Lattice Dynamics and Phonons: AFLOW-APL

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Textbooks on Phonons

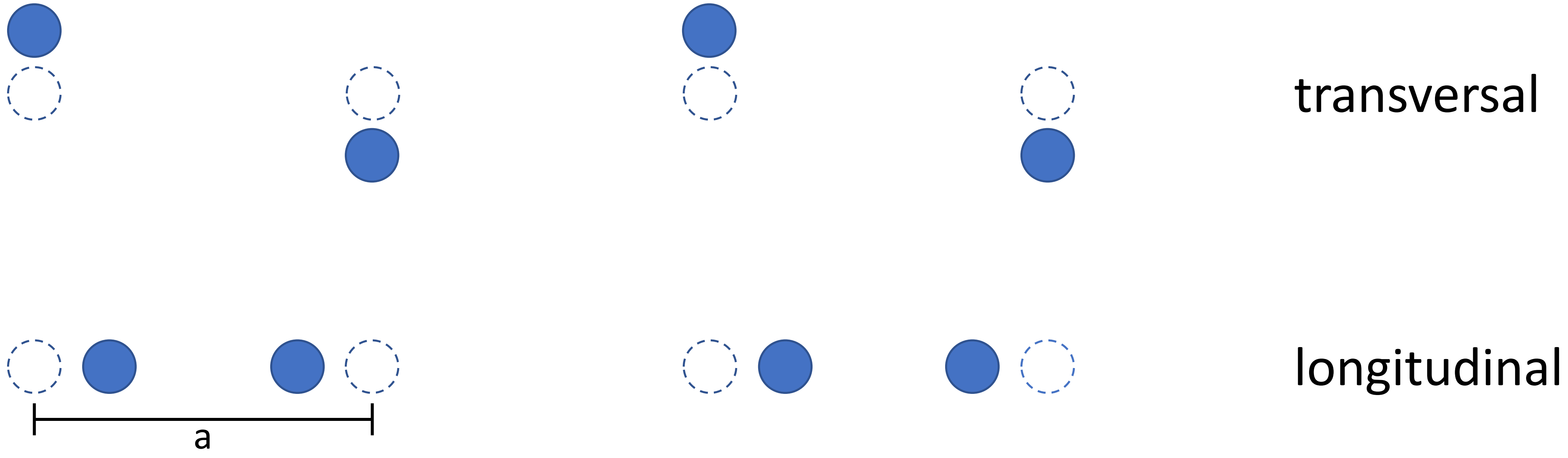
- Introductory:
  - *Solid State Physics* (Ashcroft and Mermin)
  - *Introduction to Solid State Physics* (Kittel)
  - *Fundamentals of the Physics of Phonons, Vol. 1* (Sólyom)
- Theory of phonons:
  - *Theory of Lattice Dynamics in the Harmonic Approximation* (Maradudin)
  - *Thermodynamics of Crystals* (Wallace)
  - *Physics of Phonons* (Srivastava)
  - *Electrons and Phonons* (Ziman)

What are Phonons?

- Phonons describe vibrational motions of atoms on a lattice (lattice vibrations)
- They are a collective property (not confined to unit cell)
- Responsible/important for a many physical properties
  - Thermal properties, thermal conductivity
  - Electrical conductivity, thermoelectricity, superconductivity
  - Phase stability

Phonons in a Monoatomic Basis

- Each atom has 3 degrees of freedom (*x*, *y*, *z*)
- Two transversal and one longitudinal oscillation

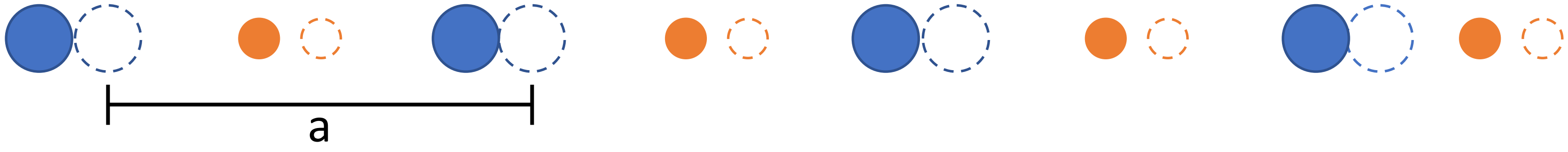


$$\lambda = 2a; \mathbf{q} = \frac{2\pi}{a}\left(\frac{1}{2}, 0, 0\right)$$

Phonons in a Diatomic Basis

Atoms can oscillate in phase (acoustic phonons, long wavelengths)

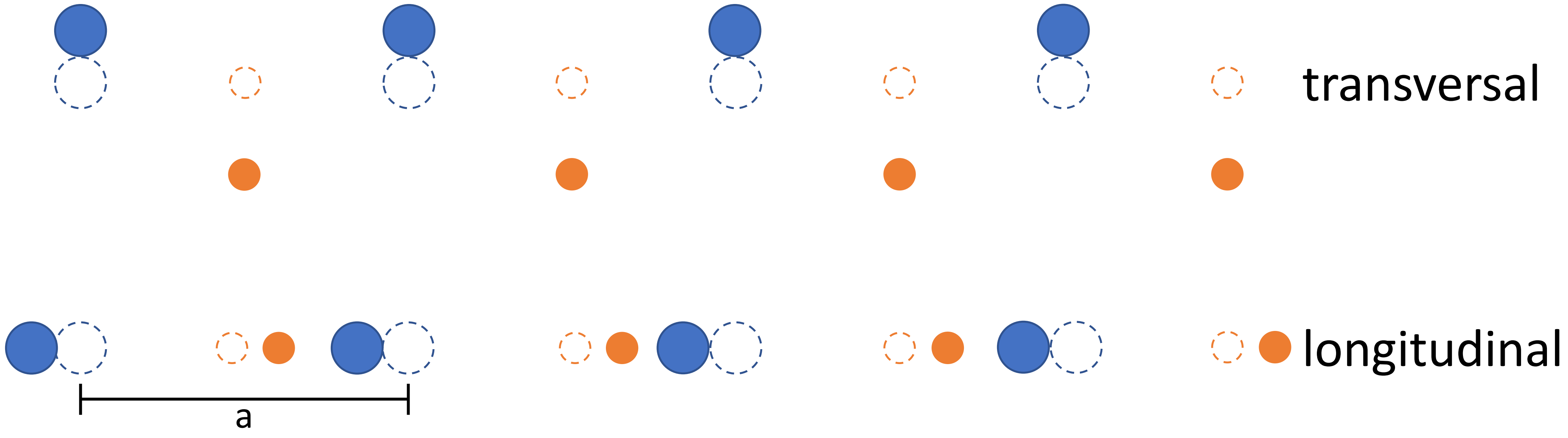
transversal



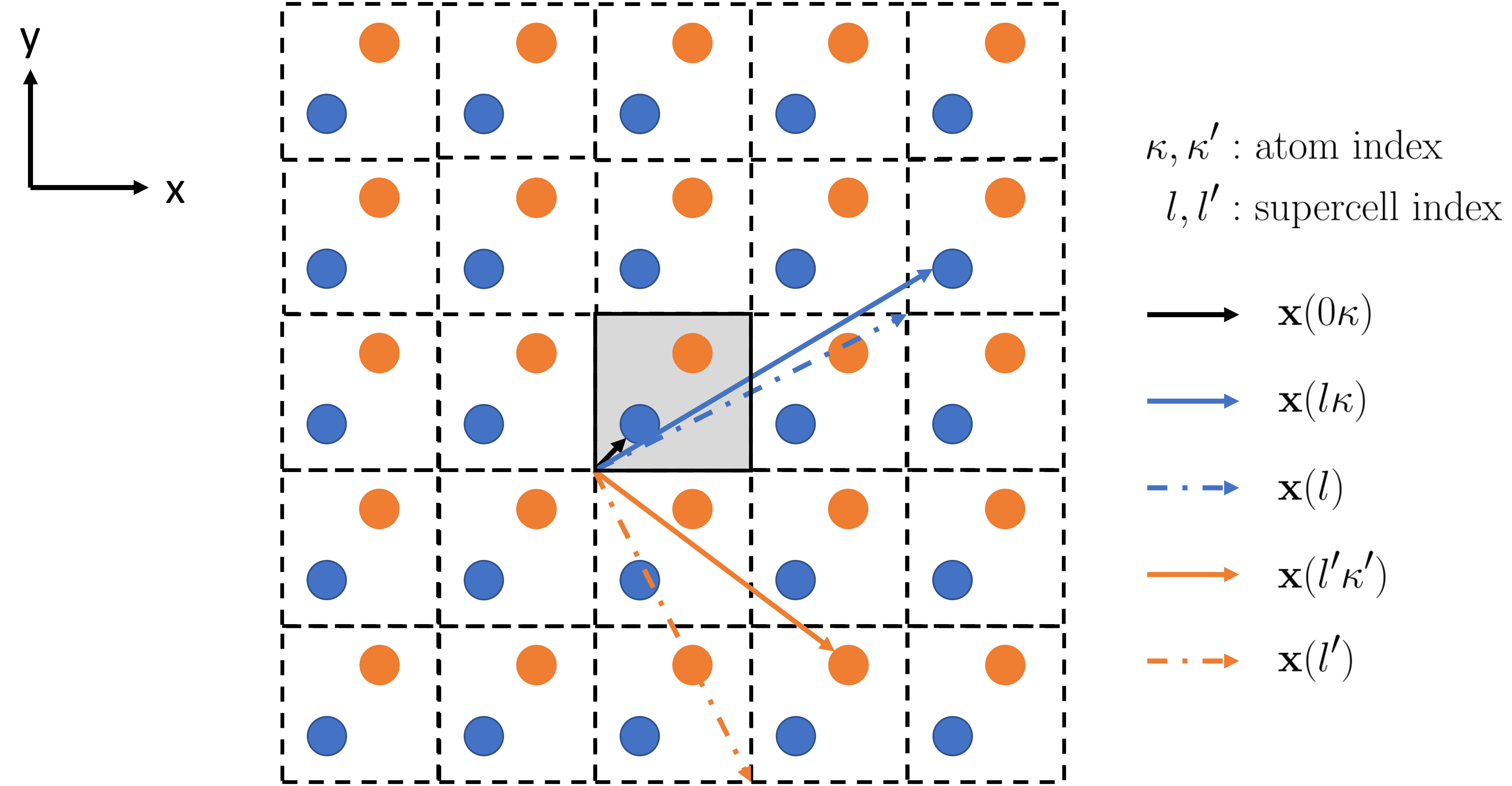
longitudinal

Phonons in a Diatomic Basis

Atoms can oscillate out of phase (optical phonons, long wavelengths)



Supercells


y
x
κ, κ' : atom index
l, l' : supercell index
$\mathbf{x}(0\kappa)$
$\mathbf{x}(l\kappa)$
$\mathbf{x}(l)$
$\mathbf{x}(l'\kappa')$
$\mathbf{x}(l')$

The Harmonic Approximation

- Potential energy:

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

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

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

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:

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

The Harmonic Approximation

- Equation of motion:

$$M\ddot{u}_\alpha(l\kappa) = -\frac{\partial \Phi}{\partial u_\alpha(l\kappa)}$$

- Which has the solution:

$$u_\alpha(l\kappa) = \frac{u_\alpha(\kappa)}{\sqrt{M_\kappa}} \exp\left[i\mathbf{q}\cdot\mathbf{x}(l) - i\omega t\right]$$

- Plugging solution into each side:

$$M_\kappa \ddot{u}_\alpha(l\kappa) = -\omega^2 u_\alpha(\kappa)\sqrt{M_\kappa} \exp\left[i\mathbf{q}\cdot\mathbf{x}(l) - i\omega t\right]$$

$$-\frac{\partial \Phi}{\partial u_\alpha(l\kappa)} = -\sum_{l'\kappa'\beta} \Phi_{\alpha\beta}(l\kappa; l'\kappa') u_\beta(l'\kappa') = -\sum_{l'\kappa'\beta} \Phi_{\alpha\beta}(l\kappa; l'\kappa') \frac{u_\beta(\kappa')}{\sqrt{M_{\kappa'}}} \exp\left[i\mathbf{q}\cdot\mathbf{x}(l') - i\omega t\right]$$

The Harmonic Approximation

- The equation of motion is thus:

$$-\omega^2 u_\alpha(\kappa)\sqrt{M_\kappa}\exp\left[i\mathbf{q}\cdot\mathbf{x}(l)-i\omega t\right] = -\sum_{l'\kappa'\beta}\Phi(l\kappa;l'\kappa')\frac{u_\beta(\kappa')}{\sqrt{M'_\kappa}}\exp\left[i\mathbf{q}\cdot\mathbf{x}(l')-i\omega t\right]$$

- Rearrange:

$$\begin{aligned}\omega^2 u_\alpha(\kappa) &= \sum_{l'\kappa'\beta}\frac{\Phi_{\alpha\beta}(l\kappa;l'\kappa')}{\sqrt{M_\kappa M_{\kappa'}}}\exp\left[i\mathbf{q}\cdot\left(\mathbf{x}(l')-\mathbf{x}(l)\right)\right]u_\beta(\kappa')\\ &= \sum_{\kappa'\beta}u_\beta(\kappa')\sum_{l'}\frac{\Phi_{\alpha\beta}(l\kappa;l'\kappa')}{\sqrt{M_\kappa M_{\kappa'}}}\exp\left[i\mathbf{q}\cdot\left(\mathbf{x}(l')-\mathbf{x}(l)\right)\right]\\ &= \sum_{\kappa'\beta}D_{\alpha\beta}\left(\kappa\kappa'|\mathbf{q}\right)u_\beta(\kappa')\end{aligned}$$

The Harmonic Approximation

- Equation of motion becomes an eigenvalue problem:

$$\boxed{\omega_\lambda^2 \mathbf{e}_\lambda = D(\mathbf{q})\mathbf{e}_\lambda}$$

$$\lambda = \{\mathbf{q}; j\}$$
$$j : 1, 2, \ldots, 3N$$

- Dynamical matrix ($3N_{\text{atoms}} \times 3N_{\text{atoms}}$ matrix):

$$D\left(\kappa\kappa'|\mathbf{q}\right) = \sum_{l'} \frac{\Phi(l\kappa; l'\kappa')}{\sqrt{M_\kappa M_{\kappa'}}} \exp\left[i\mathbf{q}\cdot\left(\mathbf{x}(l') - \mathbf{x}(l)\right)\right]$$

- Atomic displacements:

$$\mathbf{u}(l\kappa) = \frac{\mathbf{e}_\lambda(\kappa)}{\sqrt{M_\kappa}} \exp\left[i\mathbf{q}\cdot\mathbf{x}(l) - i\omega t\right]$$

The Harmonic Approximation – Summary

- Potential energy in the harmonic approximation

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

- Equation of motion

$$M \ddot{u}_\alpha(l\kappa) = -\frac{\partial \Phi}{\partial u_\alpha(l\kappa)}$$

- Becomes an eigenvalue problem

$$\omega_\lambda^2 \mathbf{e}_\lambda = D(\mathbf{q}) \mathbf{e}_\lambda$$

- With the dynamical matrix

$$D\left(\kappa\kappa'|\mathbf{q}\right) = \sum_{l'} \frac{\Phi(l\kappa; l'\kappa')}{\sqrt{M_\kappa M_{\kappa'}}} \exp\left[i\mathbf{q} \cdot \left(\mathbf{x}(l') - \mathbf{x}(l)\right)\right]$$

Calculating Force Constants

- Definition of force constants:

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

- Central difference method for derivatives:

$$f'(x) = \frac{f(x_0 + \Delta x) - f(x_0 - \Delta x)}{2\Delta x}$$

$$\Phi_{\alpha\beta}(l\kappa; l'\kappa') = \frac{\frac{\partial \Phi(u_\alpha(l\kappa)+\Delta u)}{\partial u_\beta(l'\kappa')} - \frac{\partial \Phi(u_\alpha(l\kappa)-\Delta u)}{\partial u_\beta(l'\kappa')}}{2\Delta u}$$

$$= -\frac{F_\beta(l'\kappa', u_\alpha(l\kappa) + \Delta u) - F_\beta(l'\kappa', u_\alpha(l\kappa) - \Delta u)}{2\Delta u}$$

Recall: $\frac{\partial \Phi}{\partial u_\beta(l'\kappa')} = -F_\beta(l'\kappa')$

Calculating Force Constants

- Strategy:
  1. Relax unit cell structure – forces must be as close to zero as possible!
  2. Create supercell structures with displaced atoms
  3. Calculate forces using DFT
  4. Determine force constants
  5. Calculate dynamical matrix and solve the eigenvalue problem
- Simplifications:
  - Translational invariance: only distort atoms in the unit cell
  - Use symmetry to reduce the number of distortions
- Supercell size:
  - Must be large enough to capture all interactions
  - Atoms should not interact with their periodic images

Example: Aluminum

- Create the aflow.in file:

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

- Change the following settings in the file:

```
[AFLOW_APL]KPPRA=1000
[AFLOW_APL]MINATOMS=100
[AFLOW_APL]POLAR=OFF
[AFLOW_VASP_FORCE_OPTION]SPIN=OFF
```

- Run aflow and look at the file aflow.apl.fccalc_state.out.xz

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

Example: Aluminum

- Inside the exercise directory, cd to Al and run aflow

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

- Plot phonon dispersions and densities of states:

```
aflow --plotphdispdos --print=png --outfile=Al_phdispdos
```

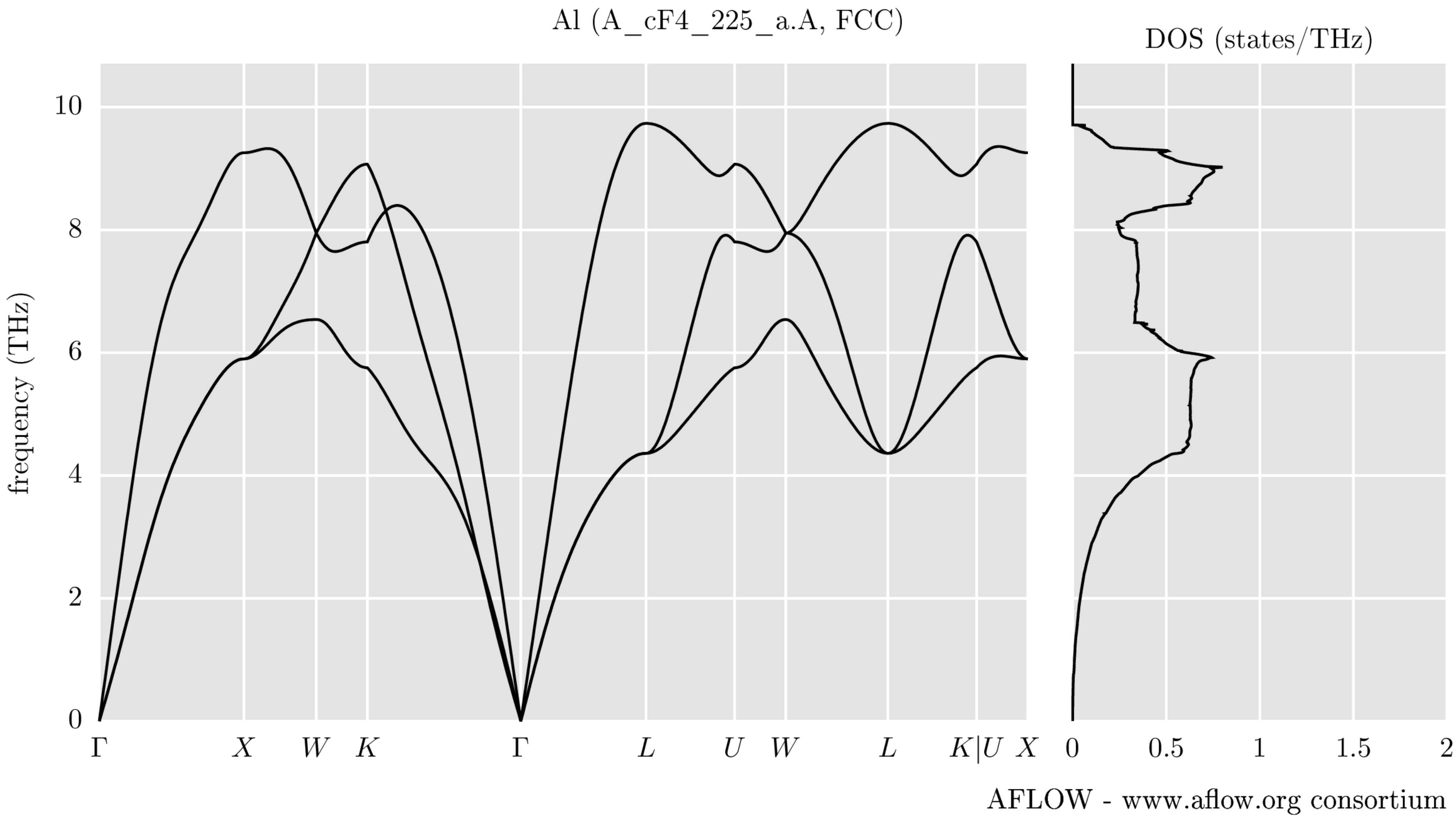
- Check out the following property files and get the properties at 300 K:

```
aflow.apl.thermodynamic_properties.out.xz
aflow.apl.displacements.out.xz
```

- Plot the thermodynamic properties:

```
aflow --plotthermo --print=png --outfile=Al
```

Example: Aluminum



Thermodynamic Properties

Zero-point energy
$$U_0 = \int_0^\infty \frac{\hbar\omega}{2} g(\omega) d\omega$$

Free energy
$$F_{\text{vib}} = U_0 + k_B T \int_0^\infty \ln\left[1 - \exp\left(\frac{\hbar\omega}{k_B T}\right)\right] g(\omega) d\omega$$

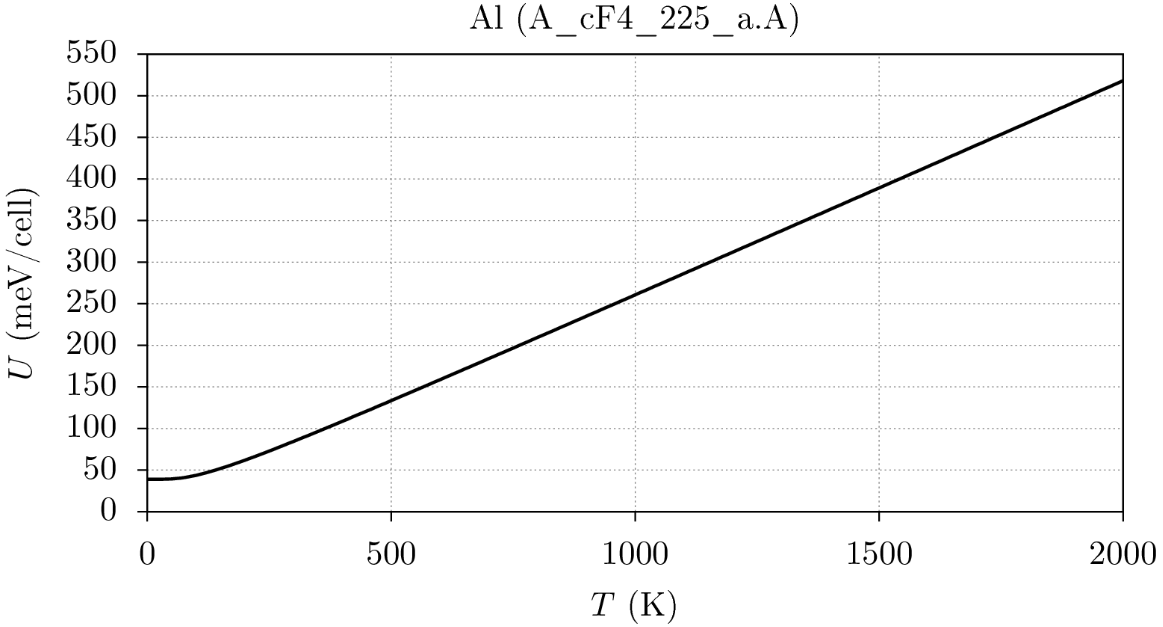
Internal energy
$$U_{\text{vib}} = F_{\text{vib}} - \left(\frac{\partial F_{\text{vib}}}{\partial F}\right)_V = U_0 + \int_0^\infty \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} g(\omega) d\omega$$

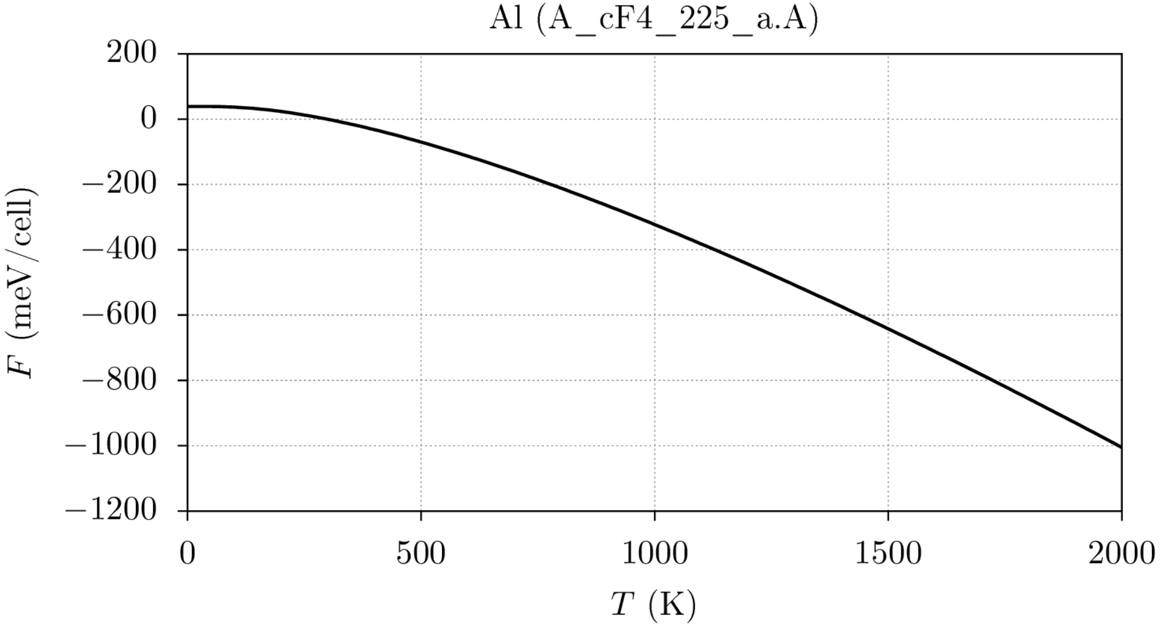
Entropy
$$S_{\text{vib}} = -\left(\frac{\partial F_{\text{vib}}}{\partial T}\right)_V = \frac{F_{\text{vib}} - U_{\text{vib}}}{T}$$

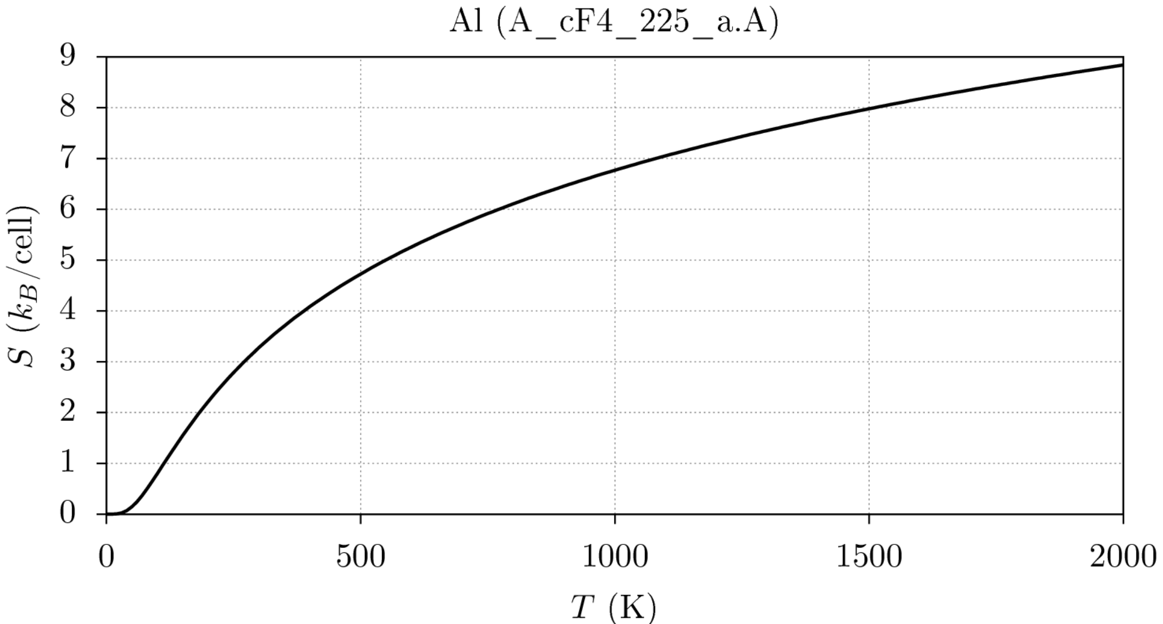
Isochoral heat capacity
$$C_V = \left(\frac{\partial U_{\text{vib}}}{\partial T}\right)_V = k_B \int_0^\infty \left(\frac{\hbar\omega}{2k_B T}\right)^2 \sinh^{-2} \frac{\hbar\omega}{2k_B T} g(\omega) d\omega$$

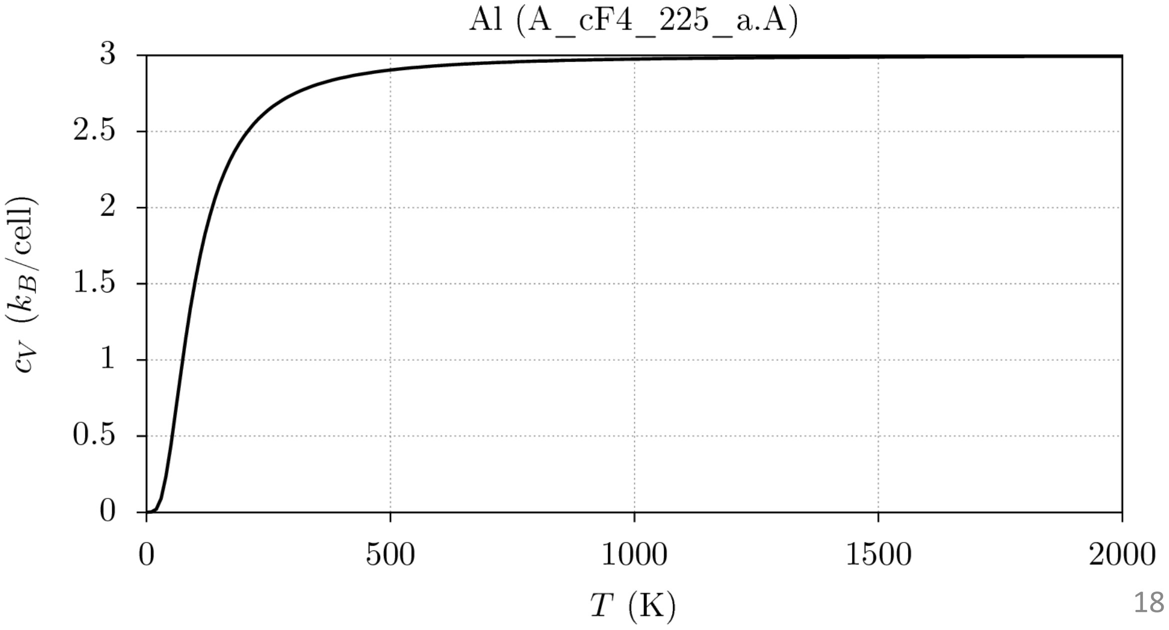
Mean square displacements
$$\left\langle |u^\alpha(j,T)|^2 \right\rangle = \frac{\hbar}{N_q M_j} \sum_\lambda \omega_\lambda^{-1} \left(\frac{1}{2} + n_\lambda\right) \left|\mathbf{e}_\lambda^\alpha(j)\right|^2$$

Thermodynamic Properties









Phonon Numbers

- Phonons are bosons → follow the Bose-Einstein distribution
- Low frequencies (acoustic phonons) dominate at low temperatures

$$\langle n_\lambda \rangle = \frac{1}{\exp\left(\frac{h\nu_\lambda}{k_B T}\right) - 1}$$

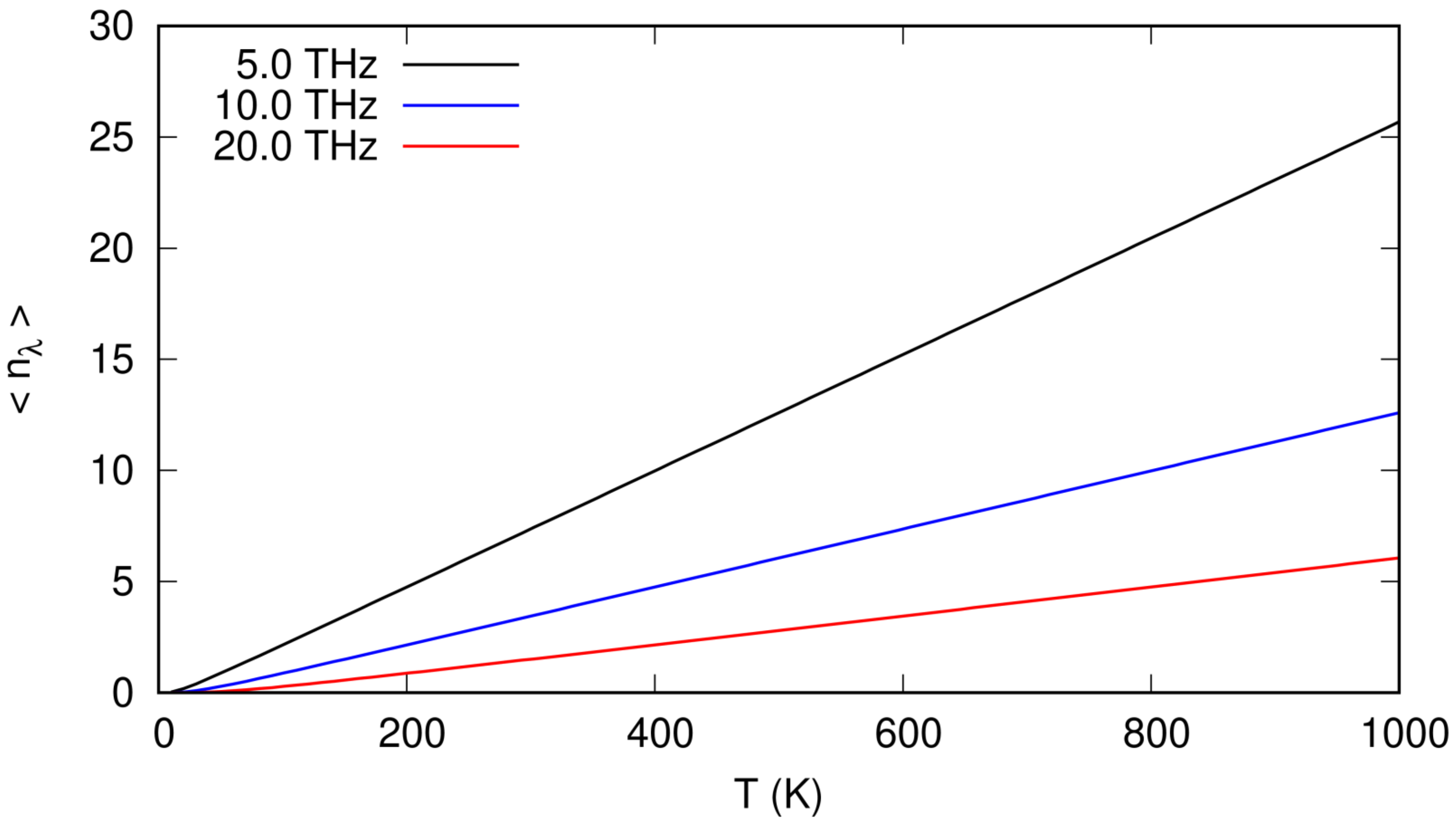
λ : phonon mode

h : Planck constant

ν : frequency

k_B : Boltzmann constant

T : temperature



Exercises

1. Pick one of the following compounds: MgO, BAs, ZnS, NbC. Add the line `[AFLOW_APL]DOS_PROJECT=ON` to the aflow.in file and run aflow:

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

2. Which displacements were created to calculate the force constants (check aflow.apl.fccalc_state.out)?
3. Determine the average mean square displacements and the isochoral heat capacity at 300 K for these compounds (see aflow.apl.displacements.out and aflow.apl.thermodynamic_properties.out).
4. Plot the combined phonon dispersion/projected DOS plot using:

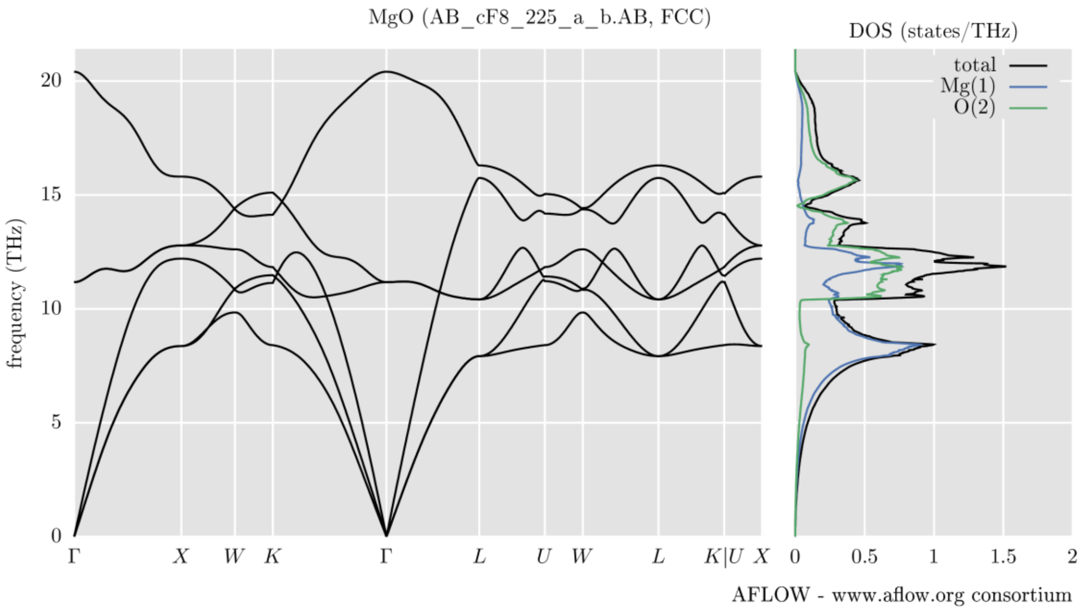
```
aflow --plotphdispdos --print=png --projection=atoms --outfile=filename
```

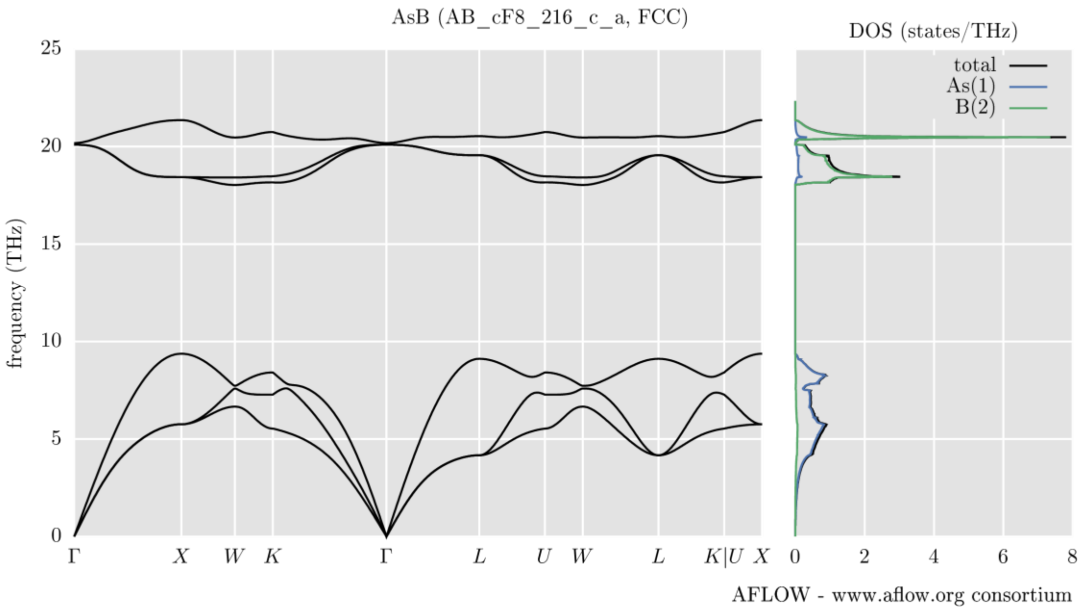
Exercises

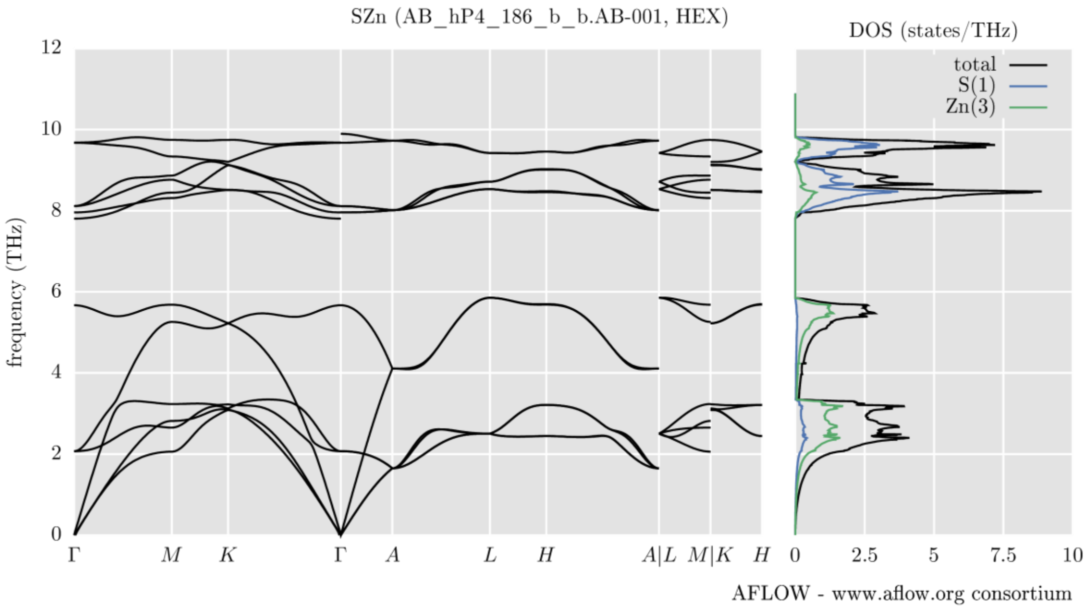
2. Which displacements were created to calculate the force constants?
   - MgO, BAs, NbC: (0, 0.70711, 0.70711) for all atoms (face diagonal)
   - ZnS: (0.31543, -0.54634, 0.77590) for both atoms (body diagonal)
3. Determine the average mean square displacements and the isochoral heat capacity at 300 K for these compounds

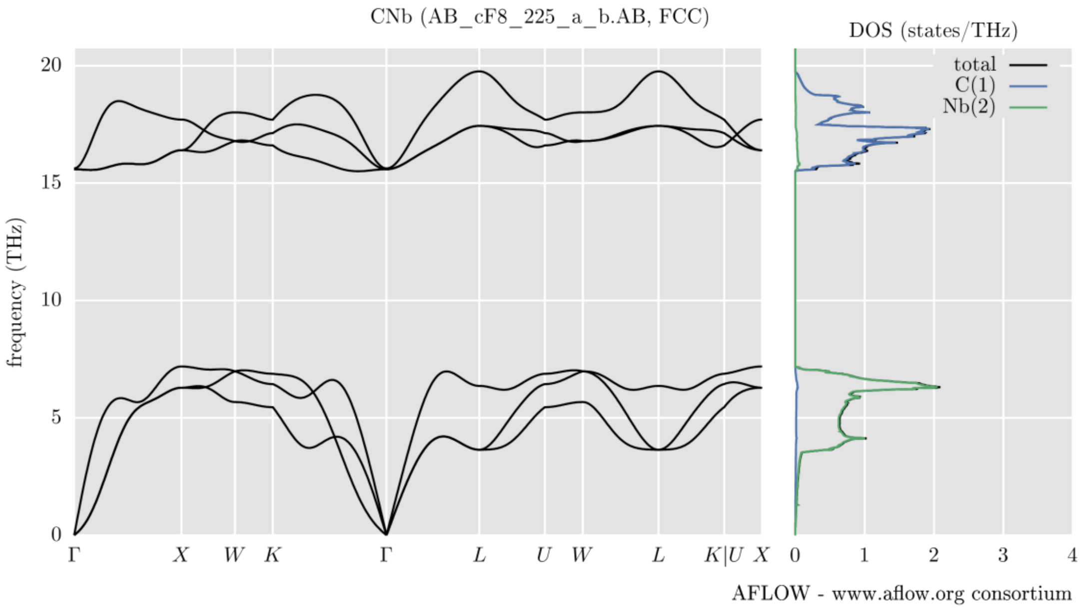
Material	Mean square displacements (Å^2)	c_V (k_B/cell)	No. atoms	c_V (k_B/atom)
MgO	Mg: (0.00421, 0.00421, 0.00421) O: (0.00418, 0.00418, 0.00418)	4.54	2	2.27
Bas	B: (0.00435, 0.00435, 0.00435) As: (0.00305, 0.00305, 0.00305)	4.20	2	2.10
ZnS	Zn: (0.01151, 0.01152, 0.01124) S: (0.00890, 0.00890, 0.00826)	10.92	4	2.73
NbC	Nb: (0.00311, 0.00311, 0.00311) C: (0.00360, 0.00360, 0.00360)	4.47	2	2.23

Projected Phonon DOS

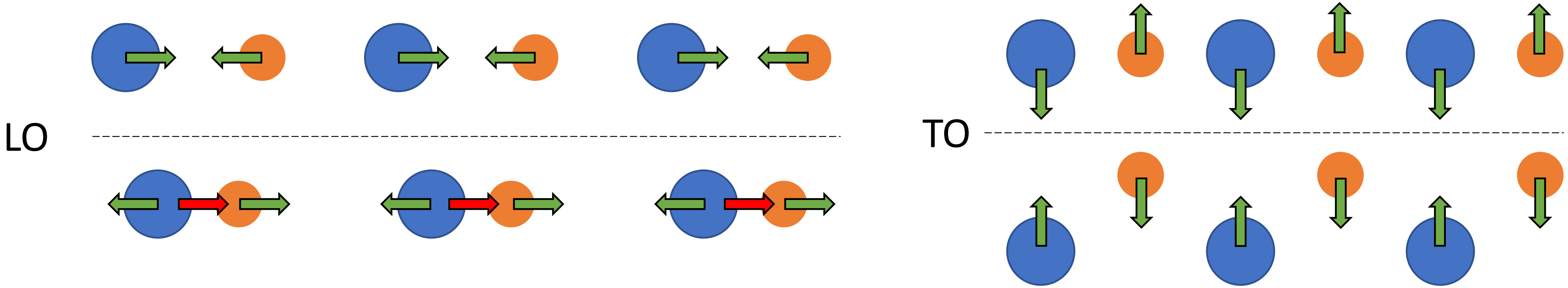








Polar Materials



- In polar materials, displacements generate an electric field
  - LO modes add additional restoring force → higher frequency (LO-TO splitting)
  - Occurs at long wavelengths (small **q**) due to long-range Coulomb interactions
  - Splitting occurs *near* the Γ point (not directly at Γ though)
- Non-analytical correction (NAC) must be added to the dynamical matrix

$$\tilde{D}^{ij}_{\alpha\beta}(\mathbf{q}) = \frac{4\pi}{V} \cdot \frac{[\mathbf{q} \cdot Z^*(i)]_\alpha [\mathbf{q} \cdot Z^*(j)]_\beta}{\mathbf{q} \cdot \varepsilon_\infty \cdot \mathbf{q}}$$

Z^* : effective charge tensor

ε_∞ : dielectric tensor

V : volume

Polar Materials

- Check out the file aflow.apl.polar.xml.xz and note the Born effective charges and the dielectric tensor
- Open the aflow.in file and set `[AFLOW_APL]POLAR=OFF`
- Run aflow using:

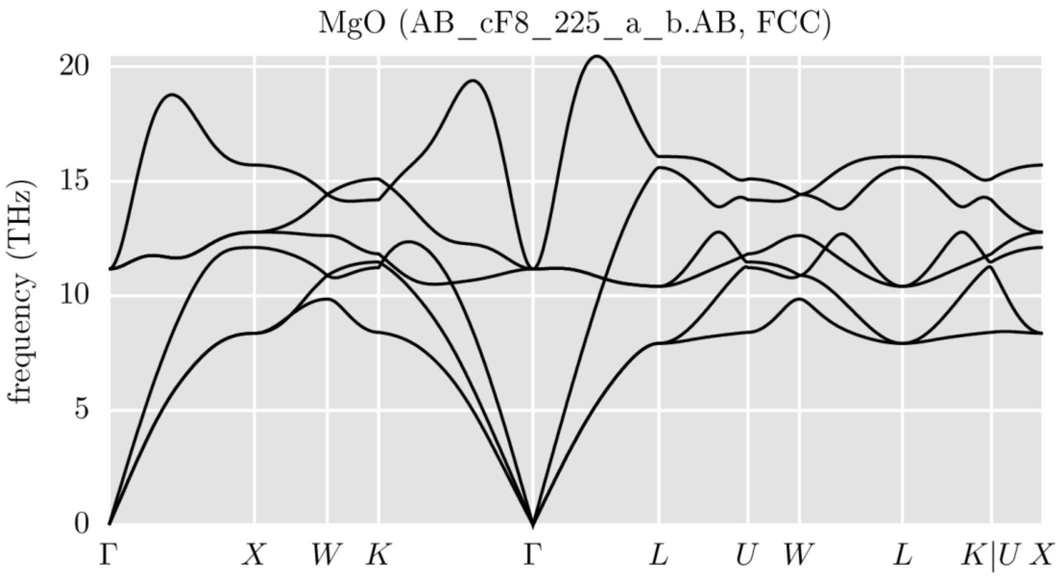
```
aflow --run --use_LOCK=nonpolar.LOCK -D ./
```

- Plot the phonon dispersions:

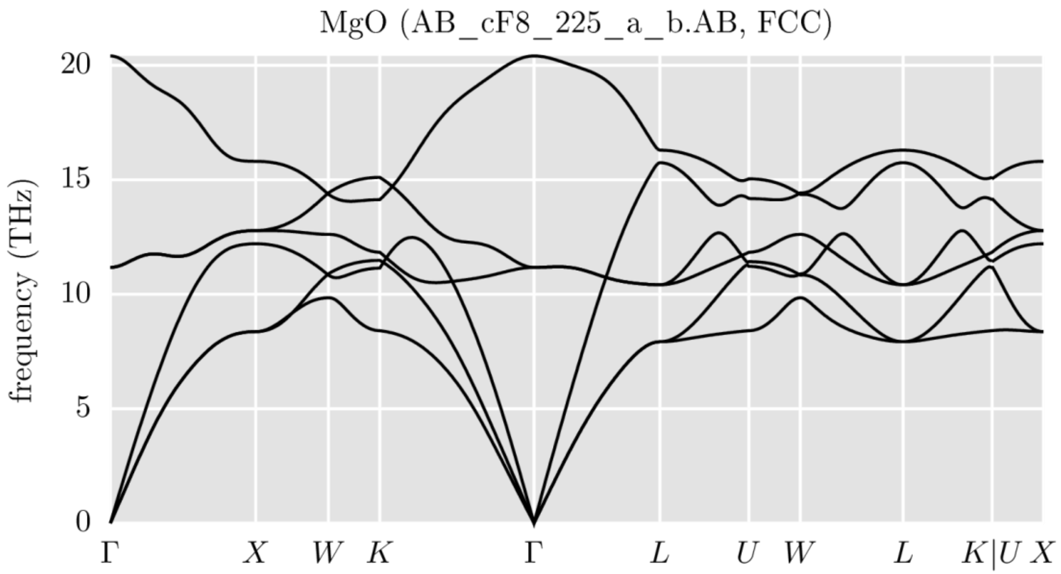
```
aflow --plotphdisp --print=png --outfile=filename
```

Polar Materials

Without NAC



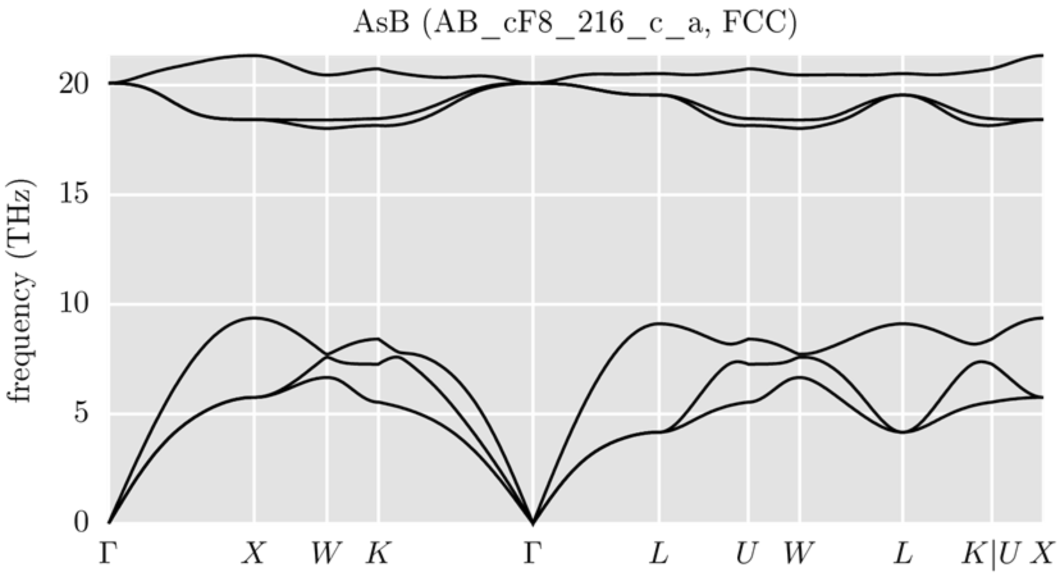
With NAC



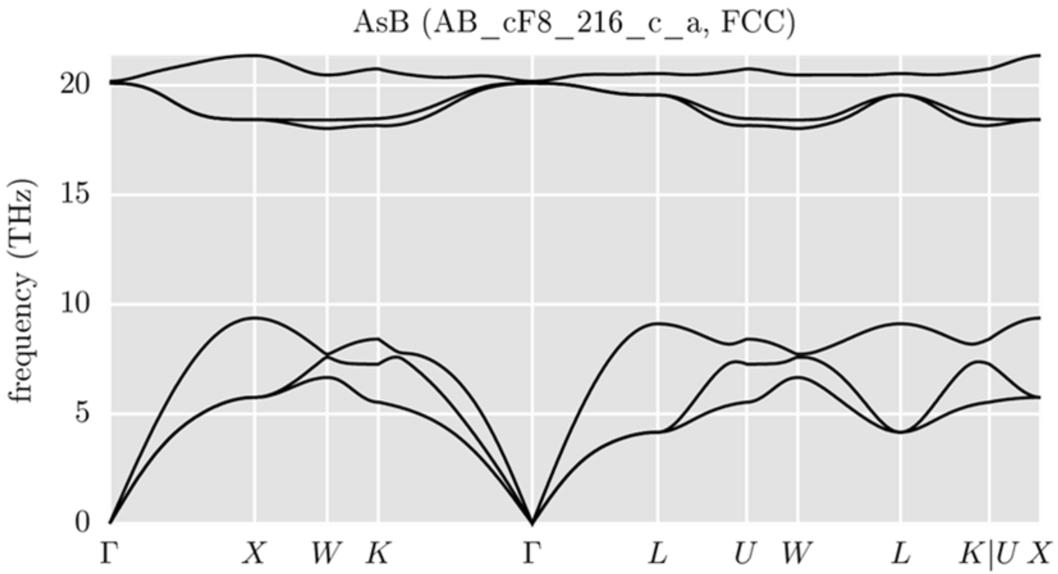
$$Z^*_{\mathrm{Mg}} = \begin{pmatrix} 1.984 & 0 & 0 \\ 0 & 1.984 & 0 \\ 0 & 0 & 1.984 \end{pmatrix}, Z^*_{\mathrm{O}} = \begin{pmatrix} -1.984 & 0 & 0 \\ 0 & -1.984 & 0 \\ 0 & 0 & -1.984 \end{pmatrix}, \varepsilon_\infty = \begin{pmatrix} 3.209 & 0 & 0 \\ 0 & 3.209 & 0 \\ 0 & 0 & 3.209 \end{pmatrix}$$

Polar Materials

Without NAC



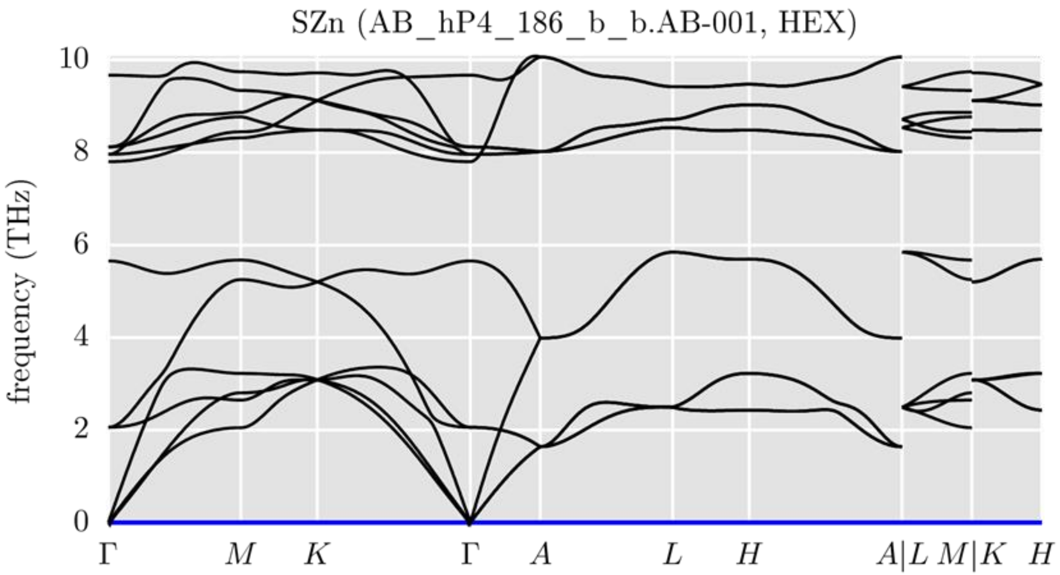
With NAC



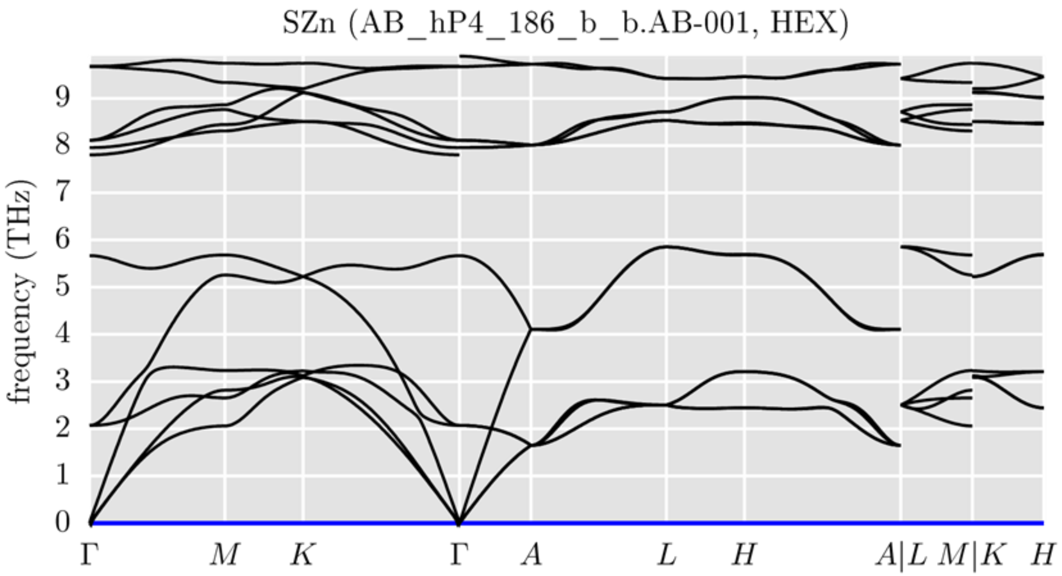
$$Z_{\mathrm{B}}^{*} = \begin{pmatrix} -0.454 & 0 & 0 \\ 0 & -0.454 & 0 \\ 0 & 0 & -0.454 \end{pmatrix}, Z_{\mathrm{As}}^{*} = \begin{pmatrix} 0.454 & 0 & 0 \\ 0 & 0.454 & 0 \\ 0 & 0 & 0.454 \end{pmatrix}, \varepsilon_{\infty} = \begin{pmatrix} 9.843 & 0 & 0 \\ 0 & 9.843 & 0 \\ 0 & 0 & 9.843 \end{pmatrix}$$

Polar Materials

Without NAC



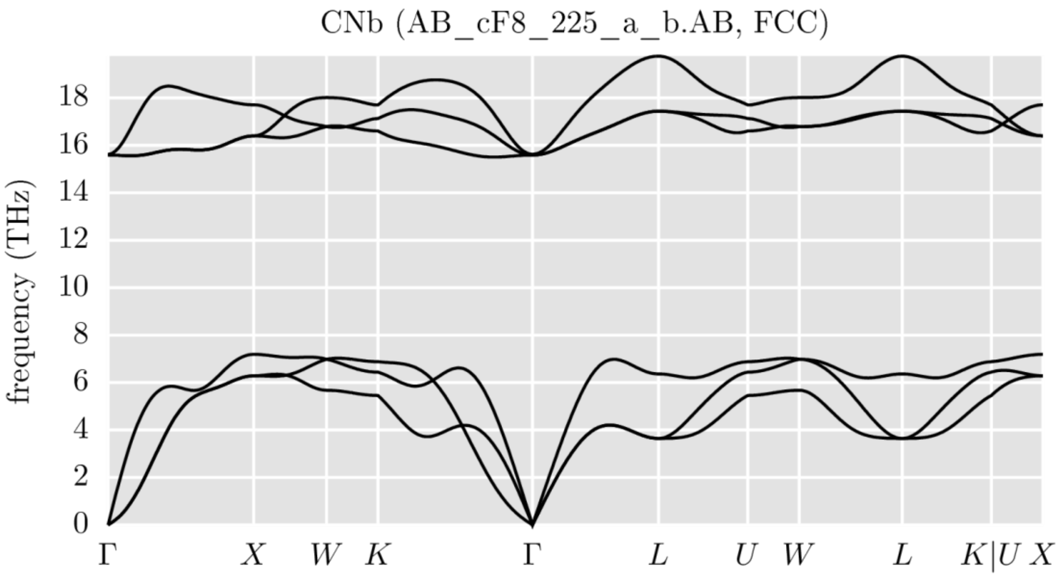
With NAC



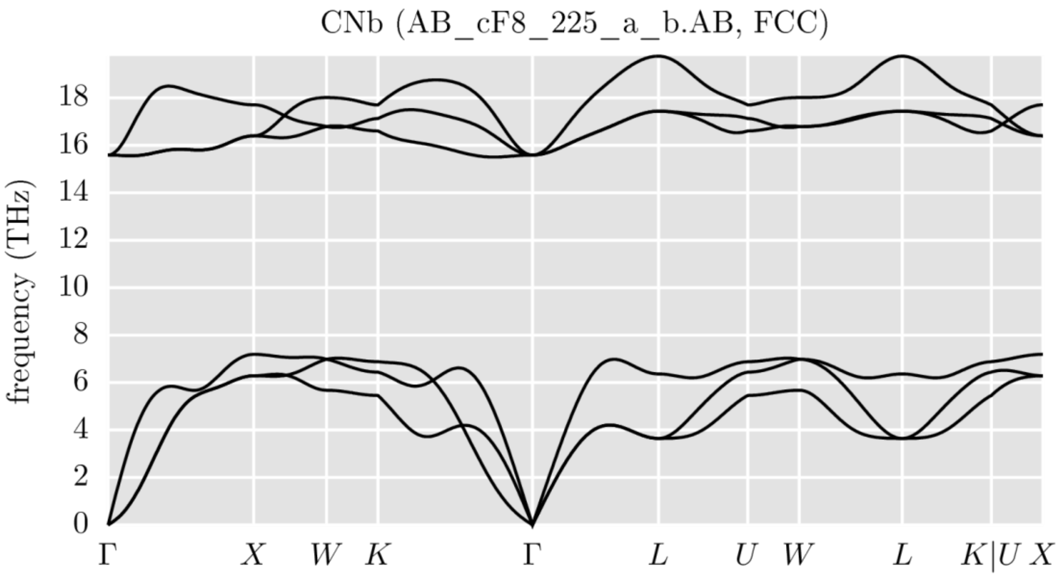
$$Z^*_{\mathrm{Zn}} = \begin{pmatrix} 1.967 & 0 & 0 \\ 0 & 1.967 & 0 \\ 0 & 0 & 1.967 \end{pmatrix}, Z^*_{\mathrm{S}} = \begin{pmatrix} -1.967 & 0 & 0 \\ 0 & -1.967 & 0 \\ 0 & 0 & -1.967 \end{pmatrix}, \varepsilon_\infty = \begin{pmatrix} 5.777 & 0 & 0 \\ 0 & 5.777 & 0 \\ 0 & 0 & 5.777 \end{pmatrix}$$

Polar Materials

Without NAC



With NAC



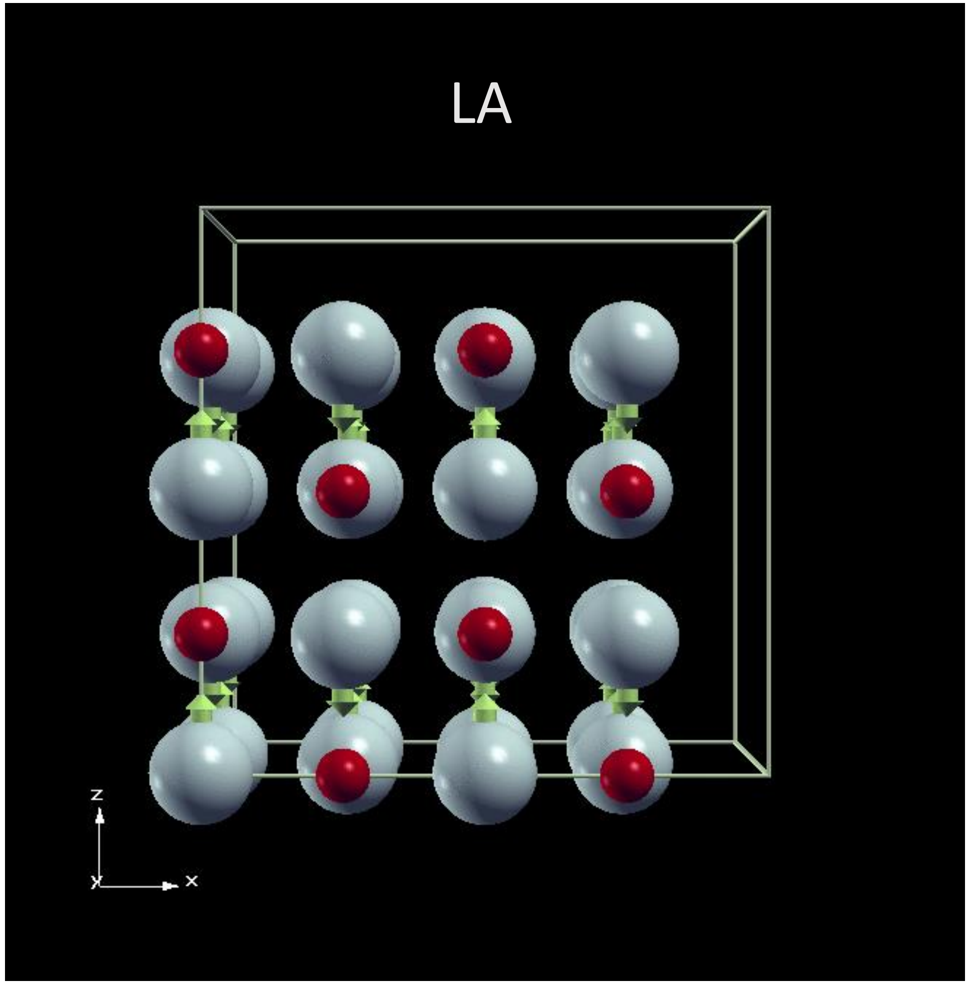
$$Z^*_{\mathrm{Nb}} = \begin{pmatrix} 0.410 & 0 & 0 \\ 0 & 0.410 & 0 \\ 0 & 0 & 0.410 \end{pmatrix}, Z^*_{\mathrm{C}} = \begin{pmatrix} -0.410 & 0 & 0 \\ 0 & -0.410 & 0 \\ 0 & 0 & -0.410 \end{pmatrix}, \varepsilon_\infty = \begin{pmatrix} 27.19 & 0 & 0 \\ 0 & 27.19 & 0 \\ 0 & 0 & 27.19 \end{pmatrix}$$

Visualizing Phonons (MgO, *X* point)

$$\mathbf{u}(l\kappa) = \frac{A}{\sqrt{M_\kappa}} \exp\left[i\mathbf{q}\cdot\mathbf{x}(l) - i\omega_\lambda t\right]\mathbf{e}_\lambda(\kappa)$$

$$\mathbf{b}_1 = \frac{4\pi}{a}\left(-\frac{1}{2}\hat{x} + \frac{1}{2}\hat{y} + \frac{1}{2}\hat{z}\right)$$
$$\mathbf{b}_2 = \frac{4\pi}{a}\left(\frac{1}{2}\hat{x} - \frac{1}{2}\hat{y} + \frac{1}{2}\hat{z}\right)$$
$$\mathbf{b}_3 = \frac{4\pi}{a}\left(\frac{1}{2}\hat{x} + \frac{1}{2}\hat{y} - \frac{1}{2}\hat{z}\right)$$

$$X : \left(\frac{1}{2}, \frac{1}{2}, 0\right) \qquad \mathbf{q} = \frac{2\pi}{a}\hat{z}$$

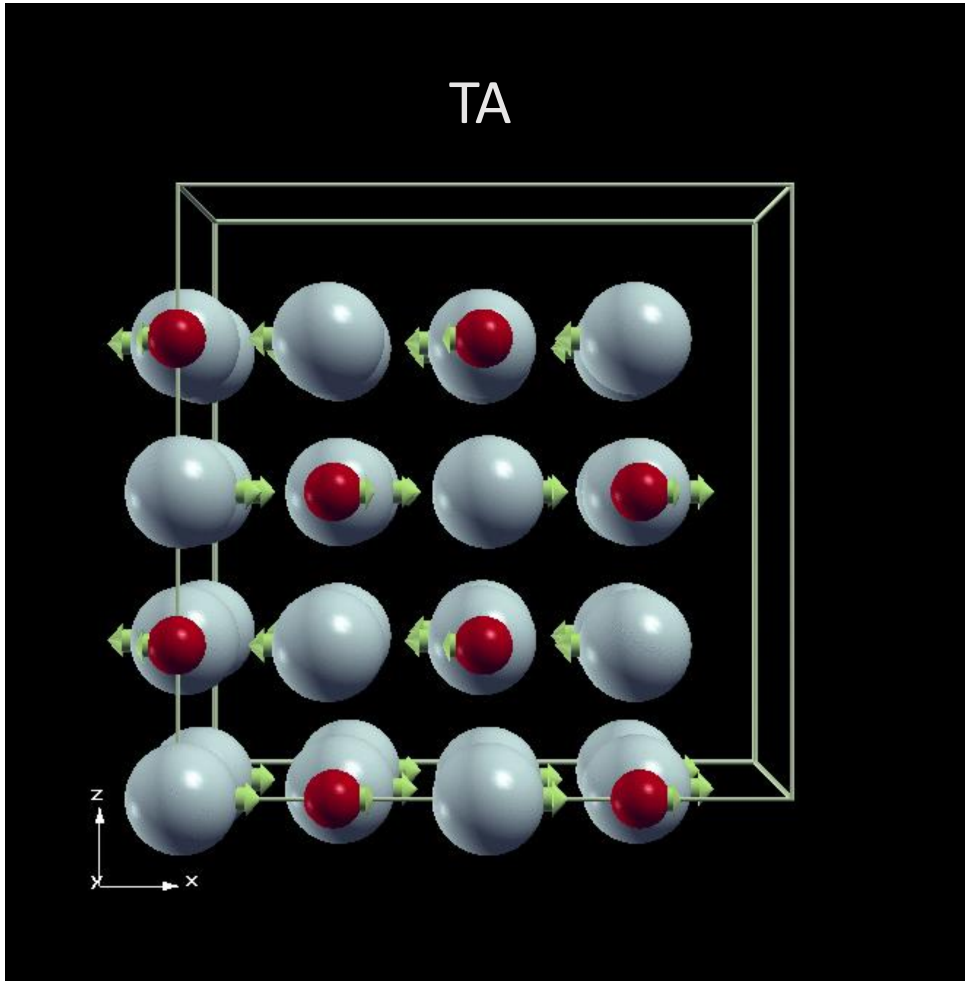


Visualizing Phonons (MgO, *X* point)

$$\mathbf{u}(l\kappa) = \frac{A}{\sqrt{M_\kappa}} \exp\left[i\mathbf{q}\cdot\mathbf{x}(l) - i\omega_\lambda t\right] \mathbf{e}_\lambda(\kappa)$$

$$\mathbf{b}_1 = \frac{4\pi}{a}\left(-\frac{1}{2}\hat{x} + \frac{1}{2}\hat{y} + \frac{1}{2}\hat{z}\right)$$
$$\mathbf{b}_2 = \frac{4\pi}{a}\left(\frac{1}{2}\hat{x} - \frac{1}{2}\hat{y} + \frac{1}{2}\hat{z}\right)$$
$$\mathbf{b}_3 = \frac{4\pi}{a}\left(\frac{1}{2}\hat{x} + \frac{1}{2}\hat{y} - \frac{1}{2}\hat{z}\right)$$

$$X : \left(\frac{1}{2}, \frac{1}{2}, 0\right) \qquad \mathbf{q} = \frac{2\pi}{a}\hat{z}$$

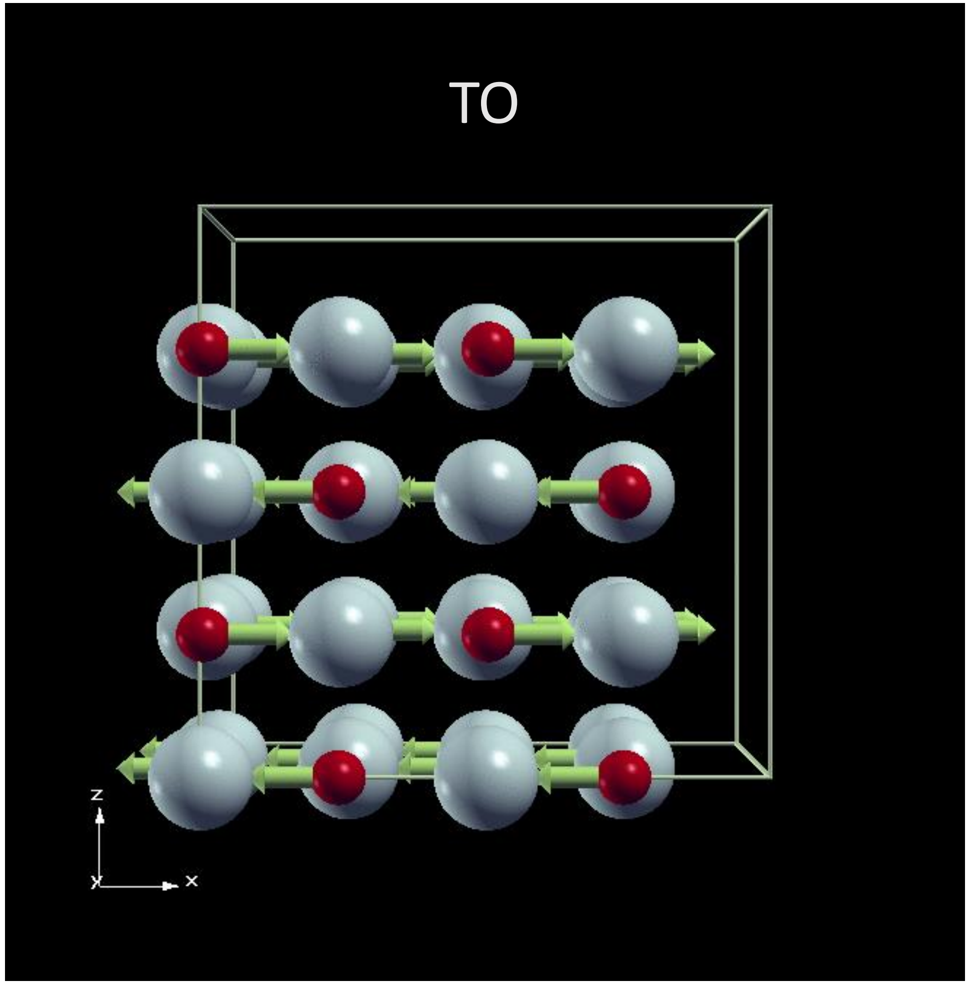


Visualizing Phonons (MgO, *X* point)

$$\mathbf{u}(l\kappa) = \frac{A}{\sqrt{M_\kappa}} \exp\left[i\mathbf{q}\cdot\mathbf{x}(l) - i\omega_\lambda t\right] \mathbf{e}_\lambda(\kappa)$$

$$\mathbf{b}_1 = \frac{4\pi}{a}\left(-\frac{1}{2}\hat{x} + \frac{1}{2}\hat{y} + \frac{1}{2}\hat{z}\right)$$
$$\mathbf{b}_2 = \frac{4\pi}{a}\left(\frac{1}{2}\hat{x} - \frac{1}{2}\hat{y} + \frac{1}{2}\hat{z}\right)$$
$$\mathbf{b}_3 = \frac{4\pi}{a}\left(\frac{1}{2}\hat{x} + \frac{1}{2}\hat{y} - \frac{1}{2}\hat{z}\right)$$

$$X : \left(\frac{1}{2}, \frac{1}{2}, 0\right) \qquad \mathbf{q} = \frac{2\pi}{a}\hat{z}$$

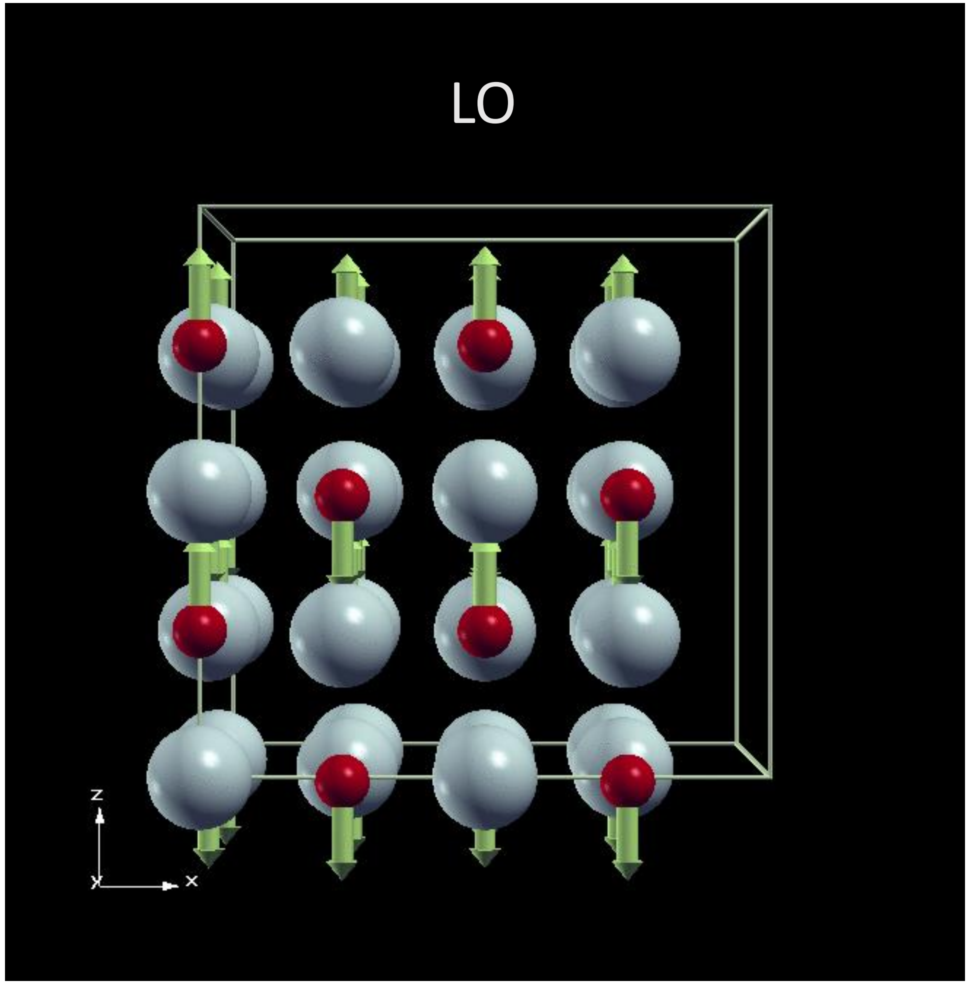


Visualizing Phonons (MgO, *X* point)

$$\mathbf{u}(l\kappa) = \frac{A}{\sqrt{M_\kappa}} \exp\left[i\mathbf{q}\cdot\mathbf{x}(l) - i\omega_\lambda t\right] \mathbf{e}_\lambda(\kappa)$$

$$\mathbf{b}_1 = \frac{4\pi}{a}\left(-\frac{1}{2}\hat{x} + \frac{1}{2}\hat{y} + \frac{1}{2}\hat{z}\right)$$
$$\mathbf{b}_2 = \frac{4\pi}{a}\left(\frac{1}{2}\hat{x} - \frac{1}{2}\hat{y} + \frac{1}{2}\hat{z}\right)$$
$$\mathbf{b}_3 = \frac{4\pi}{a}\left(\frac{1}{2}\hat{x} + \frac{1}{2}\hat{y} - \frac{1}{2}\hat{z}\right)$$

$$X : \left(\frac{1}{2}, \frac{1}{2}, 0\right) \qquad \mathbf{q} = \frac{2\pi}{a}\hat{z}$$



Visualizing Phonons

- Generate XCRYSDEN scene files

```
aflow --visualize_phonons --q=0.5,0.5,0.0 --scell=2x2x2
```

- Open XCRYSDEN
- File → Open Structure → Open AXSF – choose any axsf file
- Adjust the appearance:
  - Display → Forces
  - Display → Coordinate System
  - Display → Unit of Repetition → Translational asymmetric unit
  - Modify → Force Settings → adjust “Length Factor” so that arrows are smaller
  - Optional: Modify → Atomic Radii → Set “Chemical connectivity factor” to 0

Visualizing Phonons

- Modify → Animation Control
  - Set the current slide to 1
  - Expand “Animated GIF/MPEG/AVI”
  - Set “Movie format” to “Animated-GIF”
  - Unset “Edit flags or parameter-file before enoding”
  - Click on “Start Recording Animation”
  - Click the right double-arrow button
  - When on the final slide, click on “Stop Recording Animation”
  - Save the file

Phase Stability

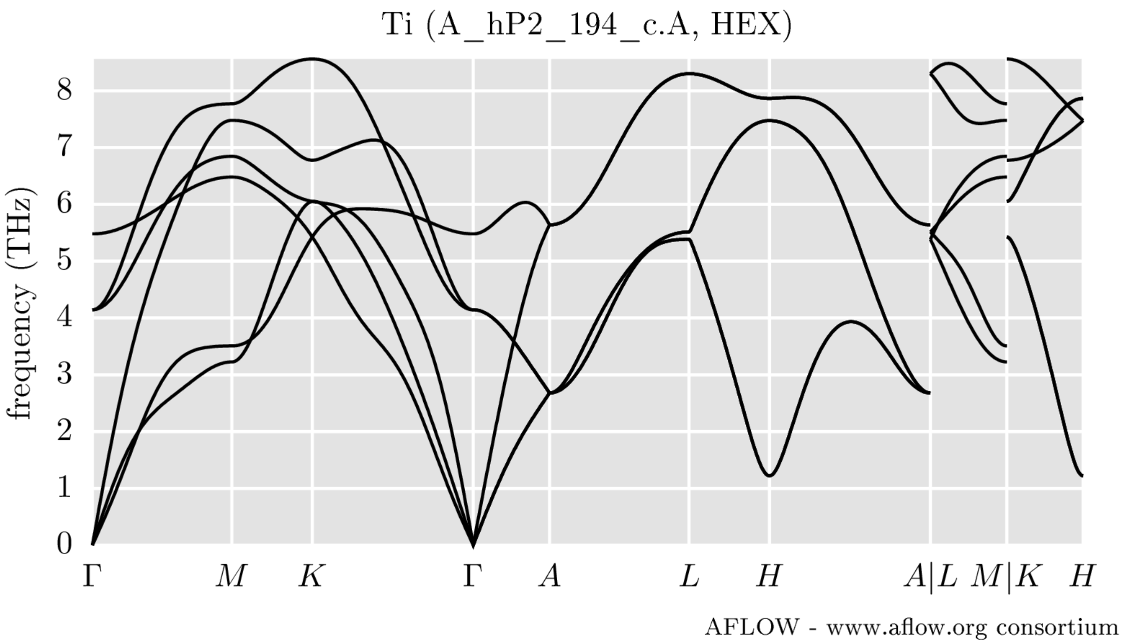
- In equilibrium, displacements increase potential energy $\rightarrow$ forces are restorative
- If not in equilibrium (unstable structures), displacements can decrease potential energy $\rightarrow$ forces are not restorative
- This leads to $\omega^2 < 0$ $\rightarrow$ frequencies become imaginary

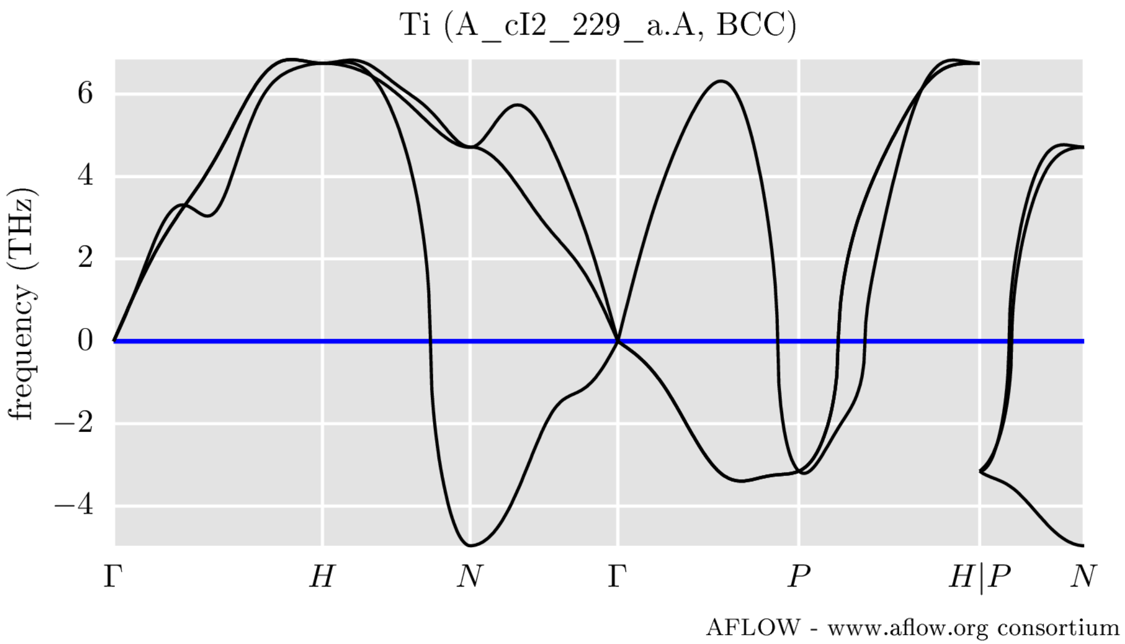
Example: BCC Titanium

- β-Ti (bcc) unstable at room temperature
- Occurs above 1155 K → stabilized by large displacements

$$N : \left(0, 0, \frac{1}{2}\right) \rightarrow 1 \times 1 \times 2 \text{ supercell}$$

$$P : \left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right) \rightarrow 4 \times 4 \times 4 \text{ supercell}$$





Expansion to the Harmonic Approximation

- Quasi-harmonic approximation (QHA):
  - Phonon calculations at different volumes
  - Can calculate thermal expansion and mechanical properties
- Higher order contributions (anharmonicity):
  - Phonon-phonon interactions → thermal conductivity (AFLOW-AAPL)
  - Renormalization effects → self-consistent phonons