The Quasi-Harmonic Approximation: AFLOW-QHA

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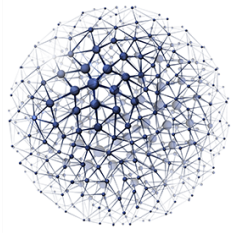

AFLOW
Automatic - FLOW for Materials Discovery

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Textbooks

- Introductory:
  - *Introduction to Lattice Dynamics* (Dove)
  - *Computational Thermodynamics of Materials* (Liu and Wang)
- Advanced:
  - *Thermodynamics of Crystals* (Wallace)
  - *Thermophysical Properties of Materials* (Grimvall)
  - *Equations of State of Solids for Geophysics and Ceramic Science* (Anderson)

The Harmonic Approximation

- Potential energy:

$$\Phi = \Phi_0 + \sum_{l\kappa\alpha} \Phi_\alpha(l\kappa) u_\alpha(l\kappa) + \frac{1}{2} \sum_{\substack{l\kappa\alpha \\ l'\kappa'\beta}} \Phi_{\alpha\beta}(l\kappa; l'\kappa') u_\alpha(l\kappa) u_\beta(l'\kappa') + \dots$$

$$\Phi_\alpha(l\kappa) = \left. \frac{\partial \Phi}{\partial u_\alpha(l\kappa)} \right|_0 = -F_\alpha(l\kappa)|_0 = 0$$

$$\Phi_{\alpha\beta}(l\kappa; l'\kappa') = \left. \frac{\partial^2 \Phi}{\partial u_\alpha(l\kappa) \partial u_\beta(l'\kappa')} \right|_0$$

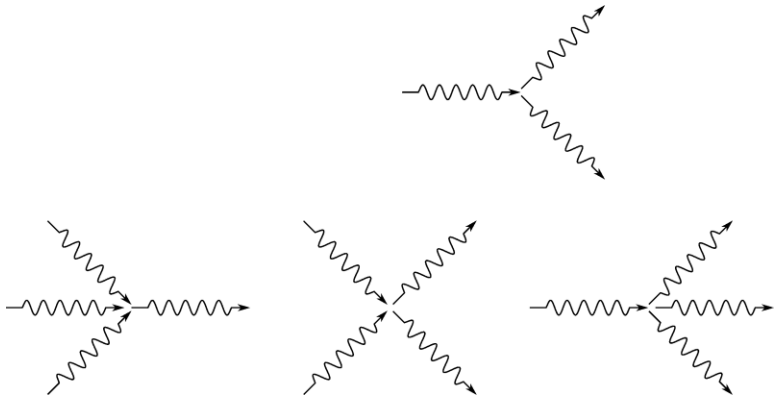
Φ : potential energy
u_α : atomic displacement
α, β : Cartesian coordinates
$F_\alpha(l\kappa)|_0$: equilibrium force
$\Phi_{\alpha\beta}(l\kappa; l'\kappa')$: harmonic force constant

- Harmonic approximation: truncate after quadratic term:

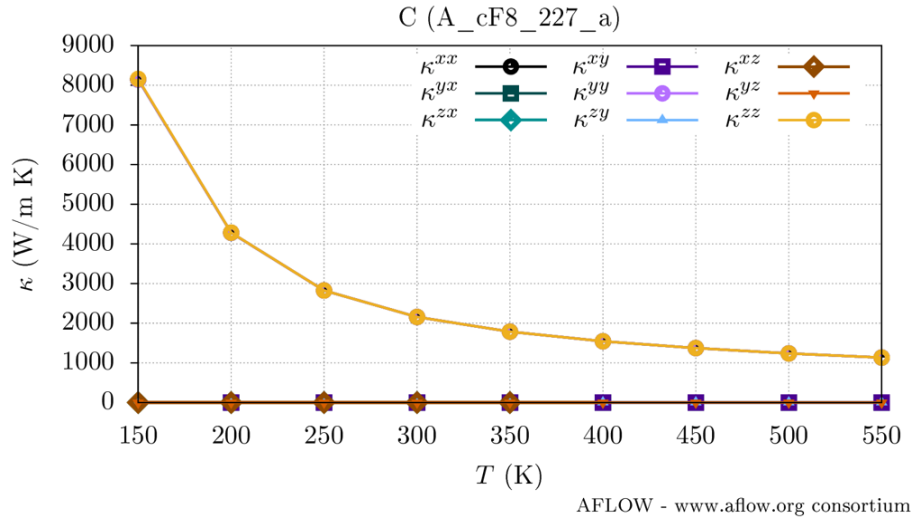
$$\Phi = \Phi_0 + \frac{1}{2} \sum_{\substack{l\kappa\alpha \\ l'\kappa'\beta}} \Phi_{\alpha\beta}(l\kappa; l'\kappa') u_\alpha(l\kappa) u_\beta(l'\kappa')$$

Anharmonicity

- Phonons start to interact: phonon scattering



- Leads to finite thermal conductivity



Anharmonicity

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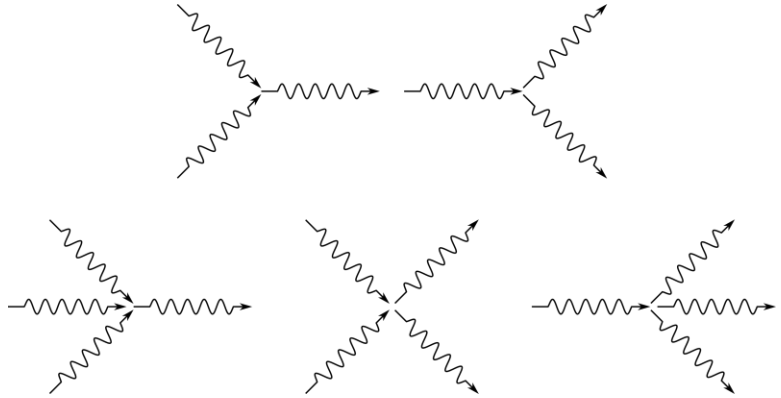
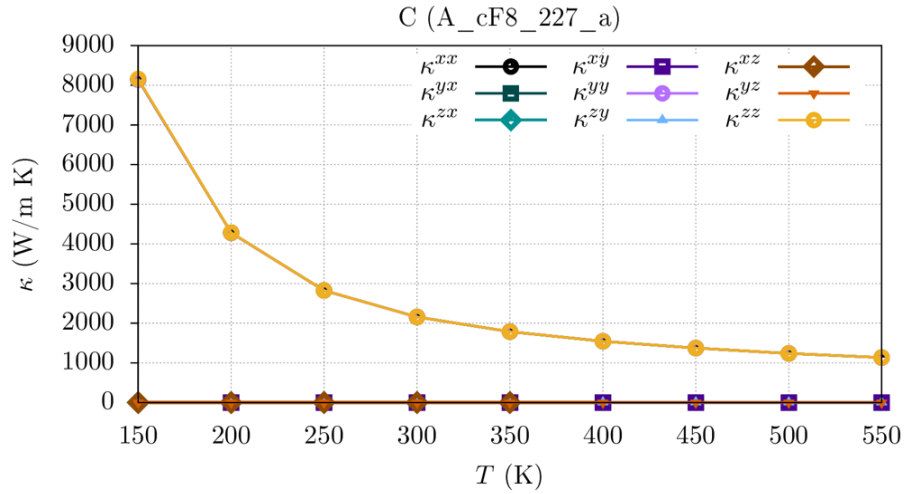
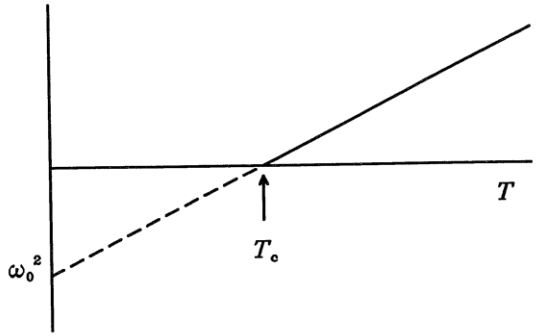


- Leads to finite thermal conductivity

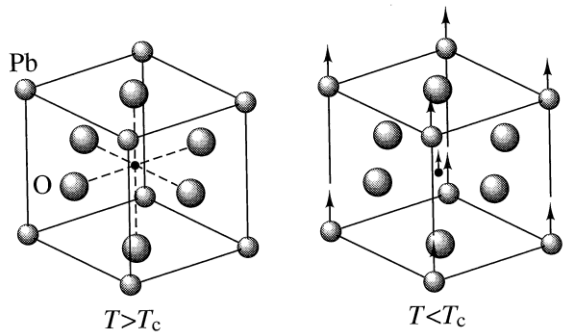


Anharmonicity

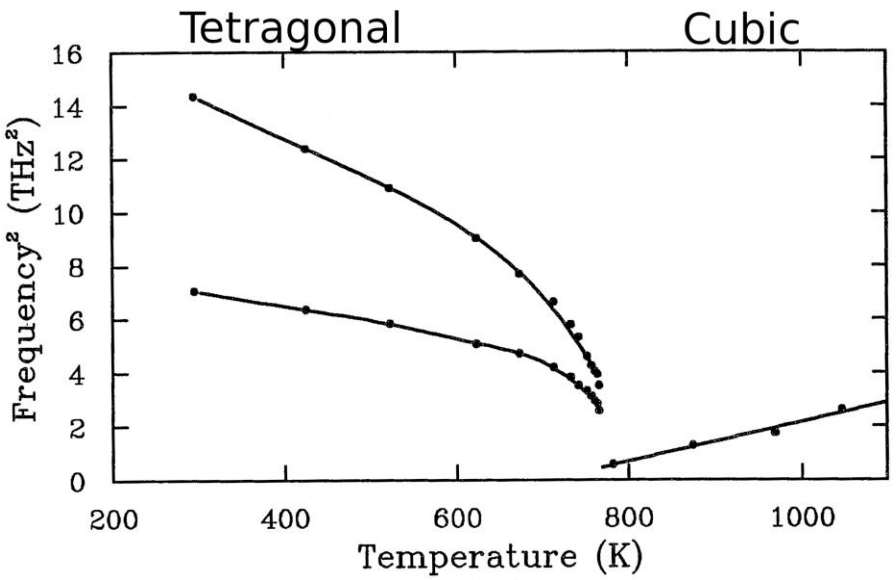
- Temperature dependence of phonon frequencies



- Phase transitions (displacive)



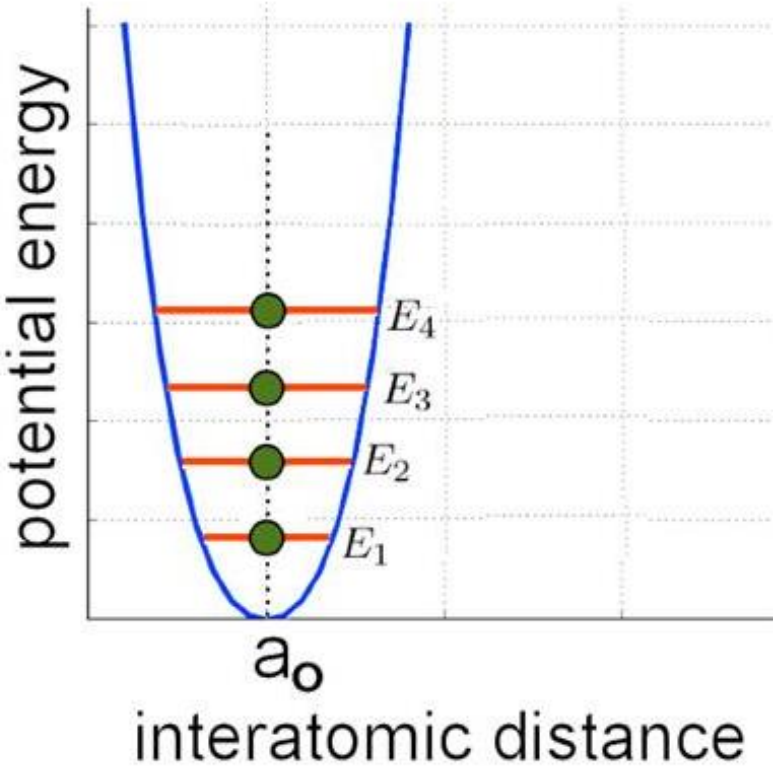
Cubic Tetragonal



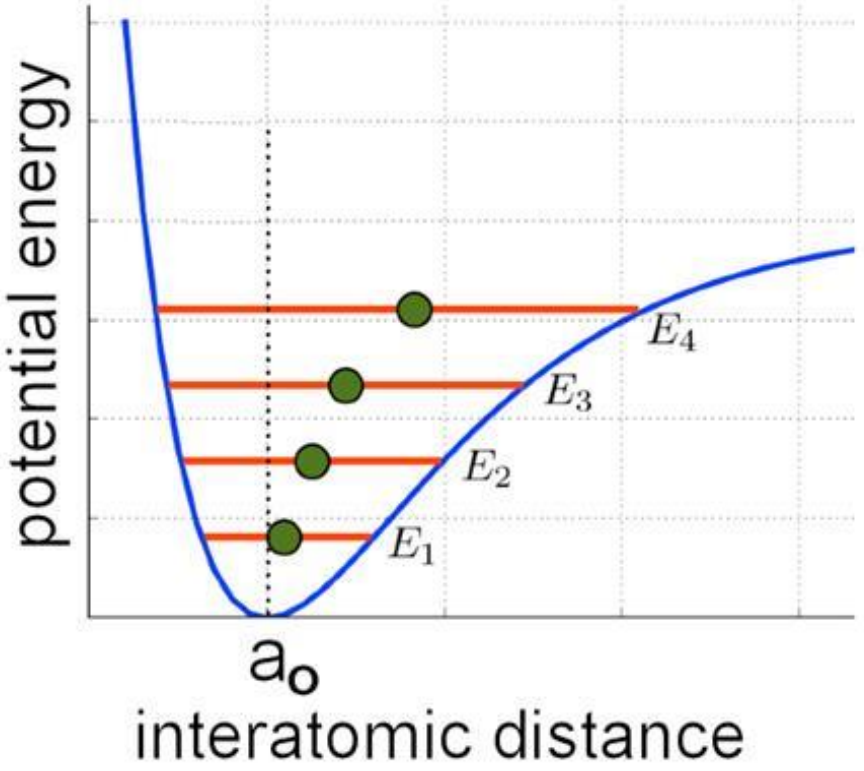
Introduction to Lattice Dynamics (Dove)

Anharmonicity

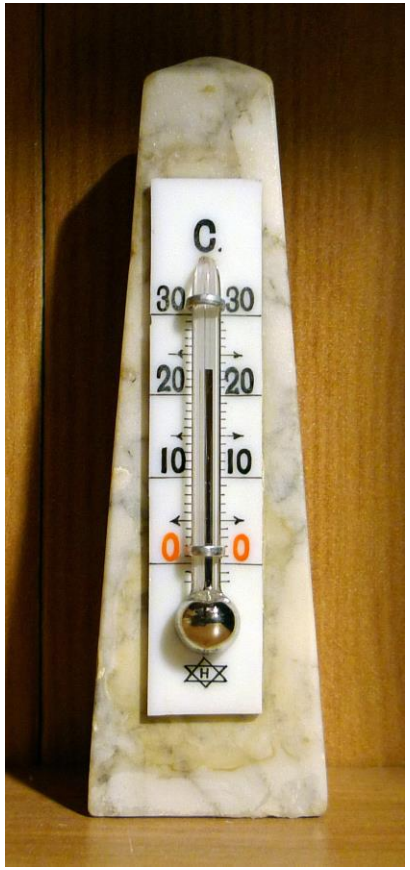
- Harmonic potential: no thermal expansion



- Anharmonic potential: thermal expansion



Thermal expansion



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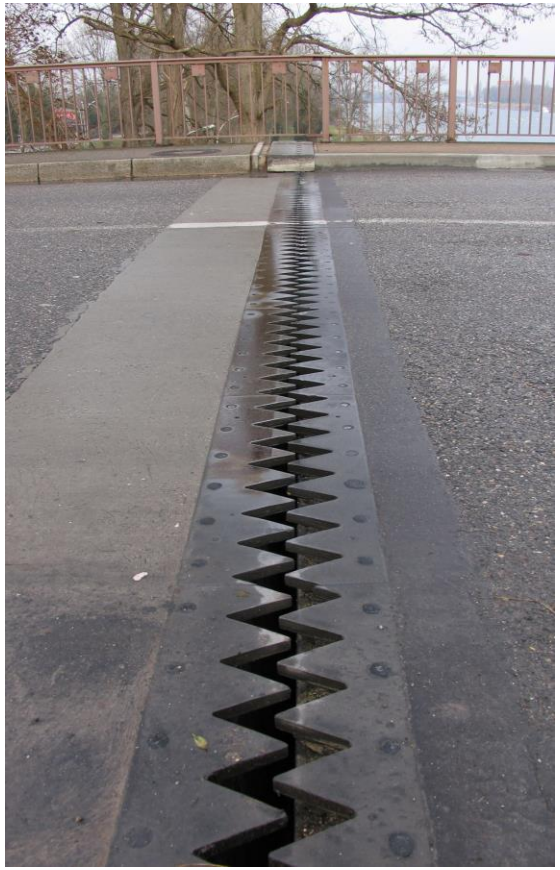

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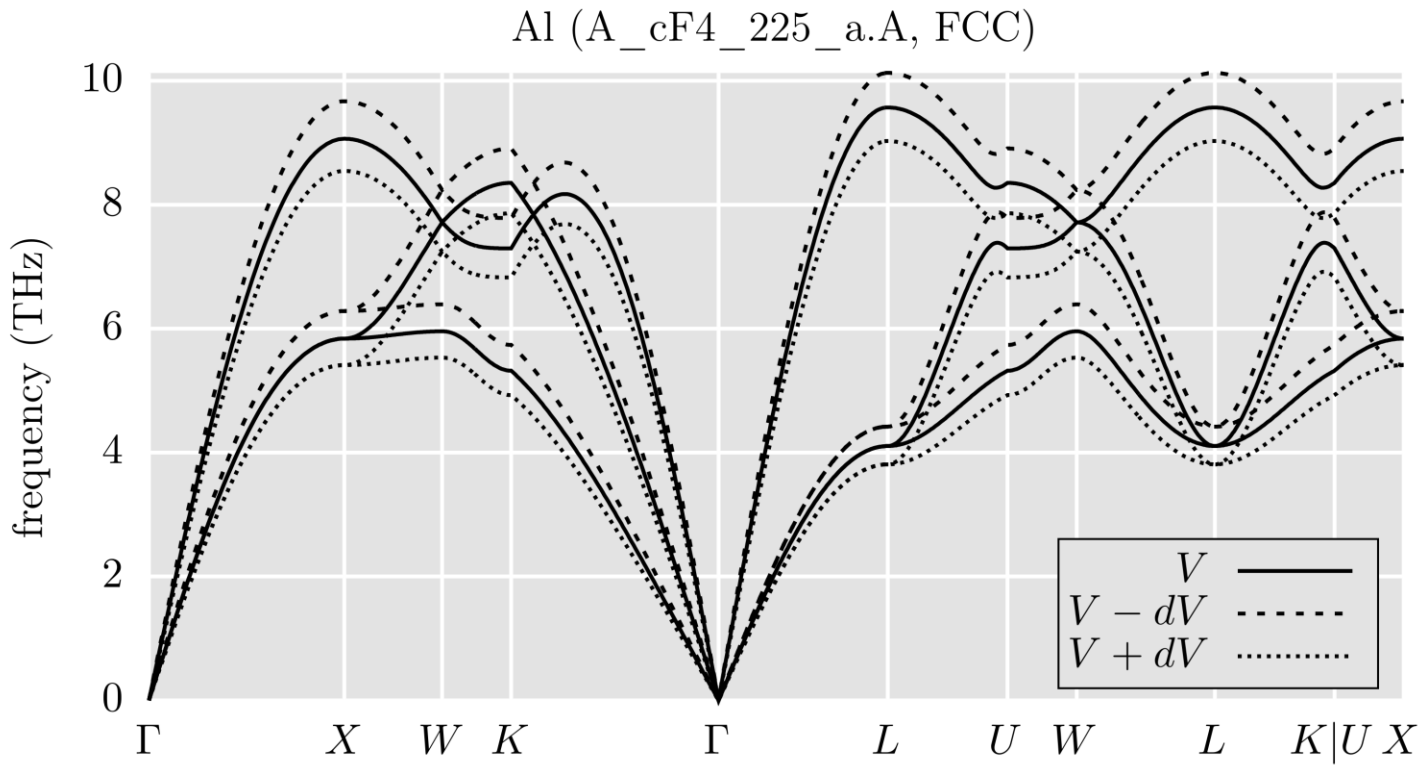
The Quasi-Harmonic Approximation

- Including anharmonicity exactly is computationally demanding
- Quasi-Harmonic Approximation (QHA): phonon frequencies depend only on volume

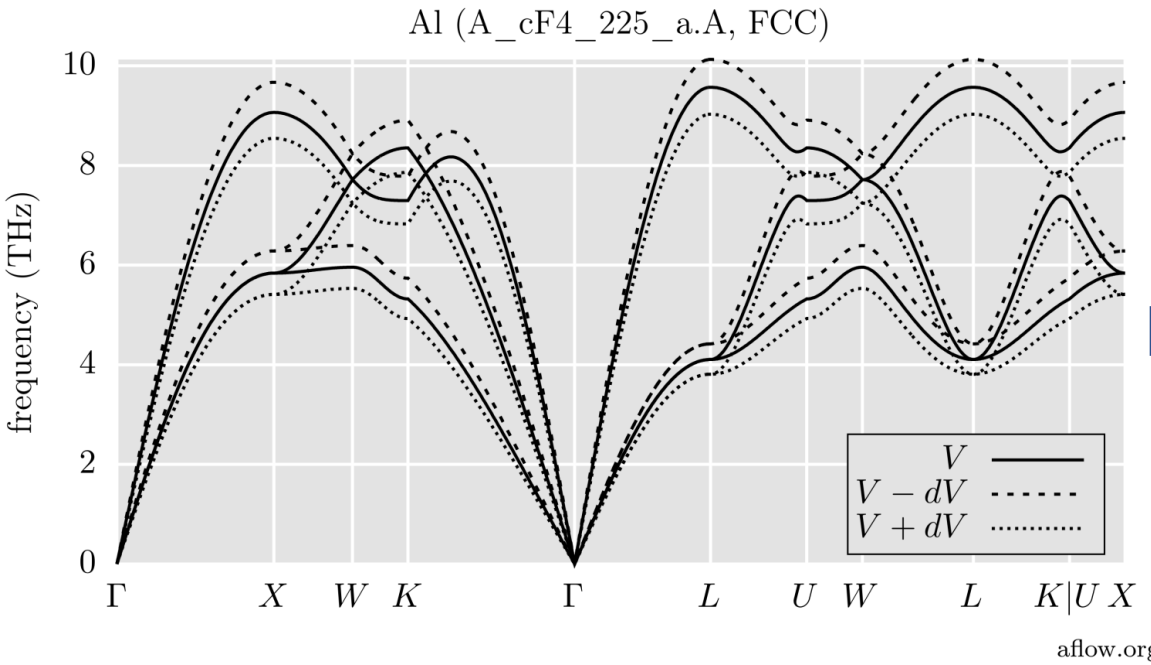


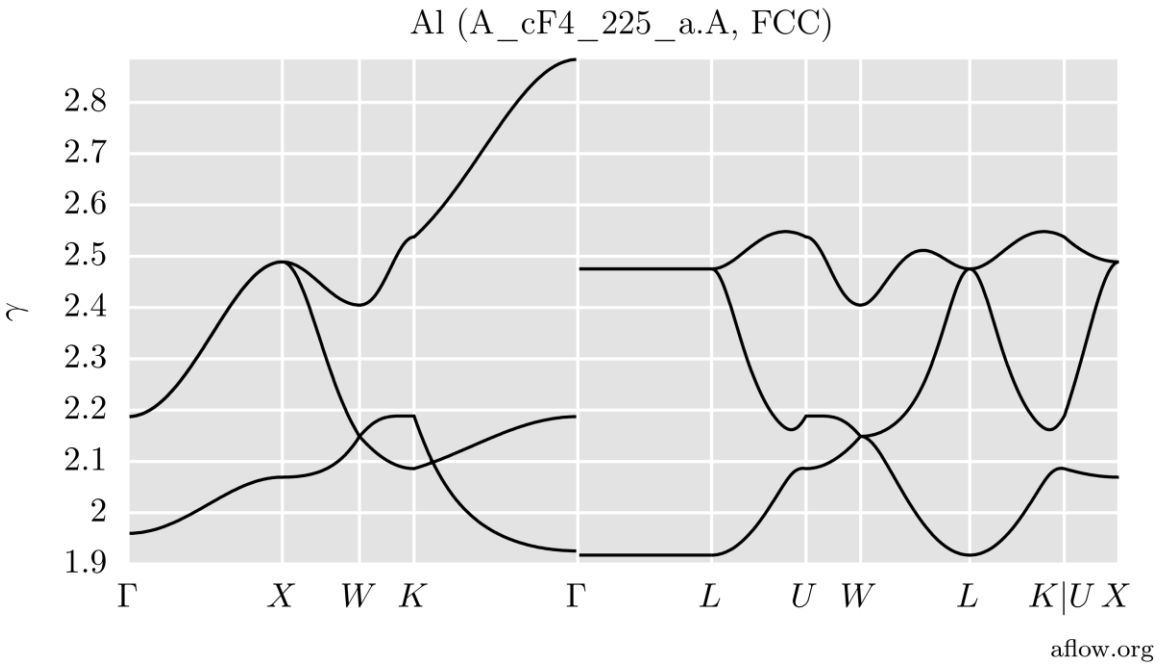
Microscopic Grüneisen parameters

- Mode-dependent Grüneisen parameter

$$\gamma_{i,\vec{q}}(V) = -\frac{V}{\omega_{i,\vec{q}}(V)} \frac{\partial \omega_{i,\vec{q}}(V)}{\partial V}$$

- Quantifies the degree of anharmonic contributions to each phonon

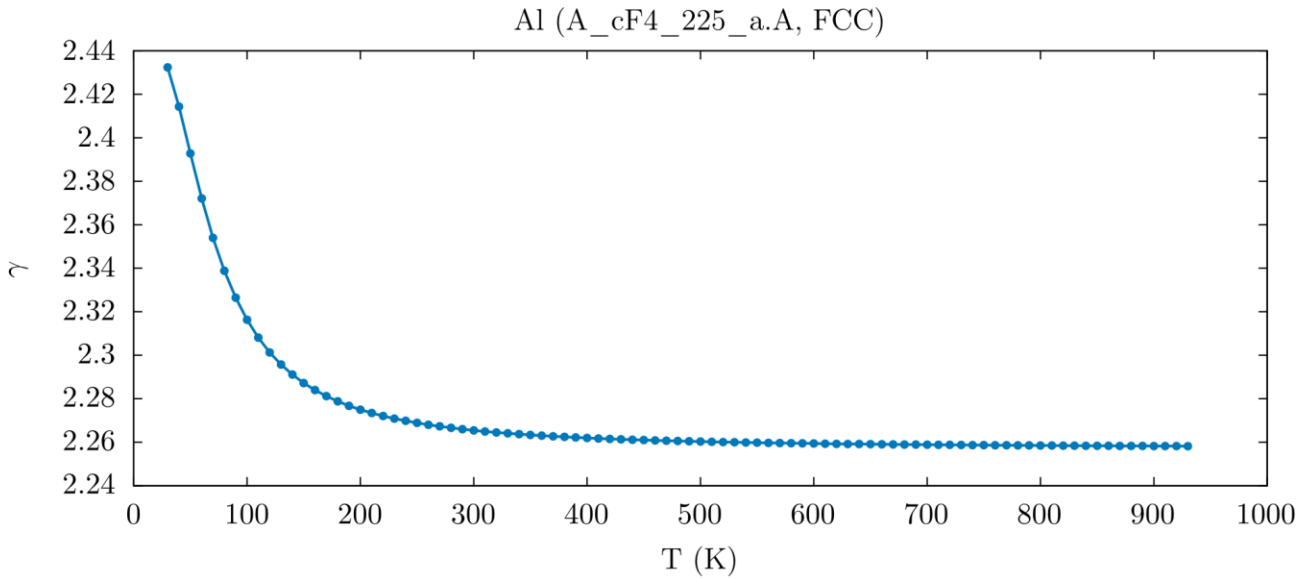




Average Grüneisen parameter

- Weighted average:

$$\gamma = \frac{\sum_{i,\vec{q}} \gamma_{i,\vec{q}} C_{V_{i,\vec{q}}}}{\sum_{i,\vec{q}} C_{V_{i,\vec{q}}}}$$



- Used to estimate thermal conductivity and thermal expansion

$$\kappa_{\mathrm{ph}} \propto \frac{1}{\gamma^2 T}$$

Example: Aluminum

- Create the aflow.in file:

```
aflow --aflow_proto=A_cF4_225_a:Al --module=qha
```

- Change the relevant APL settings in the file:

```
[AFLOW_APL]MINATOMS=100
[AFLOW_APL]POLAR=OFF
[AFLOW_APL]RELAX=OFF
```

- To enable mode-dependent Grüneisen parameter calculation:

```
[AFLOW_QHA]GP_FINITE_DIFF=ON
[AFLOW_QHA]EOS=OFF
```

- Run aflow and look at the directory structure

```
aflow --run -D ./
```

Exercise 1

Setup will be done for aluminum with face-centered cubic structure.

- Go to the directory `Ex1`
- Run the following command to generate the `aflow.in` file:

```
aflow --aflow_proto=A_cF4_225_a:Al --module=qha
```

- Go inside `AFLOWDATA/Al:PAW_PBE/A_cF4_225_a.A`
- Make sure that `[AFLOW_QHA]CALC` is uncommented
- Make the following changes:

```
[AFLOW_APL]RELAX=OFF
[AFLOW_QHA]EOS=OFF
[AFLOW_QHA]GP_FINITE_DIFF=ON
[AFLOW_QHA]GP_DISTORTION=3
```

- Run the following command to start the QHA preprocessing step:

```
aflow --run
```

Note that 3 directories are created, each with an aflow.in file inside.

Exercise 2

Calculation will be done for aluminum with face-centered cubic structure.

- Go to the directory `Ex2` and open the `aflow.in` file
- Uncomment `[AFLOW_QHA]CALC`
- Make the following changes:

```
[AFLOW_QHA]EOS=OFF
[AFLOW_QHA]GP_FINITE_DIFF=ON
[AFLOW_QHA]GP_DISTORTION=3
```

- Run the following command to start the QHA calculation:

```
aflow --run
```

In case of a successful run, three output files should be present:

```
aflow.qha.gp.avg.out.xz
aflow.qha.gp.disp.out.xz
aflow.qha.gp.mesh.out.xz
```

- We will plot the Grueneisen parameter dispersions from the `aflow.qha.gp.disp.out.xz` file
- For this, use the following command:

```
aflow --plotgrueneisendispersion
```

or, shorter:

```
aflow --plotgrdisp
```

- Examine the `aflow.qha.gp.avg.out.xz` file and determine the value of the average Grueneisen parameter (gamma) at T = 300 K and T = 930 K.

Thermodynamic Properties

Free energy

$$F(V,T) = E_0(V) + F_{\mathrm{elec}}(V,T) + F_{\mathrm{vib}}(V,T)$$

The static energy obtained by the DFT calculation: $E_0(V)$

Electronic contribution to the free energy:

$$F_{\mathrm{elec}}(V,T) = U_{\mathrm{elec}}(V,T) - TS_{\mathrm{elec}}(V,T)$$

$$U_{\mathrm{elec}}(V,T) = 2\int_0^\infty g_E(V,E)\mathcal{F}(E,T)EdE$$

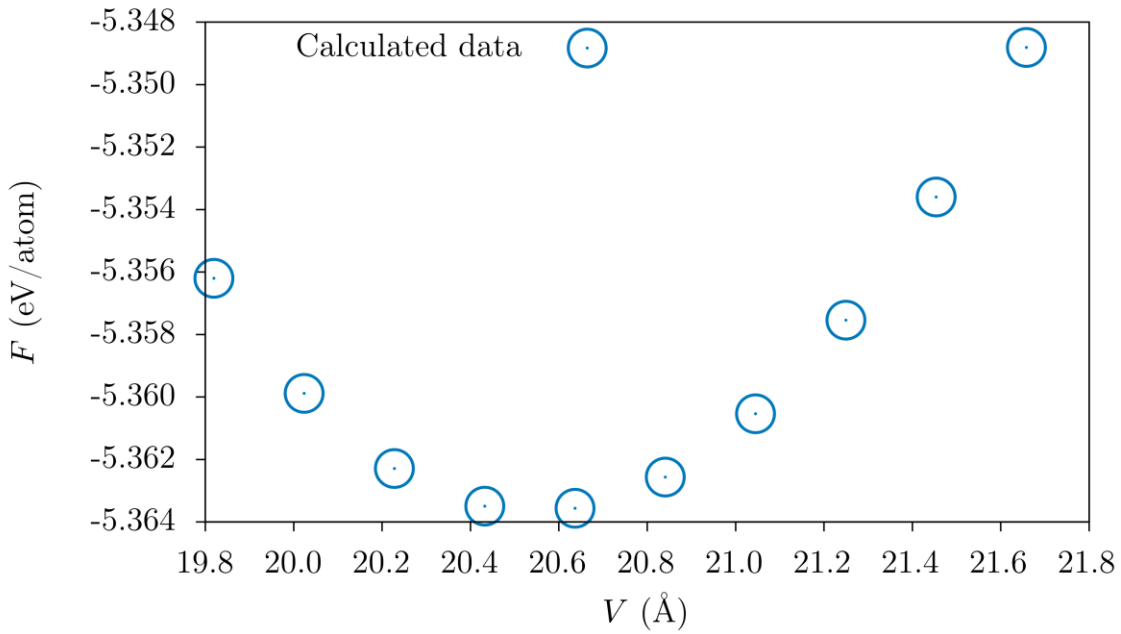
$$S_{\mathrm{elec}}(V,T) = -2k_{\mathrm{B}}\int_0^\infty g_E(V,E)\Big[\mathcal{F}(E,T)\ln\mathcal{F}(E,T) + \big(1-\mathcal{F}(E,T)\big)\ln\big(1-\mathcal{F}(E,T)\big)\Big]dE$$

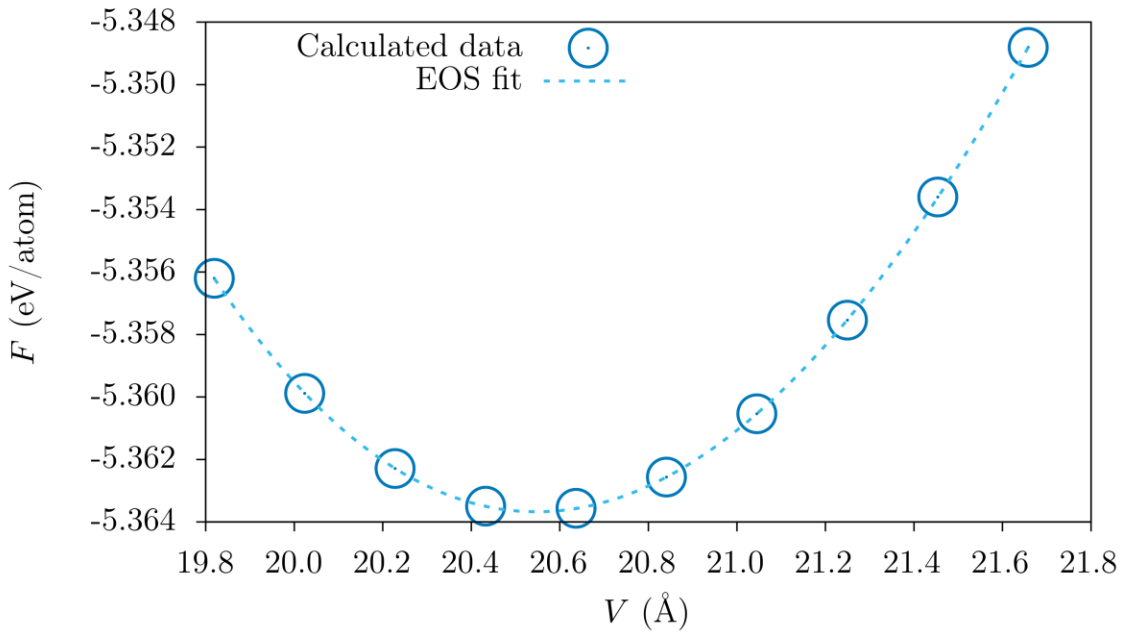
Vibrational contribution to the free energy:

$$F_{\mathrm{vib}}(V,T) = k_{\mathrm{B}}T\int_0^\infty \ln\left(2\sinh\frac{\hbar\omega}{2k_{\mathrm{B}}T}\right)g(V,\omega)d\omega$$

Equation of state

- We have a discrete set of free energy data points, but we need a continuous energy-volume relation
- Solution: fit to the equation of state (EOS)





Equation of state

- Murnaghan EOS (at least 4 volumes)

  `[AFLOW_QHA]EOS_MODEL=M`

$$F(V) = F_{eq} + \frac{BV_{eq}}{B'(B'-1)}\left(\frac{V}{V_{eq}}\right)^{1-B'} + \frac{BV}{B'} - \frac{BV_{eq}}{B'-1}$$

- Birch-Murnaghan EOS (at least 3 volumes for the lowest order)

  `[AFLOW_QHA]EOS_MODEL=BM2,BM3,BM4`

$$F(V) = \sum_{i=0}^{n} f_i V^{-\frac{2}{3}i}$$

- Stabilized jellium EOS (at least 4 volumes)

  `[AFLOW_QHA]EOS_MODEL=SJ`

$$F(V) = \sum_{i=0}^{3} f_i V^{-\frac{1}{3}i}$$

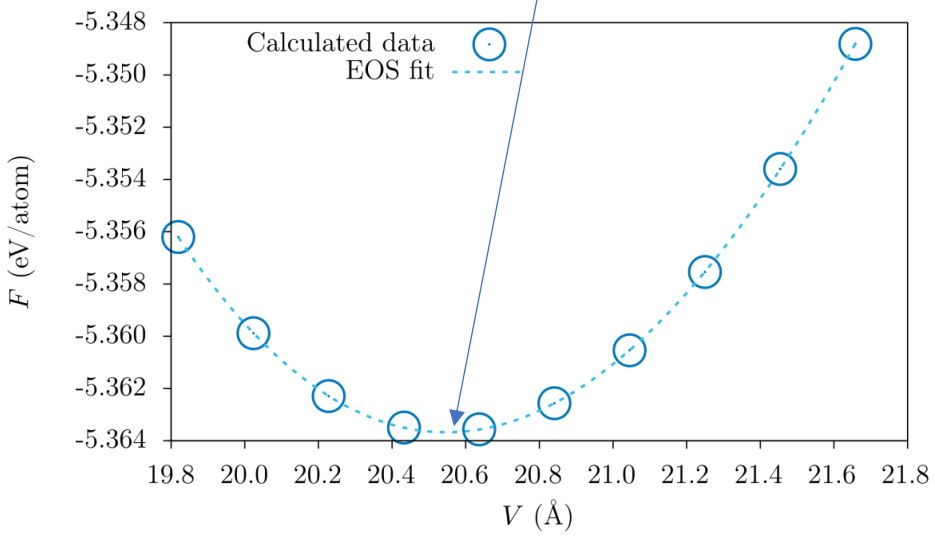
Thermodynamic Properties

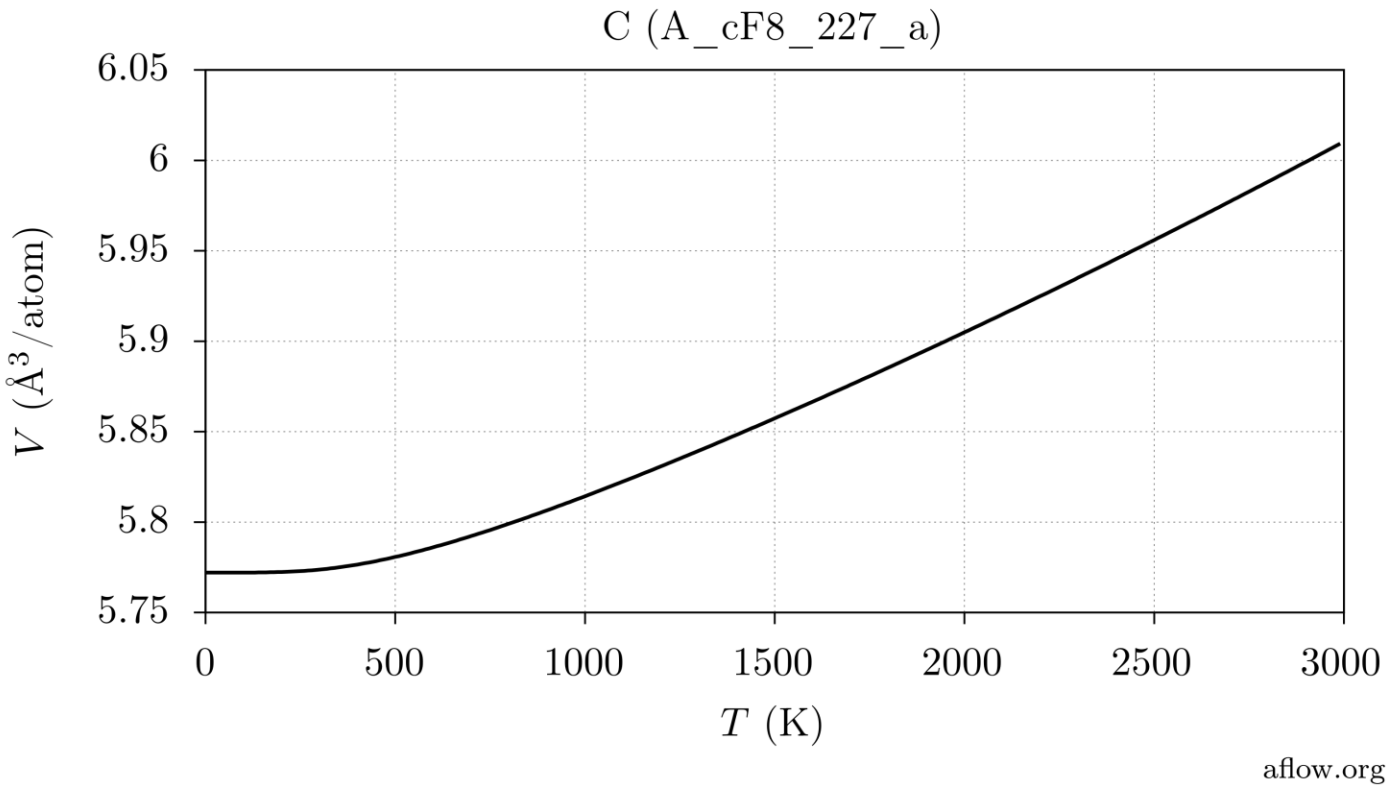
Free energy

$$F(V,T) = E_0(V) + F_{\text{elec}}(V,T) + F_{\text{vib}}(V,T)$$

Equilibrium volume

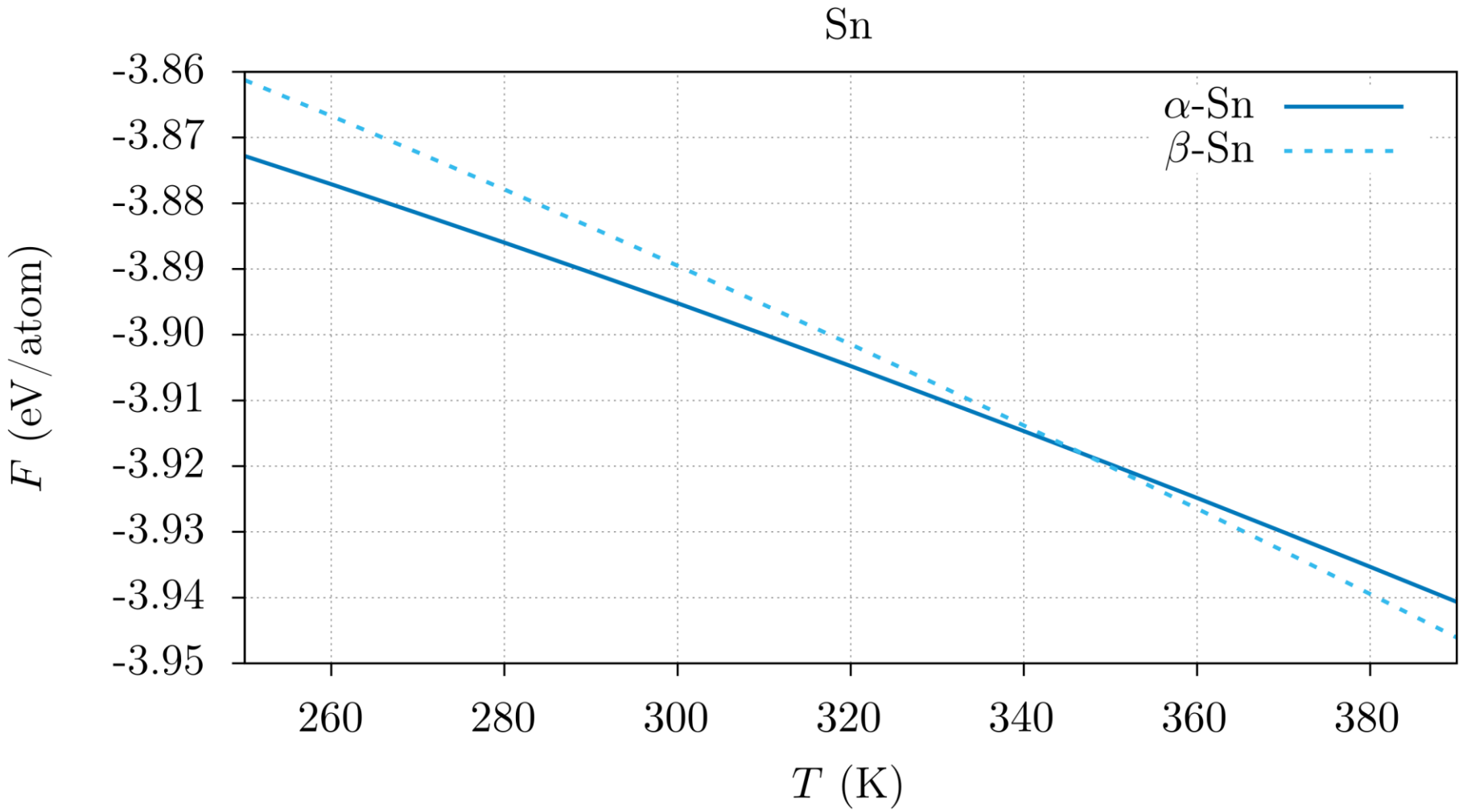
$$V_{\text{eq}}(T) = \arg\min_V F(V,T)$$





T-dependent free energy

- Compare $F(V_{eq},T)$ of various structures to study phase transitions



Thermodynamic Properties

Free energy

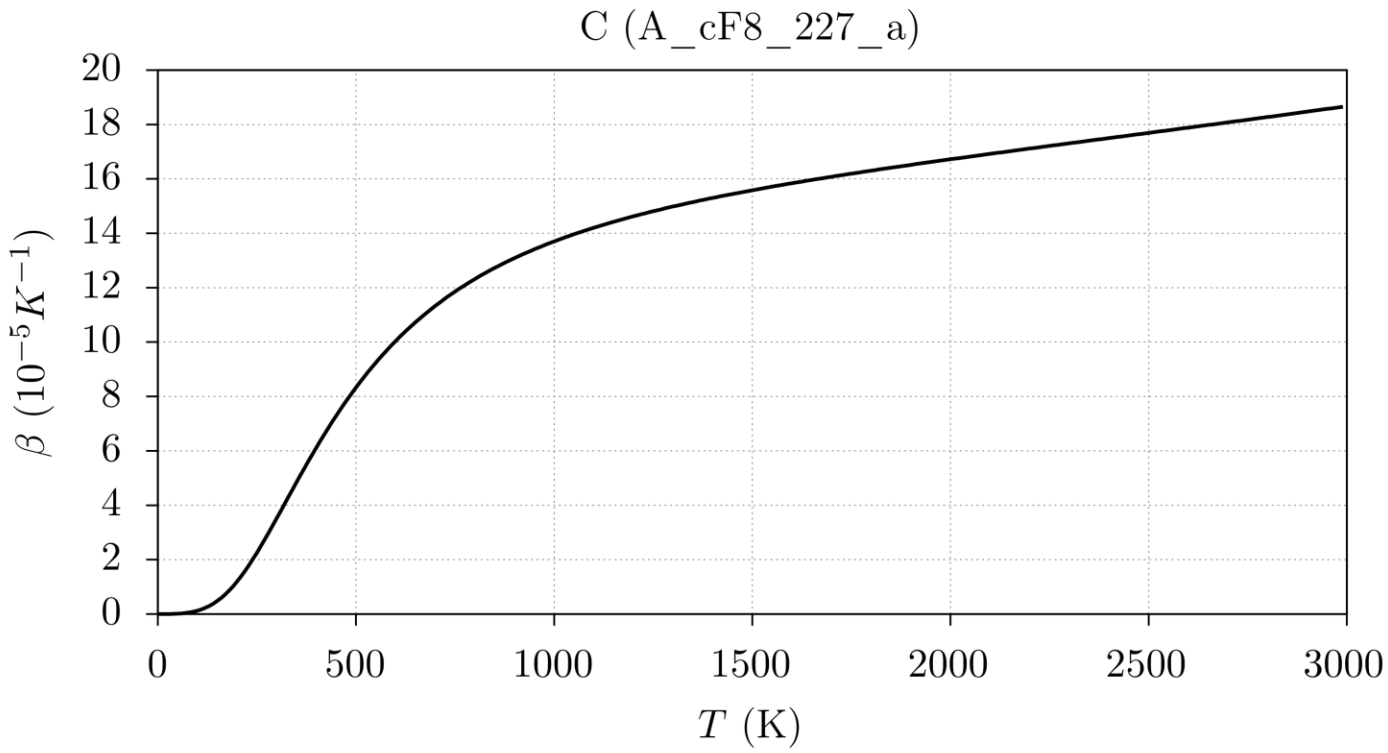
$$F(V,T) = E_0(V) + F_{\text{elec}}(V,T) + F_{\text{vib}}(V,T)$$

Equilibrium volume

$$V_{\text{eq}}(T) = \arg\min_V F(V,T)$$

Thermal expansion

$$\beta = \frac{d\ln(V_{\text{eq}})}{dT} = \frac{1}{V_{\text{eq}}}\frac{dV_{\text{eq}}}{dT}$$



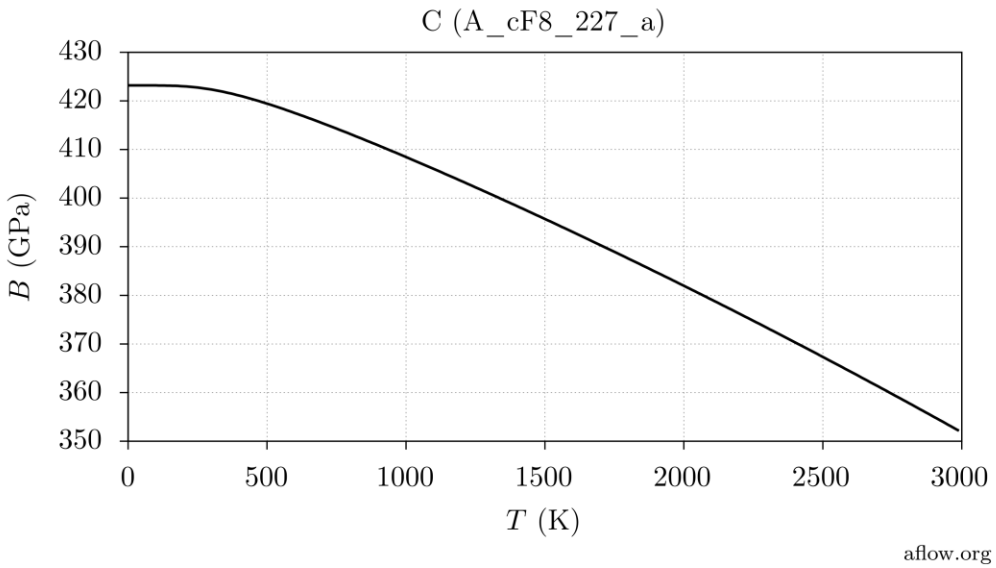
Thermodynamic Properties

Free energy

$$F(V,T) = E_0(V) + F_{\text{elec}}(V,T) + F_{\text{vib}}(V,T)$$

Bulk modulus

$$B = V\frac{\partial^2 F(V,T)}{\partial V^2}$$



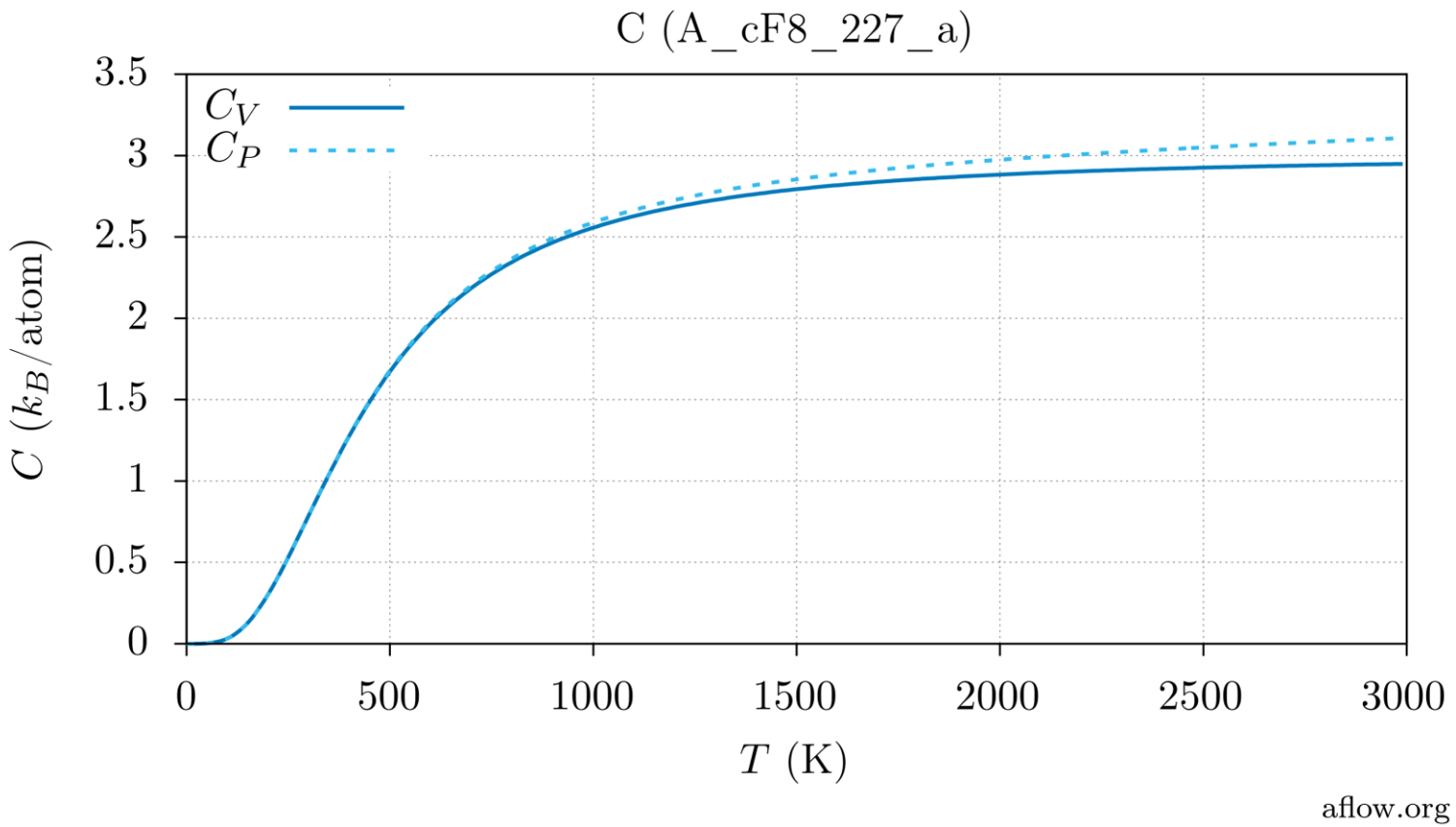
A material with B = 100 GPa loses 1% of its volume when subjected to 1 GPa pressure

Name	B (GPa)
Diamond	443
Steel	160
Granite	50
NaCl	24
Chalk	9

Thermodynamic Properties

Free energy

$$F(V,T) = E_0(V) + F_{\text{elec}}(V,T) + F_{\text{vib}}(V,T)$$



Isochoric heat capacity (constant volume)

$$C_V = -T\frac{\partial^2 F(V,T)}{\partial T^2}$$

Isobaric heat capacity (constant pressure)

$$C_P = C_V + V_{\text{eq}} B \beta^2 T$$

Thermodynamic Properties

Free energy

$$F(V,T) = E_0(V) + F_{\text{elec}}(V,T) + F_{\text{vib}}(V,T)$$

Equilibrium volume

$$V_{\text{eq}}(T) = \arg\min_V F(V,T)$$

Thermal expansion

$$\beta = \frac{d\ln(V_{\text{eq}})}{dT} = \frac{1}{V_{\text{eq}}}\frac{dV_{\text{eq}}}{dT}$$

Bulk modulus

$$B = V\frac{\partial^2 F(V,T)}{\partial V^2}$$

Isochoric heat capacity (constant volume)

$$C_V = -T\frac{\partial^2 F(V,T)}{\partial T^2}$$

Isobaric heat capacity (constant pressure)

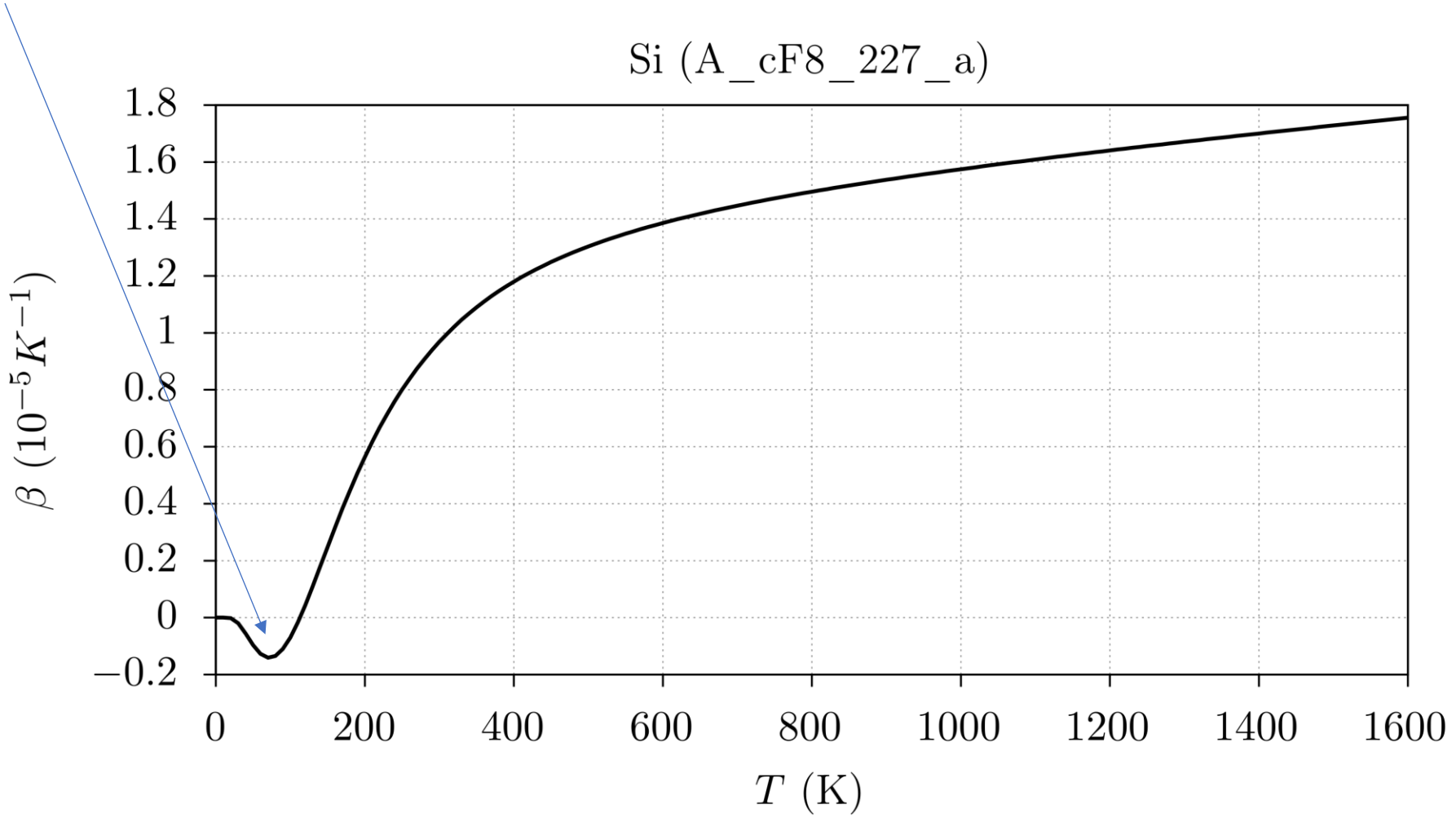
$$C_P = C_V + V_{\text{eq}} B \beta^2 T$$

Grüneisen parameter

$$\gamma = \frac{\beta B V_{\text{eq}}}{C_V}$$

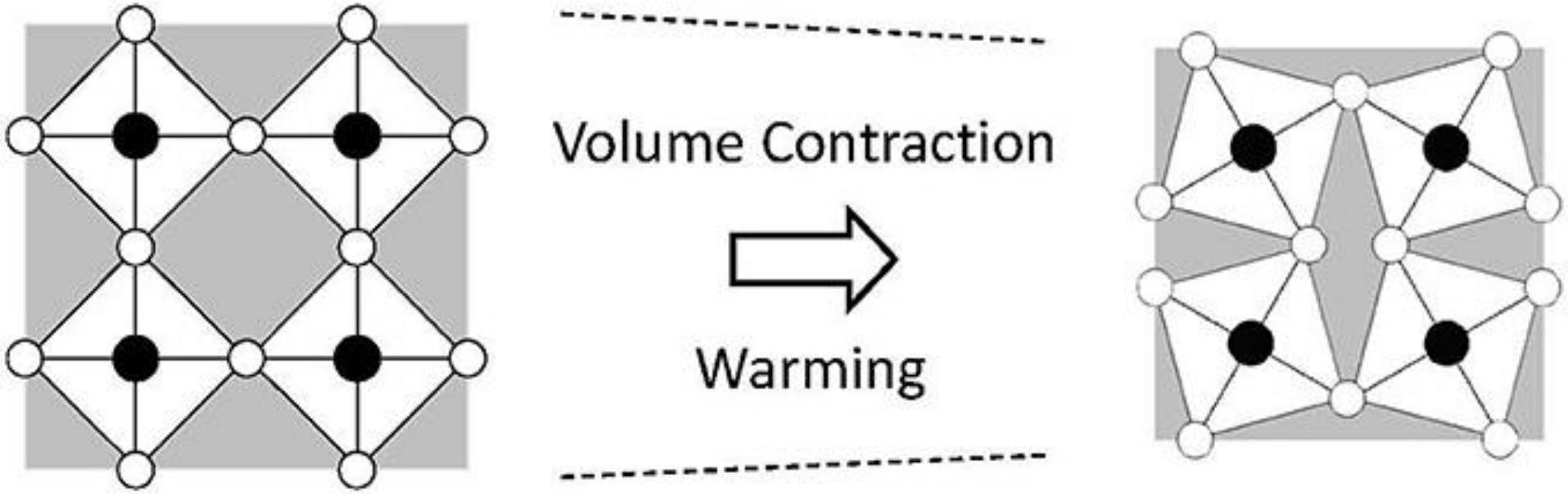
Negative thermal expansion

- Solids change its size under heating (usually they expand)
- Negative thermal expansion: compression under heating



Negative thermal expansion

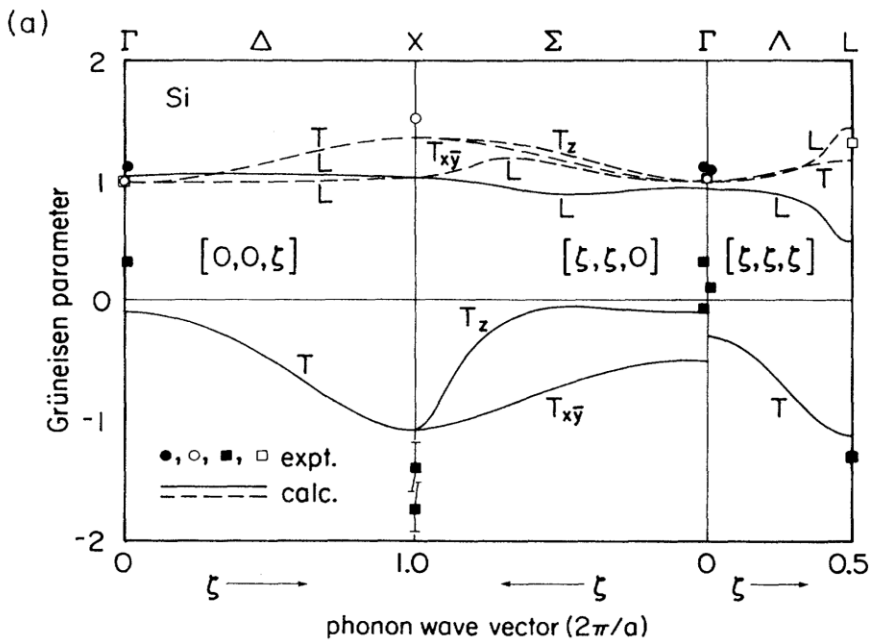
- Solids change its size under heating (usually they expand)
- Negative thermal expansion: compression under heating



Takenaka K (2018) Front. Chem. 6:267. doi: 10.3389/fchem.2018.00267

Negative thermal expansion

- The negative values of mode Grüneisen parameter pinpoint modes responsible for the NTE



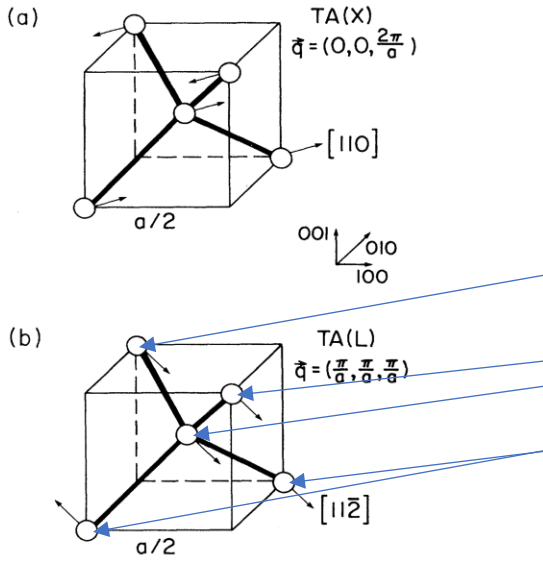
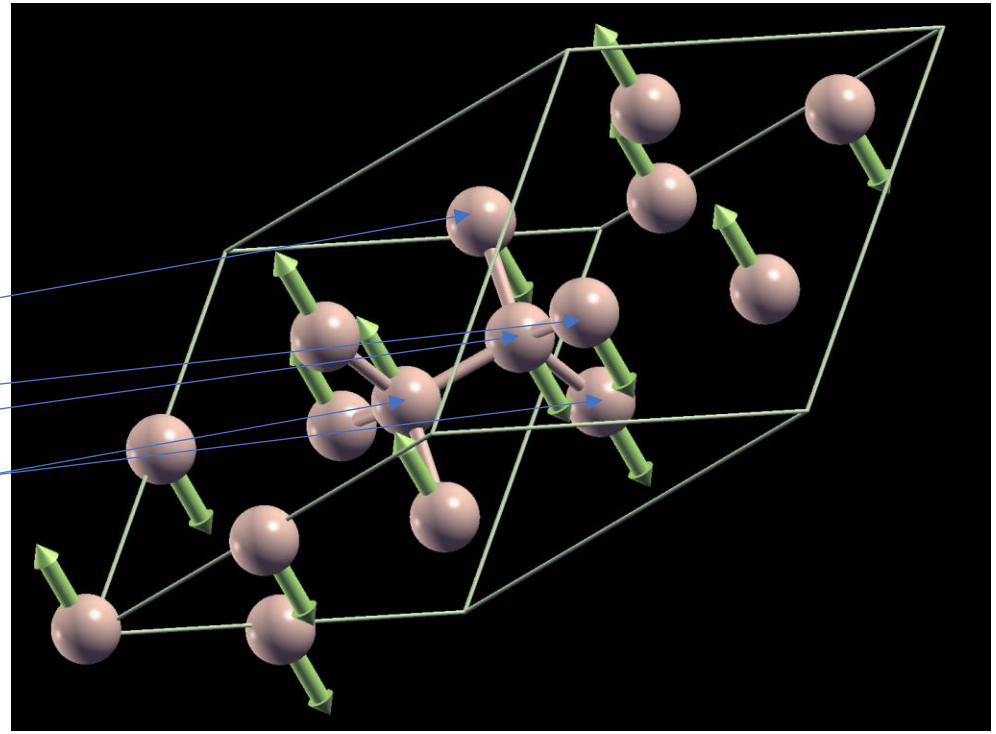
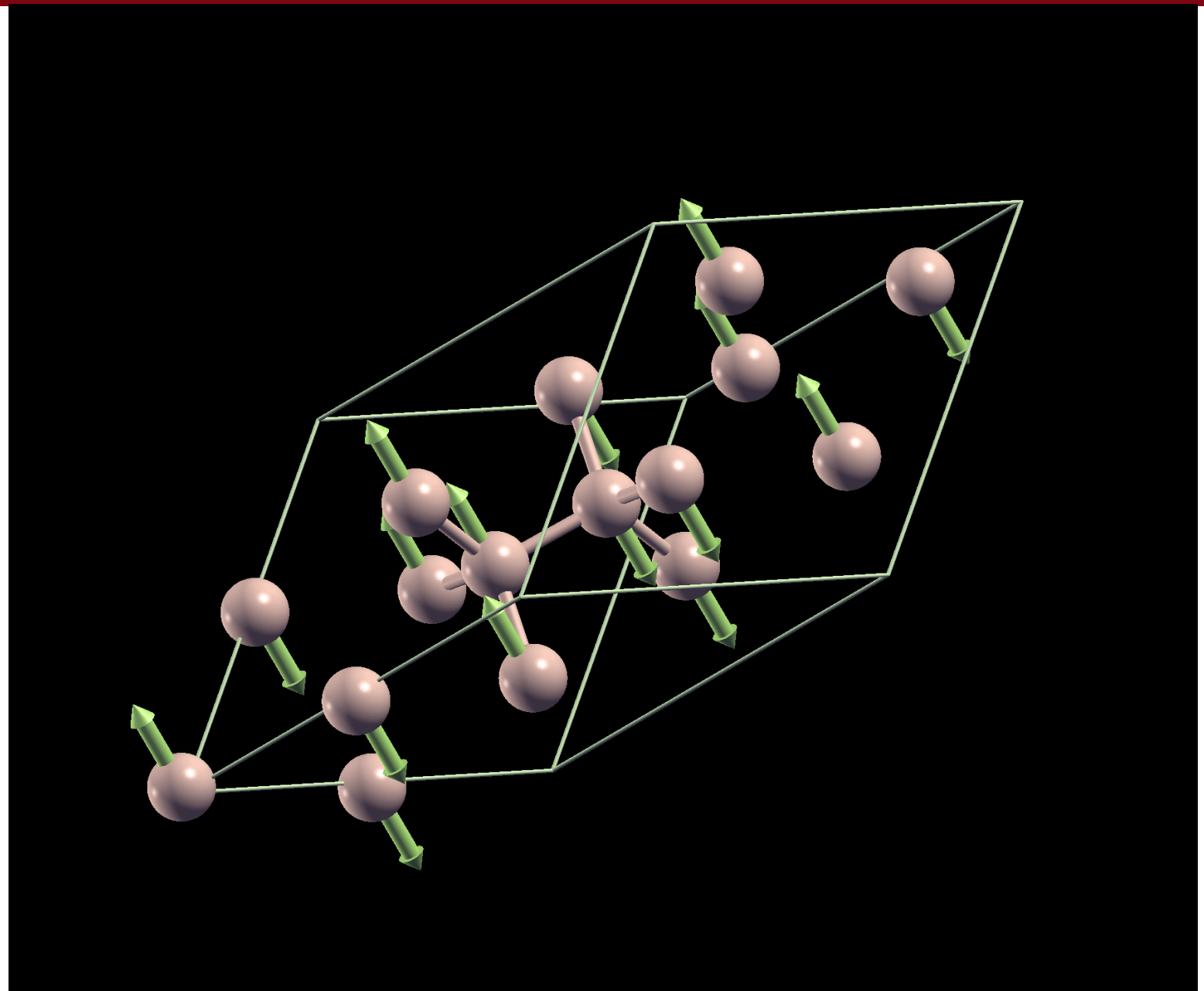


FIG. 4. Vibrational motion corresponding to the (a) TA(X) mode and (b) TA(L) mode in the diamond structure. The displacements of the ions are along the [110] direction in (a) and along the $[11\bar{2}]$ direction in (b).



Xu C.H. (1991) Phys. Rev. B **43**, 5024. https://doi.org/10.1103/PhysRevB.43.5024

Negative thermal expansion



Exercise 3

Setup will be done for silicon with diamond structure

- Go to the directory `Ex3`
- Run the following command to generate the `aflow.in` file:

```
aflow --aflow_proto=A_cF8_227_a:Si --module=qha
```

- Go to the AFLOWDATA/Si:PAW_PBE/A_cF8_227_a.A directory
- Make sure that `[AFLOW_QHA]CALC` is uncommented
- Make the following changes:

```
[AFLOW_APL]POLAR=OFF
[AFLOW_APL]RELAX=OFF
[AFLOW_QHA]EOS_DISTORTION_RANGE=-3:6:1
```

- How many volumes do you expect?
- Run the following command to start the QHA preprocessing step:

```
aflow --run
```

- Check if your expectation was correct.

Exercise 4

Calculation will be done for silicon with diamond structure.

- Go to the directory `Ex4` and open the `aflow.in` file
- Uncomment `[AFLOW_QHA]CALC`
- Make the following changes:

```
[AFLOW_QHA]EOS_DISTORTION_RANGE=-3:6:1
```

In case of the successful run, the `afow.qha.thermo.out.xz` file should be present

- Plot thermodynamic data:

```
aflow --plotthermoqha
```

- Examine the produced pdf files, notice the coefficient of thermal expansion is negative at low temperature
- Open the aflow.qha.thermo.out.xz file and determine the value of the thermal expansion (beta) at T = 70 K and T = 300 K, the bulk modulus (B) at T = 0 K and the isochoric heat capacity (Cv) at T = 1200 K.