

# ALAMODE講習会

## - TSUBAME 3.0を用いた講習会 -

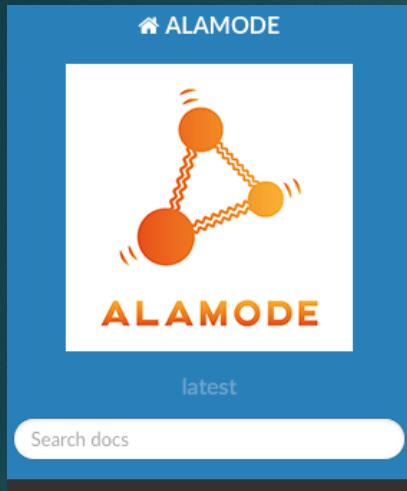
Lecturer: Terumasa Tadano (NIMS, Japan)  
June 28<sup>th</sup>, 2022

Download this slide from below:  
[https://github.com/ttadano/alamode\\_tutorial  
/tree/main/hands-on\\_TSUBAME2022](https://github.com/ttadano/alamode_tutorial/tree/main/hands-on_TSUBAME2022)

# Outline

1. Overview of ALAMODE software and functionality of ALM (30 mins.)
2. **Hands-on session** 1: Extraction of harmonic/anharmonic force constants ( ~40 mins.)
3. **Hands-on session** 2: Using python wrapper of ALM (~20 mins.)  
(lunck break)
4. Overview of functionality of ANPHON (30 mins.)
5. **Hands-on session** 3: Thermal conductivity calculation using ANPHON (~ 30 mins.)  
(short break)
6. **Hands-on session** 4: Finite-temperature phonon calculation using ANPHON (~ 90mins.)

# ALAMODE



Docs » 1. About

 Edit on GitHub

## 1. About

### 1.1. What is ALAMODE?

ALAMODE is an open source software designed for analyzing lattice anharmonicity and lattice thermal conductivity of solids. By using an external DFT package such as VASP and Quantum ESPRESSO, you can extract harmonic and anharmonic force constants straightforwardly with ALAMODE. Using the calculated anharmonic force constants, you can also estimate lattice thermal conductivity, phonon linewidth, and other anharmonic phonon properties from first principles.

<https://alamode.readthedocs.io/>

- ▶ An open source software to compute anharmonic properties of phonons
- ▶ MIT license
- ▶ Latest version: 1.4.0 (Released June 21<sup>st</sup>, 2022)
- ▶ Developer: Terumasa Tadano
- ▶ Contributors (alphabetical order):
  - R. Masuki (Structure optimization at finite temperature)
  - T. Nishimoto (Ewald method),
  - Y. Oba (Anharmonic free-energy),
  - Y. Tanaka (Interface with OpenMX),
  - A. Togo (Code refactoring, API implementation)

# Main features

## I. Extraction of harmonic/anharmonic force constants from DFT

Hands-on : 1, 2

- ▶ K. Esfarjani and H. T. Stokes, Phys. Rev. B **77**, 144112 (2008).
- ▶ T. Tadano, Y. Gohda, and S. Tsuneyuki, JPCM **26**, 225402 (2014).

## 2. Lattice thermal conductivity based on the Peierls-Boltzmann theory

Hands-on : 3

- ▶ Peierls, “Quantum theory of solids”, Oxford press (1955).
- ▶ D. A. Broido, A. Ward, and N. Mingo, Phys. Rev. B **72**, 14308 (2005).

## 3. Finite-temperature phonons based on the self-consistent phonon theory

Hands-on: 4

- ▶ T. Tadano and S. Tsuneyuki, Phys. Rev. B **92**, 054301 (2015); J. Phys. Soc. Jpn. **87**, 041015 (2018).
- ▶ Y. Oba, T. Tadano, R. Akashi, and S. Tsuneyuki, Phys. Rev. Materials **3**, 033601 (2019).

- ▶ ALAMODE requires an external DFT/FF code that can calculate forces for extracting force constants.
- ▶ Interface scripts for the following codes are included in tools/ directory:  
[VASP](#), [Quantum-ESPRESSO \(QE\)](#), [OpenMX](#), [xTAPP](#), and [LAMMPS](#).  
Also, an interface with [GULP](#) is provided by the GULP team.

## Required libraries

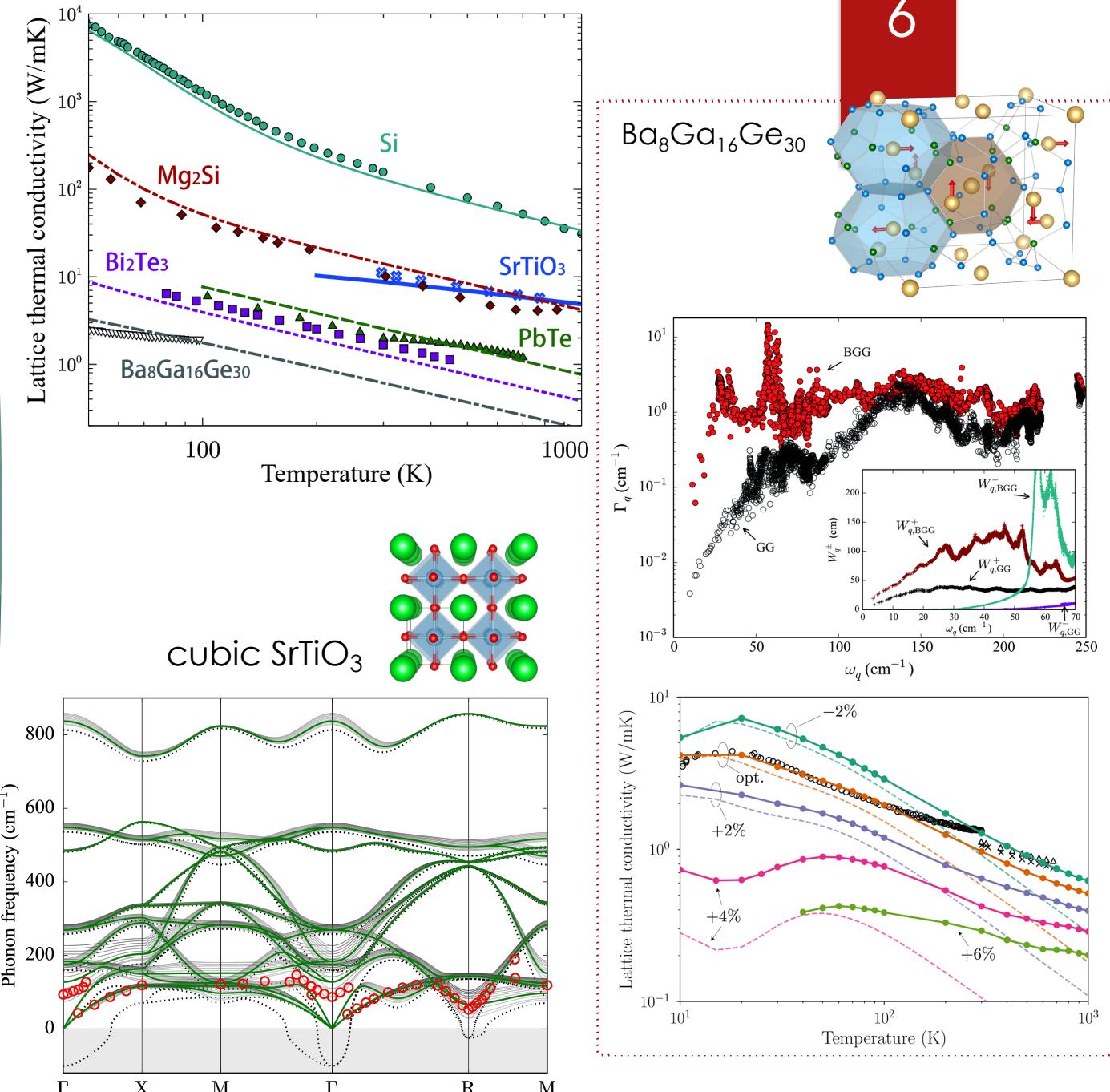
- C++ compiler (Intel compiler is recommended.)
- LAPACK library
- MPI library
- [Boost C++ library](#)
- [FFTW library](#)
- [Eigen3 library](#)
- [spglib](#)

# Applications

- ▶ Thermal conductivity of silicon,  $\text{Mg}_2\text{Si}$ ,  $\text{PbTe}$ ,  $\text{Bi}_2\text{Te}_3$ , etc.
- ▶ Thermal conductivity of clathrate  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$   
PRL **114**, 095501 (2015); PRL **120**, 105902 (2018)
- ▶ Finite-temperature phonons of cubic  $\text{SrTiO}_3$   
PRB **92**, 054301 (2015); JPSJ **87**, 041015 (2018)
- ▶ Anharmonic free-energy calculation of  $\text{ScF}_3$   
PRMater **3**, 033601(2019).

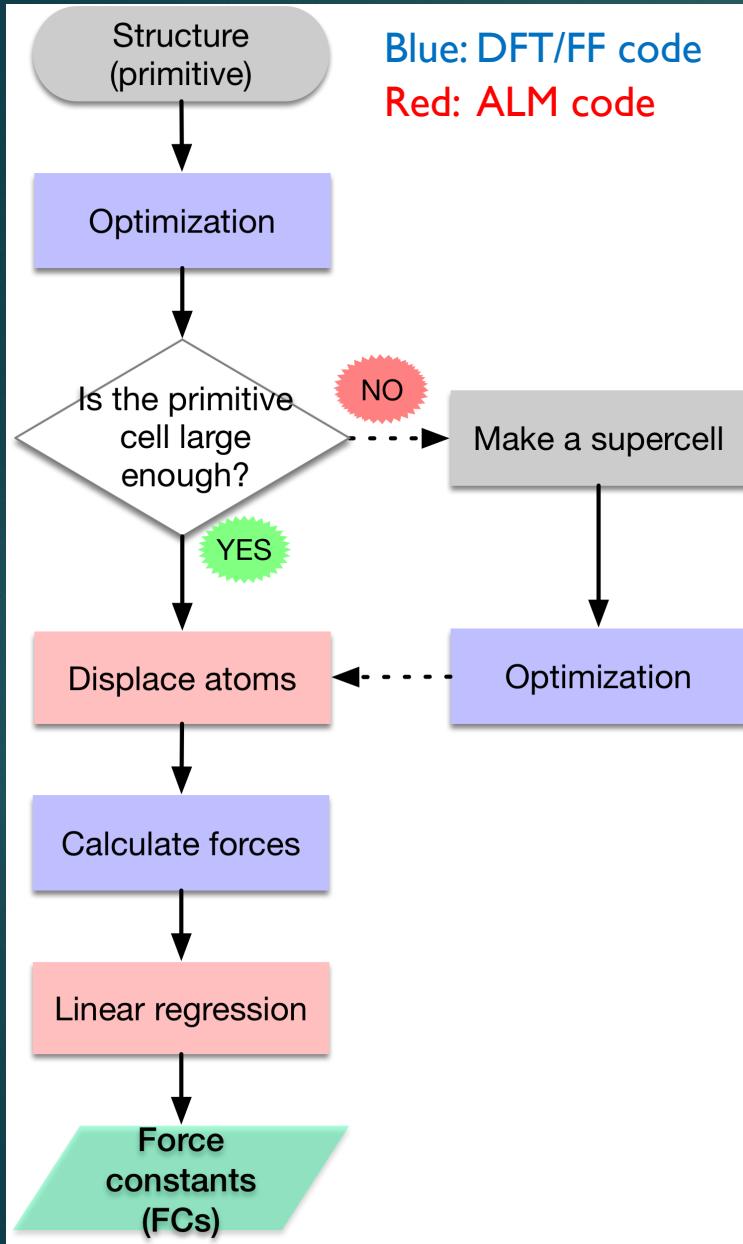
More applications can be found at

<https://scholar.google.co.jp/scholar?oi=bibs&hl=en&cites=121760967892518950>  
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# ALAMODE workflow

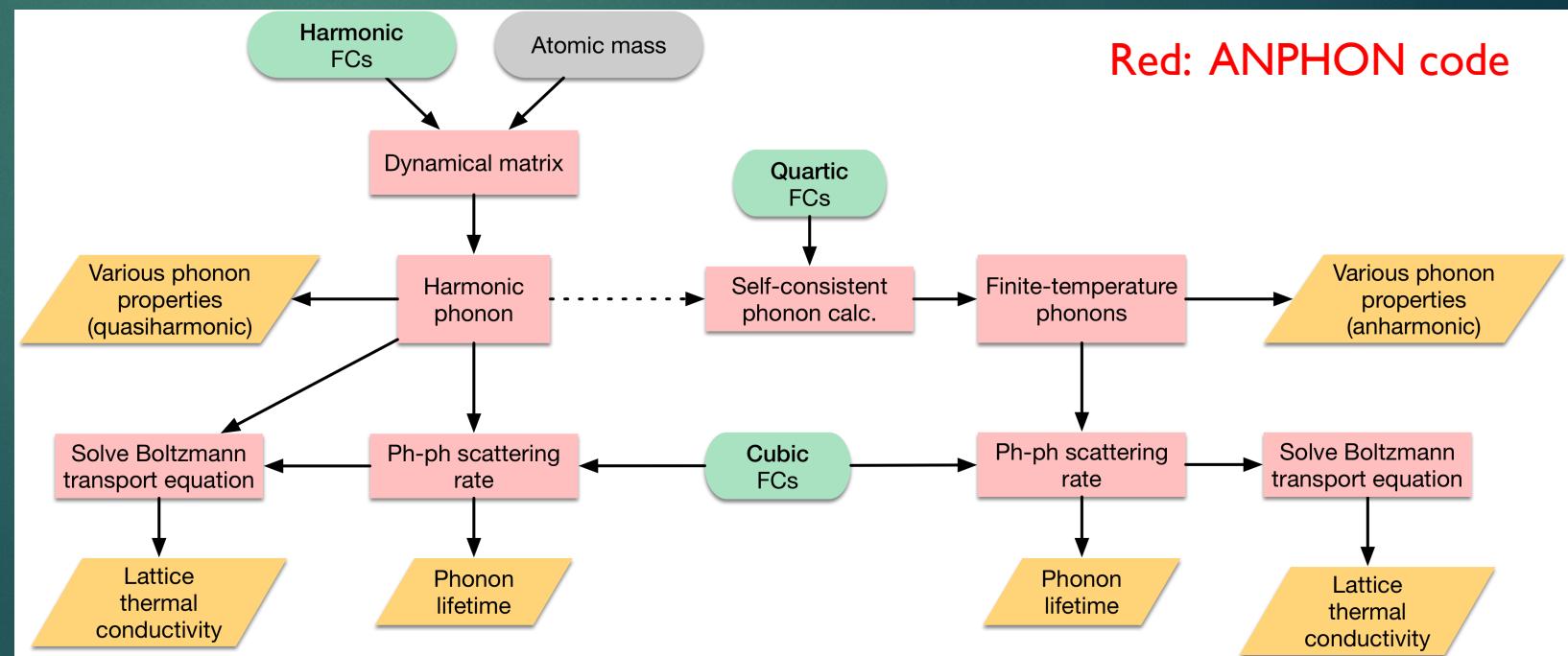
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ALAMODE package includes two independent codes:

**ALM** : Force constant calculator, OpenMP

**ANPHON**: Phonon property calculator, MPI+OpenMP



# Taylor expansion of potential energy surface

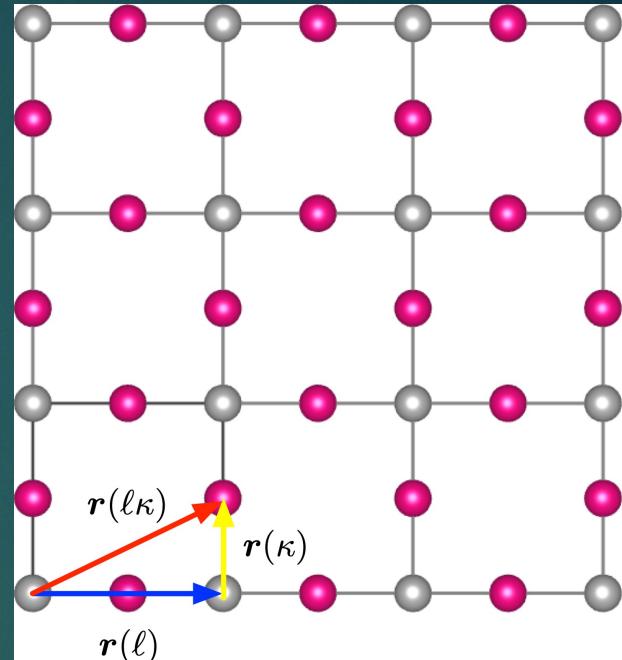
8

## Assumption

- ▶ Born-Oppenheimer approximation
- ▶ Potential energy is an analytic function of atomic displacements
- ▶ Displacements are small enough compared to the interatomic distance

$$\begin{aligned} U - U_0 &= U_2 + U_3 + U_4 + \dots \\ &= \frac{1}{2} \sum_{\{\ell, \kappa, \mu\}} \Phi_{\mu_1 \mu_2}(\ell_1 \kappa_1; \ell_2 \kappa_2) \times u_{\mu_1}(\ell_1 \kappa_1) u_{\mu_2}(\ell_2 \kappa_2) \\ &\quad + \frac{1}{3!} \sum_{\{\ell, \kappa, \mu\}} \Phi_{\mu_1 \mu_2 \mu_3}(\ell_1 \kappa_1; \ell_2 \kappa_2; \ell_3 \kappa_3) \times u_{\mu_1}(\ell_1 \kappa_1) u_{\mu_2}(\ell_2 \kappa_2) u_{\mu_3}(\ell_3 \kappa_3) \\ &\quad + \frac{1}{4!} \sum_{\{\ell, \kappa, \mu\}} \Phi_{\mu_1 \mu_2 \mu_3 \mu_4}(\ell_1 \kappa_1; \ell_2 \kappa_2; \ell_3 \kappa_3; \ell_4 \kappa_4) \times u_{\mu_1}(\ell_1 \kappa_1) u_{\mu_2}(\ell_2 \kappa_2) u_{\mu_3}(\ell_3 \kappa_3) u_{\mu_4}(\ell_4 \kappa_4) + \dots \end{aligned}$$

$\mu = x, y, z$   
 $\ell$  : Cell index  
 $\kappa$  : Atom index



$\mathbf{u}(\ell \kappa) = \mathbf{R}(\ell \kappa) - \mathbf{R}^0(\ell \kappa)$  where  $\mathbf{R}^0(\ell \kappa)$  is the atomic position optimized by DFT ( $T = 0$  K).

# Interatomic force constant (IFC)

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$n$ th-order IFC is defined as

$$\Phi_{\mu_1 \dots \mu_n}(\ell_1 \kappa_1; \dots; \ell_n \kappa_n) = \frac{\partial^n U}{\partial u_{\mu_1}(\ell_1 \kappa_1) \cdots \partial u_{\mu_n}(\ell_n \kappa_n)} \Big|_{\{u\}=0}$$

Second-order (harmonic) term  $\rightarrow$  Lattice dynamics at  $T = 0$  K.

Third-order (cubic) term  $\rightarrow$  Phonon-phonon scattering, thermal expansion, ...

Fourth-order (quartic) term  $\rightarrow$  Lattice dynamics at finite temperature, ...

# Harmonic approximation (HA)

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$$U - U_0 = U_2 + U_3 + U_4 + \dots \approx U_2$$

$$\begin{aligned} H_0 &= T + U_2 \\ &= \sum_{\ell_1, \kappa_1, \mu_1} \frac{\{p_{\mu_1}(\ell_1 \kappa_1)\}^2}{2M_{\kappa_1}} + \frac{1}{2} \sum_{\{\ell, \kappa, \mu\}} \Phi_{\mu_1 \mu_2}(\ell_1 \kappa_1; \ell_2 \kappa_2) u_{\mu_1}(\ell_1 \kappa_1) u_{\mu_2}(\ell_2 \kappa_2) \end{aligned}$$

↓ Fourier transform  $u(\ell \kappa) = N^{-1/2} \sum_{\mathbf{q}} u(\kappa; \mathbf{q}) e^{i \mathbf{q} \cdot \mathbf{r}(\ell)}$   
 $p(\ell \kappa) = N^{-1/2} \sum_{\mathbf{q}} p(\kappa; \mathbf{q}) e^{i \mathbf{q} \cdot \mathbf{r}(\ell)}$

$$= \sum_{\mathbf{q}, \kappa} \frac{\mathbf{p}^*(\kappa; \mathbf{q}) \cdot \mathbf{p}(\kappa; \mathbf{q})}{2M_{\kappa}} + \frac{1}{2} \sum_{\mathbf{q}, \kappa, \kappa'} \mathbf{u}^*(\kappa; \mathbf{q}) \cdot \Phi(\kappa \kappa'; \mathbf{q}) \mathbf{u}(\kappa'; \mathbf{q})$$

↓ Normal coordinate  $u(\kappa; \mathbf{q}) = \frac{1}{\sqrt{M_{\kappa}}} \sum_j e(\kappa; \mathbf{q}j) Q_{\mathbf{q}j}$   
 $p(\kappa; \mathbf{q}) = \sqrt{M_{\kappa}} \sum_j e(\kappa; \mathbf{q}j) P_{\mathbf{q}j}$

$$= \frac{1}{2} \sum_{\mathbf{q}, j} P_{\mathbf{q}j}^* P_{\mathbf{q}j} + \frac{1}{2} \sum_{\mathbf{q}, j} \omega_{\mathbf{q}j}^2 Q_{\mathbf{q}j}^* Q_{\mathbf{q}j}$$

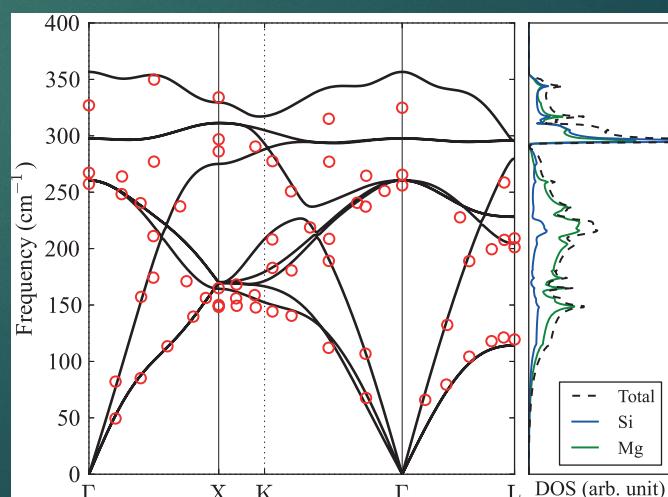
↓ Second quantization

$$= \sum_{\mathbf{q}, j} \hbar \omega_{\mathbf{q}j} \left( b_{\mathbf{q}j}^\dagger b_{\mathbf{q}j} + \frac{1}{2} \right)$$

Dynamical matrix

$$D_{\mu\nu}(\kappa \kappa'; \mathbf{q}) = \frac{1}{\sqrt{M_{\kappa} M_{\kappa'}}} \sum_{\ell'} \Phi_{\mu\nu}(0 \kappa; \ell' \kappa') e^{i \mathbf{q} \cdot \mathbf{r}(\ell)}$$

$$\omega_{\mathbf{q}j}^2 = (\mathbf{e}_{\mathbf{q}j}^*)^T D(\mathbf{q}) \mathbf{e}_{\mathbf{q}j}.$$



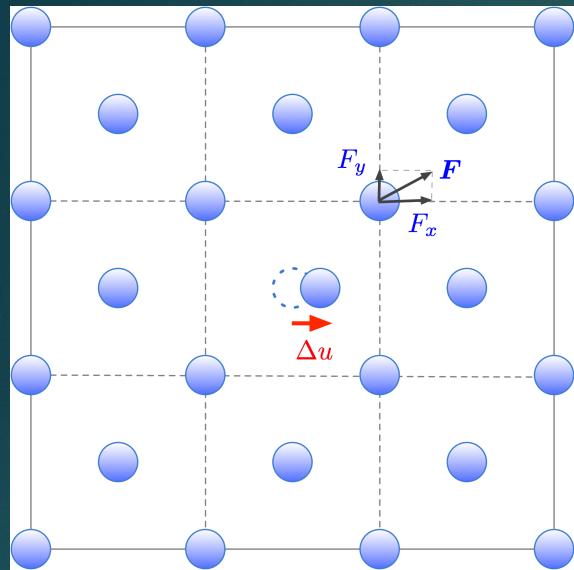
# First-principles calculation of IFCs

| Method   | DFPT [1,2]<br>(density functional perturbation theory)   | Direct method [3]   |
|----------|--|---|
| Pros.    | <ul style="list-style-type: none"><li>Efficient calculation of phonons at <math>q \neq 0</math> with a primitive cell</li><li>Able to compute dielectric constants, Born effective charges</li></ul>         | <ul style="list-style-type: none"><li>Easy to implement</li><li>Able to compute fourth- and higher-order IFCs</li><li>Meta-GGA, vdW functional, and hybrid functional can be used</li></ul> |
| Cons.    | <ul style="list-style-type: none"><li>Difficult to implement</li><li>(Currently) up to cubic IFCs</li><li>Beyond LDA (hybrid functional, etc.) calculation is not supported in available softwares</li></ul> | <ul style="list-style-type: none"><li>Need a supercell to calculate phonons at <math>q \neq 0</math></li></ul>  |
| Software | <ul style="list-style-type: none"><li>Quantum ESPRESSO</li><li>Abinit</li><li>VASP (only <math>q=0</math>)</li></ul>   | <ul style="list-style-type: none"><li>Phonopy</li><li>PHONON</li><li><b>ALAMODE</b></li><li>...</li></ul>   |

- [1] P. Giannozzi *et al.*, PRB **43**, 7231 (1991). [2] X. Gonze, PRB **55**, 10337 (1997).  
[3] K. Parlinski, Z. Q. Li, and Y. Kawazoe, PRL **78**, 4063 (1997).

# Direct method (finite difference)

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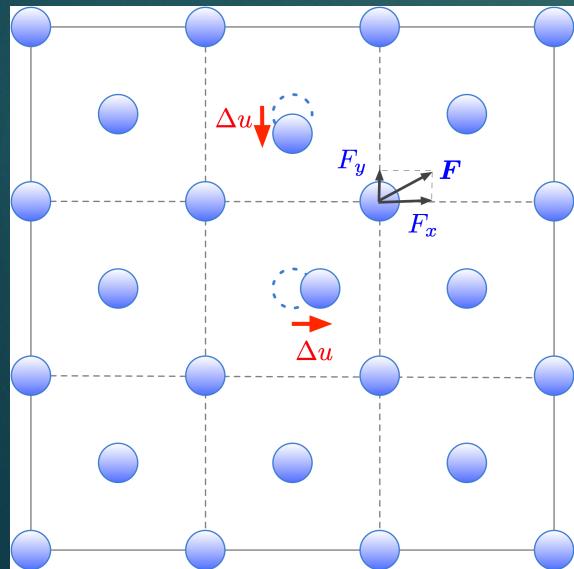


Harmonic IFCs

$$u_1 \equiv u_{\mu_1}(\ell_1 \kappa_1)$$

$$\Phi_{\mu_1 \mu_2}(\ell_1 \kappa_1; \ell_2 \kappa_2) = \Phi(1; 2)$$

$$= \frac{\partial^2 U}{\partial u_1 \partial u_2} = -\frac{\partial F_2}{\partial u_1} \approx -\frac{F_2(u_1 = +\Delta u) - F_2(u_1 = -\Delta u)}{2\Delta u}$$



Cubic IFCs

$$\Phi(1; 2; 3) = \frac{\partial^3 U}{\partial u_1 \partial u_2 \partial u_3} = -\frac{\partial F_3}{\partial u_1 \partial u_2}$$

$$\approx -\frac{1}{4(\Delta u)^2} [F_3(u_1 = u_2 = \Delta u) + F_3(u_1 = u_2 = -\Delta u) - F_3(u_1 = \Delta u, u_2 = -\Delta u) - F_3(u_1 = -\Delta u, u_2 = \Delta u)]$$

# Direct method (linear regression)

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Taylor expansion (Anharmonic lattice model: ALM)

$$U_{\text{ALM}} - U_0 = U_2 + U_3 + U_4 + \dots$$

$$\begin{aligned} &= \frac{1}{2} \sum_{1,2} \Phi(1;2) u_1 u_2 + \frac{1}{3!} \sum_{1,2,3} \Phi(1;2;3) u_1 u_2 u_3 + \frac{1}{4!} \sum_{1,2,3,4} \Phi(1;2;3;4) u_1 u_2 u_3 u_4 + \dots \\ &= \Phi \cdot \mathbf{b} \end{aligned}$$

$$\Phi = [\Phi_1, \Phi_2, \dots, \Phi_N]^T \quad N: \text{The number of independent IFCs}$$

Forces in ALM

$$\mathbf{F}_{\text{ALM}} = -\frac{\partial U_{\text{ALM}}}{\partial \mathbf{u}} = -\frac{\partial \mathbf{b}^T}{\partial \mathbf{u}} \Phi = A \Phi \quad A = \begin{bmatrix} -u_1^x & -\frac{1}{2} u_1^x u_2^x & -\frac{1}{3!} u_1^x u_2^x u_3^x & \dots \\ \vdots & \vdots & \vdots & \vdots \\ -u_{N_s}^z & -\frac{1}{2} u_{N_s}^z u_{N_s-1}^z & -\frac{1}{3!} u_{N_s}^z u_{N_s-1}^z u_{N_s-2}^z & \dots \end{bmatrix}$$

$N_s$  : The number of atoms in the supercell

# Direct method (linear regression)

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Ordinary least-squares (OLS)  $\Phi_{\text{OLS}} = \arg \min_{\Phi} \frac{1}{2N_d} \|\mathbb{A}\Phi - \mathcal{F}_{\text{DFT}}\|_2^2$

$\mathbb{A} \in \mathbb{R}^{M \times N}$  :Sensing matrix  $\mathbb{A}^T = [A^T(\mathbf{u}_1), \dots, A^T(\mathbf{u}_{N_d})]$   
where  $M = 3N_s \times N_d$

$\mathcal{F}$  :Vector comprising  $M$  force components

To determine all components of  $\Phi_{\text{OLS}}$  uniquely,  $\mathbb{A}^T \mathbb{A}$  must be a full-rank matrix.

Necessary displacement patterns can be generated systematically based on symmetry arguments or molecular dynamics simulations (TT, JPCM **26**, 225402 (2014)).

# Symmetry relationships between IFCs

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Permutation

$$\Phi_{\mu_1\mu_2\mu_3}(\ell_1\kappa_1; \ell_2\kappa_2; \ell_3\kappa_3) = \Phi_{\mu_1\mu_3\mu_2}(\ell_1\kappa_1; \ell_3\kappa_3; \ell_2\kappa_2) = \dots$$

Periodicity

$$\Phi_{\mu_1\mu_2\dots\mu_n}(\ell_1\kappa_1; \ell_2\kappa_2; \dots; \ell_n\kappa_n) = \Phi_{\mu_1\mu_2\dots\mu_n}(0\kappa_1; \ell_2 - \ell_1\kappa_2; \dots; \ell_n - \ell_1\kappa_n).$$

Space group symmetry

$$\sum_{\nu_1, \dots, \nu_n} \Phi_{\nu_1\dots\nu_n}(L_1K_1; \dots; L_nK_n) O_{\nu_1\mu_1} \cdots O_{\nu_n\mu_n} = \Phi_{\mu_1\dots\mu_n}(\ell_1\kappa_1; \dots; \ell_n\kappa_n),$$

These symmetry relationships are fully utilized in ALM to reduce the number of independent IFCs.

Translational invariance (a.k.a acoustic sum rule: ASR)

$$\sum_{\ell_1 \kappa_1} \Phi_{\mu_1 \mu_2 \dots \mu_n}(\ell_1 \kappa_1; \ell_2 \kappa_2; \dots; \ell_n \kappa_n) = 0$$

The ASR must be satisfied accurately. If the deviation from the ASR is large, the resulting phonon dispersion curves and/or lattice thermal conductivity values are unreliable.

OLS with equality constraint

$$\Phi_{\text{OLS}} = \arg \min_{\Phi} \frac{1}{2N_d} \|\mathbb{A}\Phi - \mathcal{F}_{\text{DFT}}\|_2^2 \quad \text{subject to} \quad C\Phi = 0$$

The matrix  $\mathbb{A}$  can be large when higher-order and long-distance anharmonic terms are included in ALM. We need a lot of RAM to solve the OLS problem directly.

Necessary environment:

RAM: > 4 GB

CPU: Single core is sufficient, but multicore is preferable.

Detailed installation method is described in

<https://alamode.readthedocs.io/en/latest/install.html>

**Today**, we will use the compiled binaries on TSUBAME.

```
> echo "[ -f /gs/hs0/tgz-hpci-apps/.bash_alamode_setup ] && . /gs/hs0/tgz-hpci-  
apps/.bash_alamode_setup" >> ~/.bashrc  
> . ~/.bashrc
```

# Copy hands-on files

Please copy the input files for the hands-on session from  
`/gs/hs0/tgz-hpc1-apps/`

```
> cd  
> cd t3workspace  
> cp -r $WORK/alamode_handson2022.tar.bz2 .  
> tar -xvf alamode_handson2022.tar.bz2  
> cd alamode_handson2022
```

If you don't have an access to TSUBAME3.0, the same files can be downloaded from  
[https://github.com/ttadano/alamode\\_tutorial](https://github.com/ttadano/alamode_tutorial)

```
> cd somewhere_to_place_files  
> git clone https://github.com/ttadano/alamode_tutorial.git  
> cd alamode_tutorial/hands-on_TSUBAME2022
```

```
> tree -L 2  
.|- 1_force_constant_silicon  
|   |- data  
|   |- hands-on_1.ipynb  
|   |- ref  
|   |- work  
|- 2_force_constant_graphene  
|   |- Extra_hands-on_1.ipynb  
|   |- data  
|   |- hands-on_2.ipynb  
|   |- ref  
|   |- work  
|- 3_thermal_conductivity_silicon  
|   |- hands-on_3.ipynb  
|   |- ref  
|   |- work  
|- 4_thermal_conductivity_graphene  
|   |- hands-on_4.ipynb  
|   |- ref  
|   |- work  
|- 5_self_consistent_phonon_ST0  
|   |- data  
|   |- hands-on_5.ipynb  
|   |- ref  
|   |- work  
|- 6_thermal_conductivity_ST0  
|   |- data  
|   |- hands-on_6.ipynb  
|   |- ref  
|   |- work
```

## Topics

- ▶ Calculation of harmonic/anharmonic IFCs of bulk silicon

## Details

- ▶ Use VASP for explanation
- ▶  $a = 5.403 \text{ \AA}$
- ▶ PBEsol xc functional

```
> cd 1_force_constant_silicon/work/  
> ls  
primitive.POSCAR.vasp
```

# 1.1 Create a supercell

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Currently (ver. 1.4.0), creation of a supercell structure is not supported by ALAMODE. So please create the structure by using any of the following approaches:

1. Use VESTA
2. Use `pymatgen.Structure.make_supercell` method
3. Write a simple script by yourself

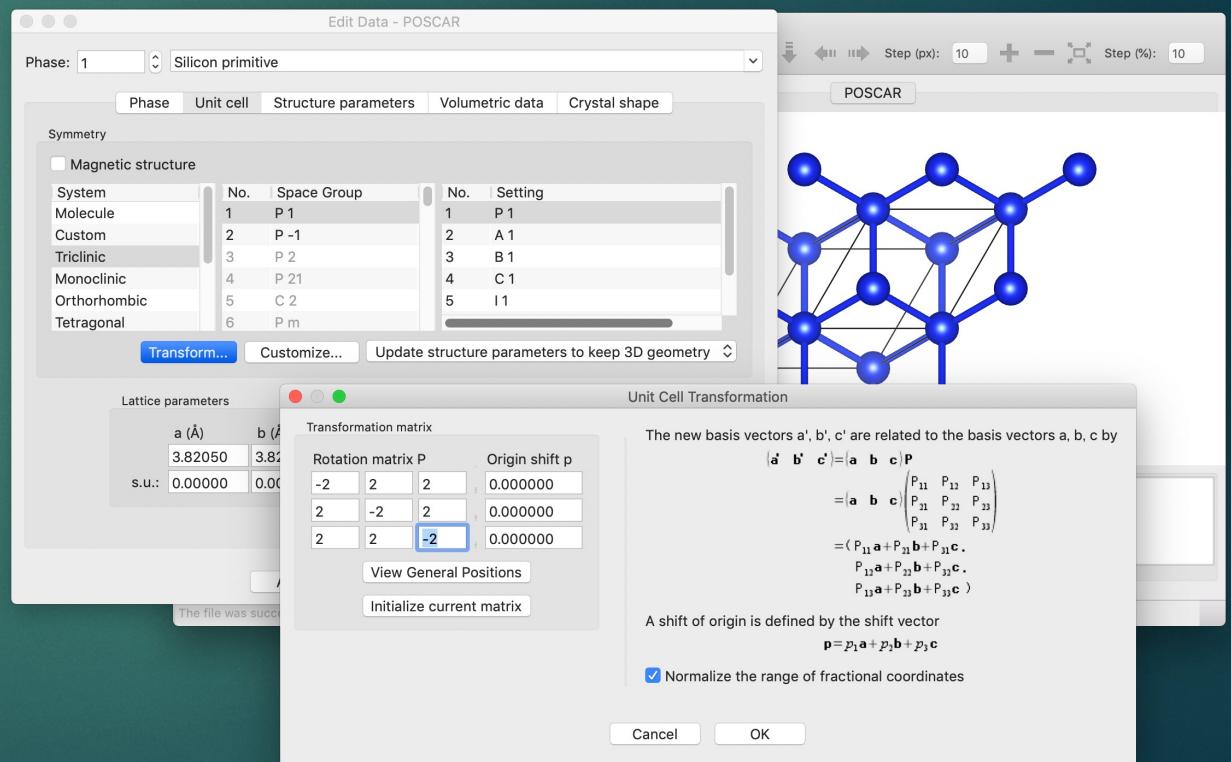
In VESTA:

Edit → Edit data → Unit cell → Transform

Rotation matrix P:

|    |    |    |
|----|----|----|
| -2 | 2  | 2  |
| 2  | -2 | 2  |
| 2  | 2  | -2 |

File → Export Data → File type VASP  
→ Save as “si222.POSCAR”



# 1.1 Create a supercell (pymatgen)

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```
from pymatgen.core import Structure

scaling_matrix = [[-2, 2, 2],
                  [ 2,-2, 2],
                  [ 2, 2,-2]]

# Make POSCAR of supercell
Structure.from_file('primitive.POSCAR.vasp')
Structure.make_supercell(structure, scaling_matrix)
```

```
> cp ./ref/makedisp_vasp.py .
> python makedisp_vasp.py
> less SPOSCAR
Si64
1.000
 10.80600000000000  0.00000000000000  0.00000000000000
  0.00000000000000 10.80600000000000  0.00000000000000
  0.00000000000000  0.00000000000000 10.80600000000000

Si
64
Direct
...
```

# 1.2 Create an ALM input and run ALM

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File: ALM0.in

```
&general
  PREFIX = si222
  MODE = suggest
  NAT = 64; NKD = 1
  KD = Si
/
# Define the Taylor
# expansion potential

&interaction
  NORDER = 1 # harmonic
/
&cutoff
  Si-Si None
/
```

```
# Supercell structure
&cell
  1.88972612545783
  10.806  0.000  0.000
  0.000  10.806  0.000
  0.000  0.000  10.806
/
# Fractional coordinates
# of 64 atoms, which must
# be exactly the same as
# si222.POSCAR.vasp
&position
  1  0.5000  0.0000  0.0000
  1  0.7500  0.2500  0.0000
  ...
  1  0.1250  0.8750  0.8750
/
```

terminal

```
> alm ALM0.in > ALM0.log
> grep "Space group" ALM0.log
Space group: Fd-3m (227)
> grep "Number of disp. patterns" ALM0.log
Number of disp. patterns for HARMONIC : 1
```

Tips:

- ▶ Space group symmetry is very important. Please check if the detected symmetry is correct.
- ▶ Recommended to use 15 decimal digits for the &cell and &position field. (e.g.  $\sqrt{3}/2$  should be 0.86602540378443, not 0.866025.)

# 1.3 Generate displaced structures

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```
> python -m displace --VASP SPOSCAR --mag 0.01 --prefix harm -pf si222.pattern_HARMONIC

> less harm1.POSCAR
  Disp. Num. 1 ( 0.010000 Angstrom, 1 : +x)
1.0
  10.805999755900000    0.000000000000000    0.000000000000000
  0.000000000000000    10.805999755900000    0.000000000000000
  0.000000000000000    0.000000000000000    10.805999755900000
Si
64
Direct
  0.500925411808255    0.000000000000000    0.000000000000000
  0.750000000000000    0.250000000000000    0.000000000000000
  0.750000000000000    0.000000000000000    0.250000000000000
...
```

## Tips:

- ▶ Set the magnitude of displacements small enough to exclude anharmonic effects in the calculated atomic forces. Typical value of `--mag` is 0.01–0.04.

# 1.4 Anharmonic force constants

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File: ALM0.in

```
# Up to cubic IFCs
&interaction
  NORDER = 2
/
&cutoff
  Si-Si  None 7.3
/
```

```
# Up to quartic IFCs
&interaction
  NORDER = 3
  NBODY = 2 3 3
/
&cutoff
  Si-Si  None 7.3 7.3
/
```

```
← (Edit ALM0.in and run ALM again)
> python -m displace --VASP SPOSCAR --mag 0.04 --prefix cubic -pf
  si222.pattern_ANHARM3
> python -m displace --VASP SPOSCAR --mag 0.08 --prefix quartic -pf
  si222.pattern_ANHARM4
```

- ▶ A triplet cluster  $(i, j, k)$  is included in the model when all of the pair distances are smaller than the cutoff radius.

$$r_{ij}, r_{jk}, r_{ki} \leq r_c$$

The same rule applies to fourth- and higher-order

- ▶ NBODY-tag is useful to reduce the number of anharmonic (>3) IFCs.

<https://alamode.readthedocs.io/en/latest/almdir/inputalm.html>  
#alm-nbody

# 1.5 Calculate forces with a DFT/FF code

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File: run\_vasp.sh

```
#!/bin/bash

# harmonic
cp harm1.POSCAR POSCAR
exec vasp
mv OUTCAR harm1.OUTCAR
mv vasprun.xml vasprun_harm1.xml

# cubic
for ((i=1;i<=16;i++))
do
num=`echo $i | awk '{printf("%02d",$1)}'`
cp cubic${num}.POSCAR POSCAR
exec vasp
mv OUTCAR cubic${num}.OUTCAR
mv vasprun.xml vasprun_cubic${num}.xml
done
```

## Tips:

- ▶ Calculation of forces for the displaced configurations is one of the most expensive part of the procedure
- ▶ This part can be run in parallel

# 1.6 Parse displacement-force datasets

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```
> python -m extract --VASP SPOSCAR ../data/vasprun_harmonic1.xml > DFSET_harmonic
> python -m extract --VASP SPOSCAR ../data/vasprun_cubic*.xml > DFSET_cubic

> less DFSET_harmonic
# Filename: vasprun_cubic01.xml, Snapshot: 1, E_pot (eV): -381.42981293
  0.0755891      0.0000000      0.0000000      -2.08143550E-02 -0.00000000E+00  0.00000000E+00
  0.0000000      0.0000000      0.0000000      3.04690602E-04  2.97841791E-04  1.51655908E-04
  0.0000000      0.0000000      0.0000000      3.04690602E-04  1.51655908E-04  2.97841791E-04
...
```



$u_x$



$u_y$



$u_z$



$F_x$



$F_y$



$F_z$

Displacements in units of Bohr

Forces in units of Ryd/Bohr

# 1.7 Extract force constants

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```
> cp ALM0.in ALM1.in
  (Edit ALM1.in →)
> alm ALM1.in > ALM1.log
> grep "Fitting error" ALM1.log
Fitting error (%) : 0.569031

> cp ALM0.in ALM2.in
> (Edit ALM2.in →)
> alm ALM2.in > ALM2.log
Fitting error (%) : 0.12064

> ls si222_cubic.*
si222_cubic.fcs si222_cubic.xml
```

File: ALM1.in

```
&general
  PREFIX = si222
  MODE = opt
  NAT = 64; NKD = 1
  KD = Si
/
&interaction
  NORDER = 1
/
&optimize
  DFSET = DFSET_harmonic
/
```

File: ALM2.in

```
&general
  PREFIX = si222_cubic
  MODE = opt
  NAT = 64; NKD = 1
  KD = Si
/
&interaction
  NORDER = 2
/
&optimize
  DFSET = DFSET_cubic
  FC2XML = si222.xml
/
```

Tips:

- ▶ Numerical noises in forces, residual forces (linear term of Taylor expansion), and anharmonicity result in a large fitting error.

## Topics

- ▶ Calculation of harmonic/anharmonic IFCs of **graphene**

## Details

- ▶ Use VASP for explanation
- ▶ LDA xc functional
- ▶ 5x5x1 supercell

```
> cd 2_force_constant_graphene/work/
> less primitive.POSCAR.vasp
P6/mmm (191) C128
1.000
      2.44650000000000  0.00000000000000  0.00000000000000
     -1.22325000000000  2.11873115035863  0.00000000000000
      0.00000000000000  0.00000000000000  15.00000000000000

C
2
Direct
      0.66666666666667  0.33333333333333  0.00000000000000
      0.33333333333333  0.66666666666667  0.00000000000000
```

## 2.1 Fitting harmonic terms

```
> python makedisp_vasp.py
> cp ALM0.in ALM1.in
(edit ALM1.in)
> python -m extract --VASP SPOSCAR ../data/vasprun_harmonic?.xml > DFSET_harmonic
> alm ALM1.in > ALM1.log
> grep "Fitting error" ALM1.log
Fitting error (%) : 1.74943

> python -m extract --VASP SPOSCAR ../data/vasprun_random??.xml > DFSET_random
```

## 2.2 Anharmonic terms

30

File: ALM0.in

```
# Up to quartic IFCs
&interaction
  NORDER = 3
  NBODY = 2 3 3
/
&cutoff
  ** None 8.1 8.1
/
```

```
(edit ALM0.in; see left)
> alm ALM0.in > ALM0.log
> grep "Number of disp" ALM0.log
  Number of disp. patterns for HARMONIC : 4
  Number of disp. patterns for ANHARM3 : 119
  Number of disp. patterns for ANHARM4 : 1132
```

The number of displacement patterns is **119** for computing the **third-order** terms and  $119+1132=1251$  for computing up to the **fourth-order** terms. **This is expensive!**

A more efficient approach

- ▶ Use **compressive sensing** approach
- ▶ Displace **all atoms** in the supercell (randomly)

## 2.3 Compressive sensing

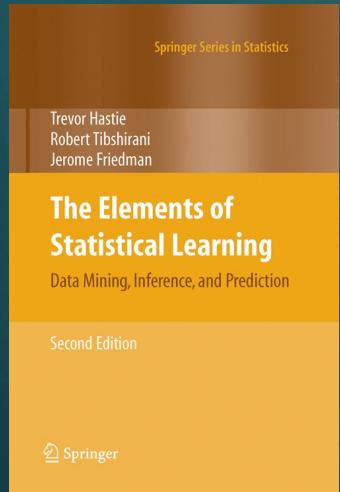
31

$$\text{Elastic-net } \Phi_{\text{enet}} = \underset{\Phi}{\operatorname{argmin}} \frac{1}{2N_d} \|\mathbb{A}\Phi - \mathcal{F}_{\text{DFT}}\|_2^2 + \alpha\beta\|\Phi\|_1 + \frac{1}{2}\alpha(1-\beta)\|\Phi\|_2^2$$

$\beta = 1$  : LASSO

$\beta = 0$  : Ridge regression

$\alpha$  is a hyperparameter that controls the trade-off between the sparsity and accuracy of the model. An optimal value of  $\alpha$  can be estimated by cross validation (CV).



See statistical learning textbooks for more details of CV and enet.

<https://web.stanford.edu/~hastie/ElemStatLearn/>

## 2.4 Cross-validation

32

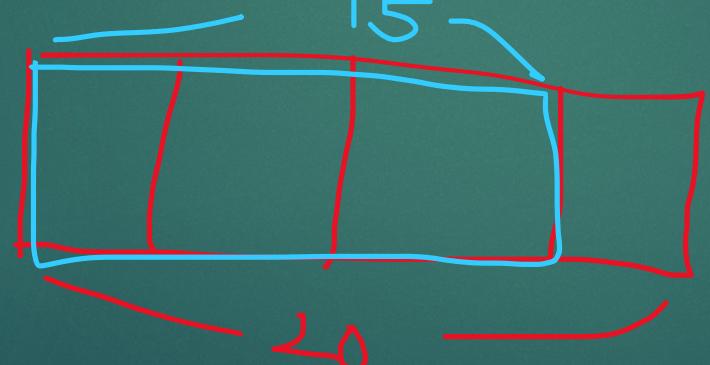
File: CV.in

```
&general
PREFIX = graphene_anharm
MODE = optimize
NAT = 50; NKD = 1
KD = C
/
&interaction
NORDER = 3
NBODY = 2 3 3
/
&cutoff
*-* None 8.1 8.1
/
```

```
&optimize
LMODEL = enet
NDATA = 20
DFSET = DFSET_random
FC2XML = super551.xml
```

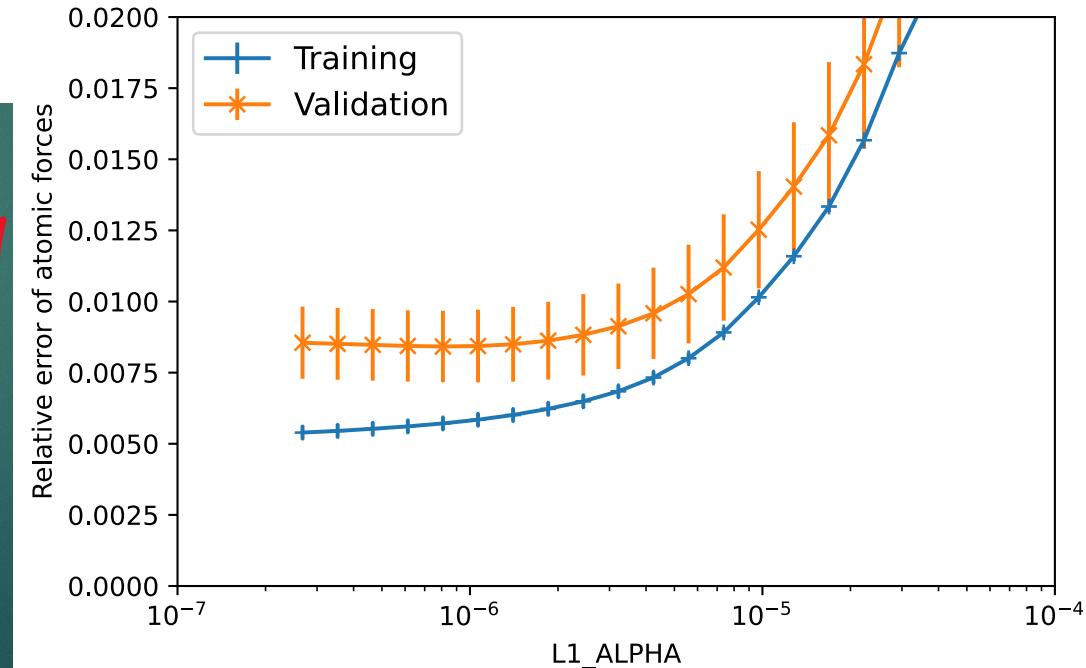
CV = 4

```
L1_RATIO = 1.0 #LASSO
CONV_TOL = 1.0e-8
/
```



- Anharmonic terms up to **fourth-order**
- 20 training datasets and **4-fold CV**

```
> cp ALM0.in CV.in
(edit CV.in)
> alm CV.in > CV.log &
(This takes 1-2 mins.)
(plot graphene_anharm.csvscore using a
plotting software)
```



## 2.5 Enet optimization

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File: opt.in

```
&general
PREFIX = graphene_anharmonic
MODE = optimize
NAT = 100; NKD = 1
KD = C
/
...
&optimize
LMODEL = enet
NDATA = 20
DFSET = ../data/DFSET_random
FC2XML = super551.xml

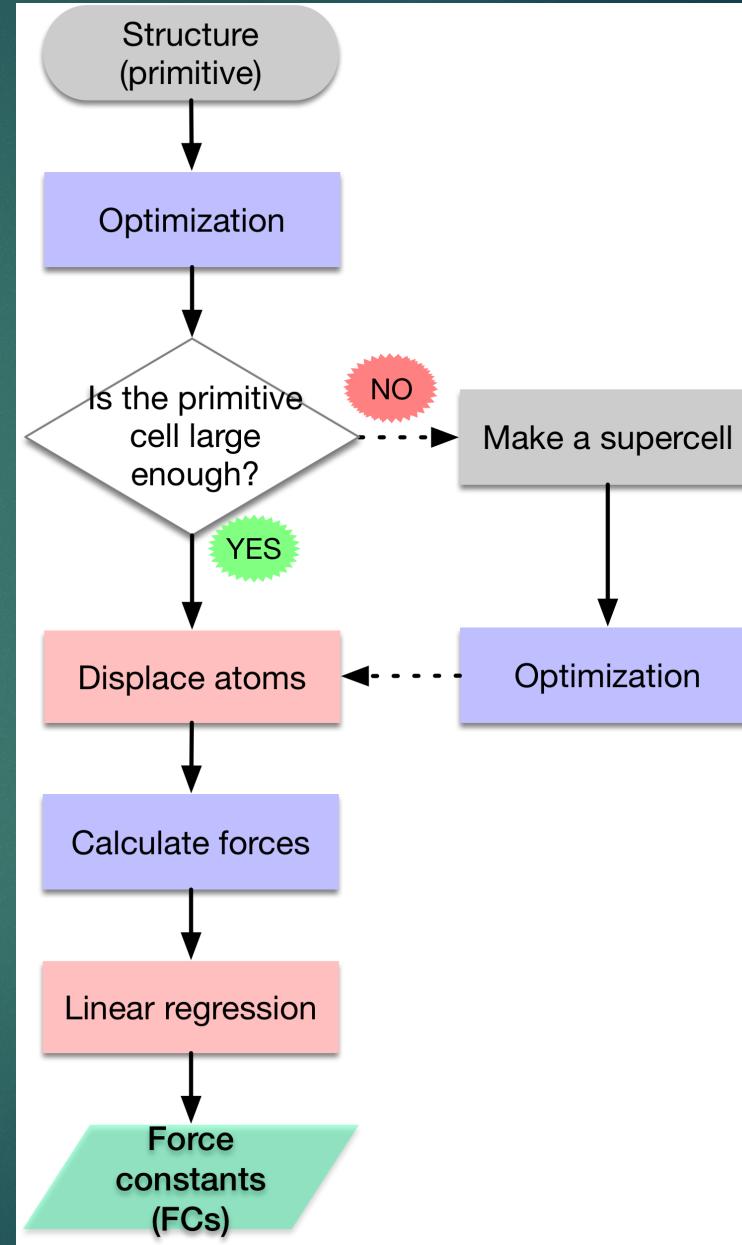
CV = 0 # switch off CV
L1_RATIO = 1.0 #LASSO
L1_ALPHA = 3.81092e-06

CONV_TOL = 1.0e-8
/
```

```
> cp CV.in opt.in
← (Edit opt.in)
> alm opt.in > opt.log
> less opt.log
```

# Summary of ALM

- ▶ Extraction of harmonic/cubic force constants of silicon by least-squares fitting.
- ▶ Extraction of anharmonic force constants of graphene by compressive sensing
- ▶ We use VASP as a DFT engine today. It can be replaced with other DFT codes and LAMMPS.
- ▶ The most expensive part is the calculation of atomic forces by DFT. Run this part in parallel in computer clusters or supercomputers.



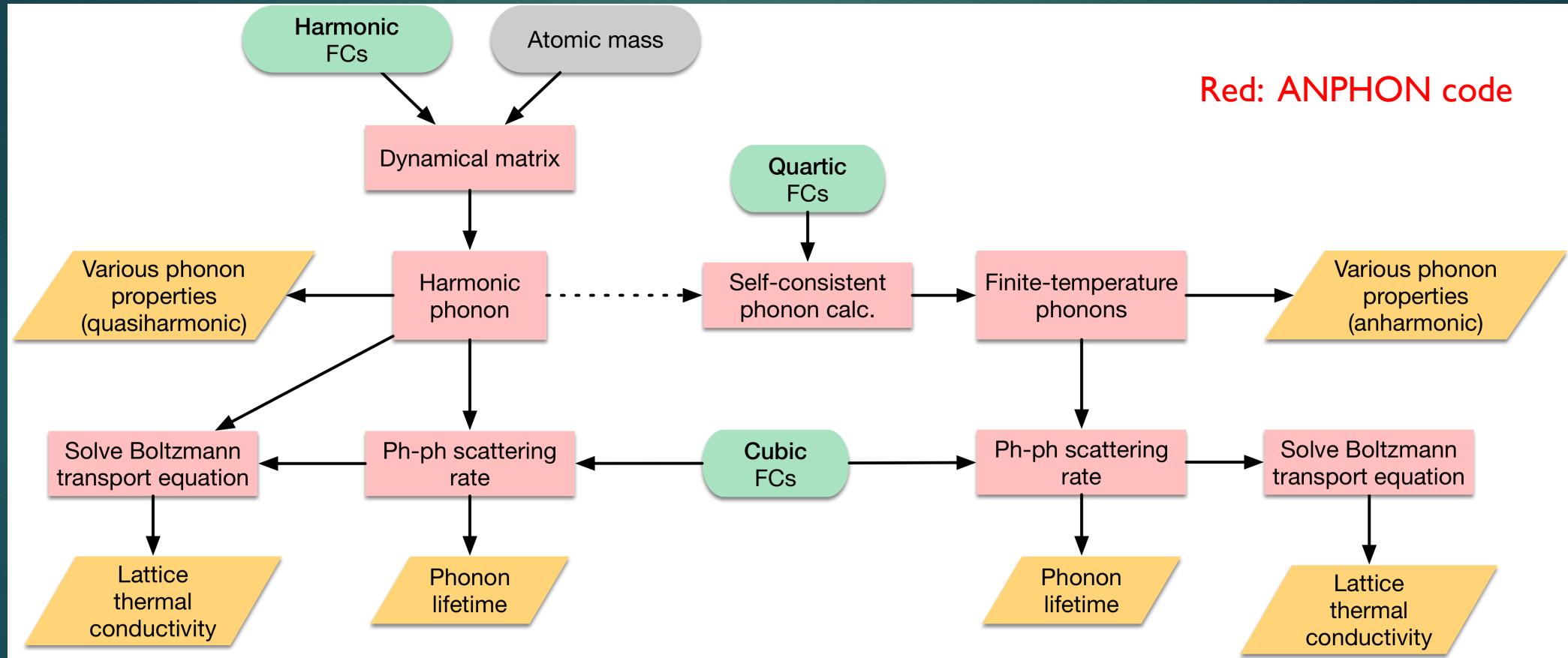
Using python wrapper of ALM.

Open **2\_force\_constant\_graphene/Extra\_hands-on\_1.ipynb** from jupyterlab

# Overview of ANPHON code

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**ANPHON:** Phonon property calculator, MPI+OpenMP



Exact dynamical matrix in an infinite-size crystal

$$\bar{D}_{\mu\nu}(\kappa\kappa'; \mathbf{q}) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \sum_L^\infty \bar{\Phi}_{\mu\nu}(0\kappa; L\kappa') e^{i\mathbf{q}\cdot\mathbf{r}(L)} = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \sum_{\ell'} \sum_{L_s}^\infty \bar{\Phi}_{\mu\nu}(0\kappa; L_s + \ell'\kappa') e^{i\mathbf{q}\cdot(\mathbf{r}(L_s) + \mathbf{r}(\ell'))}$$

Dynamical matrix constructed from IFCs inside a supercell

$$D_{\mu\nu}(\kappa\kappa'; \mathbf{q}) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \sum_{\ell'} \Phi_{\mu\nu}(0\kappa; \ell'\kappa') e^{i\mathbf{q}\cdot\mathbf{r}(\ell')} = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \sum_{\ell'} \left[ \sum_{L_s}^\infty \bar{\Phi}_{\mu\nu}(0\kappa; L_s + \ell'\kappa') \right] e^{i\mathbf{q}\cdot\mathbf{r}(\ell')}$$

The dynamical matrix becomes exact, i.e.  $D_{\mu\nu}(\kappa\kappa'; \mathbf{q}) = \bar{D}_{\mu\nu}(\kappa\kappa'; \mathbf{q})$ , when  $e^{i\mathbf{q}\cdot\mathbf{r}(L_s)} = 1$  is satisfied for all  $L_s$ . The momentum  $\mathbf{q}$  satisfying this condition is called **commensurate  $\mathbf{q}$  point**.

# Non-analytic (NA) correction

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In insulators (semiconductors), the ion-ion Coulomb interaction is long-range

$$D_{\mu\nu}^{\text{NA}}(\kappa\kappa'; \mathbf{q}) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \frac{4\pi e^2}{\Omega} \frac{(Z_\kappa^* \mathbf{q})_\mu (Z_{\kappa'}^* \mathbf{q})_\nu}{\mathbf{q} \cdot \epsilon^\infty \mathbf{q}},$$

Parlinski's approach (K. Parlinski, Z. Q. Li, and Y. Kawazoe, PRL **81**, 3298 (1998))

$$D(\mathbf{q}) + D^{\text{NA}}(\mathbf{q}) \exp(-q^2/\sigma^2),$$

Mixed-space approach (Y. Wang *et al.*, JPCM **22**, 202201 (2010))

$$D(\mathbf{q}) + D^{\text{NA}}(\mathbf{q}) \frac{1}{N} \sum_{\ell'} \exp [i\mathbf{q} \cdot (\mathbf{r}(\ell') - \mathbf{r}(\ell))]$$

Ewald summation method (X. Gonze and C. Lee, PRB **55**, 66389 (1997))

$$\hat{H}_0 = \sum_{\mathbf{q}, j} \hbar \omega_{\mathbf{q}j} \left( b_{\mathbf{q}j}^\dagger b_{\mathbf{q}j} + \frac{1}{2} \right)$$

- ▶ Phonon is **non-interacting**  $\rightarrow$  **infinite** lifetime  $\rightarrow$  **infinite** thermal conductivity
- ▶ Phonon is **volume-independent**  $\rightarrow$  **no** thermal expansion
- ▶ Phonon is **temperature-independent**  $\rightarrow$  **no** (displacive) structural phase transition
- ▶ **Fails** to explain phonons of high-temperature phases

# Boltzmann transport theory (BTE)

- Semiclassical approach to simulate energy transport of quasi-particles. For phonon transport it is given as

$$-\mathbf{v}_q \cdot \nabla T \left( \frac{\partial \mathbf{n}_q}{\partial T} \right) = \sum_{q'} P_{q,q'} + \sum_{q',q''} P_{q,q',q''} + \dots$$

↓ Linearization

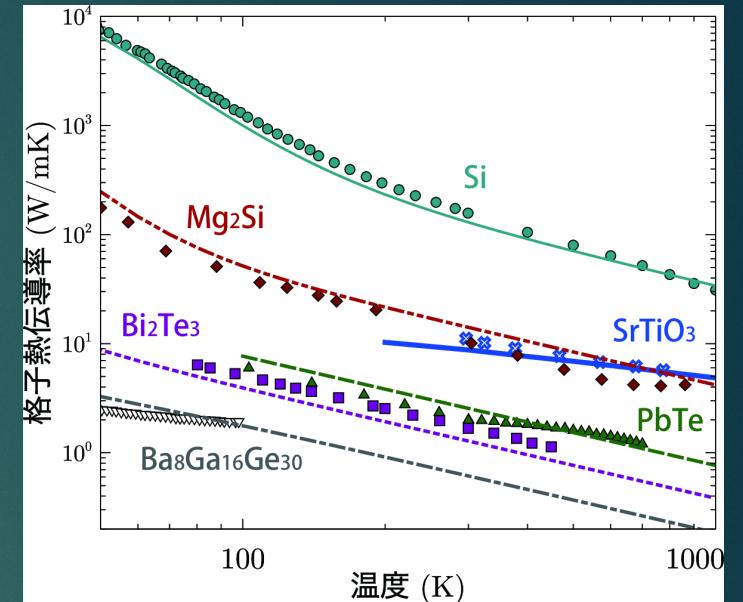
Once the phonon frequencies, group velocities, polarization vectors, and the scattering probabilities  $\Lambda$  are given, the above linearized-BTE can be solved **iteratively** or **directly**.

# Lattice thermal conductivity

- ▶ Fourier's law  $\mathbf{j} = -\kappa \nabla T$
- ▶ Phonon gas model  $\mathbf{j} \approx \mathbf{j}_{\text{QP}} = \frac{1}{NV} \sum_{\mathbf{q}j} \hbar \omega_{\mathbf{q}j} \mathbf{v}_{\mathbf{q}j} \mathbf{n}_{\mathbf{q}j}.$

Finally, we obtain the lattice thermal conductivity

$$\kappa = -\frac{\hbar}{NVk_{\text{B}}T} \sum_q \omega_q \mathbf{v}_q \otimes \mathbf{f}_q n_q (n_q + 1).$$



In ALAMODE, the single-mode relaxation-time approximation (RTA) is used:

$$\begin{aligned} \kappa_{\text{RTA}} &= \frac{\hbar^2}{NVk_{\text{B}}T^2} \sum_q \omega_q^2 \mathbf{v}_q \otimes \mathbf{v}_q n_q (n_q + 1) \tau_q \\ &= \frac{1}{NV} \sum_q c_q \mathbf{v}_q \otimes \mathbf{v}_q \tau_q \end{aligned}$$

# Perturbative treatment of anharmonicity

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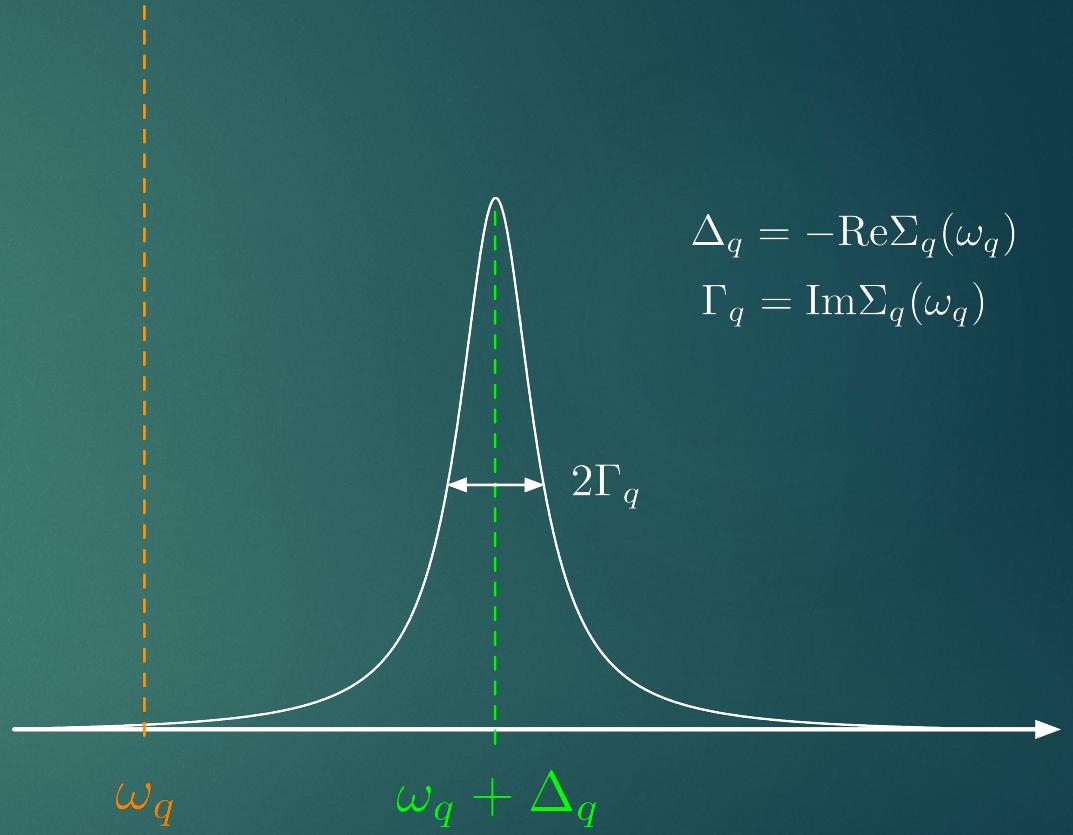
$$\hat{H} = \hat{H}_0 + \hat{U}_3 + \hat{U}_4 + \dots$$

$$[G_q(\omega)]^{-1} = [G_q^0(\omega)]^{-1} - \Sigma_q(\omega)$$

$$G_{\mathbf{q}jj'}^0(\omega) = \frac{2\omega_{\mathbf{q}j}}{\omega_{\mathbf{q}j}^2 - \omega^2} \delta_{jj'}$$

- ▶ Non-zero phonon linewidth  $\rightarrow$  finite lifetime
- ▶ Phonon frequency shift

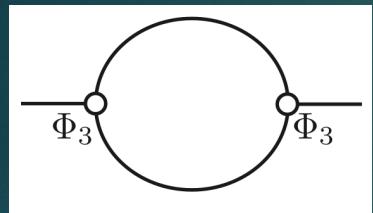
A systematic approximation of the phonon self-energy is necessary.



# Anharmonic phonon self-energy

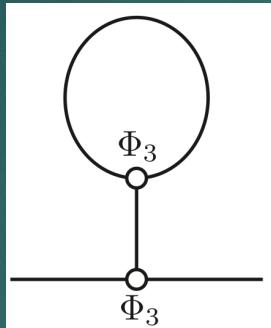
43

Self-energies up to the second order



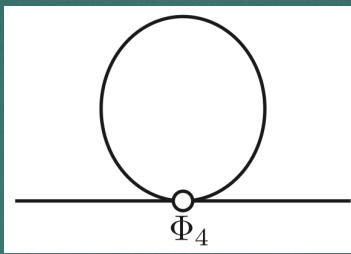
Bubble

Gives frequency shift and linewidth



Tadpole

Give frequency shift only



Loop

A. A. Maradudin and A. E. Fein, Phys. Rev **128**, 2589 (1962).

Tadpole self-energy is non-zero

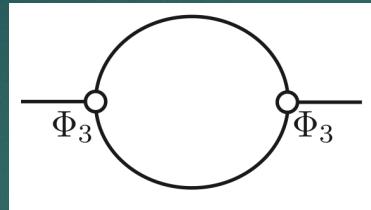
- ▶ only when the atomic coordinates can change without breaking the crystal symmetry

Loop self-energy is

- ▶ generally non-zero
- ▶ included in the self-consistent phonon theory (explained later)

# Bubble self-energy

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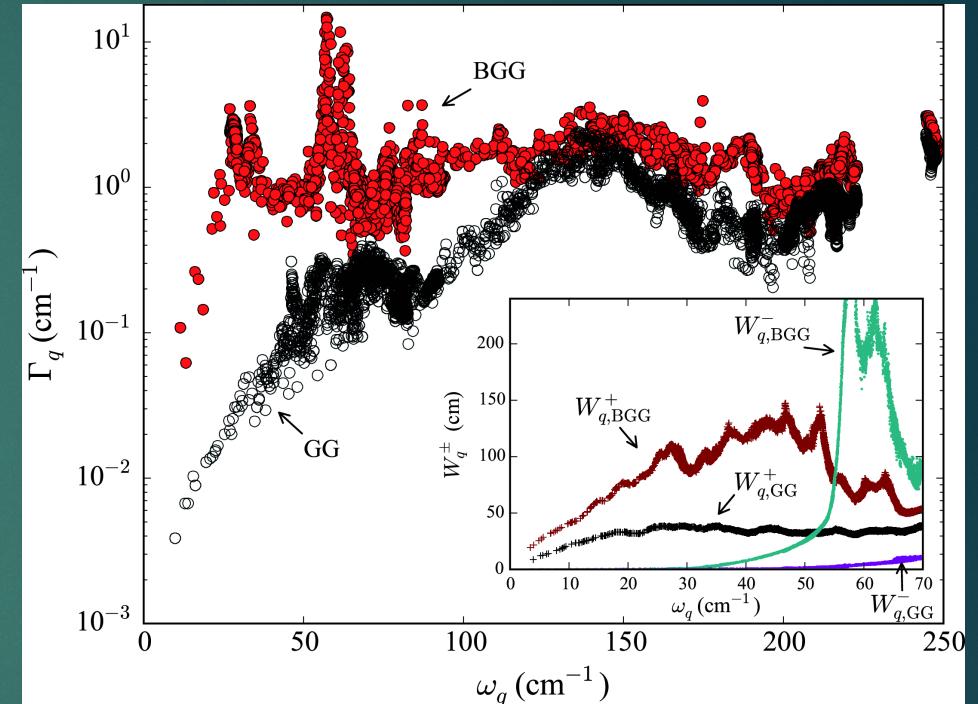


Bubble

$$\Gamma_q^{(B)} = \text{Im}\Sigma_q^{(B)}(\omega_q)$$

$$\begin{aligned} &= \frac{\pi}{2N} \sum_{q',q''} \frac{\hbar|\Phi_3(-q, q', q'')|^2}{8\omega_q\omega_{q'}\omega_{q''}} \times \Delta(-\mathbf{q} + \mathbf{q}' + \mathbf{q}'') \\ &\quad \times [(n_{q'} + n_{q''} + 1)\delta(\omega_q - \omega_{q'} - \omega_{q''}) \\ &\quad - 2(n_{q'} - n_{q''})\delta(\omega_q - \omega_{q'} + \omega_{q''})] \end{aligned}$$

$$\tau_q = \frac{\hbar}{2\Gamma_q}$$



- The bubble diagram gives the three-phonon scattering probability

# Parallelization performance

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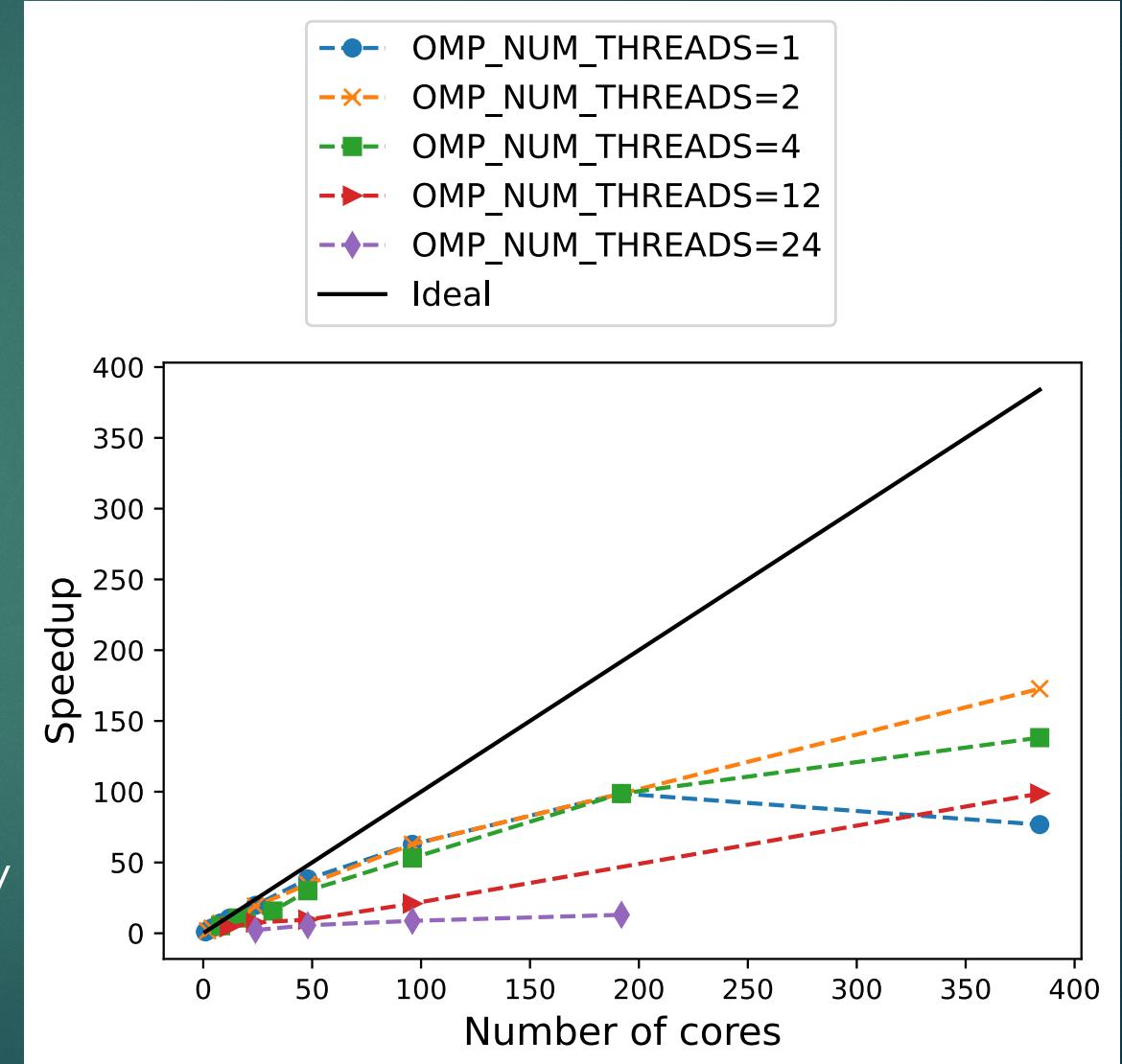
$$\Gamma_q^{(B)} = \frac{\pi}{2N} \sum_{q',q''} \frac{\hbar |\Phi_3(-q, q', q'')|^2}{8\omega_q \omega_{q'} \omega_{q''}} \times \Delta(-q + q' + q'')$$
$$\times [(n_{q'} + n_{q''} + 1)\delta(\omega_q - \omega_{q'} - \omega_{q''}) - 2(n_{q'} - n_{q''})\delta(\omega_q - \omega_{q'} + \omega_{q''})]$$

MPI

OpenMP  
(over double loop of  
band index)

## Benchmark:

- Si thermal conductivity
- $20^3$  qpoints
- NIMS simulator



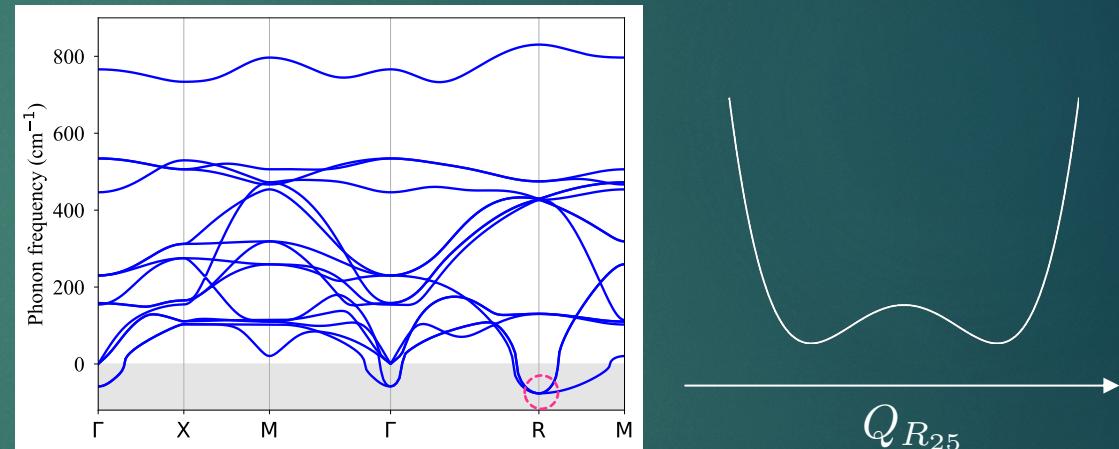
# Limitation of the perturbative treatment

46

- ▶ The perturbative approach becomes inaccurate when the anharmonicity is strong and even breaks down when the harmonic phonon is unstable ( $\omega_q^2 < 0$ )

When the phonon frequency is imaginary, we cannot define the non-interacting Hamiltonian:

$$\hat{H}_0 = \sum_{\mathbf{q}, j} \hbar \omega_{\mathbf{q} j} \left( b_{\mathbf{q} j}^\dagger b_{\mathbf{q} j} + \frac{1}{2} \right)$$



- ▶ A nonperturbative approach is desired.

# Self-consistent phonon (SCP) theory

N. R. Werthamer, Phys. Rev. B 1, 572 (1970)

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Let us assume an effective one-body Hamiltonian exists:  $\tilde{H}_0 = \sum_{\mathbf{q}, j} \hbar \Omega_{\mathbf{q}j} (a_{\mathbf{q}j}^\dagger a_{\mathbf{q}j} + \frac{1}{2})$

Introduce an operator  $\rho$  defined as  $\rho = \frac{e^{-\beta \tilde{H}_0}}{\text{Tr} e^{-\beta \tilde{H}_0}}$

Then, the following **Gibbs inequality** holds:  $F[\rho] = \tilde{F}_0 + \langle H - \tilde{H}_0 \rangle_0 \geq F$

$F$ : exact anharmonic free-energy

The self-consistent phonon (SCP) frequency is obtained via  $\frac{\delta F[\rho]}{\delta \rho} = 0$

- ▶ SCP theory is the “Hartree-Fock” theory for phonons (mean-field theory)

## ► Stochastic self-consistent harmonic approximation (SSCHA)

- Use conjugate gradient method to update  $\rho$  and  $F[\rho]$  by repeatedly calculating atomic forces in supercells.
- The gradient of  $F[\rho]$  is calculated stochastically.
- Full anharmonicity included

I. Errea et al., PRB **89**,  
064302 (2014).

## ► Self-consistent phonon approach based on force constants (SCP)

- Compute  $\delta F[\rho]/\delta \rho = 0$  analytically and derive the self-consistent equation by truncating the higher-order anharmonic terms.

$$\langle H - \tilde{H}_0 \rangle_0 = \langle H_0 - \tilde{H}_0 + U_3 + U_4 + \dots \rangle_0 \approx \langle H_0 - \tilde{H}_0 + U_4 \rangle_0$$

- Efficient calculation of  $\rho$  and  $F[\rho]$  at various temperature
- Higher-order terms (sixth, eighth, ...) are neglected.
- Implemented in ALAMODE

TT and S. Tsuneyuki,  
PRB 92, 054301 (2015).

# An intuitive view of SCP calculation

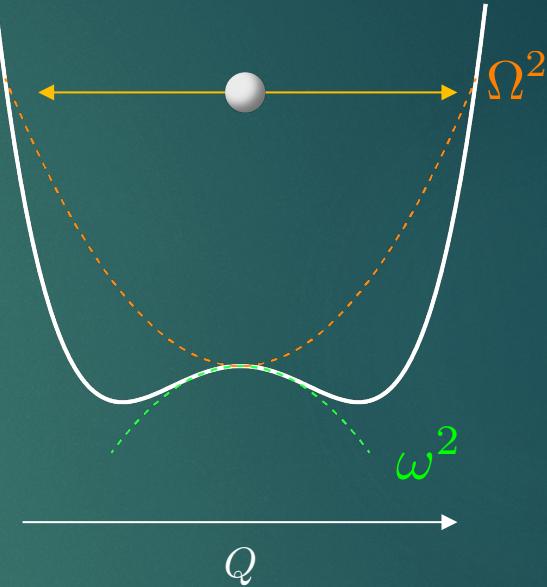
49

Effective 2<sup>nd</sup>-order IFC

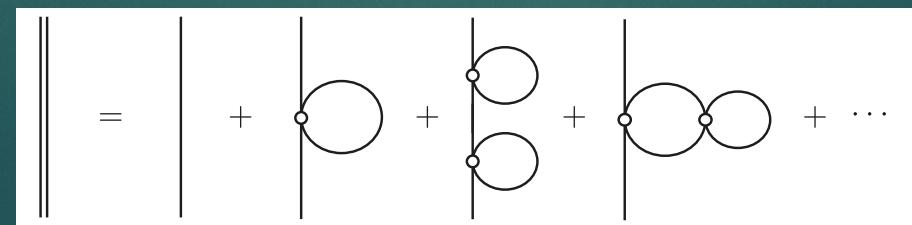
$$\tilde{\Phi}_{ij}(T) = \Phi_{ij} + \frac{1}{4} \sum_{kl} \Phi_{ijkl} \langle u_k u_l \rangle$$

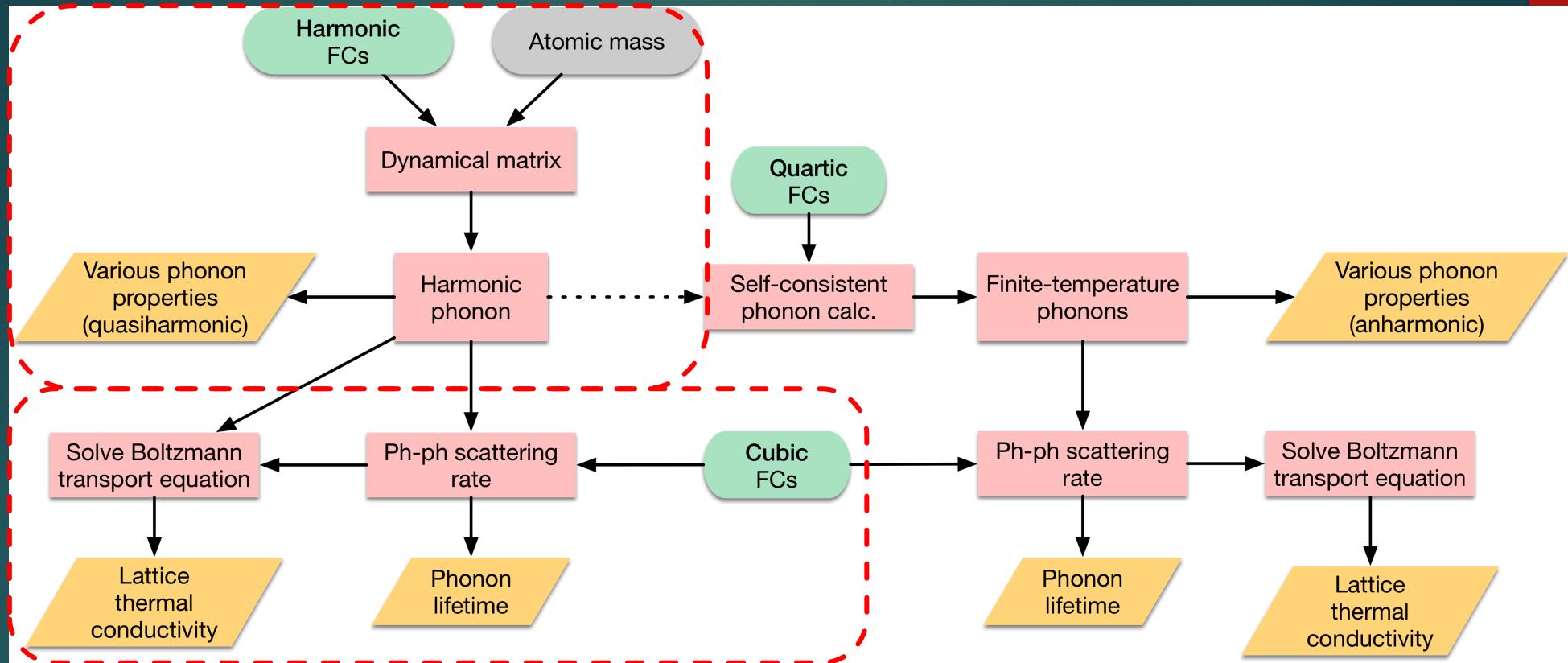
Bare 2<sup>nd</sup>-order IFC

MSD  
(T-dependent)



- ▶ Diagrammatically, the SCP propagator include an infinite set of Feynman diagrams that can be generated from the loop diagram:





## Topics

- ▶ Phonon calculation of bulk silicon (harmonic level)
- ▶ Lattice thermal conductivity calculation of bulk silicon
- ▶ Lattice thermal conductivity calculation of graphene

# 3.1 Calculate phonon dispersion curves

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File: phband.in

```
&general
PREFIX = Si
MODE = phonons
NKD = 1; KD = Si
FCSXML = si222_cubic.xml
/
&cell
10.21019
0.0 0.5 0.5
0.5 0.0 0.5
0.5 0.5 0.0
/
&kpoint
1
G 0.0 0.0 0.0 X 0.5 0.5 0.0 51
X 0.5 0.5 1.0 G 0.0 0.0 0.0 51
G 0.0 0.0 0.0 L 0.5 0.5 0.5 51
/
```

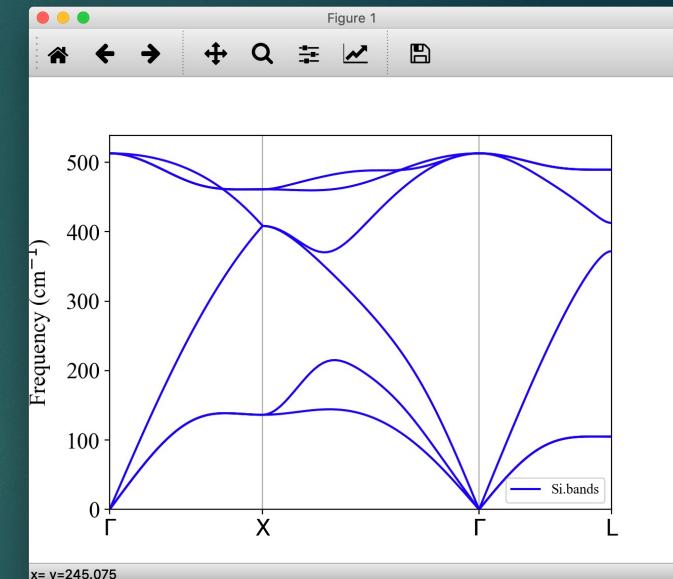
```
> cd ../../3_thermal_conductivity_silicon/work/
> cp ../../1_force_constant_silicon/work/si222_cubic.xml .
←(Create phband.in)
> anphon phband.in > phband.log
```

## Important

- ▶ Primitive lattice vectors must be given in the &cell field.

## Tips

- ▶ The k-point path is given in the fractional coordinate of the primitive reciprocal lattice vector
- ▶ Useful tool: Seek-path  
<https://www.materialscloud.org/work/tools/seekpath/>



### 3.2 Calculate phonon DOS

File: phdos.in

&general

```
PREFIX = Si # use "Si2" for ISMEAR=1
MODE = phonons; NKD = 1; KD = Si
FCSXML = si222_cubic.xml
EMIN = 0; EMAX = 550; DELTA_E = 1
# Tetrahedron
ISMEAR = -1
# Gaussian broadening
#ISMEAR = 1; EPSILON = 7.0
```

/

&cell

```
10.21019
0.0 0.5 0.5
0.5 0.0 0.5
0.5 0.5 0.0
```

/

&kpoint

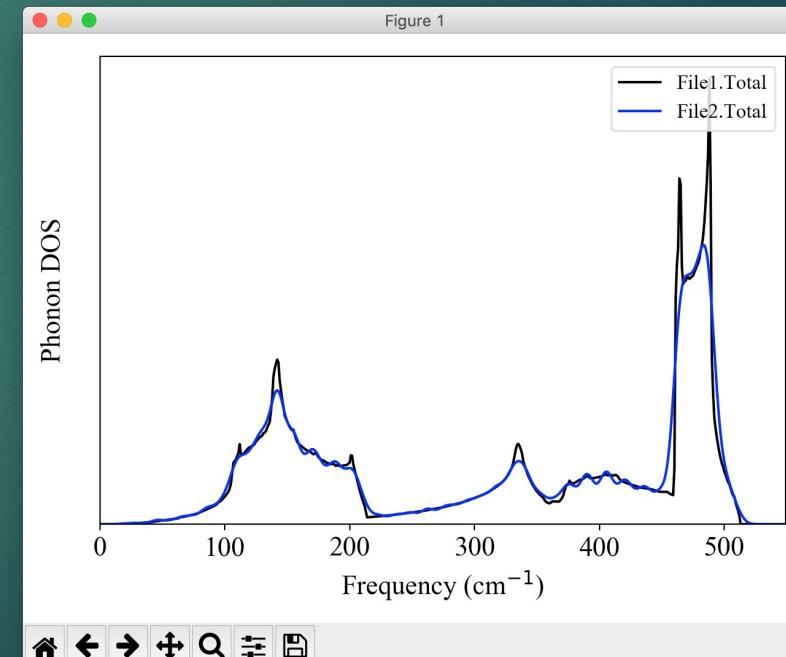
```
2
20 20 20
```

/

$$\text{DOS}(\omega) = \frac{1}{N_q} \sum_{\mathbf{q},j} \delta(\omega - \omega_{\mathbf{q}j}).$$

52

```
> cp phband.in phdos.in
(Edit phdos.in)
> anphon phdos.in > phdos.log
```

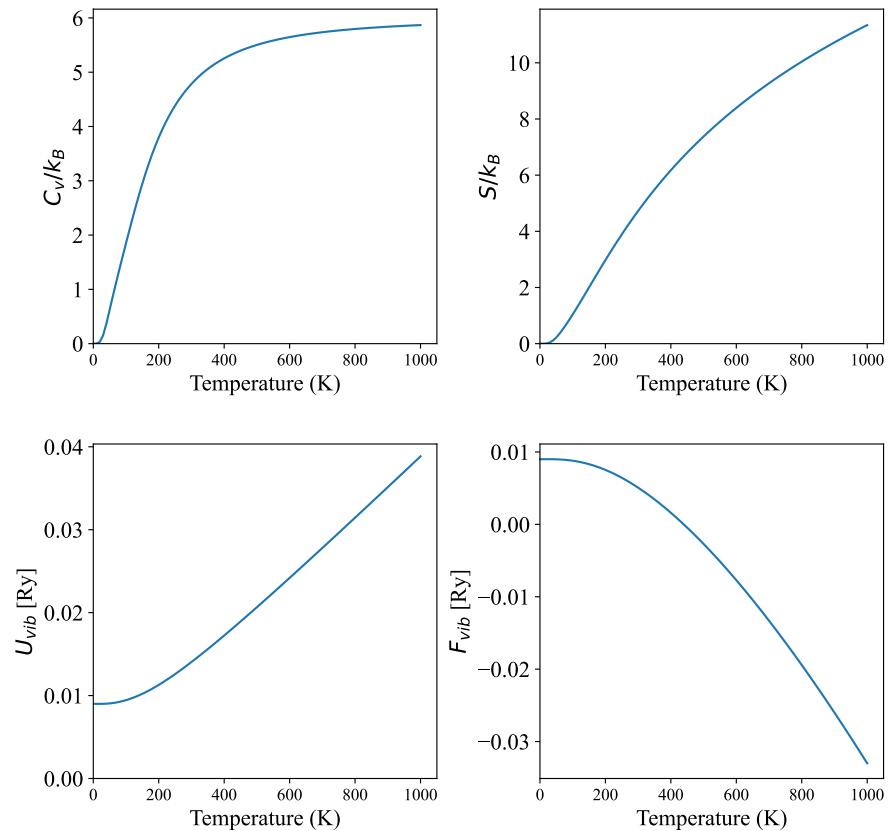


Tetrahedron (ISMEAR=-1) v.s. Gaussian broadening (ISMEAR=1)

### 3.3 Thermodynamics functions

```
> less Si.thermo
# Temperature [K], Heat capacity / kB, Entropy / kB, Internal energy [Ry], Free energy (QHA)
[Ry]
 0.000000 0.000000e+00 -0.000000e+00 9.000983e-03 9.000983e-03
 10.000000 2.505659e-03 6.437732e-04 9.001016e-03 9.000976e-03
 20.000000 3.315056e-02 8.601184e-03 9.001845e-03 9.000755e-03
 30.000000 1.547310e-01 4.127771e-02 9.007206e-03 8.999362e-03
 40.000000 3.696073e-01 1.136006e-01 9.023455e-03 8.994675e-03
 50.000000 6.243941e-01 2.231466e-01 9.054848e-03 8.984182e-03
...

```



### 3.4 Mean square displacements

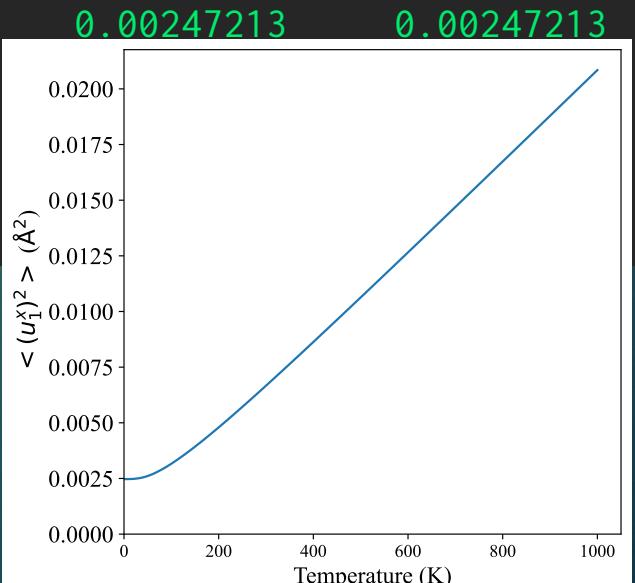
File: phdos.in

```
&analysis  
PRINTMSD = 1  
DOS = 0  
/
```

$$\langle u_\mu^2(\kappa) \rangle = \frac{\hbar}{M_\kappa N_q} \sum_{\mathbf{q}, j} \frac{1}{\omega_{\mathbf{q}j}} |e_\mu(\kappa; \mathbf{q}j)|^2 \left( n_{\mathbf{q}j} + \frac{1}{2} \right),$$

```
> (Add the &analysis option)  
> anphon phdos.in > phdos.log  
> less Si.msd  
# Mean Square Displacements at a function of temperature.  
# Temperature [K], <(u_{1}^{x})^{2}>, <(u_{1}^{y})^{2}>, <(u_{1}^{z})^{2}>, .... [Angstrom^2]
```

|     |            |            |            |            |
|-----|------------|------------|------------|------------|
| 0   | 0.00247213 | 0.00247213 | 0.00247213 | 0.00247213 |
| 10  | 0.00247304 | 0.00247304 | 0.00247304 | 0.00247304 |
| 20  | 0.00248178 | 0.00248178 | 0.00248178 | 0.00248178 |
| 30  | 0.0025045  | 0.0025045  | 0.0025045  | 0.0025045  |
| ... |            |            |            |            |



# 3.5 Lattice thermal conductivity (LTC)

File: kappa.in

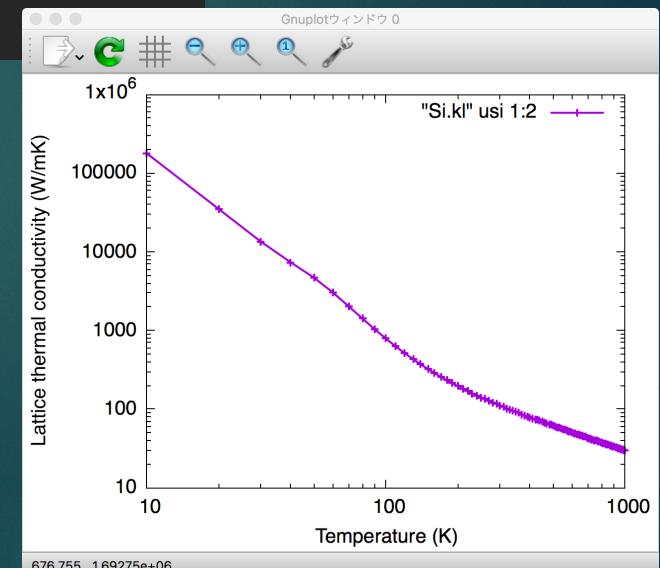
```
&general
PREFIX = Si_q10
MODE = RTA
NKD = 1; KD = Si
FCSXML = si222_cubic.xml
ISMEAR = -1
/
&cell
10.21019
0.0 0.5 0.5
0.5 0.0 0.5
0.5 0.5 0.0
/
&kpoint
2
10 10 10
/
```

- ▶ BTE with the three-phonon scattering process only

$$\kappa_{\text{ph}}^{\mu\nu}(T) = \frac{1}{\Omega N_q} \sum_{\mathbf{q},j} c_{\mathbf{q}j}(T) v_{\mathbf{q}j}^{\mu} v_{\mathbf{q}j}^{\nu} \tau_{\mathbf{q}j}(T) \quad \tau_{\mathbf{q}j}^{-1} = \tau_{\mathbf{q}j, \text{anh}}^{-1}$$

```
> cp phdos.in kappa.in
← (Edit RTA.in)
> export OMP_NUM_THREADS=1
> mpirun anphon kappa.in > kappa.log

(plot Si_q10.kl)
```



- ▶ LTC diverges in the  $T \rightarrow 0$  limit when only the three-phonon scattering is considered with `ISMEAR=-1`.

# 3.6 LTC with phonon-isotope scattering

- Isotope impurities introduce the mass difference, which works as a scattering center of propagating phonons. The phonon self-energy associated with the phonon-isotope scattering can be calculated perturbatively as (PRB **27**, 858 (1983))

$$\Gamma_{\mathbf{q}j}^{\text{iso}}(\omega) = \frac{\pi}{4N_q} \omega_{\mathbf{q}j}^2 \sum_{\mathbf{q}_1, j_1} \delta(\omega - \omega_{\mathbf{q}_1 j_1}) \sum_{\kappa} g_2(\kappa) |\mathbf{e}^*(\kappa; \mathbf{q}_1 j_1) \cdot \mathbf{e}(\kappa; \mathbf{q}j)|^2,$$

$$g_2(\kappa) = \sum_i f_i(\kappa) \left(1 - \frac{m_i(\kappa)}{M_{\kappa}}\right)^2$$

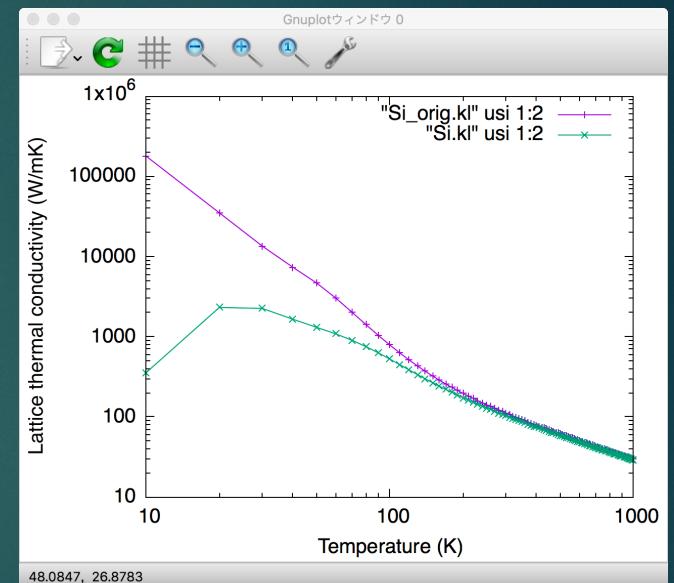
File: kappa.in

```
&analysis
ISOTOPE = 2
/
```

$g_2(\kappa)$  is calculated automatically with the natural isotopic abundance.

```
> cp Si_q10.kl Si_q10_pure.kl
← (Add &analysis field in kappa.in)
> mpirun anphon kappa.in

(compare Si_q10.kl and Si_q10_pure.kl)
```



## Tips

- When PREFIX.result exists in the working directory, the code restarts the RTA calculation and overwrites PREFIX.kl in the final step.

# 3.7 LTC with phonon-boundary scattering

- ▶ Treatment of phonon-boundary scattering is difficult and not unique. In ALAMODE, we use the following equation ( $L$  is the grain size):

$$\tau_{\mathbf{q}j,\text{ph-b}}^{-1} = \frac{2|\mathbf{v}_{\mathbf{q}j}|}{L}$$

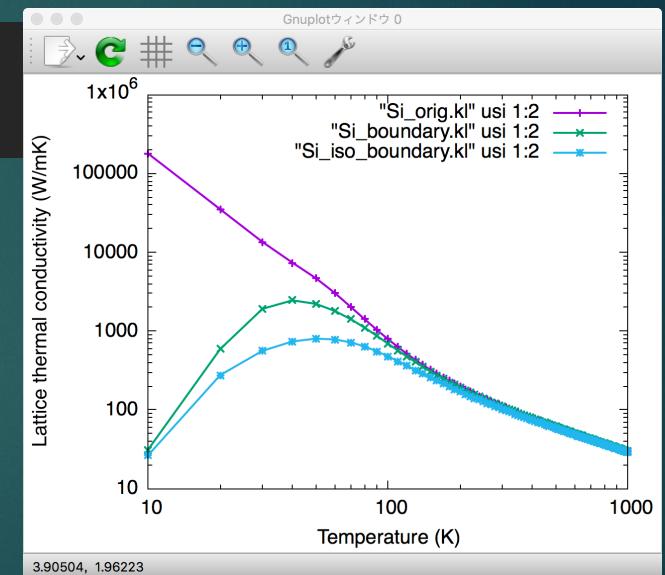
$$\tau_{\mathbf{q}j}^{-1} = \tau_{\mathbf{q}j,\text{anh}}^{-1} + \tau_{\mathbf{q}j,\text{ph-b}}^{-1}$$

```
> python -m analyze_phonons  
  --calc kappa_boundary --size 1.0e+5 Si_q10.result > Si_boundary.kl
```

$L$  in units of nm

$$\tau_{\mathbf{q}j}^{-1} = \tau_{\mathbf{q}j,\text{anh}}^{-1} + \tau_{\mathbf{q}j,\text{ph-iso}}^{-1} + \tau_{\mathbf{q}j,\text{ph-b}}^{-1}$$

```
> python -m analyze_phonons  
  --calc kappa_boundary --isotope Si.self_isotope --size 1.0e+5  
  Si_q10.result > Si_iso_boundary.kl
```



**Tips** ▶ The grain size  $L$  is somewhat arbitrary and usually set to reproduce the crystalline peak of LTC observed experimentally.

# 3.8 Lattice thermal conductivity spectrum

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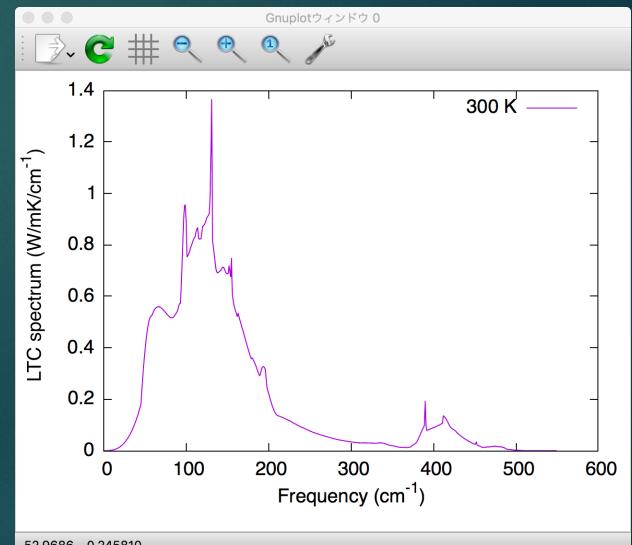
File: kappa.in

```
&general
PREFIX = Si_q10
MODE = RTA
NKD = 1; KD = Si
FCSXML = si222_cubic.xml
ISMEAR = -1
EMIN = 0; EMAX = 550;
DELTA_E = 1
/
...
&analysis
KAPPA_SPEC = 1
#ISOTOPE = 2
/
```

$$\kappa_{\text{ph}}^{\mu\mu}(\omega) = \frac{1}{\Omega N_q} \sum_{\mathbf{q}, j} c_{\mathbf{q}j} v_{\mathbf{q}j}^{\mu} v_{\mathbf{q}j}^{\mu} \tau_{\mathbf{q}j} \delta(\omega - \omega_{\mathbf{q}j})$$

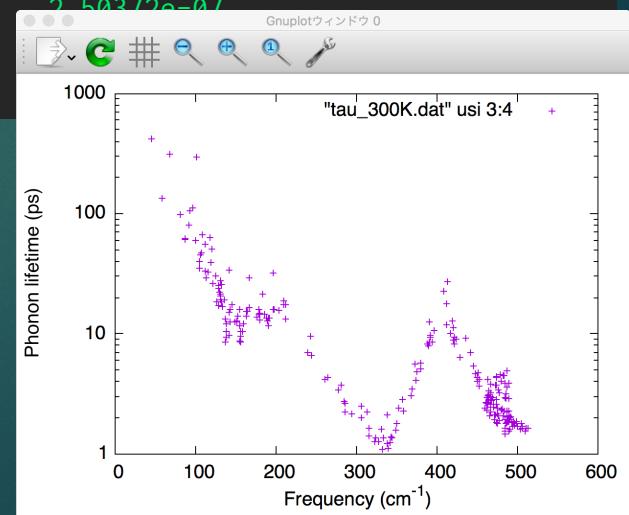
```
←(Edit kappa.in)
> anphon kappa.in
(plot Si_q10.kl_spec)
```

- Most of the contribution to the total LTC comes from the low-frequency region below  $200 \text{ cm}^{-1}$ .



### 3.9 Phonon lifetime & mean-free-path

```
> python -m analyze_phonons --calc tau --temp 300 Si_q10.result > tau_300K.dat
> less -S tau_300K.dat
# Result analyzer ver. 1.0.5
# Input file : Si_q10.result
# Phonon lifetime at temperature 300 K.
# kpoint range 1 47
# mode range 1 6
# ik, is, Frequency [cm^{-1}], Lifetime [ps], |Velocity| [m/s], MFP [nm], Multiplicity, Thermal conductivity par mode (xx, xy, ...) [W/mK]
  1  1  1.09737e-10      0      0      0  1      0      0      0
  1  2  1.09737e-10      0      0      0  1      0      0      0
  1  3  1.09737e-10      0      0      0  1      0      0      0
  1  4    512.569    1.65431      0      0  1      0      0      0
  1  5    512.569    1.65431      0      0  1      0      0      0
  1  6    512.569    1.65431      0      0  1      0      0      0
  2  1    45.18     412.002   3916.77   1613.72  8  0.734523  2.50372e-07  2.50372e-07
  2  2    45.18     412.002   3916.77   1613.72  8  0.735095  2.50372e-07  2.50372e-07
  2  3   93.2762    106.274   8603.6   914.336  8  0.902968      0
  2  4   505.052    1.70325  1342.95   2.28739  8  0.000224747      0
```



# 3.10 Cumulative thermal conductivity

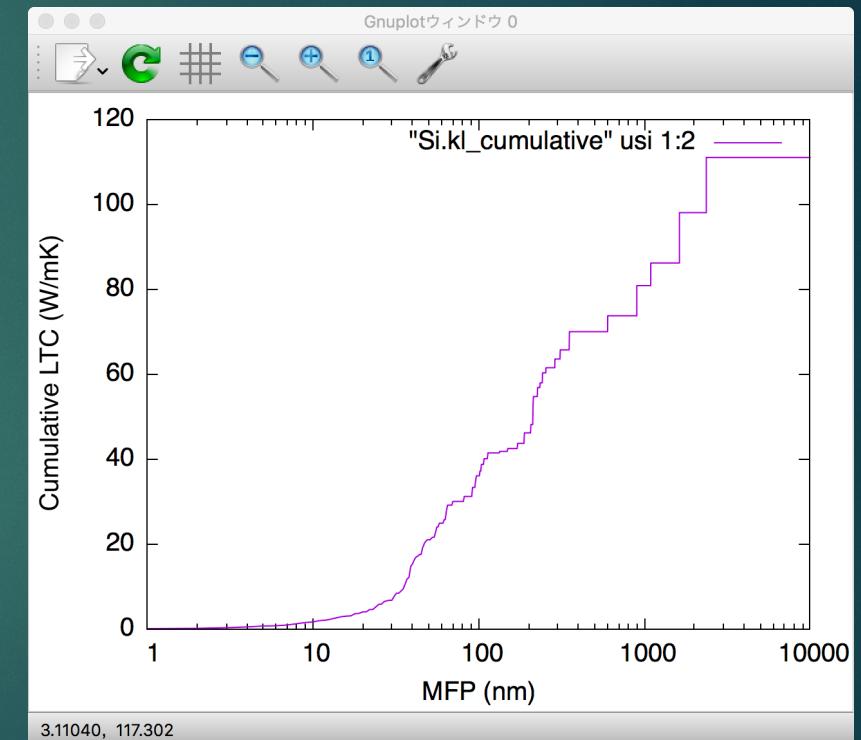
$$\kappa_{\text{ph,accum}}^{\mu\mu}(L) = \frac{1}{\Omega N_q} \sum_{\mathbf{q},j} c_{\mathbf{q}j} v_{\mathbf{q}j}^{\mu} v_{\mathbf{q}j}^{\mu} \tau_{\mathbf{q}j} \Theta(L - \frac{|v_{\mathbf{q}j}| \tau_{\mathbf{q}j}}{\text{phonon MFP}})$$

$\Theta(x)$  : Heaviside step function

```
> python -m analyze_phonons --calc cumulative --temp 300
--length 10000:1 Si.result > Si.kl_cumulative
```

(Max. of L):(Length step dL)  
in units of nm

(plot Si.kl\_cumulative using a plotting software)



The calculated LTC gradually increases with increasing the q-point mesh density and eventually reaches convergence.

## File: RTA.in

```
&general
PREFIX = Si_q15
MODE = RTA
NKD = 1; KD = Si
FCSXML = si222_cubic.xml
ISMEAR = -1
/
...
&kpoint
2
15 15 15
/
```

## Optional task:

- ▶ Perform the calculation again with a denser **q**-point grid and check how the result changes

## Tips

- ▶ The computational cost increases in proportion to  $\mathcal{O}(N_p^3 N_k^2)$  where  $N_p$  is the number of atoms in the primitive cell and  $N_k$  is the number of q points.
- ▶ RTA tends to underestimate LTC of silicon and other high-LTC materials. To achieve a perfect agreement with the experimental value, a full solution to BTE is necessary (which is not supported in ALAMODE).

If you still have time, please try phonon and thermal conductivity calculations of graphene

```
> cd ../../4_thermal_conductivity_graphene/work/  
> cp ../../2_force_constant_graphene/work/graphene_anharm.xml .
```

Follow the instruction in **hands-on\_4.ipynb**.

## Important

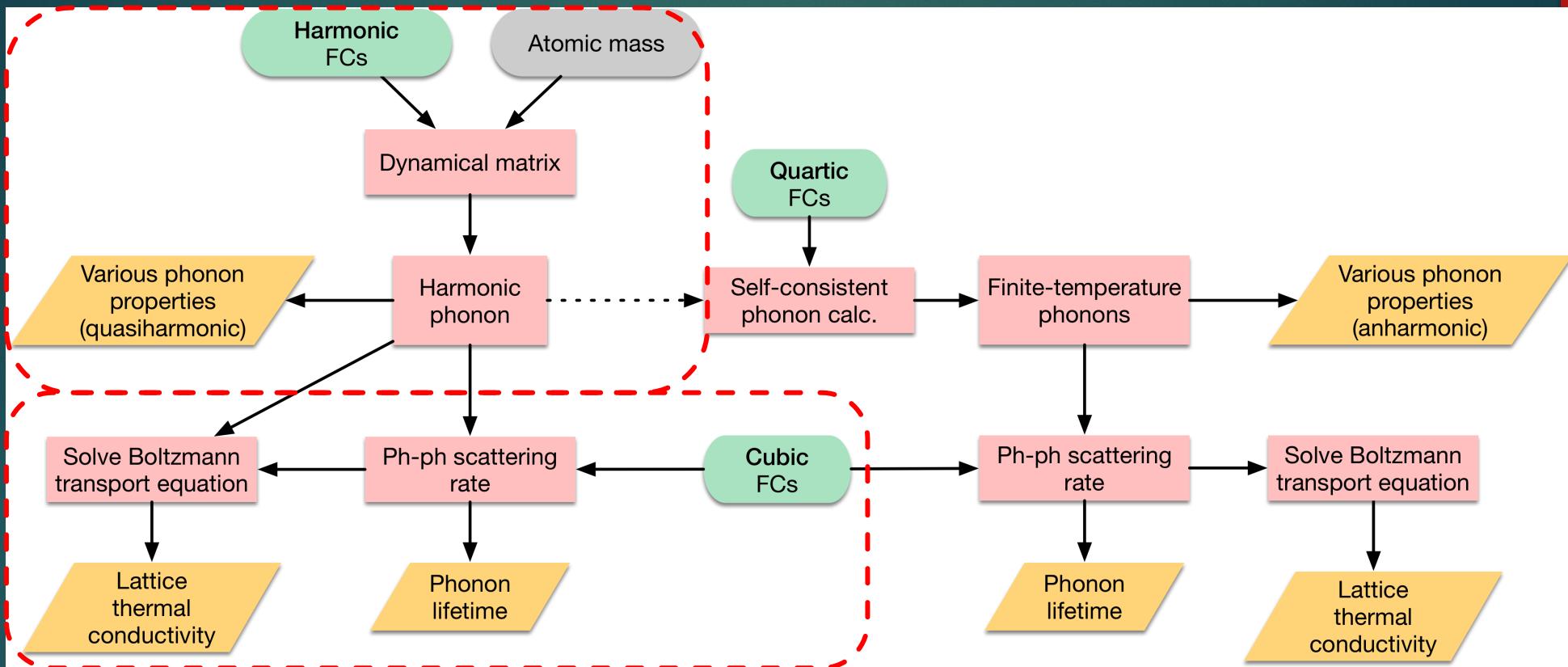
For 2D materials, you need to multiply a factor of  $c/d$  to the values in PREFIX.kl.

$c$ : The c-axis length of the simulation box

$d$ : The monolayer thickness

# Summary of part 3, 4

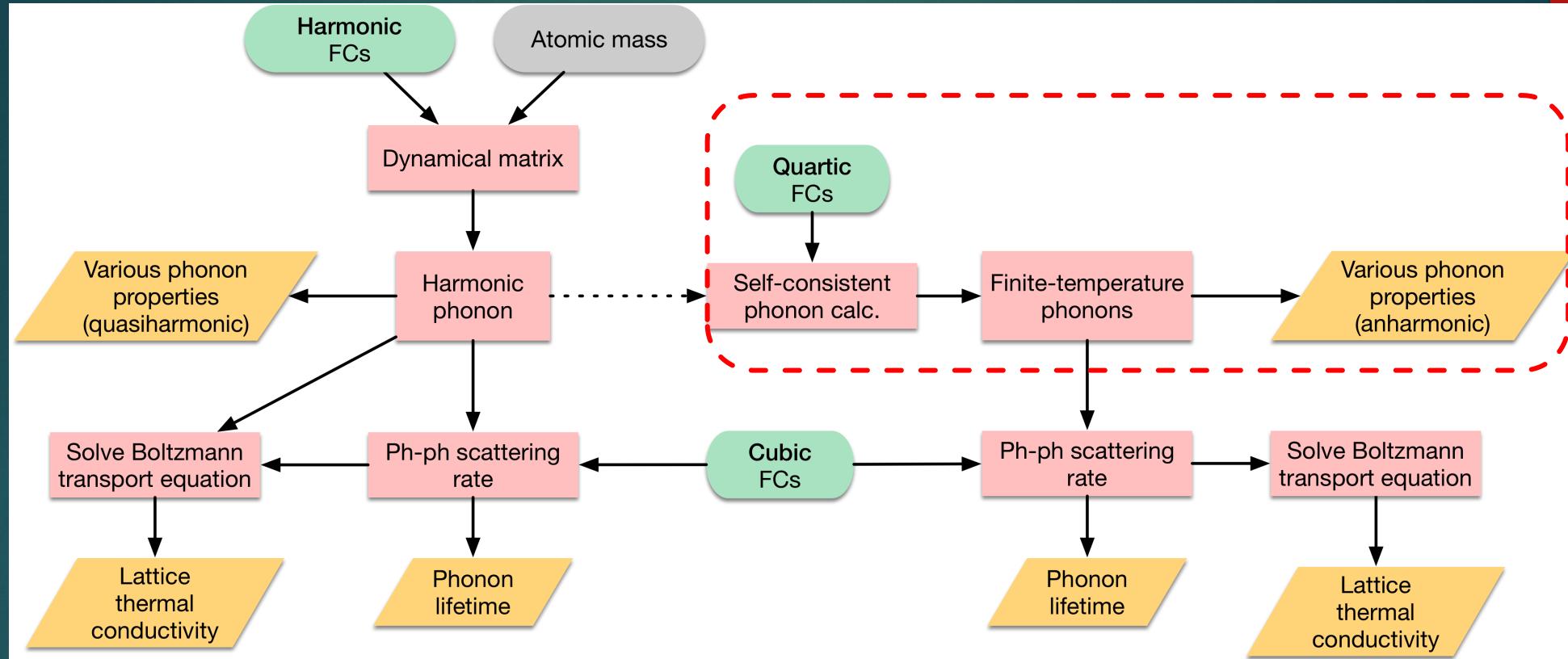
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- ▶ Harmonic phonon properties (dispersion, DOS, thermodynamic functions, mean-square displacement)
- ▶ Lattice thermal conductivity with three-phonon, ph-isotope, and ph-boundary scatterings.
- ▶ Various spectral decomposition of thermal conductivity

# Hands-on: part 5

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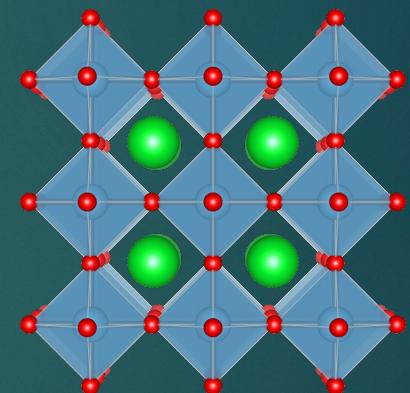
# Topics

- ▶ Phonon calculation of cubic  $\text{SrTiO}_3$  (harmonic level)
  - ▶ Self-consistent phonon calculation of cubic  $\text{SrTiO}_3$

This part requires quartic IFCs of cubic  $\text{SrTiO}_3$ , whose calculation is computationally demanding. So, we provide the [STO\\_anharm.xml](#) which contains harmonic/anharmonic IFCs necessary to run the self-consistent phonon.

## Computational details

- ▶ Original paper: T. Tadano and S. Tsuneyuki, *Phys. Rev. B* **92**, 054301 (2015); *J. Phys. Soc. Jpn.* **87**, 041015 (2018).
- ▶ VASP, PBEsol, ENCUT= 550 eV
- ▶ 2x2x2 supercell (40 atoms)
- ▶ Anharmonic IFCs are estimated by the compressive sensing lattice dynamics (LMODEL = enet)

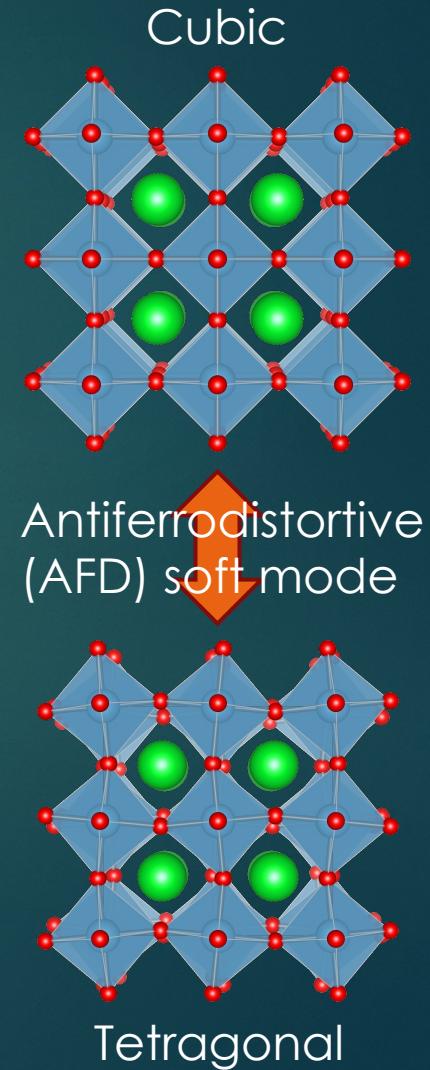
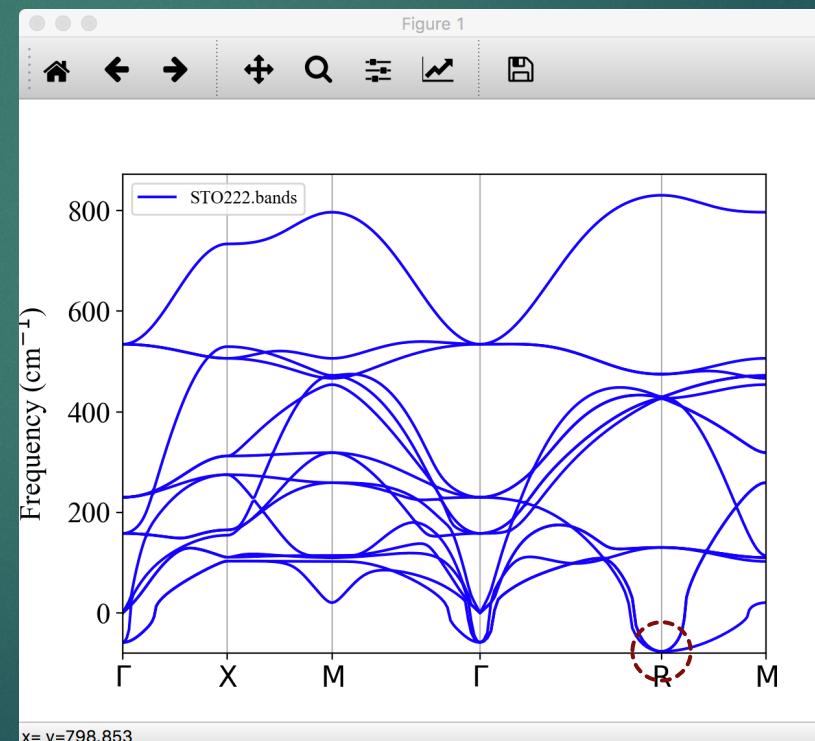


# 5.1 Harmonic IFCs & harmonic phonons

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```
> cd ../../5_self_consistent_phonon_STO/work/
> cp ./ref/ALM1.in .
> less ALM1.in
&general
  PREFIX = STO222
  MODE = opt
  NAT = 40; NKD = 3
  KD = Sr Ti O
/
&interaction
  NORDER = 1
/
&cutoff
  ** None
/
&optimize
  DFSET = ./data/DFSET_harmonic
/
...
> alm ALM1.in > ALM1.log
> grep "Fitting error" ALM1.log
Fitting error (%) : 1.53358
```

```
> cp ./ref/phband.in .
> anphon phband.in > phband.log
```



# 5.2 LO-TO splitting

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File: phband.in

```
&general
PREFIX = STO222_NA2
MODE = phonons
NKD = 3; KD = Sr Ti 0
FCSXML = STO222.xml
NONANALYTIC = 2
BORNINFO = BORN
/
...
...
```

File: STO.Born

|                   | 6.350838 | -0.000000 | -0.000000 |
|-------------------|----------|-----------|-----------|
| $\epsilon^\infty$ | 0.000000 | 6.350838  | -0.000000 |
|                   | 0.000000 | 0.000000  | 6.350838  |
| -----             |          |           |           |
| $Z_{\text{Sr}}^*$ | 2.55161  | 0.00000   | -0.00000  |
|                   | -0.00000 | 2.55161   | 0.00000   |
|                   | -0.00000 | 0.00000   | 2.55161   |
| -----             |          |           |           |
|                   | 7.34739  | 0.00000   | 0.00000   |
| $Z_{\text{Ti}}^*$ | 0.00000  | 7.34739   | -0.00000  |
|                   | 0.00000  | 0.00000   | 7.34739   |
| -----             |          |           |           |
| $Z_{\text{O}1}^*$ | -5.82005 | 0.00000   | 0.00000   |
|                   | 0.00000  | -2.04025  | -0.00000  |
|                   | -0.00000 | -0.00000  | -2.04025  |
| -----             |          |           |           |
|                   | -2.04025 | -0.00000  | -0.00000  |
| $Z_{\text{O}2}^*$ | -0.00000 | -5.82004  | 0.00000   |
|                   | 0.00000  | 0.00000   | -2.04025  |
| -----             |          |           |           |
|                   | -2.04025 | 0.00000   | 0.00000   |
| $Z_{\text{O}3}^*$ | 0.00000  | -2.04025  | 0.00000   |
|                   | 0.00000  | -0.00000  | -5.82005  |

(obtained by DFPT)

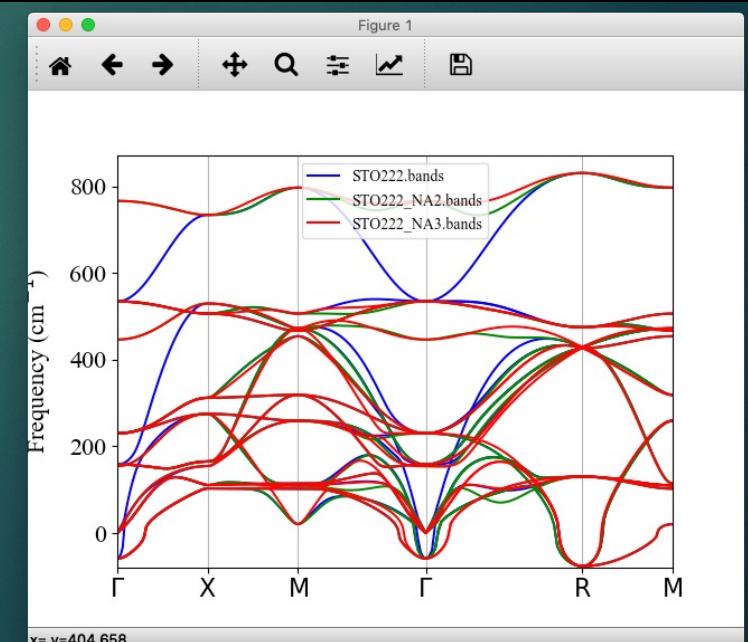
```
> python -m extract --VASP ../data/POSCAR --get
born ../data/vasprun_epsilon.xml > BORN

> anphon phband.in > phband.log
```

## Important

- The order of Born effective charges in BORNINFO file must corresponds to the order in phband.log:

```
Atomic positions in the primitive cell (fractional):
 1: 0.000000e+00  0.000000e+00  0.000000e+00  Sr
 2: 5.000000e-01  5.000000e-01  5.000000e-01  Ti
 3: 0.000000e+00  5.000000e-01  5.000000e-01  O
 4: 5.000000e-01  0.000000e+00  5.000000e-01  O
 5: 5.000000e-01  5.000000e-01  0.000000e+00  O
```



- ▶ Anharmonic force constants up to sixth-order were calculated by applying the compressive sensing approach to the training datasets generated with AIMD + random displacements.
- ▶ Solution of the compressive sensing takes ~30 mins., so we skip this part today. Please copy the XML file in the ref/ directory:

```
> cp ../ref/ST0_anharm.xml .
```

# 5.4 Self-consistent phonon (SCPH) calculation

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File: scph.in

```
&general
PREFIX = ST0_scph2-2
MODE = SCPH
NKD = 3; KD = Sr Ti 0
FCSXML = ST0_anharm.xml
NONANALYTIC = 2
BORNINFO = ST0.born
TMIN = 0; TMAX = 1000
DT = 50
/
&scph
SELF_OFFDIAG = 0
MAXITER = 500
MIXALPHA = 0.2
KMESH_INTERPOLATE = 2 2 2
KMESH_SCPH = 2 2 2
/
...
```

SCPH loop (`SELF_OFFDIAG = 0`):

Step 1. Calculate harmonic dynamical matrix and its eigenvalues and eigenvectors  $D_{\text{HA}}(\mathbf{q}) \rightarrow \{\omega_{\mathbf{q}j}^2, \mathbf{e}_{\mathbf{q}j}\}$

Step 2. Compute the fourth-order coupling coefficients in the basis of harmonic eigenvectors

$$F_{\mathbf{q}\mathbf{q}_1, iikk} = \Phi(qi; -qi; q_1k; -q_1k)$$

Step 3. Continue the following iteration until new phonon frequencies are converged

$$(\omega_{\mathbf{q}i}^{[n]})^2 = \omega_{\mathbf{q}i}^2 + \frac{1}{2} \sum_{\mathbf{q}_1, k} F_{\mathbf{q}\mathbf{q}_1, iikk} \mathcal{K}_{\mathbf{q}_1 k}^{[n-1]}$$

Temperature  
dependent term

$$\mathcal{K}_{\mathbf{q}i}^{[n]} = \alpha K_{\mathbf{q}i}^{[n]} + (1 - \alpha) K_{\mathbf{q}i}^{[n-1]}$$

$$K_{\mathbf{q}i}^{[n]} = \frac{\hbar[1 + 2n(\omega_{\mathbf{q}i}^{[n]})]}{2\omega_{\mathbf{q}i}^{[n]}} = \langle Q_{\mathbf{q}i}^{[n]*} Q_{\mathbf{q}i}^{[n]} \rangle$$

# 5.5 Run SCPH calculation

```
> export OMP_NUM_THREADS=14
> mpirun anphon scph.in > scph.log
(This takes about 5 minutes.)
> grep "conv" scph.log
Temp = 1.000000e+03 : convergence achieved in      58 iterations.
Temp = 9.500000e+02 : convergence achieved in      30 iterations.
Temp = 9.000000e+02 : convergence achieved in      30 iterations.
Temp = 8.500000e+02 : convergence achieved in      30 iterations.
Temp = 8.000000e+02 : convergence achieved in      30 iterations.
Temp = 7.500000e+02 : convergence achieved in      30 iterations.
Temp = 7.000000e+02 : convergence achieved in      31 iterations.
Temp = 6.500000e+02 : convergence achieved in      31 iterations.
Temp = 6.000000e+02 : convergence achieved in      31 iterations.
Temp = 5.500000e+02 : convergence achieved in      31 iterations.
Temp = 5.000000e+02 : convergence achieved in      31 iterations.
Temp = 4.500000e+02 : convergence achieved in      31 iterations.
Temp = 4.000000e+02 : convergence achieved in      32 iterations.
Temp = 3.500000e+02 : convergence achieved in      32 iterations.
Temp = 3.000000e+02 : convergence achieved in      32 iterations.
Temp = 2.500000e+02 : convergence achieved in      33 iterations.
Temp = 2.000000e+02 : convergence achieved in      33 iterations.
Temp = 1.500000e+02 : convergence achieved in      34 iterations.
Temp = 1.000000e+02 : convergence achieved in      49 iterations.
Temp = 5.000000e+01 : convergence achieved in      59 iterations.
Temp = 0.000000e+00 : not converged.
```

- ▶ The self-consistent loop stops when the change of the phonon frequencies becomes smaller than `TOL_SCPH` and the resulting dynamical matrix is positive semi-definite.
- ▶ In the low temperature region, the self-consistent loop (of the current algorithm) becomes unstable due to a smaller MSD factor.

## Tips

- ▶ Decreasing `MIXALPHA` and/or `DT` can improve the convergence in the low-T region

# 5.6 Output files of SCPH calculation

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```
> ls -1tr ST0_scph2-2.*  
ST0_scph2-2.scph_dymat  
ST0_scph2-2.scph_dfc2  
ST0_scph2-2.scph_bands
```

PREFIX.scph\_dymat

Anharmonic correction to the dynamical matrix

$$\Delta D(\mathbf{q}, T) = D_{\text{SCPH}}(\mathbf{q}, T) - D_{\text{HA}}(\mathbf{q})$$

is saved for the given  $\mathbf{q}$  and temperature grid.

## Note

When PREFIX.scph\_dymat exists in the working directory, the code loads  $\Delta D(\mathbf{q}, T)$  from the file instead of running a SCPH calculation from scratch.

PREFIX.scph\_dfc2

Anharmonic correction to the second-order IFCs

$$\Delta\Phi(\mathbf{r}(\ell), T) = M^{\frac{1}{2}} \Delta D(\mathbf{r}(\ell), T) M^{\frac{1}{2}}$$

is saved where  $\Delta D(\mathbf{r}(\ell), T) = \frac{1}{N_q} \sum_{\mathbf{q}} \Delta D(\mathbf{q}, T) e^{-i\mathbf{q}\cdot\mathbf{r}(\ell)}$  and  $M$  is the diagonal matrix whose elements are atomic masses.

## Note

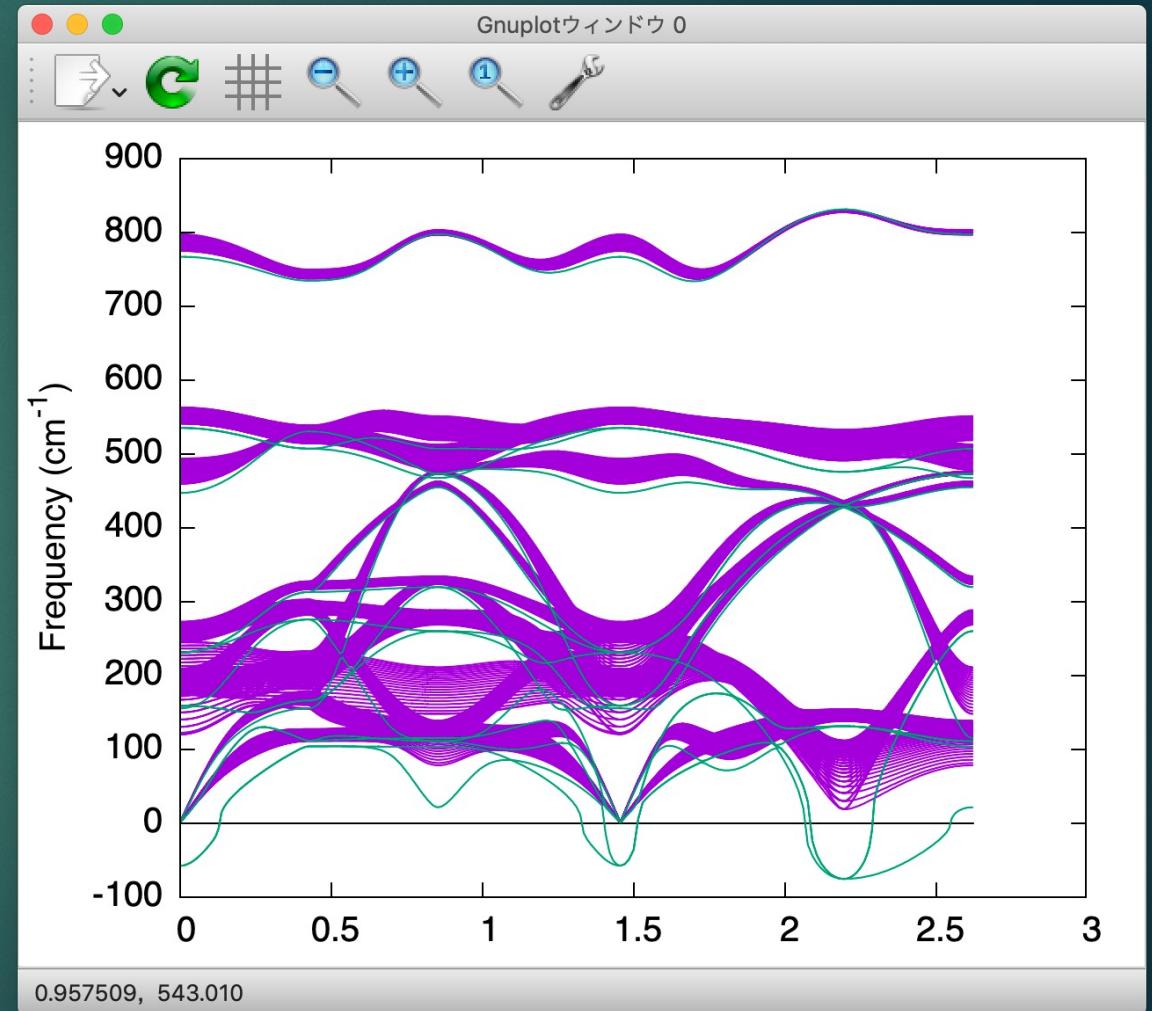
PREFIX.scph\_dfc2 is used to create effective second-order IFCs  $\tilde{\Phi}(\mathbf{r}(\ell), T) = \Phi_{\text{HA}}(\mathbf{r}(\ell)) + \Delta\Phi(\mathbf{r}(\ell), T)$

- ▶ Use dfc2 for ALAMODE XML format
- ▶ Use scph\_to\_qefc.py for QE fc format

- ▶ The  $q$  points sampled by `KMESH_INTERPOLATE` should be commensurate with the supercell size (of harmonic IFCs).
- ▶ `KMESH_SCPH` must be an integral multiple of `KMESH_INTERPOLATE`  
e.g. When `KMESH_INTERPOLATE = 2 2 2`, `KMESH_SCPH` must be `KMESH_SCPH = 2 2 2, 4 4 4, 6 6 6`, etc.
- ▶ Do not use an anisotropic  $q$  grid for isotropic systems.
- ▶ Anharmonic corrections are saved in the files even when the convergence is not achieved. Do not use the un converged results as they are not reliable.
- ▶ Currently, the SCPH iteration does not support `NONANALYTIC=3`. Please use `NONANALYTIC=2` instead. After the SCPH calculation finishes, you can switch to `NONANALYTIC=3` in the restart mode.

# 5.8 Visualize finite-T phonon dispersion

```
> gnuplot
gnuplot> set terminal qt font "Helvetica,20"
gnuplot> set ylabel "Frequency (cm^{-1})"
gnuplot> unset key
gnuplot> plot for [col=3:17] "STO_scph2-
2.scph_bands" usi 2:col w 1 lt 1
gnuplot> replot for [col=2:16]
"STO222_NA2.bands" usi 1:col w 1 lt 2
```



# Polarization mixing in SCPH

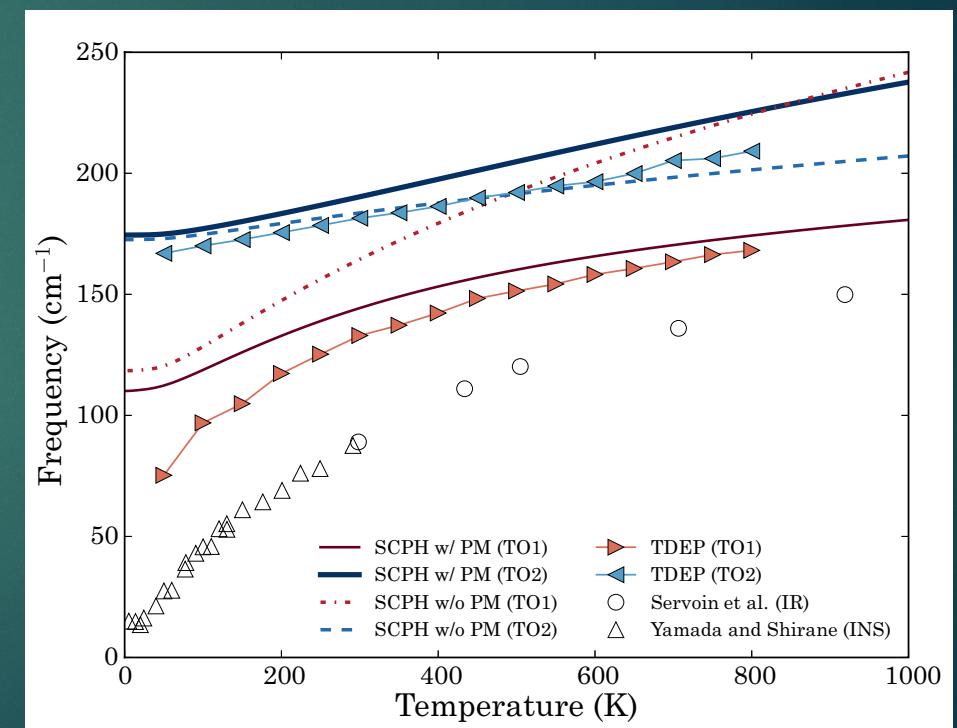
74

- ▶ The off-diagonal components of the loop diagram are considered by setting `SELF_OFFDIAG = 1`, which induces the polarization mixing (PM)
- ▶ PM occurs between phonon modes belonging to the same irreducible representation.
- ▶ PM is important in SrTiO3 at high temperatures
- ▶ `SELF_OFFDIAG = 1` is more expensive than `SELF_OFFDIAG = 0`

Complexity

$$\text{SELF\_OFFDIAG} = 0 \quad \mathcal{O}(N_q^{\text{irred.}} N_{q_1} m^2)$$

$$\text{SELF\_OFFDIAG} = 1 \quad \mathcal{O}(N_q^{\text{irred.}} N_{q_1} m^4)$$



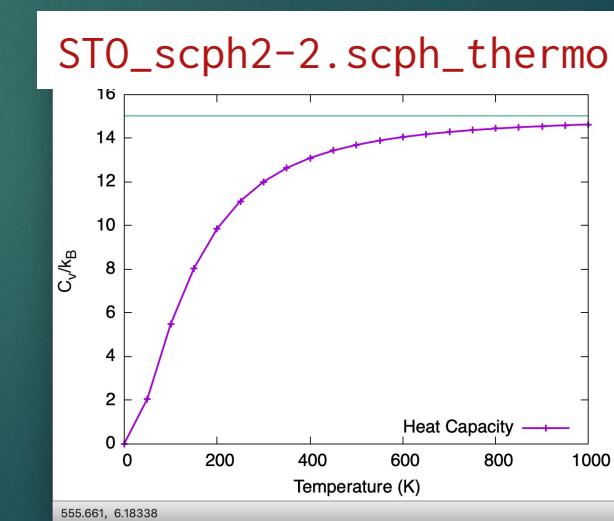
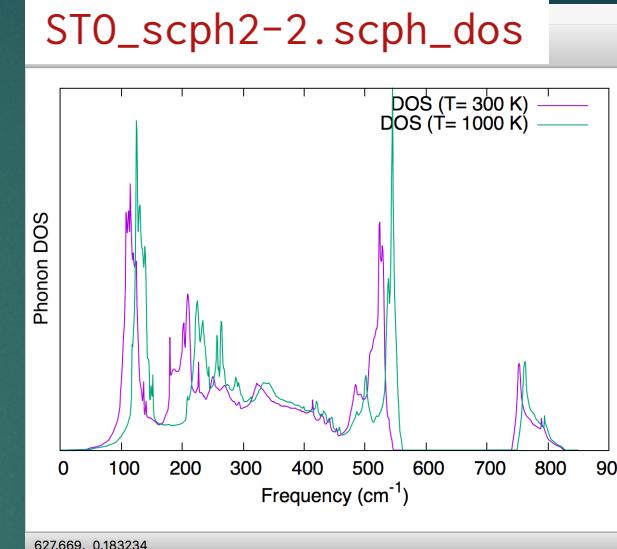
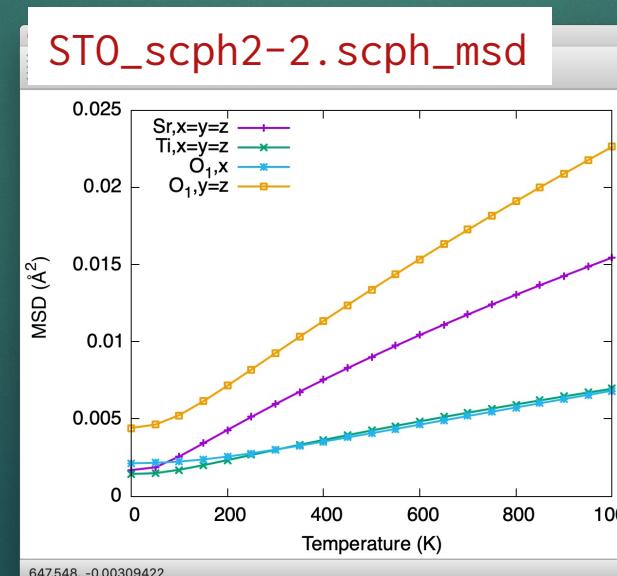
# 5.9 Finite-T phonon DOS & thermodynamic function

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File: scph.in

```
&general
PREFIX = ST0_scph2-2
MODE = SCPH
NKD = 3; KD = Sr Ti 0
FCSXML = ST0_tadano.xml
EMIN = -100; EMAX = 850;
DELTA_E = 1.0
TMIN = 0; TMAX = 1000;
DT = 50
/
&kpoint
2
10 10 10
/
&analysis
PRINTMSD = 1
/
```

```
← (Edit scph.in)
> anphon scph.in
> ls -1 ST0_scph2-2.*
ST0_scph2-2.scph_dos
ST0_scph2-2.scph_msd
ST0_scph2-2.scph_thermo
...
```



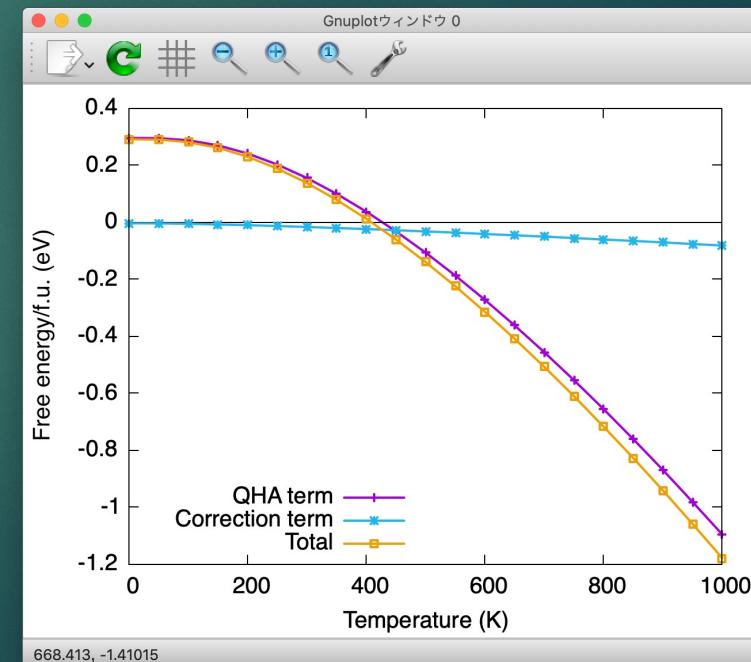
## 5.10 Vibrational free-energy with anharmonic effects

```
> less -S ST0_scph2-2.scph_thermo
# Temperature [K], Cv [in kB unit], F_{vib} (QHA term) [Ry], F_{vib} (SCPH correction) [Ry]
  0.000000  0.000000e+00  2.167446e-02  -3.378847e-04 # This line is not reliable
  50.000000 2.062933e+00  2.162180e-02  -3.577302e-04
 100.000000 5.472727e+00  2.108655e-02  -4.657560e-04
 150.000000 8.029008e+00  1.976537e-02  -6.273659e-04
 200.000000 9.847678e+00  1.765686e-02  -8.229919e-04
 250.000000 1.111219e+01  1.482308e-02  -1.044827e-03
 300.000000 1.199630e+01  1.133614e-02  -1.288477e-03
```

$$F^{\text{SCP}} = \frac{1}{N_q} \sum_{\mathbf{q}, j} \left[ \frac{\hbar \Omega_{\mathbf{q}j}}{2} + kT \log \left( 1 - e^{-\hbar \Omega_{\mathbf{q}j} / kT} \right) \right] - \frac{1}{N_q} \sum_{\mathbf{q}, j} \left[ \Omega_{\mathbf{q}j}^2 - (C_{\mathbf{q}}^\dagger \Lambda^{\text{(HA)}} C_{\mathbf{q}})_{jj} \right] \times \frac{\hbar [1 + 2n_{\mathbf{q}j}]}{2\Omega_{\mathbf{q}j}}$$

**QHA term**  

**Correction term** 



## 5.11 Classical limit (optional)

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File: scph.in

```
&general
PREFIX = ST0_scph2-2_CL
MODE = SCPH
NKD = 3; KD = Sr Ti 0
FCSXML = ST0222.xml
EMIN = -100; EMAX = 850;
DELTA_E = 1.0
TMIN = 0; TMAX = 1000;
DT = 50
CLASSICAL = 1
/
&kpoint
...
/
```

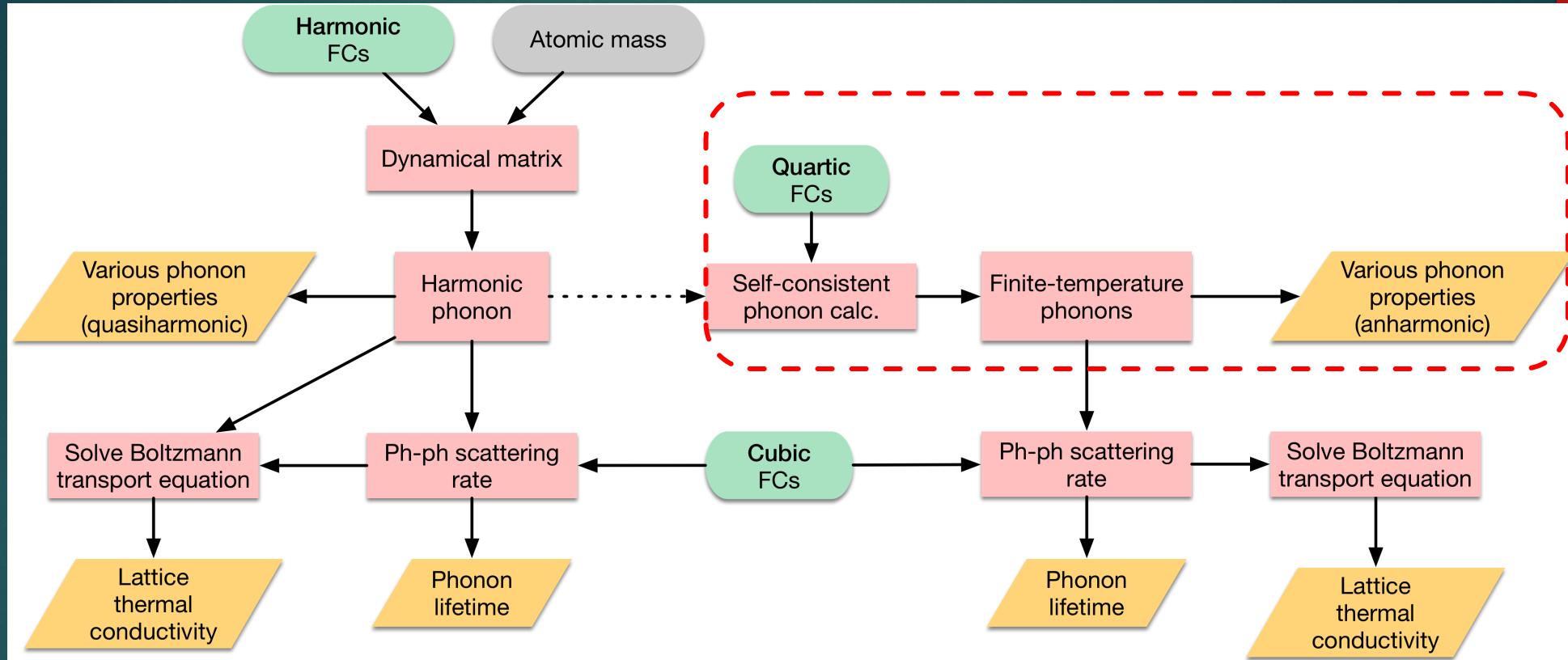
- ▶ By setting CLASSICAL=1, the code uses classical statistics instead of the quantum version.
- ▶ This flag affects SCPH results, thermodynamic functions, and lattice thermal conductivity.

### Optional task:

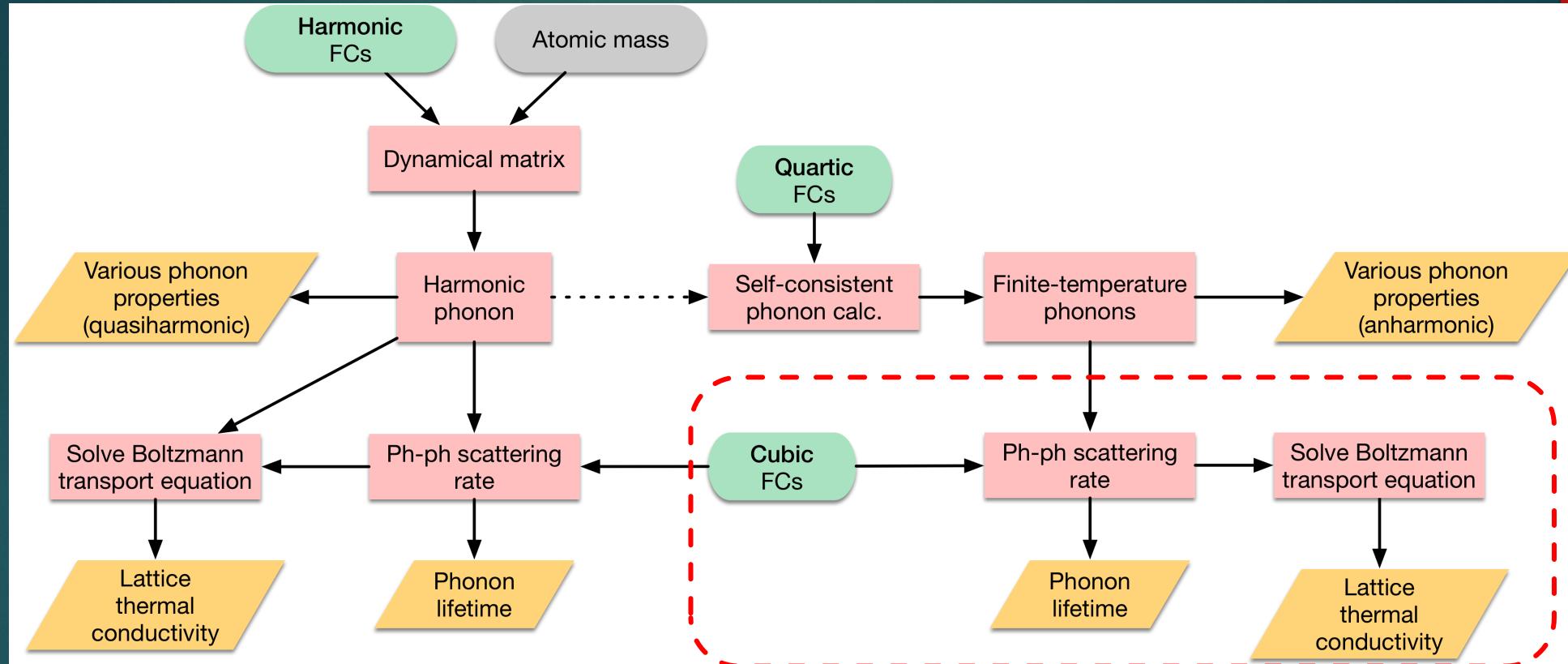
Run the SCPH calculation again with CLASSICAL=1 and check how the results change.

# 5.12 Summary of part 5

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- ▶ Harmonic and self-consistent phonon calculations of cubic SrTiO<sub>3</sub>.
- ▶ Unstable soft modes can be stabilized by quartic anharmonicity at finite temperatures.
- ▶ Anharmonic vibrational free energy



- ALAMODE supports thermal conductivity calculations on top of the SCPH solution. The procedure is explained in the next slides.

## 6.1 Create a new XML file containing renormalized harmonic force constants

```
> cd ../../6_thermal_conductivity_STO/work
> ln -s ../../5_self_consistent_phonon_ST0/work/ST0222.xml
> ln -s ../../5_self_consistent_phonon_ST0/work/ST0_anharm.xml
> ln -s ../../5_self_consistent_phonon_ST0/work/ST0_scph2-2.scph_dfc2
> ln -s ../../5_self_consistent_phonon_ST0/work/BORN
```

Calculate  $\tilde{\Phi}(\mathbf{r}(\ell), T) = \Phi_{\text{HA}}(\mathbf{r}(\ell)) + \Delta\Phi(\mathbf{r}(\ell), T)$  with dfc2

```
> dfc2
DFC2 -- a generator of renormalized harmonic FCs from SCPH outputs.
XML file containing original FC2 : ST0222.xml
Output xml filename with anharmonic correction : ST0222_scph_300K.xml
FC2 correction file from SCPH calculation : ST0_scph2-2.scph_dfc2
Target temperature : 300
```

New XML file ST0222\_scph\_300K.xml was created successfully.

One liner version

```
> dfc2 ST0222.xml ST0222_scph_300K.xml ST0_scph2-2.scph_dfc2 300
```

## 6.2 Run thermal conductivity calculation

File: kappa.in

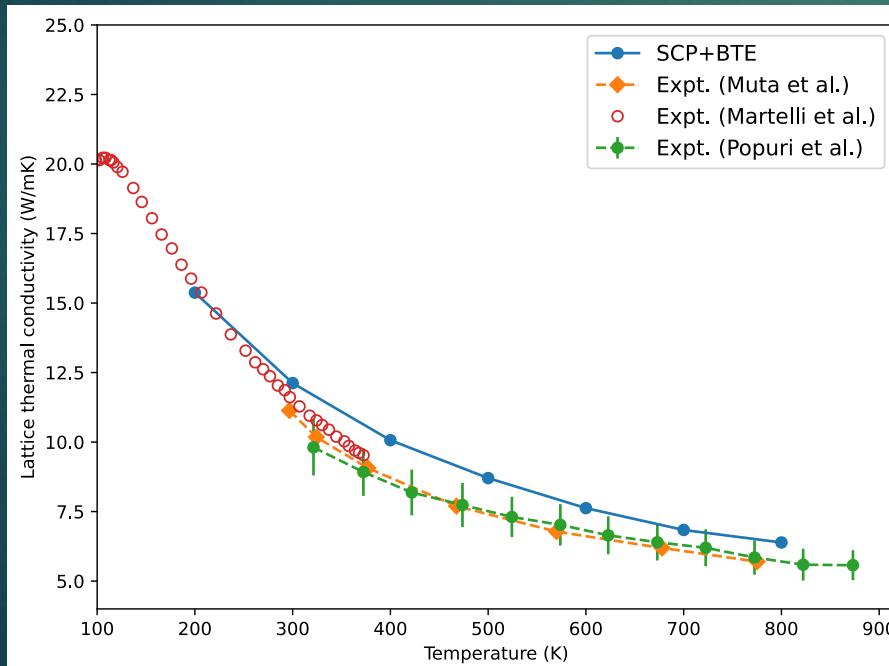
```
&general
PREFIX = ST0_scph_300K
MODE = RTA
NKD = 3; KD = Sr Ti 0
FCSXML = ST0_anharm.xml
FC2XML = ST0222_scph_300K.xml
TMIN = 300; TMAX = 300
NONANALYTIC = 3; BORNINFO = BORN
/
&cell
7.363
1.0 0.0 0.0
0.0 1.0 0.0
0.0 0.0 1.0
/
&kpoint
2
9 9 9
/
```

- ▶ Use harmonic IFCs in FC2XML and cubic IFCs in FCSXML in thermal conductivity calculation
- ▶ The result at  $T_{\text{kappa}} = T_{\text{scph}}$  is physically meaningful

```
← (Edit kappa.in)
> export OMP_NUM_THREADS=1
> mpirun anphon kappa.in > kappa.log
> cat ST0_scph_300K.kl
300.00          11.3608          0.0000         -0.0000
...
...
```

## 6.3 Run similar calculations at different temperatures

```
> cp ./ref/autocalc.sh .  
> bash ./autocalc.sh  
(this takes ~20 mins. If you don't have  
enough time, please use temp+=200 in the  
bash script.)
```



**File: autocalc.sh**

```
#!/bin/bash  
export OMP_NUM_THREADS=1  
for ((temp=200; temp<=800; temp+=100))  
do  
  dfc2 ST0222.xml ST0222_scph_${temp}K.xml ST0_scph2-2.scph_dfc2 ${temp}  
cat << EOF > kappa${temp}.in  
&general  
PREFIX = ST0_scph_${temp}K  
MODE = RTA;  
NKD = 3; KD = Sr Ti 0  
FCSXML = ST0_anharm.xml  
FC2XML = ST0222_scph_${temp}K.xml  
TMIN = ${temp}; TMAX = ${temp}  
NONANALYTIC = 3; BORNINFO = BORN  
/  
&cell  
7.363  
1.0 0.0 0.0  
0.0 1.0 0.0  
0.0 0.0 1.0  
/  
&kpoint  
2  
9 9 9  
/  
EOF  
echo "Running kappa calculation at T = " $temp  
mpirun anphon kappa${temp}.in > kappa${temp}.log  
echo "Done"  
done
```

- ▶ Fundamental theory of phonon anharmonicity
- ▶ Three major features of ALAMODE:  
force constant estimation (ALM),  
lattice thermal conductivity calculation, and  
self-consistent phonon calculation (ANPHON)
- ▶ Many functionalities not covered today: see the documentation page for details
- ▶ ALM python API is available: visit <https://github.com/ttadano/ALM>
- ▶ If you have a question, please email me (or create an issue on GitHub repository).
- ▶ Your contribution to the phonon calculation community and ALAMODE code is very welcome.

pw.x

$$\tilde{\Phi}(\mathbf{r}(\ell), T) = \Phi_{\text{HA}}(\mathbf{r}(\ell)) + \Delta\Phi(\mathbf{r}(\ell), T)$$

↓  
ph.x

```
> python -m scph_to_qe2 original.fc PREFIX.scph_dfc2 300 > new.fc
```

↓  
q2r.x  
↓  
Φ<sub>HA</sub>( $\mathbf{r}(\ell)$ )

$$\tilde{\Phi}_{\text{HA}}(\mathbf{r}(\ell), T)$$



matdyn.x



lambda.x



$\lambda, T_c$

$$\Phi_{\text{HA}}(\mathbf{r}(\ell)) \quad \Delta\Phi_{\text{HA}}(\mathbf{r}(\ell), T) \quad T \quad \tilde{\Phi}_{\text{HA}}(\mathbf{r}(\ell), T)$$