FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT

NOMAD
NOVEL MATERIALS DISCOVERY

Streamlining High-Throughput Ab Initio Green Kubo Calculations: The Example of Ga2O3

14 Nov. 2022 | Shuo Zhao(赵硕), Christian Carbogno, Matthias Scheffler

Who am I?

Na-O2 batteries

2014-2018 Bachlor in
Chemistry and Chemical Engineering

2018-2021 Master in
Physical Chemistry

2021-now

1996.3.6 Born
Hebei

Tianjin University, Tianjin
Nankai University, Tianjin

Nankai University, Tianjin

I’m here, Berlin

The Great Wall, Hebei

Tianjin Eye, Tianjin

Breakfast
狗不理 (Go believe)

1 Ab initio Green-Kubo

Introduction to aiGK

Green-Kubo formula

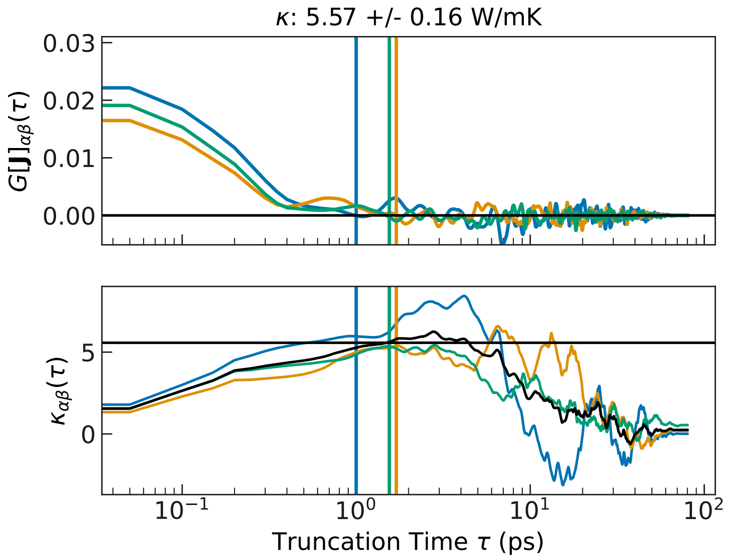
$$\kappa_{\alpha\beta} = \frac{V}{k_B T^2} \lim_{\tau \to \infty} \int_0^{\tau} \langle G[\boldsymbol{J}]_{\alpha\beta}(\tau') \rangle \, d\tau'$$

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

Ab-initio heat flux

$$\boldsymbol{J}(t) = \frac{1}{V} \frac{d}{dt} \sum_I \boldsymbol{R}_I E_I = \underbrace{\frac{1}{V} \sum_I \dot{\boldsymbol{R}}_I E_I}_{\boldsymbol{J}_c(t)=0} + \underbrace{\frac{1}{V} \sum_I \boldsymbol{R}_I \dot{E}_I}_{\boldsymbol{J}_v(t)}$$

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



C. Carbogno, R. Ramprasad, M. Scheffler, PRL **118**, 175901 (2017)

Size extrapolation

$$\kappa_{\alpha\beta}^{\text{corrected}} = \kappa_{\alpha\beta} + \kappa_{\alpha\beta}^{\text{ha-bulk}} - \kappa_{\alpha\beta}^{\text{ha}}$$

Aim:

Correcting the finite size effects in aiMD simulation

Method:

Extrapolation of BTE-like thermal conductivity at denser q-grids

C. Carbogno, R. Ramprasad, M. Scheffler, PRL **118**, 175901. (2017)
F. Knoop, M. Scheffler, C. Carbogno, arXiv:2209.01139. (2022)

Size extrapolation

Mode energy and phonon lifetime

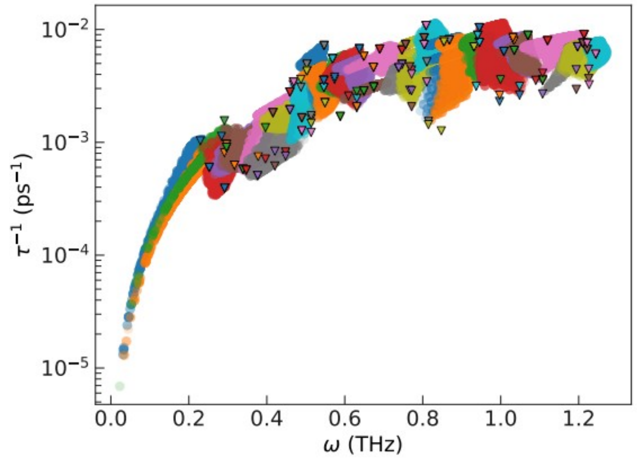
$$E_s(\boldsymbol{q},t) = \omega_s^2(\boldsymbol{q}) a_s^\dagger(\boldsymbol{q},t) a_s(\boldsymbol{q},t)$$ → from MD simulation

$$\Lambda_s(\boldsymbol{q}) = \lim_{\tau\to\infty} \frac{1}{\langle E_s^2(\boldsymbol{q})\rangle} \int_0^\tau G[\delta E_s(\boldsymbol{q},t)](\tau')d\tau'$$

Dimensionless lifetime

$$1/\Lambda_s(\boldsymbol{q}) \sim \omega_s^2(\boldsymbol{q})$$

$$\widetilde{\Lambda}_s(\boldsymbol{q}) = \omega_s^2(\boldsymbol{q})\Lambda_s(\boldsymbol{q})$$



C. Carbogno, R. Ramprasad, M. Scheffler, PRL **118**, 175901. (2017)
F. Knoop, M. Scheffler, C. Carbogno, arXiv:2209.01139. (2022)

Size extrapolation

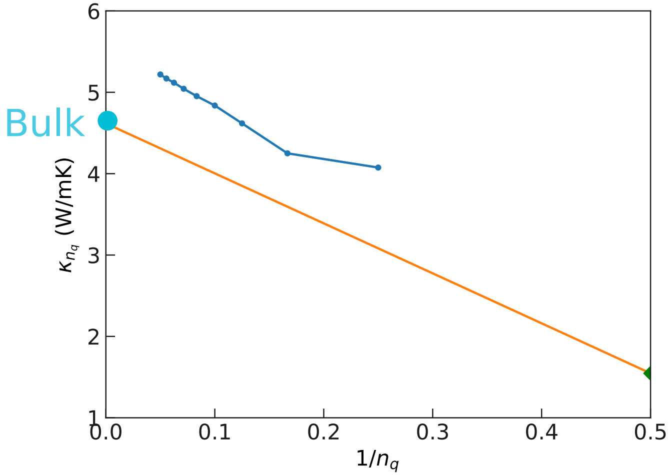
$$\kappa_{\alpha\beta}^{\text{corrected}} = \kappa_{\alpha\beta} + \kappa_{\alpha\beta}^{\text{ha-bulk}} - \kappa_{\alpha\beta}^{\text{ha}}$$

Harmonic contribution within supercell

$$\kappa_{\alpha\beta}^{\text{ha}} = \frac{k_B}{V} \sum_{s,\boldsymbol{q}} v_s^{\alpha}(\boldsymbol{q}) v_s^{\beta}(\boldsymbol{q}) \Lambda_s(\boldsymbol{q})$$

Interpolation at denser q-points

$$\kappa_{\alpha\beta}^{\text{ha-int}}(N_{\widetilde{\boldsymbol{q}}}) = \frac{k_B}{V} \frac{N_{\boldsymbol{q}}}{N_{\widetilde{\boldsymbol{q}}}} \sum_{s,\widetilde{\boldsymbol{q}}} v_s^{\alpha}(\widetilde{\boldsymbol{q}}) v_s^{\beta}(\widetilde{\boldsymbol{q}}) \Lambda_s(\widetilde{\boldsymbol{q}})$$



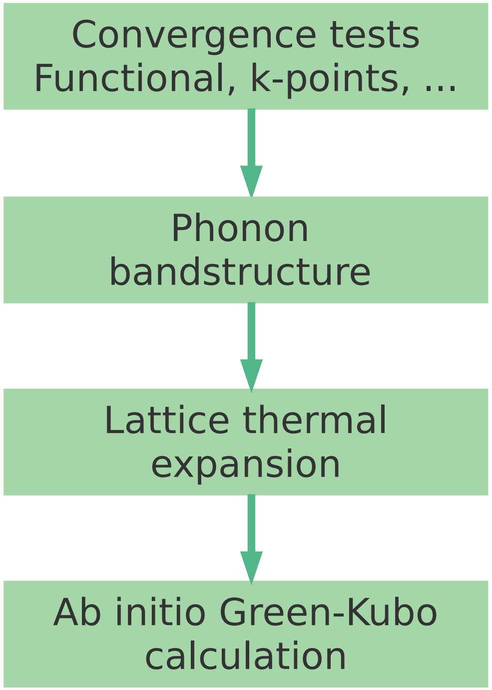
C. Carbogno, R. Ramprasad, M. Scheffler, PRL **118**, 175901. (2017)
F. Knoop, M. Scheffler, C. Carbogno, arXiv:2209.01139. (2022)

2

Streamlining aiGK

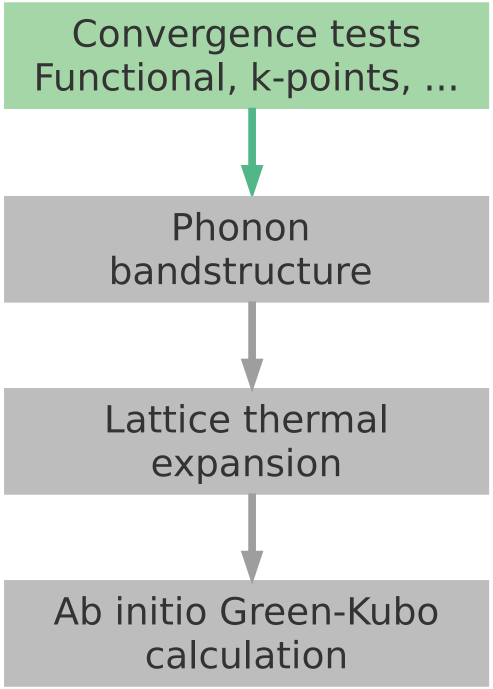
Toward high-throughput aiGK calculations

Workflow


Convergence tests
Functional, k-points, ...
Phonon
bandstructure
Lattice thermal
expansion
Ab initio Green-Kubo
calculation

2. Streamlining ab initio Green-Kubo

Workflow



K-points density convergence

~ 2.0 nkpts Å^{-1}

Basis sets & XC functionals convergence

Light setting & PBE

Lattice constants

Light setting & PBE

2. Streamlining ab initio Green-Kubo

Workflow

Convergence tests
Functional, k-points, ...

↓

Phonon
bandstructure

↓

Lattice thermal
expansion

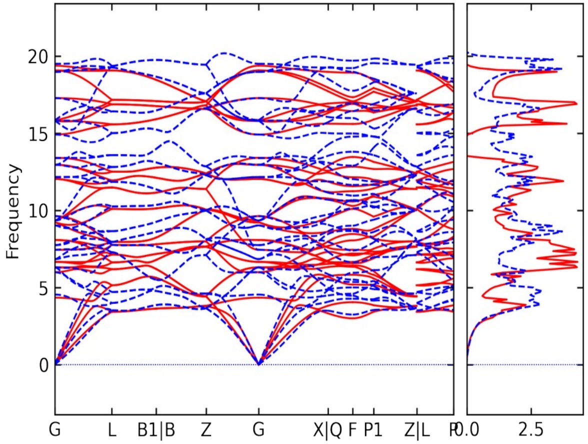
↓

Ab initio Green-Kubo
calculation

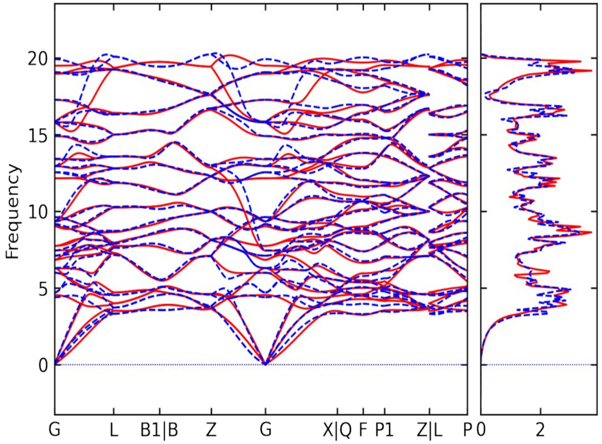
Converge phonon density of state

Tanimoto coefficient

$$f(\boldsymbol{A},\boldsymbol{B}) = \frac{\boldsymbol{A}\cdot\boldsymbol{B}}{\|\boldsymbol{A}\|^2 + \|\boldsymbol{B}\|^2 - \boldsymbol{A}\cdot\boldsymbol{B}}$$



Supercell matrix 111 vs 222



Supercell matrix 222 vs 333

Workflow

Convergence tests
Functional, k-points, ...

↓

Phonon
bandstructure

↓

Lattice thermal
expansion

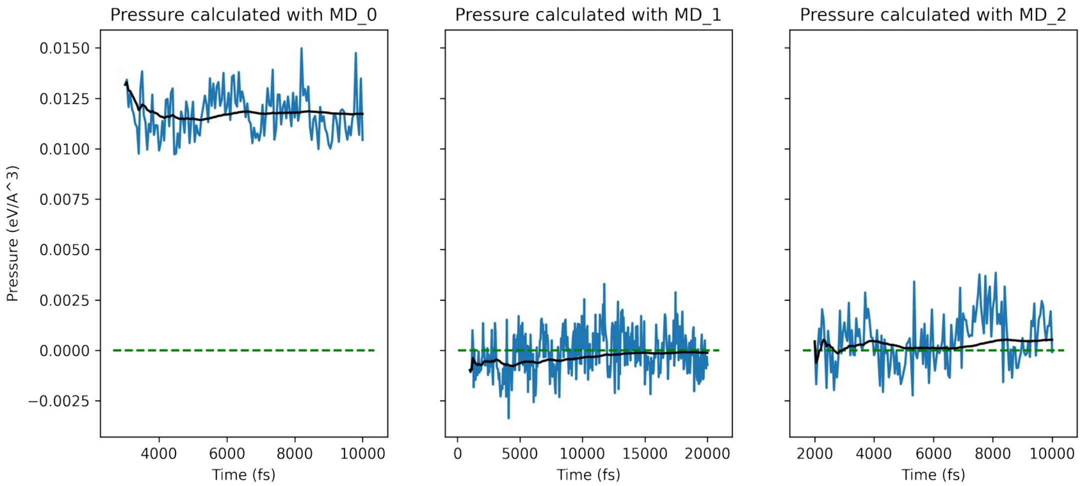
↓

Ab initio Green-Kubo
calculation

Lattice thermal expansion

Iteratively subtract residual pressure to the external pressure to relax the cell

$$\langle p_{\mathrm{Pot}} \rangle = \lim_{N_t \to \infty} \frac{1}{N_t} \sum_{n}^{N_t} p_{\mathrm{Pot}}(R(t_n))$$



Before expansion First expansion Second expansion

Harmonic sampling can be used for the first expansion

Workflow

Convergence tests
Functional, k-points, ...

↓

Phonon
bandstructure

↓

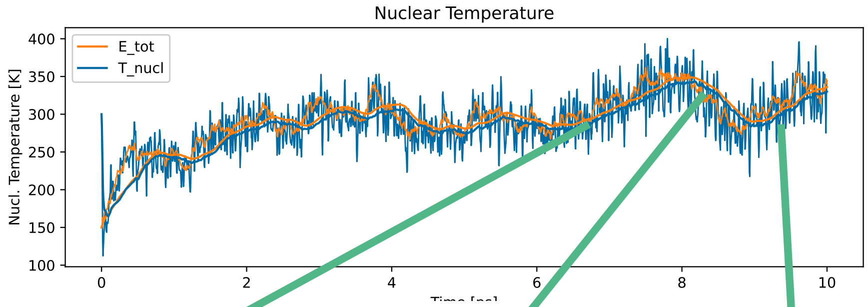
Lattice thermal
expansion

↓

Ab initio Green-Kubo
calculation

Ab initio Green-Kubo calculation

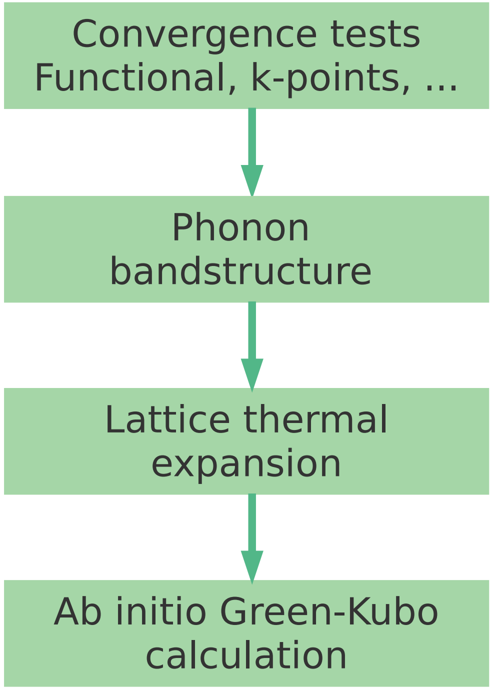
Phase space (canonical ensemble MD):



aiGK (microcanonical ensemble MD):

κ: 5.28 +/- 1.39 W/mK κ: 5.79 +/- 0.68 W/mK κ: 7.91 +/- 1.70 W/mK   ...

Workflow



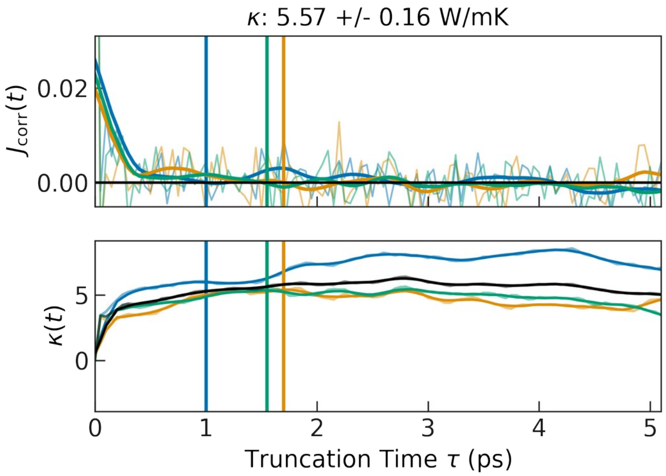
Ab initio Green-Kubo calculation

Virial heat flux

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

Green-Kubo formula

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



Workflow

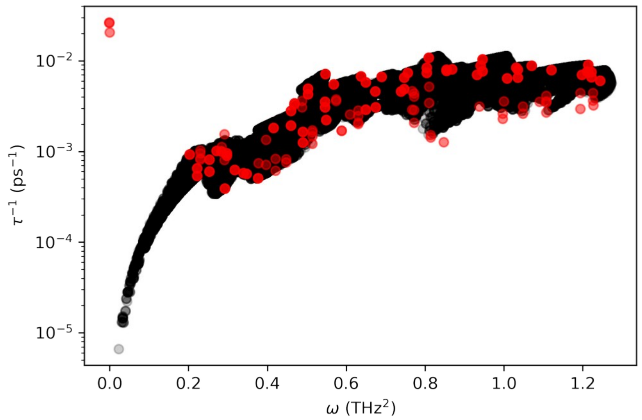
- Convergence tests
  Functional, k-points, ...
- ↓ Phonon bandstructure
- ↓ Lattice thermal expansion
- ↓ Ab initio Green-Kubo calculation

Ab initio Green-Kubo calculation

Interpolation at denser q-grids

$$\sum_{j,\beta} D_{ij}^{\alpha\beta}(\widetilde{\boldsymbol{q}})\boldsymbol{e}_{sj}^{\beta}(\widetilde{\boldsymbol{q}}) = \omega_s^2(\widetilde{\boldsymbol{q}})\boldsymbol{e}_{si}^{\alpha}(\widetilde{\boldsymbol{q}})$$

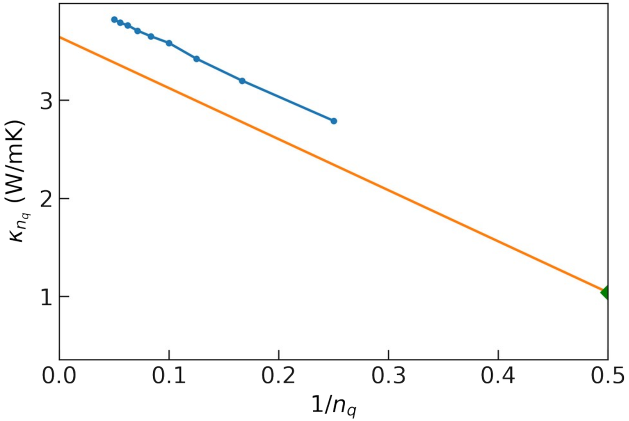
$$\Lambda_s(\widetilde{\boldsymbol{q}}) = \widetilde{\Lambda}_s(\widetilde{\boldsymbol{q}})/\omega_s(\widetilde{\boldsymbol{q}})^2$$



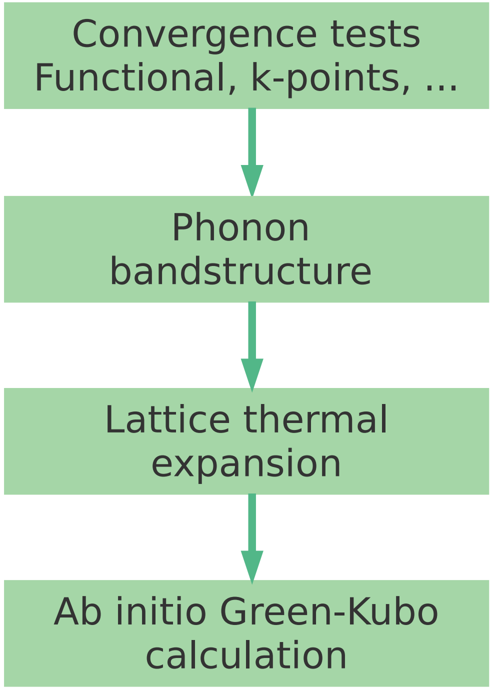
Extrapolation to bulk limit

$$\kappa_{\text{ha-int}}^{\alpha\beta} \sim 1/n_{\widetilde{\boldsymbol{q}}}$$

$$\delta\kappa_{\text{ha-int}}^{\alpha\beta} = \kappa_{\text{ha-bulk}}^{\alpha\beta} - \kappa_{\text{ha}}^{\alpha\beta}$$



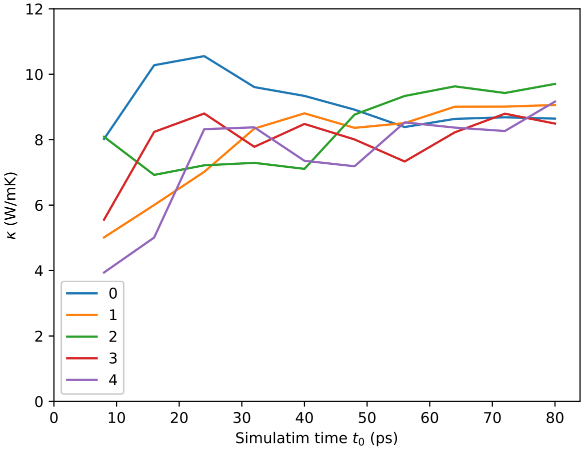
Workflow



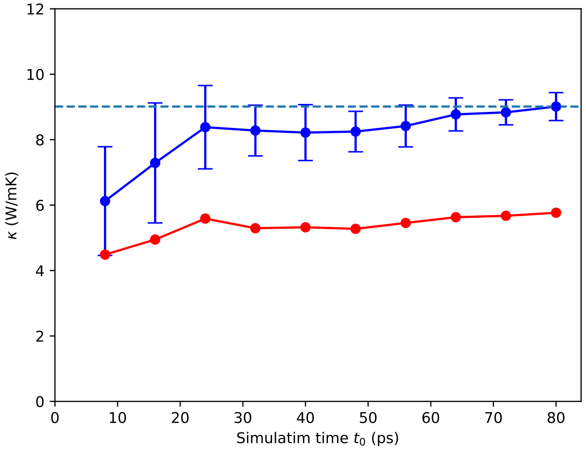
Ab initio Green-Kubo calculation

Ensemble average

$$\boldsymbol{\kappa} = \langle \boldsymbol{\kappa}_n + \delta\boldsymbol{\kappa}_{n,\text{correction}} \rangle$$



Simulation time convergence

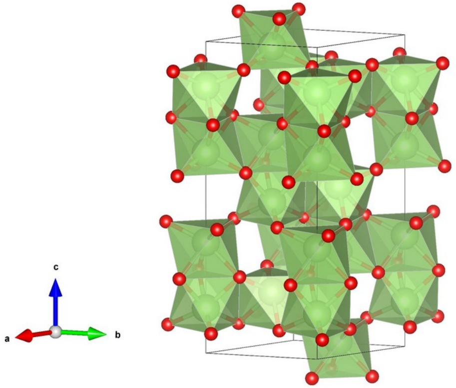


3 Example of Ga_2O_3

Structures of Ga2O3

$\alpha - Ga_2O_3$ Space Group : $R\bar{3}c(167)$

Trigonal

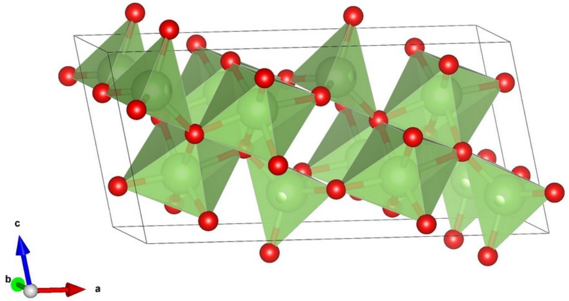


$a = 5.082$ Å, $b = 5.082$ Å, $c = 13.674$ Å

$\alpha = 90.000\ ^\circ$, $\beta = 90.000\ ^\circ$, $\gamma = 120.00\ ^\circ$

$\beta - Ga_2O_3$ Space Group : $C2/m(12)$

Monoclinic

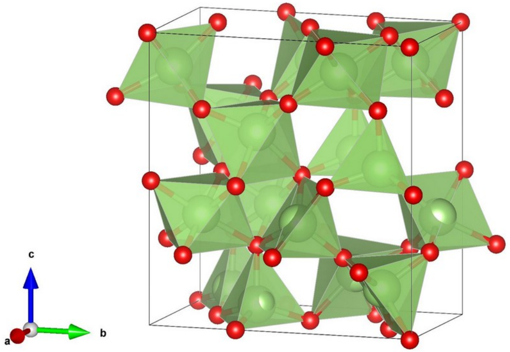


$a = 12.511$ Å, $b = 3.096$ Å, $c = 5.896$ Å

$\alpha = 90.000\ ^\circ$, $\beta = 103.66\ ^\circ$, $\gamma = 90.000\ ^\circ$

$\kappa - Ga_2O_3$ Space Group : $Pna2_1(33)$

Orthorhombic



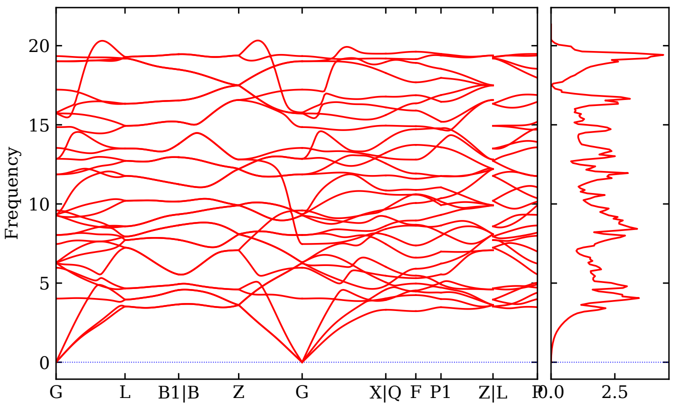
$a = 5.144$ Å, $b = 8.838$ Å, $c = 9.458$ Å

$\alpha = 90.000\ ^\circ$, $\beta = 90.000\ ^\circ$, $\gamma = 90.000\ ^\circ$

Phonon bandstructures

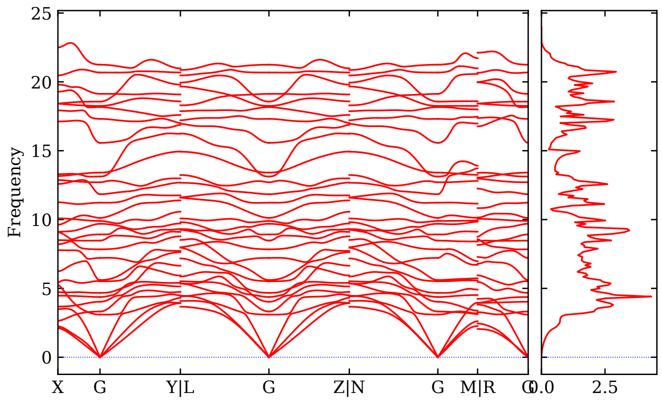
$\alpha - Ga_2O_3$ Space Group : $R\bar{3}c(167)$

Trigonal



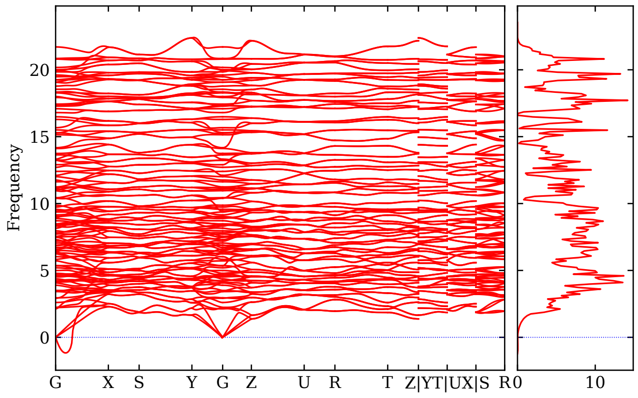
$\beta - Ga_2O_3$ Space Group : $C2/m(12)$

Monoclinic



$\kappa - Ga_2O_3$ Space Group : $Pna2_1(33)$

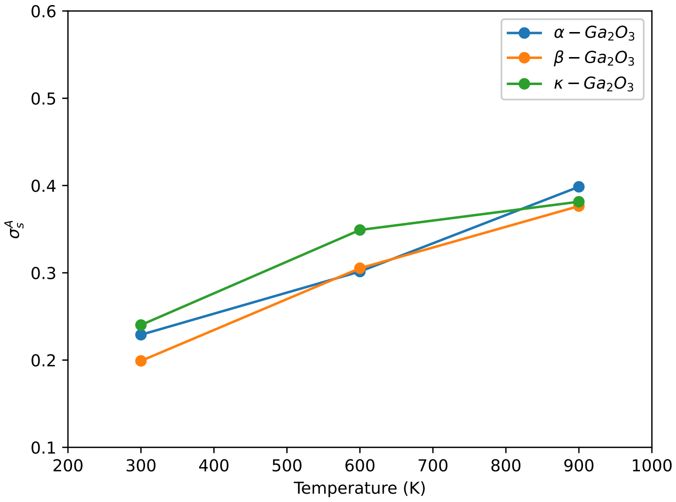
Orthorhombic



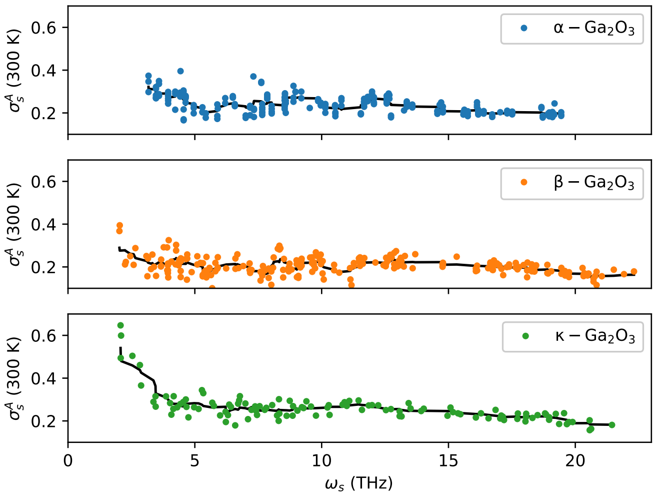
Anharmonicity

Mode-resolved anharmonicity

$$\sigma_X^A(T) = \sqrt{\frac{\sum_{x\in X} \left\langle (F_x - F_x^{(2)})^2 \right\rangle_T}{\sum_{x\in X} \langle (F_x)^2 \rangle_T}}$$



Sample-averaged

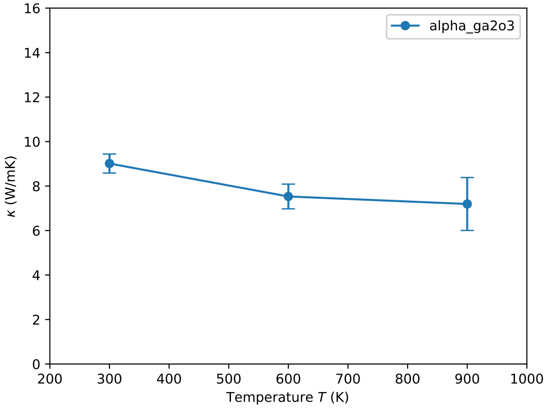


Mode-resolved anharmonicity

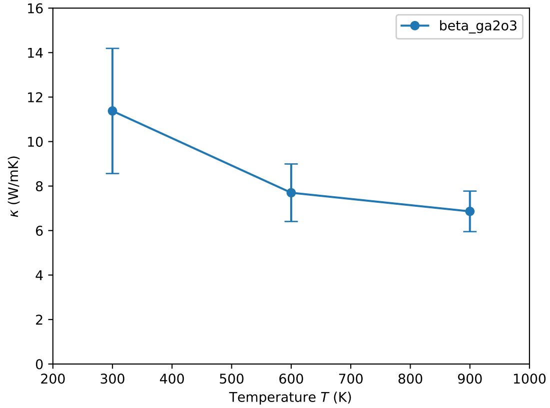
F. Knoop, T. A. Purcell, M. Scheffler, C. Carbogno, PRM, **4**, 083809. (2020)

Thermal conductivity

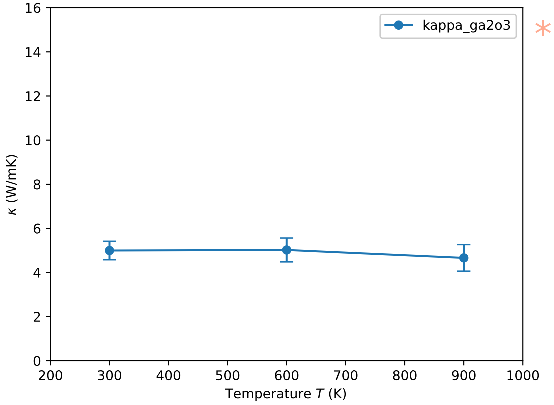
$\alpha - Ga_2O_3$ Space Group : $R\bar{3}c(167)$ | $\beta - Ga_2O_3$ Space Group : $C2/m(12)$ | $\kappa - Ga_2O_3$ Space Group : $Pna2_1(33)$



Alpha-Ga2O3 @ 300K
Comparison with Theory[1] (ShengBTE)

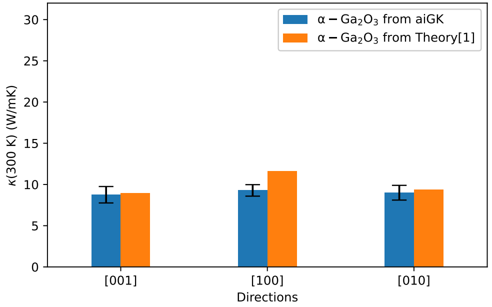


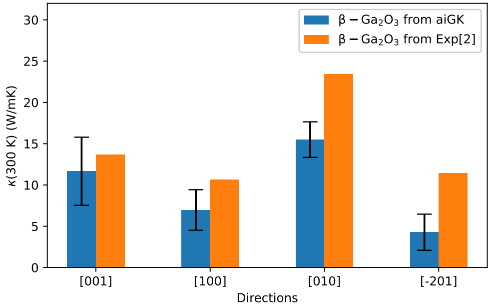
Beta-Ga2O3 @ 300K
Comparison with Exp. results[2]



*

Expecting Exp. results of kappa-Ga2O3
from Prof. Markus R. Wagner(TU Berlin)





Ref. 1: J. Vac. Sci. Technol. A40(5) Sep/Oct (2022)
Ref. 2: Appl. Phys. Lett. 106, 111909 (2015)
* Extrapolation for acoustic mode of kappa-Ga2O3 is on-going.

Anisotropic thermal conductivity

Unit vector along a direction (eg. [1 0 0])

$$v = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \end{bmatrix} \qquad v' = \frac{v}{|v|}$$

Thermal conductivity along the direction

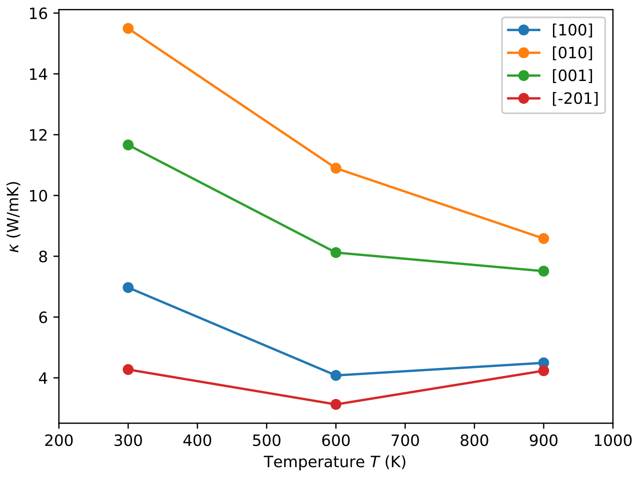
$$\kappa_{v'} = v'^T \kappa_C v'$$

Neumann's principle for kappa tensor of beta-Ga2O3

$$\boldsymbol{\kappa} = \begin{bmatrix} \kappa_{11} & 0 & \kappa_{13} \\ 0 & \kappa_{22} & 0 \\ \kappa_{13} & 0 & \kappa_{33} \end{bmatrix}$$

Independent coefficients: $\kappa_{11}, \kappa_{22}, \kappa_{33}, \kappa_{13}$

$\beta - \mathrm{Ga_2O_3}$ Space Group : C2/m(12)

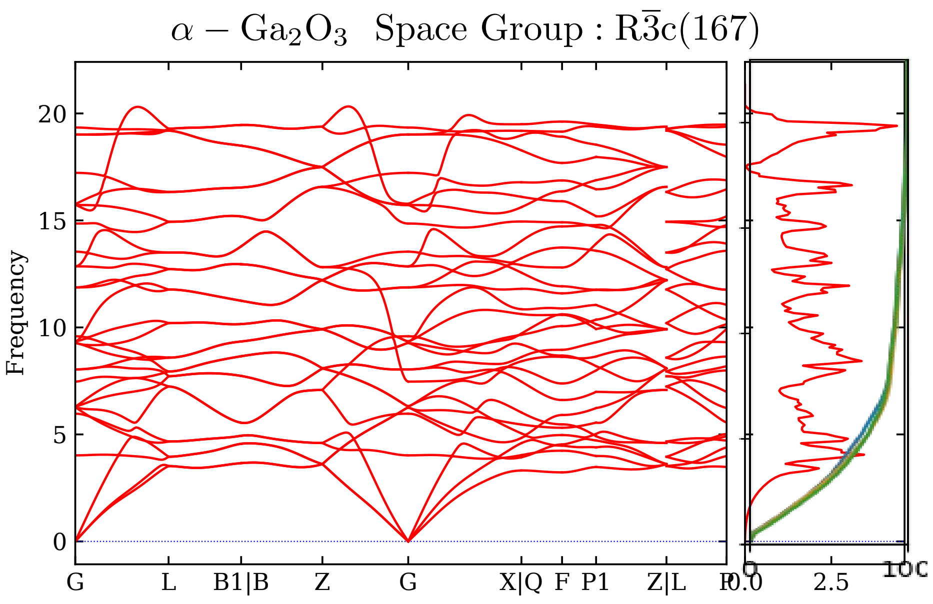


Thermal conductivity tensor of Beta-Ga2O3 @ 300 K (W/mK)

$$\boldsymbol{\kappa} = \begin{bmatrix} 6.971 & -0.033 & 4.544 \\ -0.033 & 15.496 & -0.108 \\ 4.544 & -0.108 & 11.662 \end{bmatrix}$$

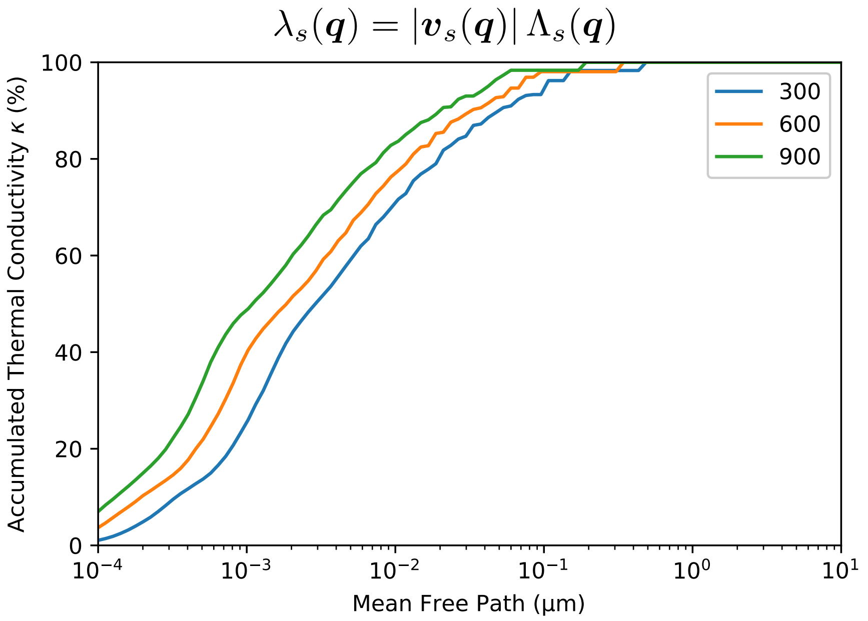
Accumulated thermal conductivity

Accumulated kappa vs. frequency



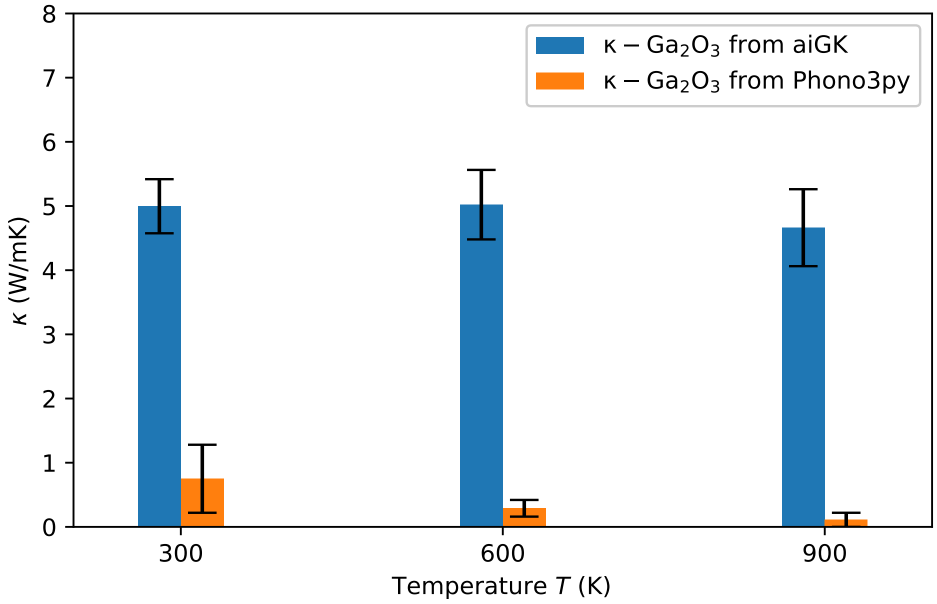
Accumulated Thermal Conductivity k(%)

Accumulated kappa vs. mean free path



Comparison with Phono3py method

Phono3py method shows much smaller thermal conductivity of kappa-Ga2O3 than aiGK method.



Conclusion

Ab initio Green-Kubo is ready to be streamlined for high-throughput calculation.

Examples of Ga_2O_3 show reasonable agreement with experiments.

Strong anharmonic materials (Kappa-Ga_2O_3) show better results than BTE-RTA methods.

Outlook

Optimizing FHI-vibes for aiGK calculation:

Ensemble average for reducing error, storage optimization, etc.

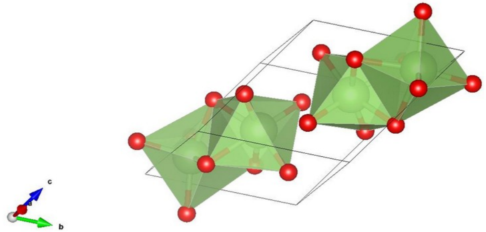
Implementation with workflow packages, for example, Fireworks, ASR, etc.

Extrapolation for materials with large primitive cell.

Thank You

Primitive cell

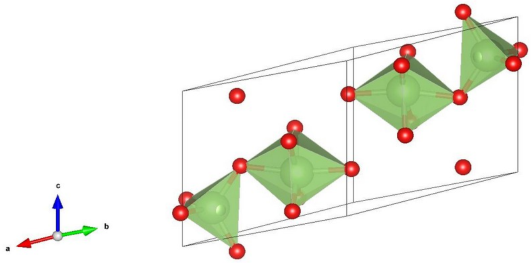
$\alpha - Ga_2O_3$ Space Group : $R\bar{3}c(167)$



$a = 5.40142$ Å, $b = 5.40142$ Å, $c = 5.40142$ Å
$\alpha = 55.9473\ °$, $\beta = 55.9473\ °$, $\gamma = 55.9473\ °$

With k grid density = 2 nkpts Å^{-1}
k-point grid: 4 4 4

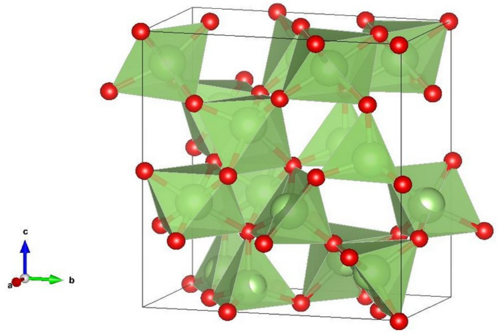
$\beta - Ga_2O_3$ Space Group : $C2/m(12)$



$a = 6.42251$ Å, $b = 6.42251$ Å, $c = 5.88231$ Å
$\alpha = 76.7536\ °$, $\beta = 103.2460\ °$, $\gamma = 152.1720\ °$

With k grid density = 2 nkpts Å^{-1}
k-point grid: 6 6 4

$\kappa - Ga_2O_3$ Space Group : $Pna2_1(33)$



$a = 5.13059$ Å, $b = 8.80758$ Å, $c = 9.42135$ Å
$\alpha = 90.0000\ °$, $\beta = 90.0000\ °$, $\gamma = 90.0000\ °$

With k grid density = 2 nkpts Å^{-1}
k-point grid: 4 2 2

Size extrapolation

Harmonic approximation

$$U = U_0 + \sum_{I,\alpha} \Phi_I^\alpha \Delta R_I^\alpha + \frac{1}{2!} \sum_{I,J,\alpha,\beta} \Phi_{IJ}^{\alpha\beta} \Delta R_I^\alpha \Delta R_J^\beta + \cdots$$

Dynamical matrix in reciprocal space

$$D_{ij}^{\alpha\beta}(\boldsymbol{q}) = \frac{1}{\sqrt{M_I M_J}} \sum_L \Phi_{IJ}^{\alpha\beta} e^{i\boldsymbol{q}\cdot(\boldsymbol{R}_i - \boldsymbol{R}_j - \boldsymbol{R}_L)}$$

$$\sum_{j,\beta} D_{ij}^{\alpha\beta}(\boldsymbol{q}) \boldsymbol{e}_{sj}^\beta(\boldsymbol{q}) = \omega_s^2(\boldsymbol{q}) \boldsymbol{e}_{si}^\alpha(\boldsymbol{q})$$

C. Carbogno, R. Ramprasad, M. Scheffler, PRL **118**, 175901. (2017)
F. Knoop, M. Scheffler, C. Carbogno, arXiv:2209.01139. (2022)

Size extrapolation

Generalized eigenvector in real space

$$\boldsymbol{e}_{s,I}(\boldsymbol{q}) = \frac{1}{\sqrt{N_{\boldsymbol{q}}}} e^{-i\boldsymbol{q}\boldsymbol{R}_I} \boldsymbol{e}_{s,i}$$

$$u_s(\boldsymbol{q}, t) = \sum_I \sqrt{M_I} \boldsymbol{e}_{s,I} \cdot \boldsymbol{U}_I(t)$$

$$p_s(\boldsymbol{q}, t) = \sum_I \frac{1}{\sqrt{M_I}} \boldsymbol{e}_{s,I} \cdot \boldsymbol{P}_I(t)$$

$$a_s(\boldsymbol{q}, t) = \frac{1}{\sqrt{2}} \left(u_s(\boldsymbol{q}, t) + \frac{i}{\omega_s(\boldsymbol{q})} p_s(\boldsymbol{q}, t) \right)$$

C. Carbogno, R. Ramprasad, M. Scheffler, PRL **118**, 175901. (2017)
F. Knoop, M. Scheffler, C. Carbogno, arXiv:2209.01139. (2022)

Ab initio Green-Kubo calculation

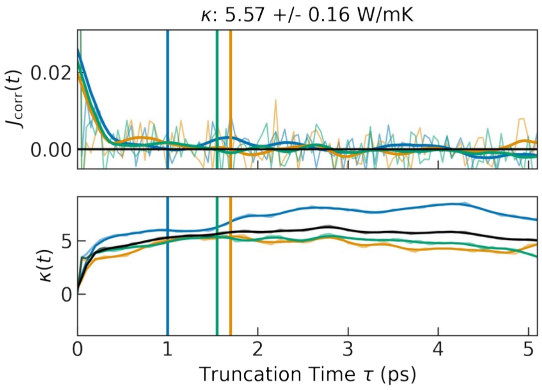
Virial heat flux

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

Gauge invariance & noise filtering

$$\boldsymbol{J}_v^{\text{gauge}}(t) = \boldsymbol{J}_v^{\text{raw}}(t) - \frac{1}{V}\sum_I \langle \sigma_I \rangle_t \, \dot{\boldsymbol{R}}_I(t) = \frac{1}{V}\sum_I \delta\sigma_I(t)\dot{\boldsymbol{R}}_I(t)$$

$$\boldsymbol{J}(t) \to \delta\boldsymbol{J}(t) = \boldsymbol{J}(t) - \langle \boldsymbol{J} \rangle_t$$



Use mean heat capacity for some cases

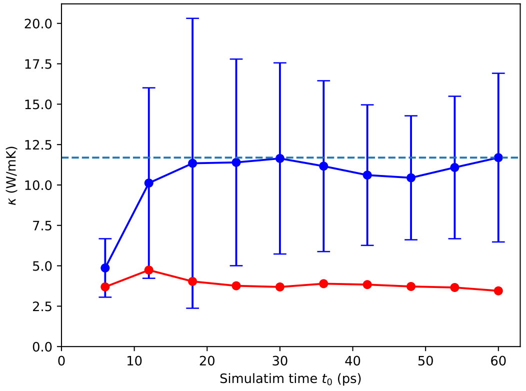
Weighted average heat capacity may fail or have large error if we have very small group velocity of lifetime

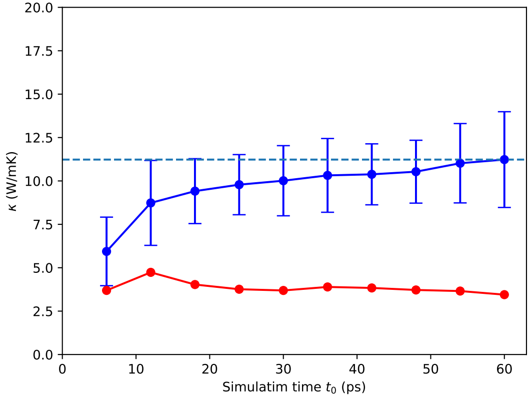
$$Cv = \frac{\sum_{sq} Cv_{sq} v^{\alpha}_{sq} v^{\beta}_{sq} \Lambda_{sq}}{\sum_{s,q} v^{\alpha}_{sq} v^{\beta}_{sq} \Lambda_{sq}}$$

Instead using mean heat capacity or classical limit will help reduce the error.

$$Cv = \langle Cv_{sq} \rangle \qquad Cv = k_B$$

Beta-Ga2O3 @ 300 K





Harmonic thermal conductivity vanishing

For some cases, group velocity within supercell gives 0

$$\boldsymbol{v}_s(\boldsymbol{q}) = \frac{\partial \omega_s(\boldsymbol{q})}{\partial \boldsymbol{q}}$$

Using BTE will leads to kappa = 0, leads to some error for extrapolation

$$\kappa_{\alpha\beta}^{\mathrm{ha}} = \frac{k_B}{V} \sum_{s,\boldsymbol{q}} v_s^{\alpha}(\boldsymbol{q}) v_s^{\beta}(\boldsymbol{q}) \Lambda_s(\boldsymbol{q})$$

Beta-Ga2O3