FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT

FHI-vibes
A Toolkit for Finding and Analyzing Thermal Insulators

ASE Workshop
Chalmers University, November 19

Florian Knoop, Tom Purcell, Maja-Olivia Lenz, Matthias Scheffler, and Christian Carbogno

Warmup

Florian Knoop

@flokno · Member since October 24, 2017

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PhD student at FHI

gitlab.com/flokno

PhD at FHI in Berlin, started January 2017:

ab initio Thermal Transport

Tools for High-Throughput Screening

Warmup

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Current Project:

Compute thermal conductivity for 100 materials

→ Starting point for developing **data science perspective** on lattice thermal conductivity (non-metals)

Outline

Part 1 — Physics

Thermal conductivity by *ab initio* Green-Kubo

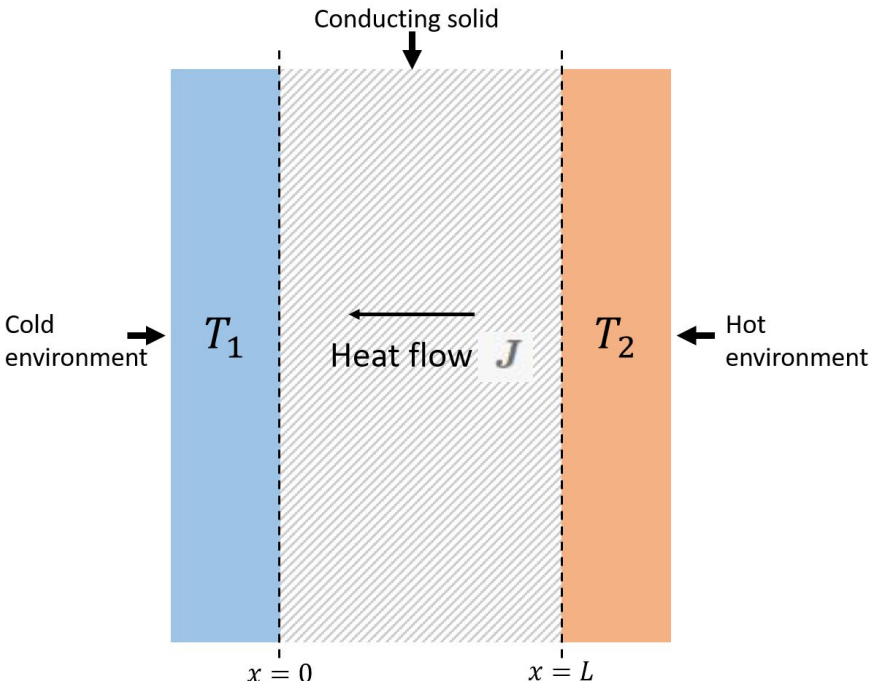
High-Throughput estimation of **Anharmonicity**

Part 2 — Tooling

FHI-vibes

Outlook

Thermal Transport



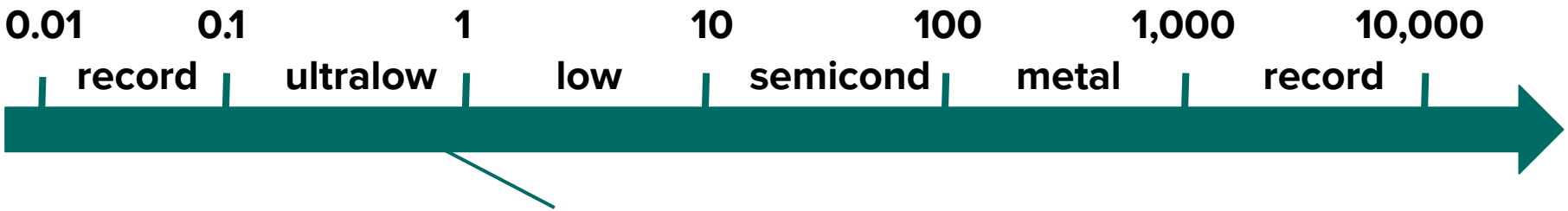
Fourier's law:

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

Thermal Conductivity

Unit:

W / m K [**Watt** per **meter Kelvin**]



Aerogels (0.02) | Wood (0.1) | **$CsPbBr_3$ (0.4)** | SnSe (0.6) | ZrO_2 (8) | MgO (60) | **Silicon (160)** | Copper (400) | Graphene (5000)

Thermal Conductivity

Unit:

W / m K [**Watt** per **meter Kelvin**]

Applications for **Thermal Insulators**:

- Thermoelectrics
- Thermal barrier coatings

Aerogels	Wood	$CsPbBr_3$	SnSe	ZrO_2	MgO	**Silicon**	Copper	Graphene
(0.02)	(0.1)	**(0.4)**	(0.6)	(8)	(60)	**(160)**	(400)	(5000)

Ab initio Green-Kubo

Real space
real time
heat flux

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

Atomic velocities
from *ab initio*
Molecular Dynamics

$$\kappa \propto \int \mathrm{d}\tau \; \langle \boldsymbol{J} \, \boldsymbol{J} \rangle \, (\tau)$$

Atomic stress
contribution
`atoms.get_stresses()`

No approximations to potential energy surface

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

Ab initio Green-Kubo

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

Fluctuation Dissipation Theorem

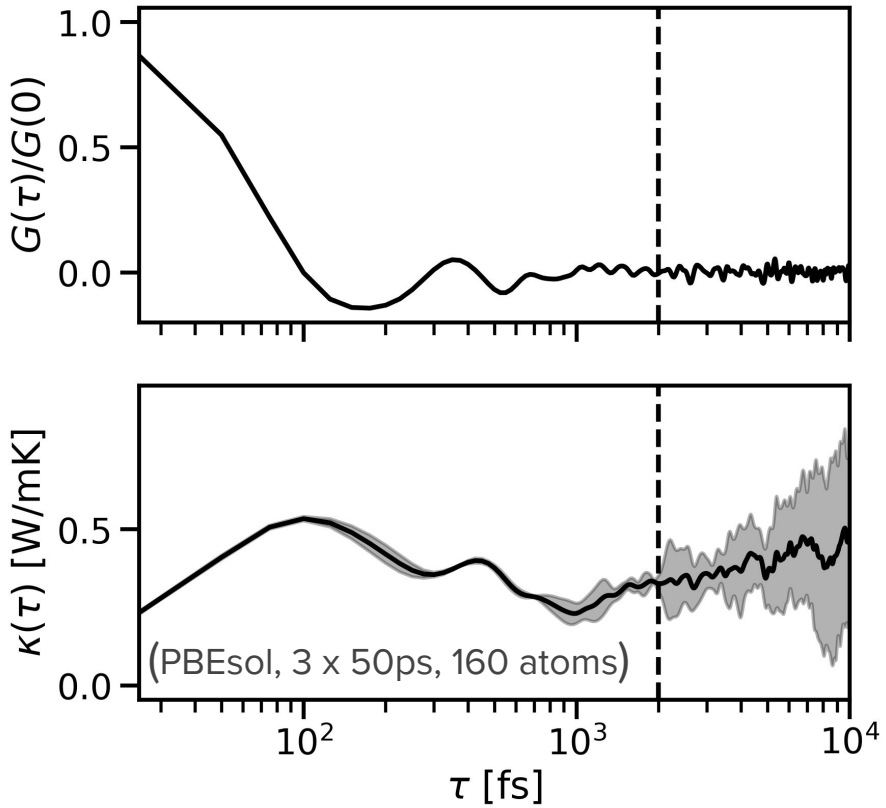
$$\kappa \propto \int \mathrm{d}\tau \; \langle \boldsymbol{J} \, \boldsymbol{J} \rangle \, (\tau)$$

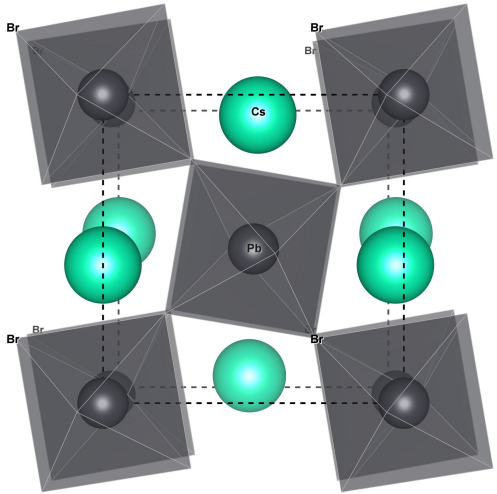
Heat Flux Autocorrelation Function

No approximations to potential energy surface

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

Results for $CsPbBr_3$ (300K)





$CsPbBr_3$ (*Pnma* 62, 20 atoms in unit cell):

κ = **0.32 ± 0.06** W/mK

(exp [1]: **0.42 ± 0.04** W/mK)

[1] Lee et al., *PNAS*, **114**, 8693 (2017)

How about Boltzmann Transport?

$$\kappa(T) = \frac{1}{V} \sum_{\boldsymbol{q}} c_{\boldsymbol{q},T} \; \boldsymbol{v}_{\boldsymbol{q}}^2 \; \tau_{\boldsymbol{q},T}$$

$$\mathcal{V}_{\text{pot}} \left(\left\{ \boldsymbol{R}^0 + \boldsymbol{u} \right\} \right) = \frac{1}{2} \, \Phi \cdot \boldsymbol{u}^2$$

How about Boltzmann Transport?

Harmonic approximation

$$\kappa(T) = \frac{1}{V} \sum_{\boldsymbol{q}} c_{\boldsymbol{q},T}\, \boldsymbol{v}_{\boldsymbol{q}}^2\, \tau_{\boldsymbol{q},T}$$

$$\mathcal{V}_{\text{pot}}\left(\{\boldsymbol{R}^0 + \boldsymbol{u}\}\right) = \frac{1}{2}\, \Phi \cdot \boldsymbol{u}^2$$

$$\Phi: \quad \mathrm{D}(\boldsymbol{q})\, |\boldsymbol{q}\rangle = \omega_{\boldsymbol{q}}^2\, |\boldsymbol{q}\rangle \Longrightarrow c_{\boldsymbol{q},T} = \frac{\partial E(T)}{\partial T}; \quad \boldsymbol{v}_{\boldsymbol{q}} = \boldsymbol{\nabla}_{\boldsymbol{q}}\, \omega_{\boldsymbol{q}}$$

How about Boltzmann Transport?

$$\kappa(T) = \frac{1}{V} \sum_{\boldsymbol{q}} c_{\boldsymbol{q},T}\ \boldsymbol{v}_{\boldsymbol{q}}^2\ \tau_{\boldsymbol{q},T}$$

Perturbative Treatment of Third Order Terms

$$\mathcal{V}_{\text{pot}}\left(\{\boldsymbol{R}^0 + \boldsymbol{u}\}\right) = \frac{1}{2}\,\Phi \cdot \boldsymbol{u}^2 + \frac{1}{3!}\,\Psi \cdot \boldsymbol{u}^3$$

$$\Phi: \quad \mathrm{D}(\boldsymbol{q})\,|\boldsymbol{q}\rangle = \omega_{\boldsymbol{q}}^2\,|\boldsymbol{q}\rangle \implies c_{\boldsymbol{q},T} = \frac{\partial E(T)}{\partial T}\,; \quad \boldsymbol{v}_{\boldsymbol{q}} = \boldsymbol{\nabla}_{\boldsymbol{q}}\,\omega_{\boldsymbol{q}}$$

$$\Psi: \quad \Sigma(\boldsymbol{q},T) \implies \tau_{\boldsymbol{q},T} = 2\,/\,\mathrm{Im}\,\Sigma(\boldsymbol{q},T)$$

How about Boltzmann Transport?

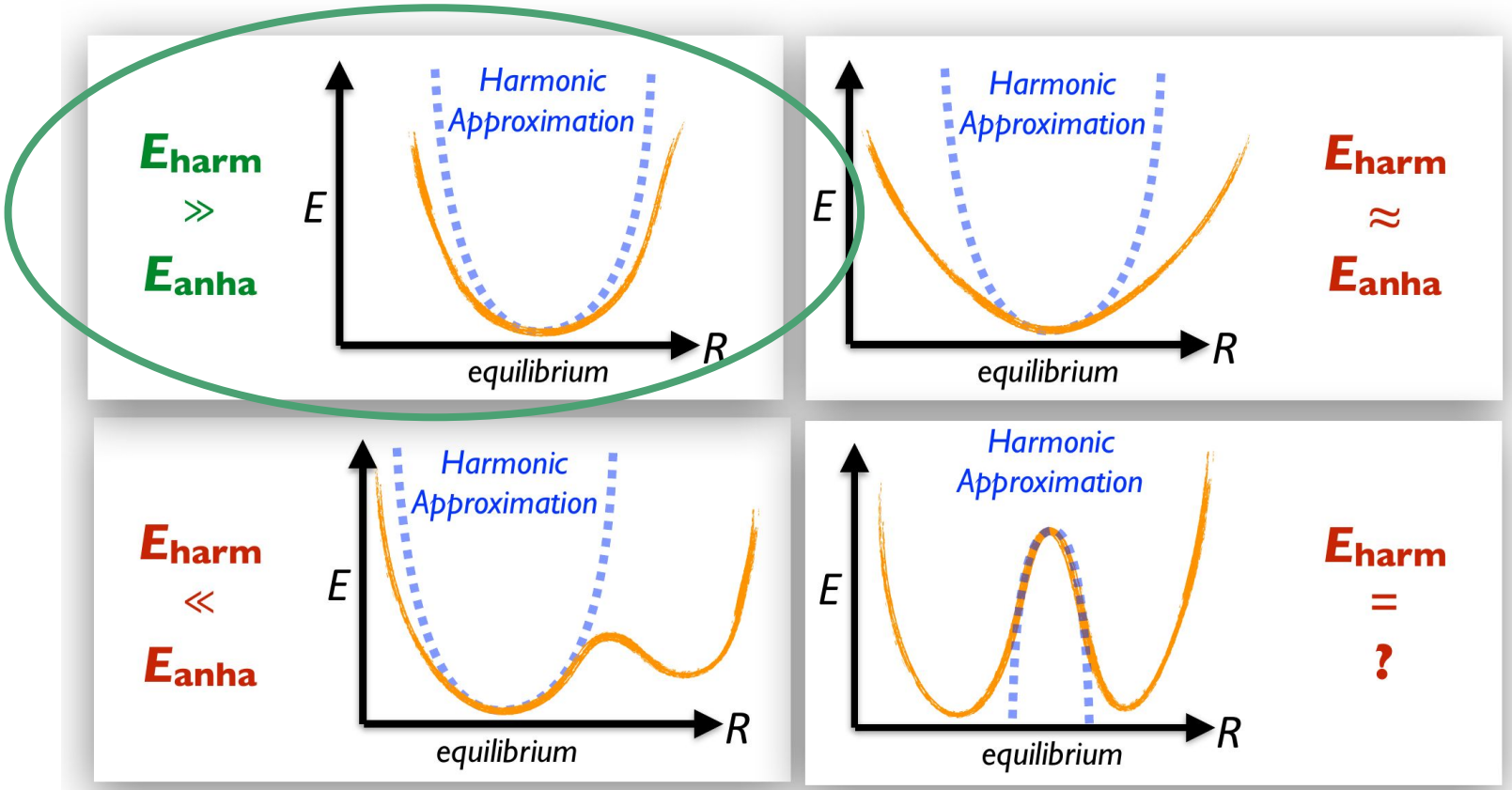
$$\kappa(T) = \frac{1}{V} \sum c_{\boldsymbol{q},T} \, \boldsymbol{v}_{\boldsymbol{q}}^2 \, \tau_{\boldsymbol{q},T}$$

Problem: Limits of perturbation theory?

$$\Phi: \quad \mathrm{D}(\boldsymbol{q}) \, |\boldsymbol{q}\rangle = \omega_{\boldsymbol{q}}^2 \, |\boldsymbol{q}\rangle \implies c_{\boldsymbol{q},T} = \frac{\partial \langle \quad \rangle}{\partial T} ; \quad \boldsymbol{v}_{\boldsymbol{q}} = \nabla_{\boldsymbol{q}} \, \omega_{\boldsymbol{q}}$$

$$\Psi: \quad \Sigma(\boldsymbol{q}, T) \implies \tau_{\boldsymbol{q},T} = 2 \, / \, \mathrm{Im} \, \Sigma(\boldsymbol{q}, T)$$

Why could perturbative treatment be insufficient?



Can we say something smart
about the nature of anharmonicity
before submitting a million core hours?
Yes we can!

Anharmonicity -- Potential Energy Surface

Nuclear Hamiltonian in adiabatic approximation:

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

Split potential into **harmonic** and **anharmonic contribution:**

$$\mathcal{V}(\boldsymbol{R}) = \mathcal{V}^{(2)} + \mathcal{V}'$$

Anharmonic Contribution!

phonopy →

$$\mathcal{V}^{(2)}(\boldsymbol{R}) = \frac{1}{2} \sum_{\substack{I,J \\ \alpha,\beta}} \Phi^{I,J}_{\alpha,\beta} \, \Delta R^{\alpha}_{I} \Delta R^{\beta}_{J}$$

Anharmonicity -- All about that force

$$\mathcal{V}(\boldsymbol{R}) = \mathcal{V}^{(2)} + \mathcal{V}'$$

$$\boldsymbol{F}_I = -\boldsymbol{\nabla}_I \mathcal{V}(\boldsymbol{R})$$

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

$$\Longrightarrow \boldsymbol{F}_I' = \boldsymbol{F}_I - \boldsymbol{F}_I^{(2)}$$

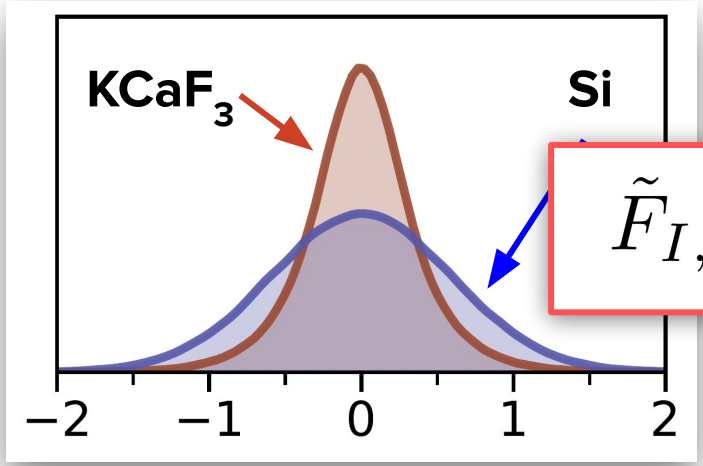
Anharmonicity of the potential ⇔ **anharmonic contribution to atomic forces**

Conclusion

Maybe it is a clever idea to **look at anharmonic forces**.

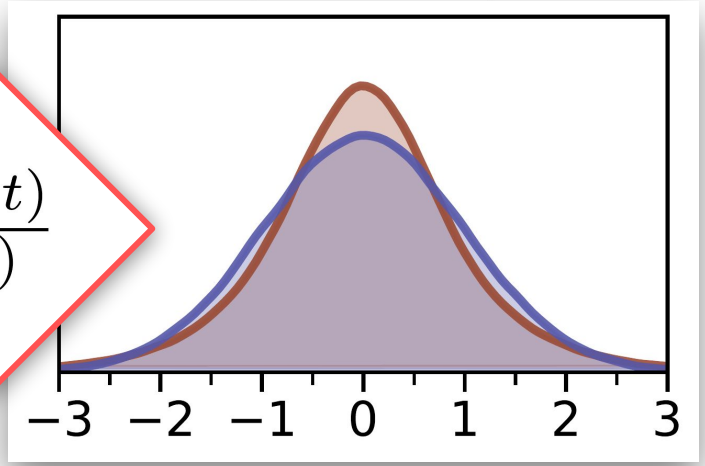
How to compare forces?

$$p\left(F_{I,\alpha}(t)\right)$$



$$\tilde{F}_{I,\alpha}(t) = \frac{F_{I,\alpha}(t)}{\sigma(\boldsymbol{F})}$$

$$p\left(\tilde{F}_{I,\alpha}(t)\right)$$

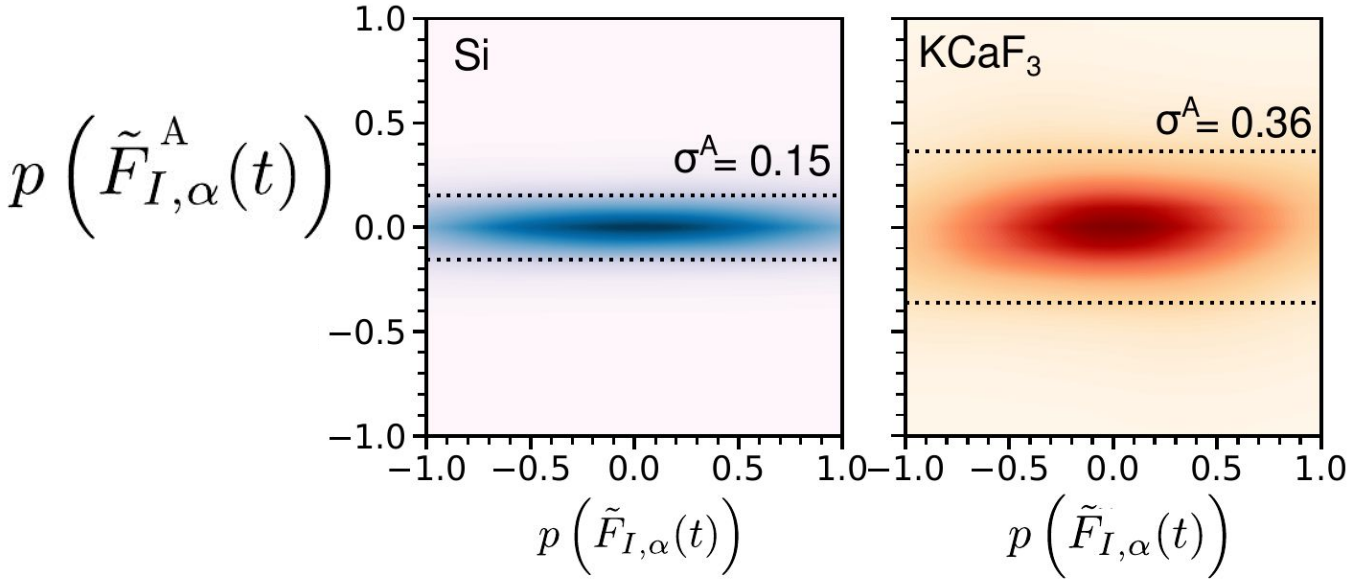


Sum up distributions of forces in each degree of freedom (atom, direction)

⇒ Variances add up

Forces observed during *ab initio* Molecular Dynamics runs

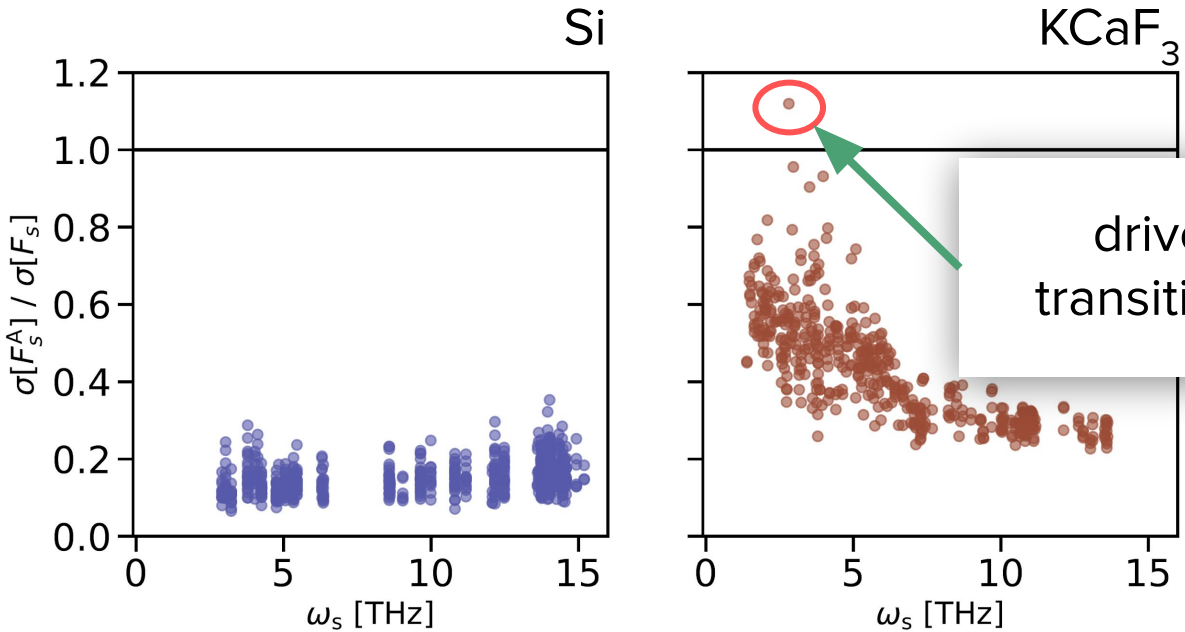
Now: Measure the Scaled Anharmonic Force



Distribution of anharmonic force contribution differs between compounds

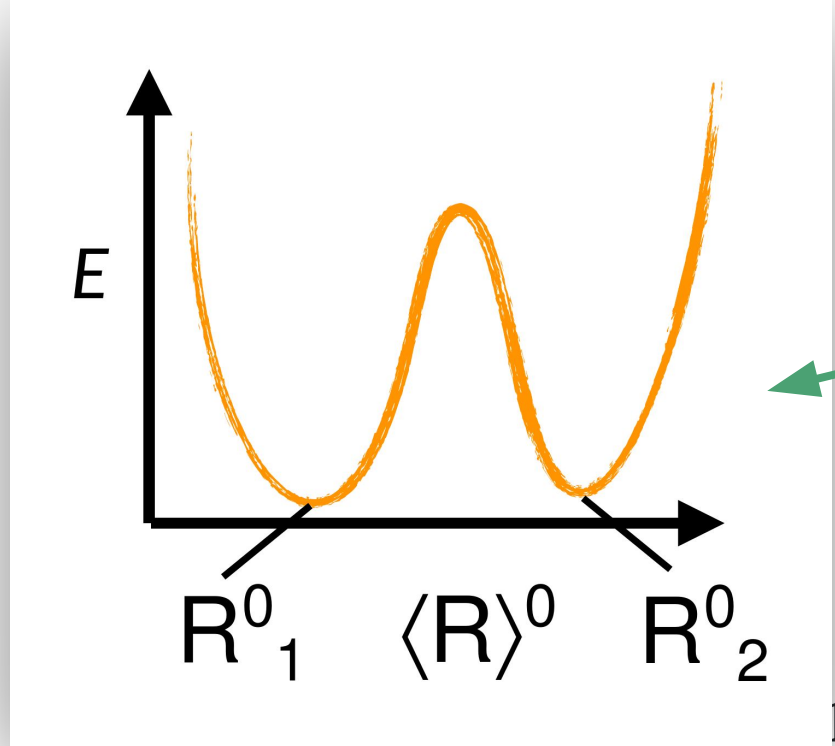
Forces observed during *ab initio* Molecular Dynamics runs

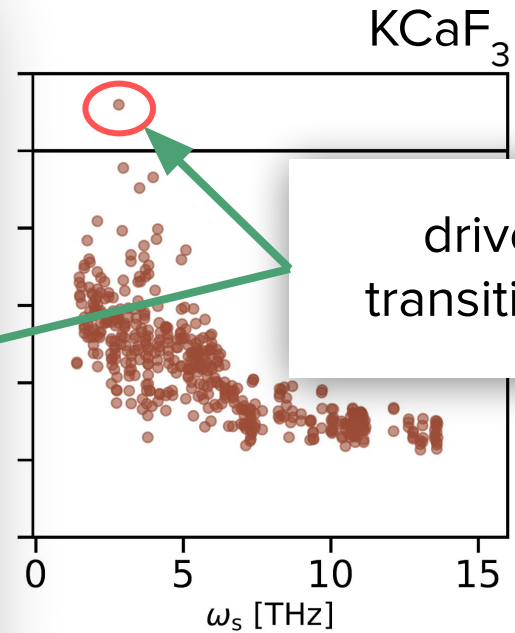
Project on Modes



$$F_s = \sum_I \frac{1}{\sqrt{M_I}} \boldsymbol{e}_{sI} \cdot \boldsymbol{F}_I$$

Project on Modes



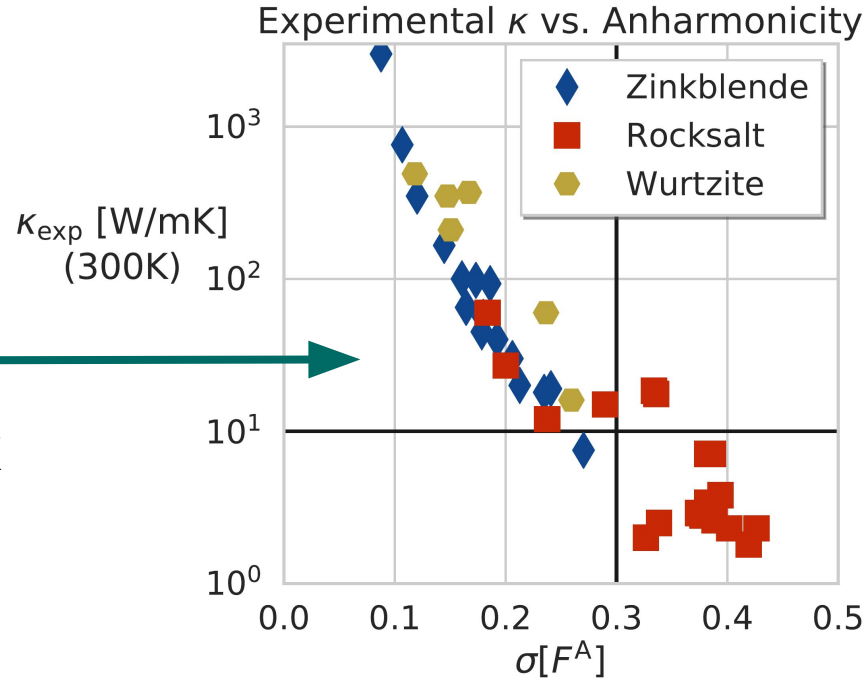


drives phase transition to cubic

$$F_s = \sum_I \frac{1}{\sqrt{M_I}} \boldsymbol{e}_{sI} \cdot \boldsymbol{F}_I$$

Anharmonicity and Thermal Conductivity

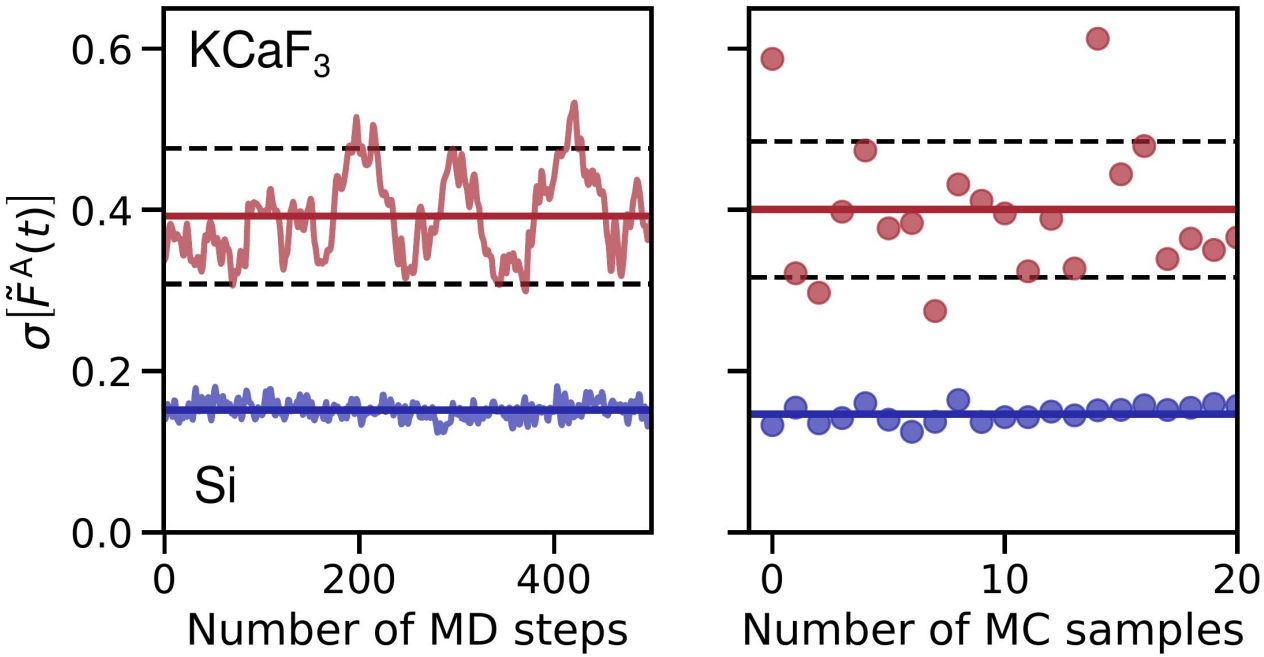
14 of 41 materials
with $\sigma^A > 0.3$,
12 of them
with $\kappa < 10$ **W/mK**



"The more anharmonic a material the lower the thermal conductivity"
is actually true!

Experimental Reference: D. Morelli, G. Slack, Thermal Conductivity Materials, Springer 2006

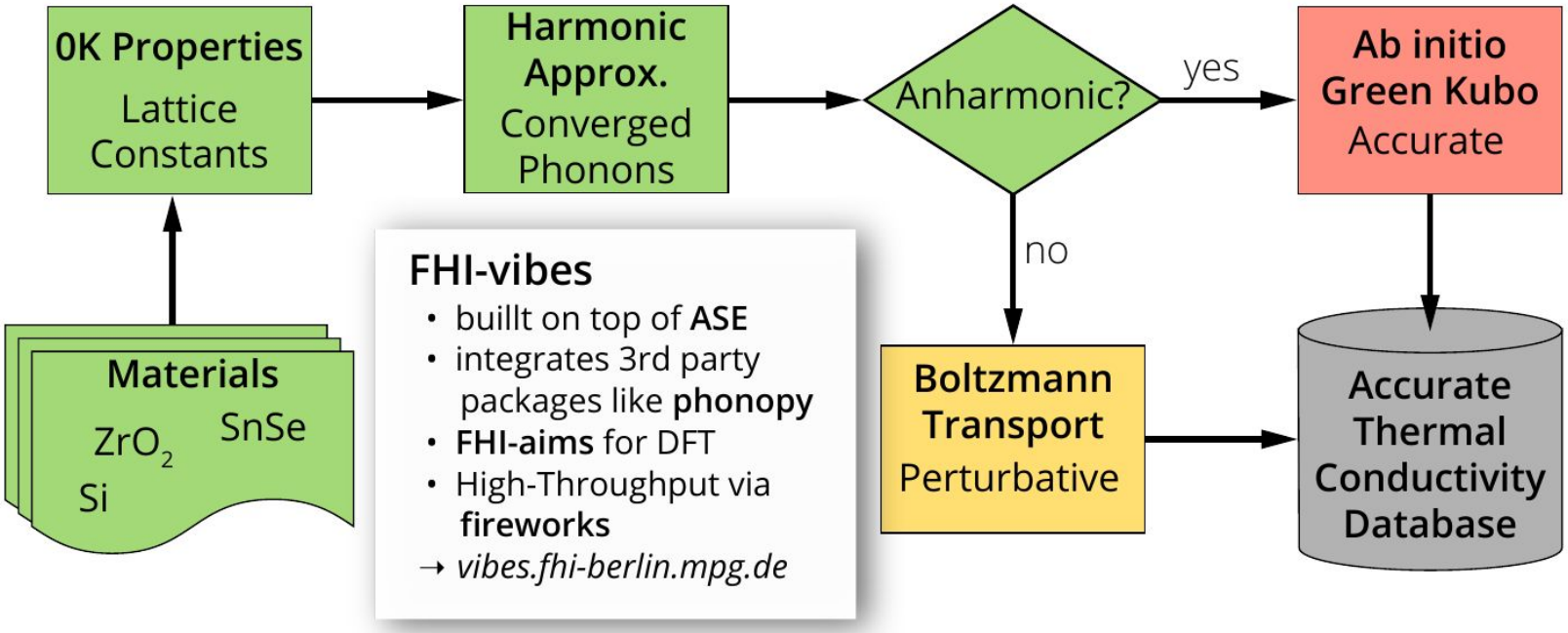
Can this be done efficiently? Yes.



Molecular Dynamics → Monte Carlo Sampling [1, 2]

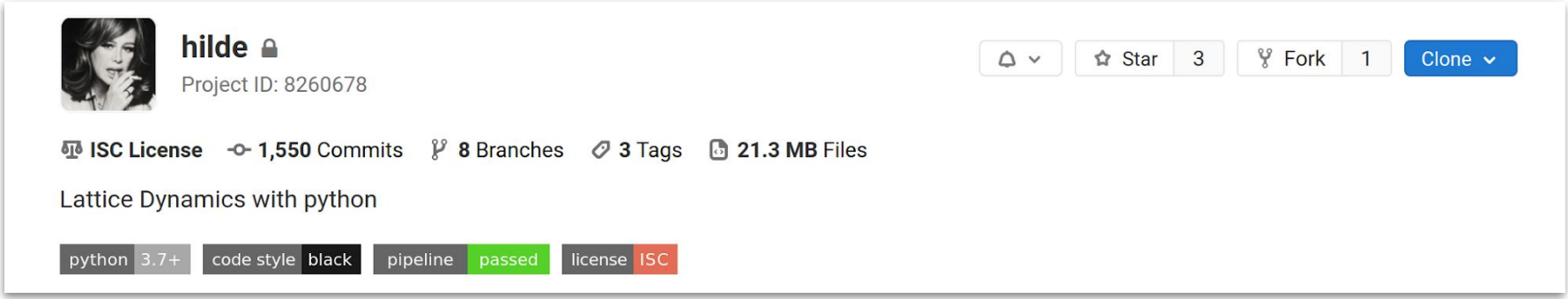
[1] D. West and S.K. Estreicher, *Phys. Rev. Lett.* **96**, 115504 (2006)
[2] M. Zacharias and F. Giustino. *Phys. Rev. B* **94**, 175901 (2017)

Our High-Throughput Approach for κ

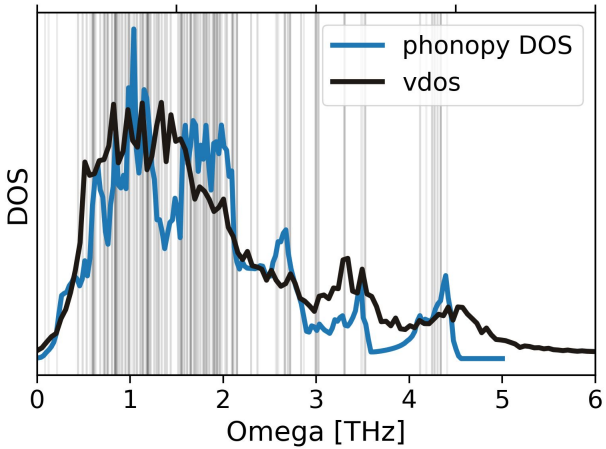


What we want from our framework

- ✓ Use existing methodologies (**phonopy**, `ase.md`)
  - **ase** makes it easy to combine functionality from different packages
- ✓ Efficient as possible DFT calculations
  - via `` `SocketIOCalculator` `` (ase **3.17**)
- x Defined input and output files for **defined workflows**
  - simple input files via python configparser
  - **self contained** output files via our own output file format
- x Command line interface
- x Cluster support (slurm submission, restarts)
- x High-Throughput functionality
  - via FireWorks, not discussed today



- **Fritz Haber Institute vibrational analysis toolkit**
  - python package for **lattice dynamics investigations with FHIaims**
  - built on top of **ase**
- Current Features
  - **phonopy** calculations ➔ Tutorial on Friday
  - **MD + heat flux** simulations
  - **toolset** for preparing, and analyzing data
  - high throughput functionality via ***fireworks***
    - ➢ Tom Purcell



Input File for MD: **md.in**

```
[geometry]
file:               geometry.in
primitive:          geometry.in.primitive
supercell:          geometry.in.supercell

[control]
xc:                 pbesol
k_grid:             [2, 2, 2]
charge_mix_param:   0.3

[basissets]
default:            light

[md]
timestep:           5
maxsteps:           2000
driver:             Langevin
temperature:        300
friction:           0.02
compute_stresses:   10
```

Input File for MD: **md.in**

for running
on the cluster

```
[...]

[slurm]
nodes:              5

[restart]
command:            vibes submit md
```

submit a job

```
➤ vibes submit md

Submitted batch job 10294567
```

Output File: **trajectory.son**

```
{<<metadata json block>>}
===
{<<structure  0 data>>}
---
{<<structure  1 data>>}
---
{<<structure  2 data>>}
---
{<<structure  3 data>>}
---
...
```

Output File: **trajectory.son**

```
{"MD": {
  "type": "molecular-dynamics",
  ...},
"calculator": {
  "calculator": "Aims",
  "calculator_parameters": {
    "xc": "pbesol",
    "k_grid": [2, 2, 2],
    ...}},
"atoms": {
  "cell":
    [[ 8.33141234000000e+00, -8.33141234000000e+00,  0.00000000000000e+00],
     [ 8.33141234000000e+00,  8.33141234000000e+00,  0.00000000000000e+00],
     [ 0.00000000000000e+00,  0.00000000000000e+00,  1.24971185100000e+01]],
  "positions":
    [[ 0.00000000000000e+00,  0.00000000000000e+00,  0.00000000000000e+00],
     [ 4.16570617000000e+00,  0.00000000000000e+00,  0.00000000000000e+00],
   …}
“primitive”: { …
…}
===
...
```

github.com/flokno/son

pypi.org/project/son

Output File: **trajectory.son**

```
{<<metadata json block>>}
===
{"atoms": {
  "info": {
    "nsteps": 0,
    "dt":  4.91134739423203e-01,
    "aims_uuid": "D985353A-F8FD-4635-A939-E129A7E6E146"},
  "positions":
    [[ 0.00000000000000e+00,  0.00000000000000e+00,  0.00000000000000e+00],
     [ 4.16570617000000e+00,  0.00000000000000e+00,  0.00000000000000e+00], ...}
---
{"atoms": {
  "info": {
    "nsteps": 1,
    "dt":  4.91134739423203e-01,
    "aims_uuid": "D985353A-F8FD-4635-A939-E129A7E6E146"},
  "positions":
    [[ 1.62463733205010e-04,  7.52668360843155e-04, -4.84513363592926e-05],
     [ 4.16666097188355e+00, -4.45877229739784e-04, -3.12871862455504e-04], ...}
---
...
```

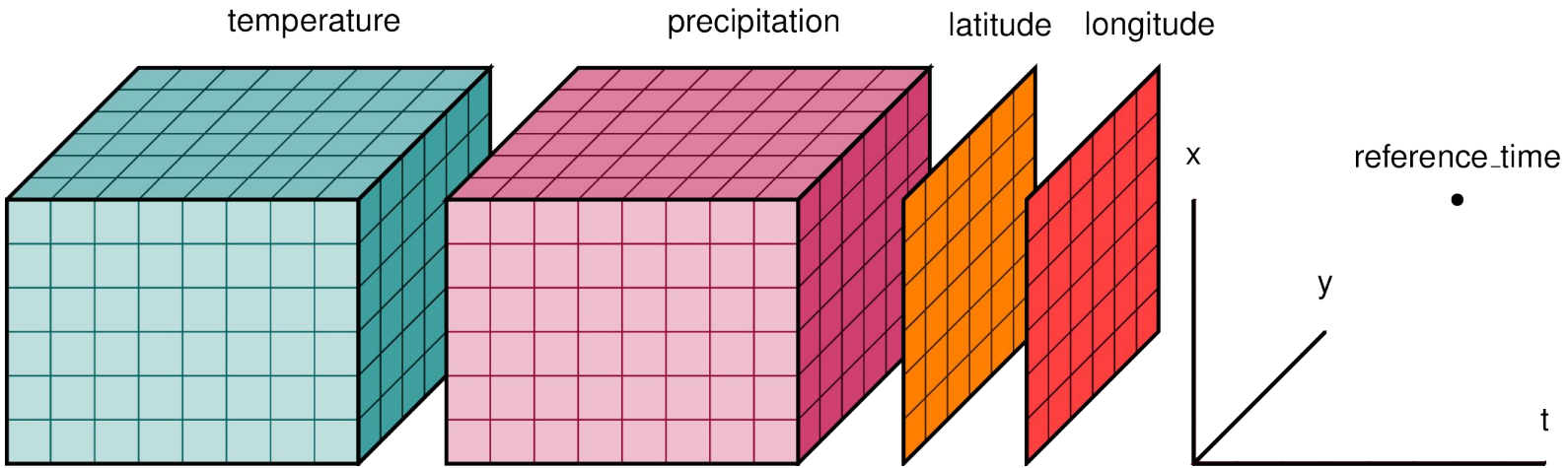
Extract data from trajectory.son

```
➤ vibes output md trajectory.son

Extract Trajectory dataset from trajectory.son
[trajectory]   Parse trajectory
[son] read file:  trajectory.son
[son] process:    |||||||||||||||||||||||||||||||||||||||  2002/2002
.. create atoms:  |||||||||||||||||||||||||||||||||||||||  2001/2001
[trajectory]   .. done in 1.639s
[trajectory]   Get positions from trajectory
[trajectory]   .. time elapsed: 0.038s
[trajectory]   Get velocities from trajectory
[trajectory]   .. time elapsed: 0.009s
[trajectory]   Get pressure from trajectory
[trajectory]   .. time elapsed: 0.308s

Trajectory dataset written to trajectory.nc
```

trajectory.nc : netCDF (hdf5) file containing an **xarray.Dataset**

¿ xarray.Dataset ?

- Similar to [pandas.DataFrame]
  - for **multi-dimensional data** (former pandas.Panel)
- Philosopy: Data should be **bundled** and **labelled**
  - compare .**xyz files**
- [xarray.pydata.org/en/stable/why-xarray.html]



¿ xarray.Dataset ?

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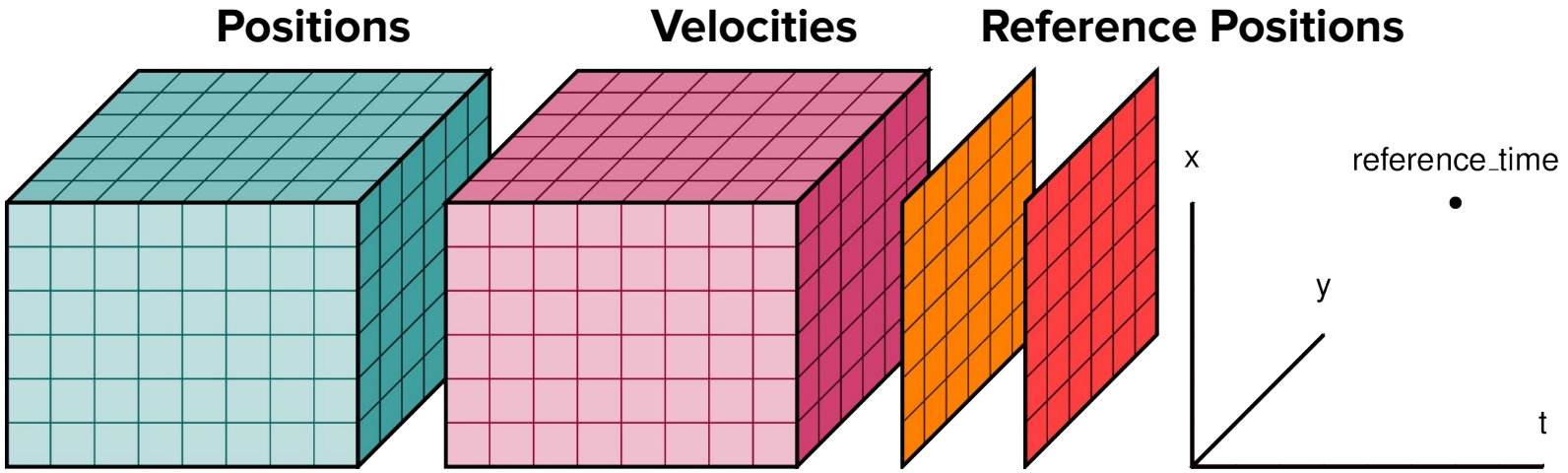


FHI-vibes: inspect trajectory dataset

```
➤ vibes info netcdf trajectory.nc

<xarray.Dataset>
Dimensions:           (I: 120, a: 3, b: 3, time: 2001)
Coordinates:
  * time              (time) float64 0.0 5.0 10.0 ... 9.99e+03 9.995e+03 1e+04
Dimensions without coordinates: I, a, b
Data variables:
    displacements     (time, I, a) float64 ...
    velocities        (time, I, a) float64 ...
    forces            (time, I, a) float64 ...
    kinetic_energy    (time) float64 ...
    potential_energy  (time) float64 ...
    stress            (time, a, b) float64 ...
    temperature       (time) float64 …
    [...]
Attributes:
    System Name:                BaHfO3
    time unit:                  fs
    timestep:                   5.000000000000001
    nsteps:                     2000
    reference atoms:            {"cell": \n[[ 8.33141234000000e+00, -8.331412...
    average atoms:              {"cell": \n[[ 8.33141234000000e+00, -8.331412...
    reference positions:        [ 0.          0.          0.          4.16570...
    reference primitive atoms:  {"cell": \n[[ 4.16570617000000e+00,  0.000000…
    [...]
```

FHI-vibes: inspect trajectory dataset

```
➤ vibes info md trajectory.nc --plot

Dataset summary for trajectory.nc:

[info]         Summarize Temperature
Simulation time:            10.000 ps (2001 steps)
Temperature:                   279.270 +/-      40.4779 K
Temperature (1st 1/3):         261.954 +/-      59.1326 K
Temperature (2st 1/3):         294.874 +/-      21.3062 K
Temperature (3st 1/3):         280.982 +/-      20.5579 K

[info]         Summarize Potential Energy
Simulation time:            10.000 ps (2001 steps)
Pot. Energy:               -15676395.140 +/-       0.6166 eV
Pot. Energy (1st 1/3):     -15676395.381 +/-       0.9148 eV
Pot. Energy (2st 1/3):     -15676394.917 +/-       0.3248 eV
Pot. Energy (3st 1/3):     -15676395.121 +/-       0.3012 eV

[info]         Summarize Pressure
Simulation time:            10.000 ps (218 of 2001 steps)
Pressure:                     0.792685 +/-   0.164142 GPa
Pressure (last 1/2):          0.792882 +/-   0.105375 GPa
Pressure (last 1/2):          0.004949 +/-   0.000658 eV/AA**3
[...]
.. summary plotted to md_summary.pdf
```

FHI-vib dataset

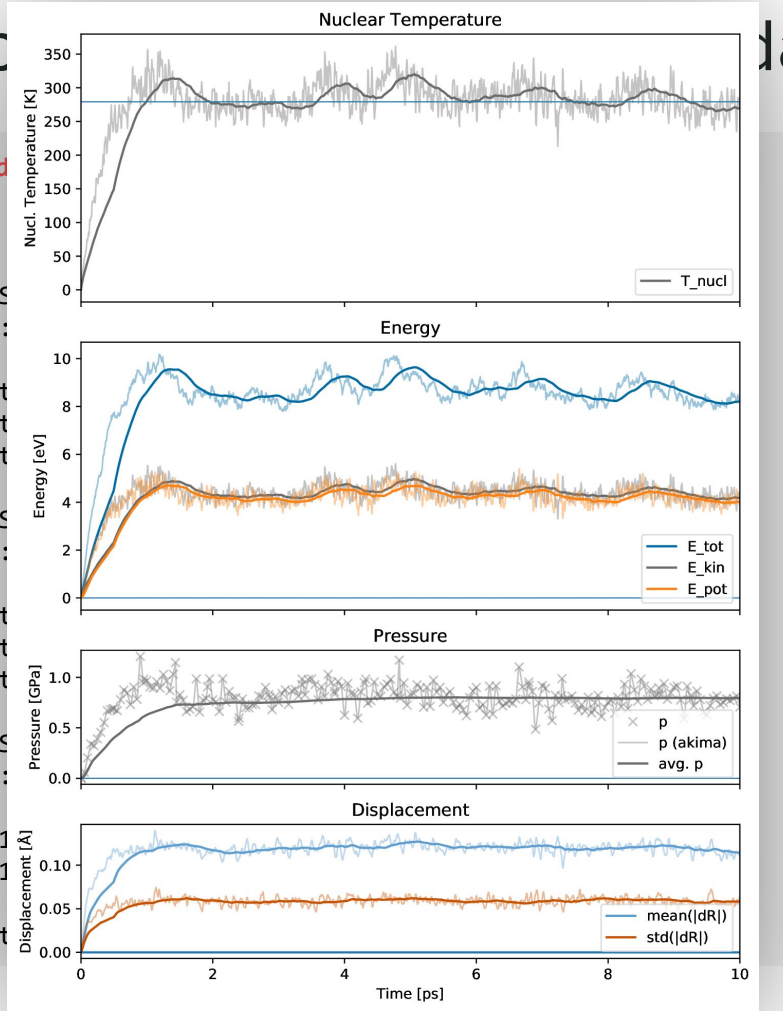
```
➤ vibes info md

Dataset summary

[info]          S
Simulation time:
Temperature:
Temperature (1st
Temperature (2st
Temperature (3st

[info]          S
Simulation time:
Pot. Energy:
Pot. Energy (1st
Pot. Energy (2st
Pot. Energy (3st

[info]          S
Simulation time:
Pressure:
Pressure (last 1
Pressure (last 1
[...]
.. summary plott
```



FHI-vibes: Outlook

- Poster Session: Let’s discuss there!
- Tutorial on Friday:
  - use FHI-vibes to perform phonopy calculations
  - inspect an MD trajectory obtained with FHI-vibes and perform postprocessing
  - interoperability with hiphive
- Further Features:
  - high-throughput functionality via Fireworks developed by Tom Purcell
- hopefully released by the end of the year
- right now: invitation to our gitlab possible

Thank you!