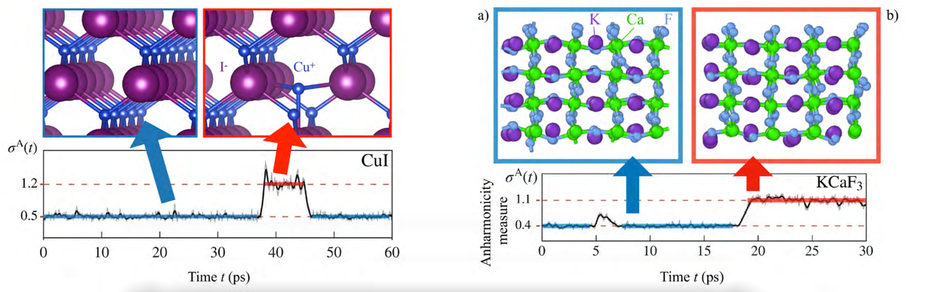


[1] FK, TAR Purcell, M Scheffler, C Carbogno, *PRMaterials* **4**, 083809 (2020)
[2] TAR Purcell, M Scheffler, LM Ghiringhelli, C Carbogno, *Arxiv:2204.12968*
[3] FK et al., *in preparation*

Non-perturbative effects in thermal insulators [1]

CuI: meta-stable Frenkel defect formation

$KCaF_3$: spontaneous octahedral tilt reorientations [2]



Potential-energy surfaces of thermal insulators are often **more complicated than fixed reference + perturbations**

[1] FK, TAR Purcell, M Scheffler, C Carbogno, *in preparation*
[2] https://youtu.be/MD89YhaOcno

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