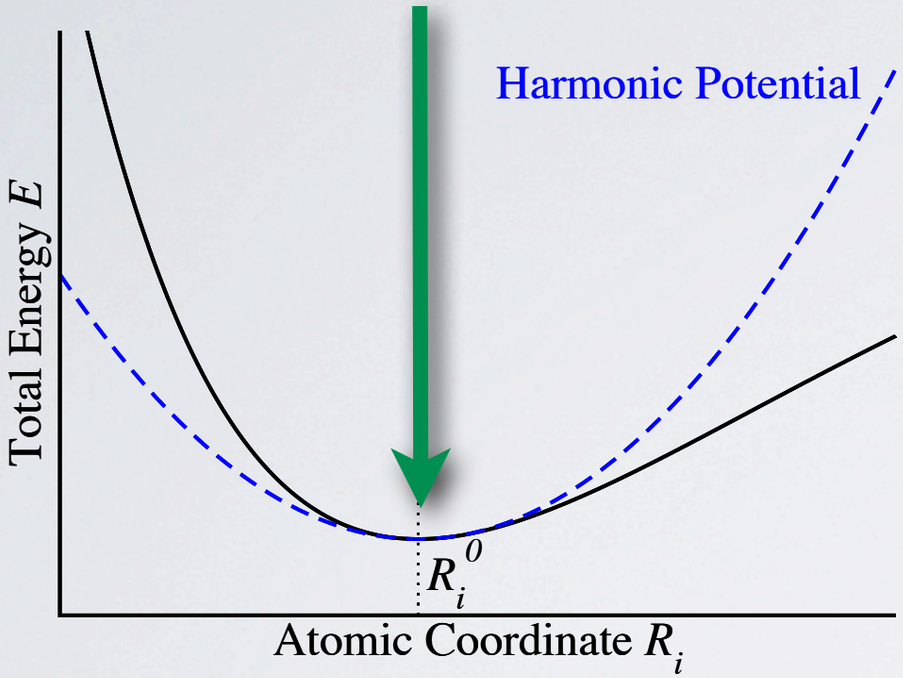
EXERCISE 1

THE HARMONIC APPROXIMATION

Static Equilibrium Position



Taylor expansion:

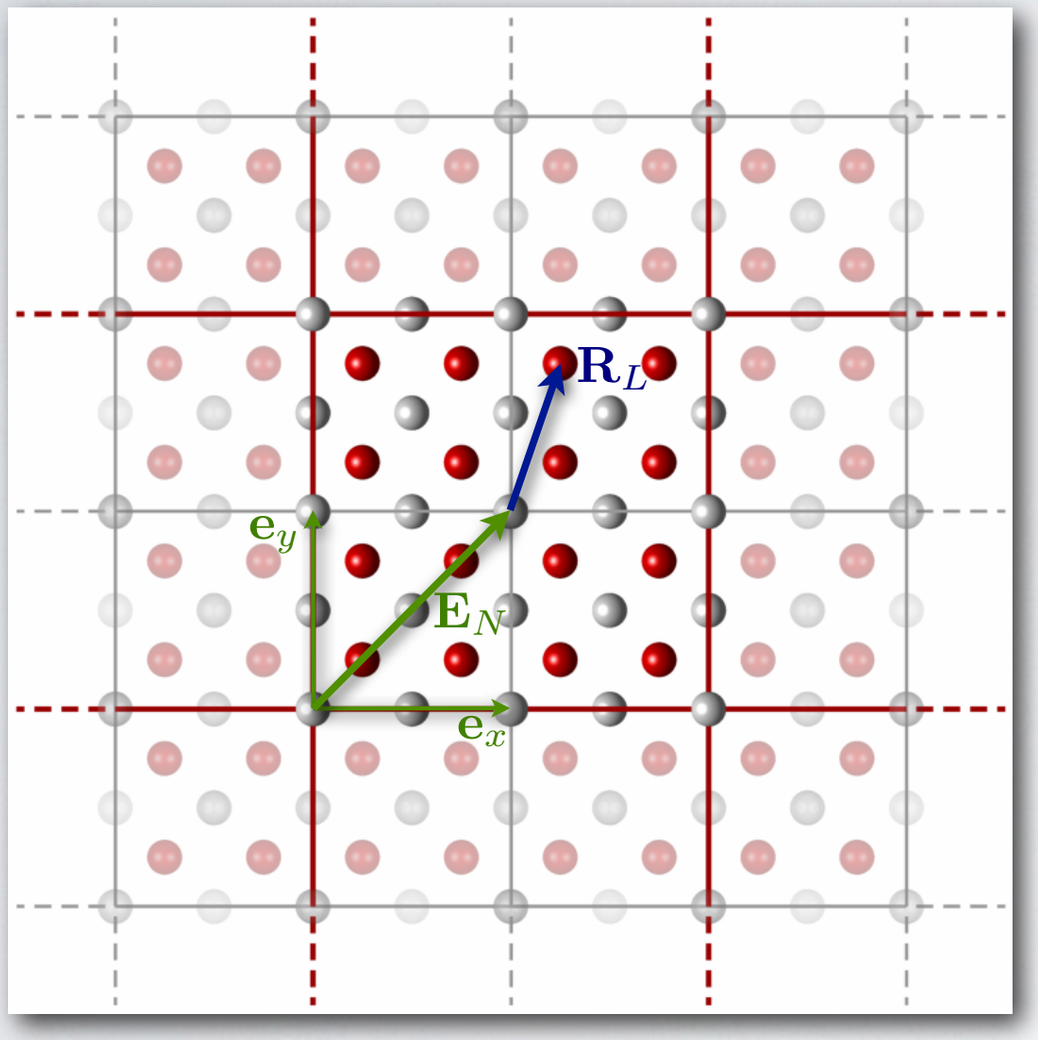
$$E \approx$$

$$E(\mathbf{R}_0) + \frac{1}{2}\sum_{i,j} \Phi^{i,j}\,(\Delta\mathbf{R}_i)(\Delta\mathbf{R}_j)$$

Determine the **Hessian** via **finite differences:**

$$\Phi_{ij} = \left.\frac{\partial^2 E}{\partial\mathbf{R}_i\partial\mathbf{R}_j}\right|_{\mathbf{R}^0} = -\left.\frac{\partial}{\partial\mathbf{R}_i}\mathbf{F}_j\right|_{\mathbf{R}^0} \approx -\frac{\mathbf{F}_j(\mathbf{R}_i^0+\varepsilon)}{\varepsilon}$$

SUPERCELL EXPANSION



Periodic Boundary Conditions
⇒ Reciprocal Space **q**

$$D_{ij}(\mathbf{q}) = \sum_{\mathbf{E}_N} \frac{e^{i(\mathbf{q}\cdot\mathbf{E}_N)}}{\sqrt{M_i M_j}} \Phi_{ij}$$

Eigenvalue problem:

$$\mathbf{D}(\mathbf{q})\ [\nu(\mathbf{q})] = \omega^2(\mathbf{q})\ [\nu(\mathbf{q})]$$

SUPERCELL EXPANSION

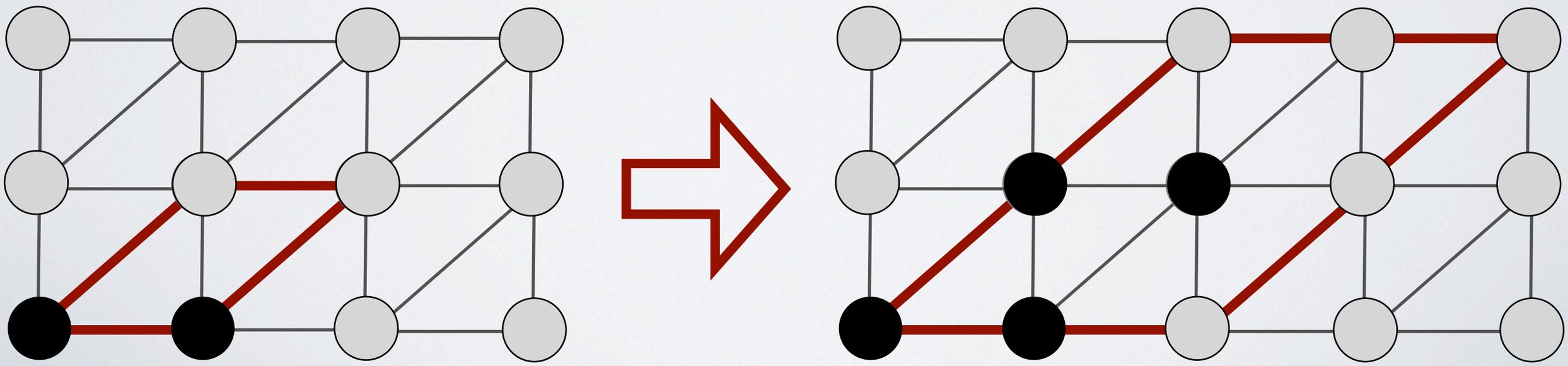
exercise_1/control.in

```
k_grid                8  8  8

phonon supercell      2  2  2
phonon displacement 0.01

phonon band  0.0   0.0   0.0    0.5   0.5   0.0   100   Gamma   X
phonon band  0.5   0.5   1.0    0.375 0.375 0.75  100   X       K
phonon band  0.375 0.375 0.75   0.0   0.0   0.0   100   K       Gamma
phonon band  0.0   0.0   0.0    0.5   0.5   0.5   100   Gamma   L

phonon dos            0    800   800    1    40
```



(a) Edit your file *control.in* so that it contains the following lines

```
k_grid                  8  8  8
phonon supercell        2  2  2
```

(b) Run *phonopy-FHI-aims* by typing

```
phonopy-FHI-aims
```

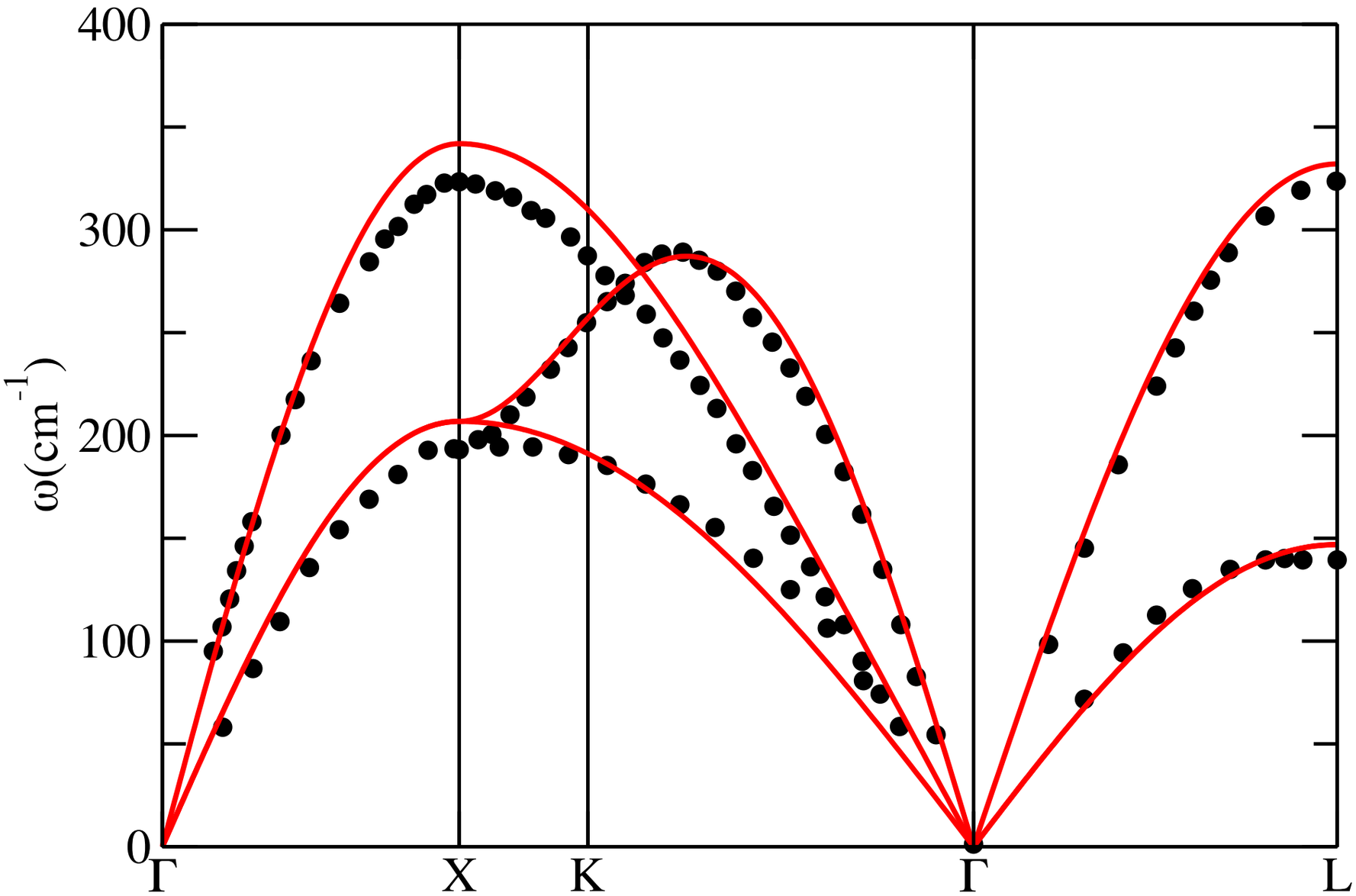
(c) Change into the directory *phonopy-FHI-aims-displacement-01* and run *FHI-aims*:

```
cd phonopy-FHI-aims-displacement-01
mpirun -np 4 aims.x > phonopy-FHI-aims-displacement-01.out
```

(d) Change into parent directory and run *phonopy-FHI-aims* again

```
cd ..
phonopy-FHI-aims
```

RESULTS



Exp.: R. Stedman and G. Nilsson, *Phys Rev* **145**, 492 (1966).

EXERCISE 11

(a) Change into directory exercise_2_a and run *phonopy-FHI-aims* by typing

```
cd exercise_2/exercise_2_a
phonopy-FHI-aims
```

(b) Change into the directory *phonopy-FHI-aims-displacement-01* and run *FHI-aims*:

```
cd phonopy-FHI-aims-displacement-01
mpirun -np 4 aims.x > phonopy-FHI-aims-displacement-01.out
```

(c) Change into parent directory and run *phonopy-FHI-aims* again

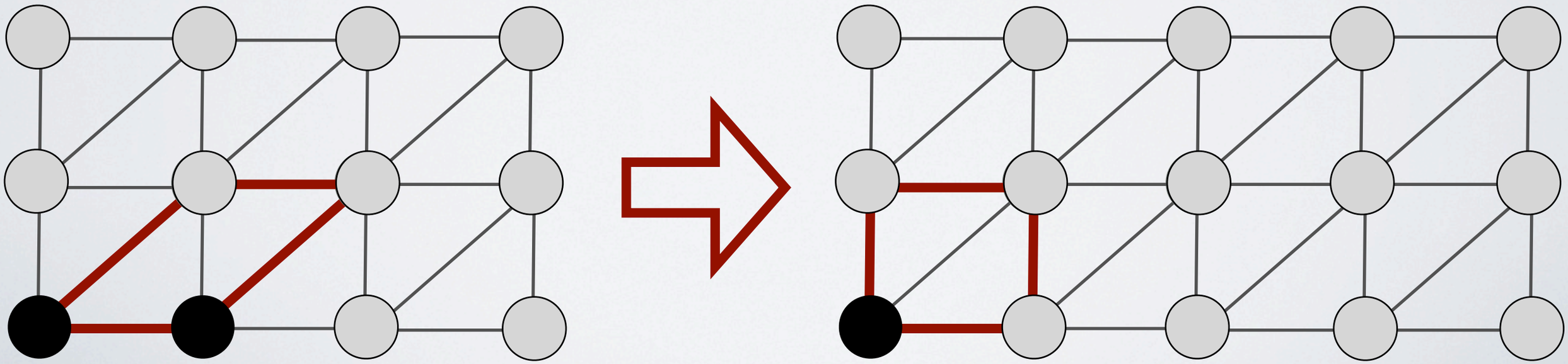
```
cd ..
phonopy-FHI-aims
```

SUPERCELL EXPANSION

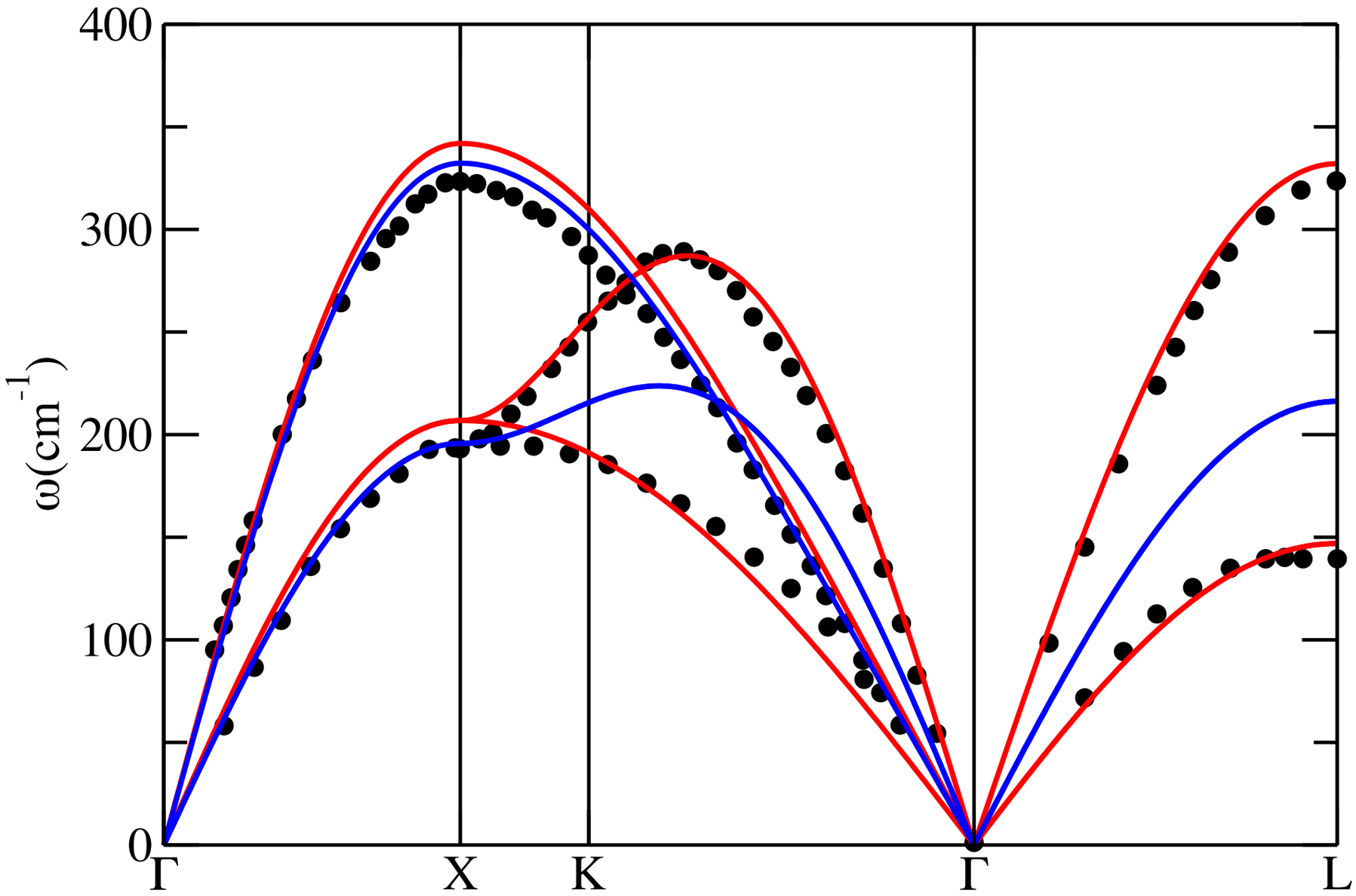
```
k_grid                    6  6  6
phonon supercell       -1 1 1  1 -1 1  1 1 -1
```

exercise_2_a/control.in

$$\hat{\mathbf{a}}_i = \begin{pmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{pmatrix} \cdot \mathbf{a}_i \quad \Longrightarrow \quad \mathbf{a}_1 = \begin{pmatrix} 0 \\ a/2 \\ a/2 \end{pmatrix} \rightarrow \hat{\mathbf{a}}_1 = \begin{pmatrix} a \\ 0 \\ 0 \end{pmatrix}$$



Exercise 2a



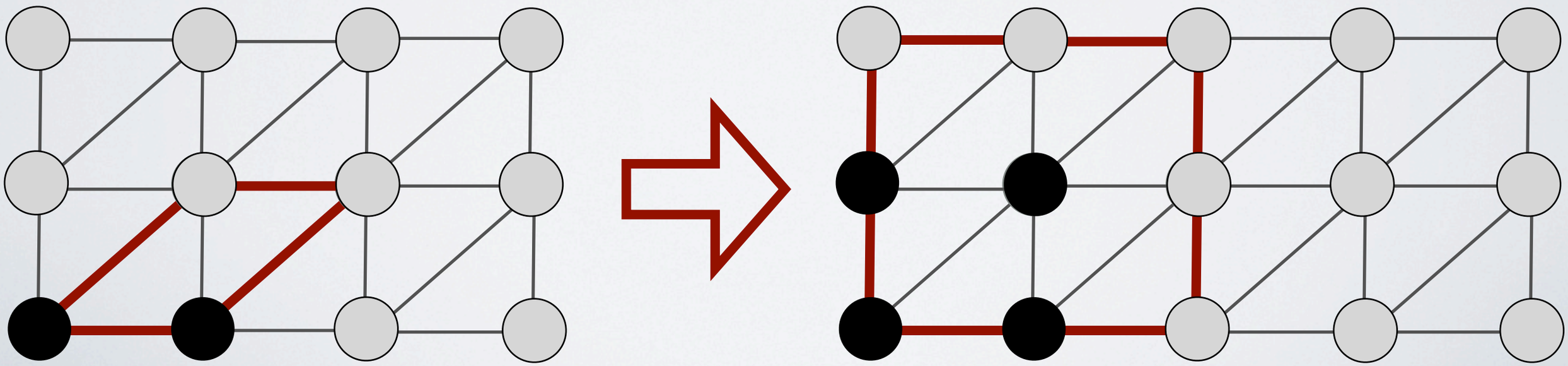
Exp.: R. Stedman and G. Nilsson, *Phys Rev* **145**, 492 (1966).

SUPERCELL EXPANSION

```
k_grid                    3  3  3
phonon supercell         -2  2  2   2 -2  2   2  2 -2
```

exercise_2_b/control.in

$$\hat{\mathbf{a}}_i = \begin{pmatrix} -2 & 2 & 2 \\ 2 & -2 & 2 \\ 2 & 2 & -2 \end{pmatrix} \cdot \mathbf{a}_i \quad \Longrightarrow \quad \mathbf{a}_1 = \begin{pmatrix} 0 \\ a/2 \\ a/2 \end{pmatrix} \rightarrow \hat{\mathbf{a}}_1 = \begin{pmatrix} 2a \\ 0 \\ 0 \end{pmatrix}$$



WORKFLOW

(a) Change into directory exercise_2_b and run *phonopy-FHI-aims* by typing

```
cd exercise_2/exercise_2_b
phonopy-FHI-aims
```

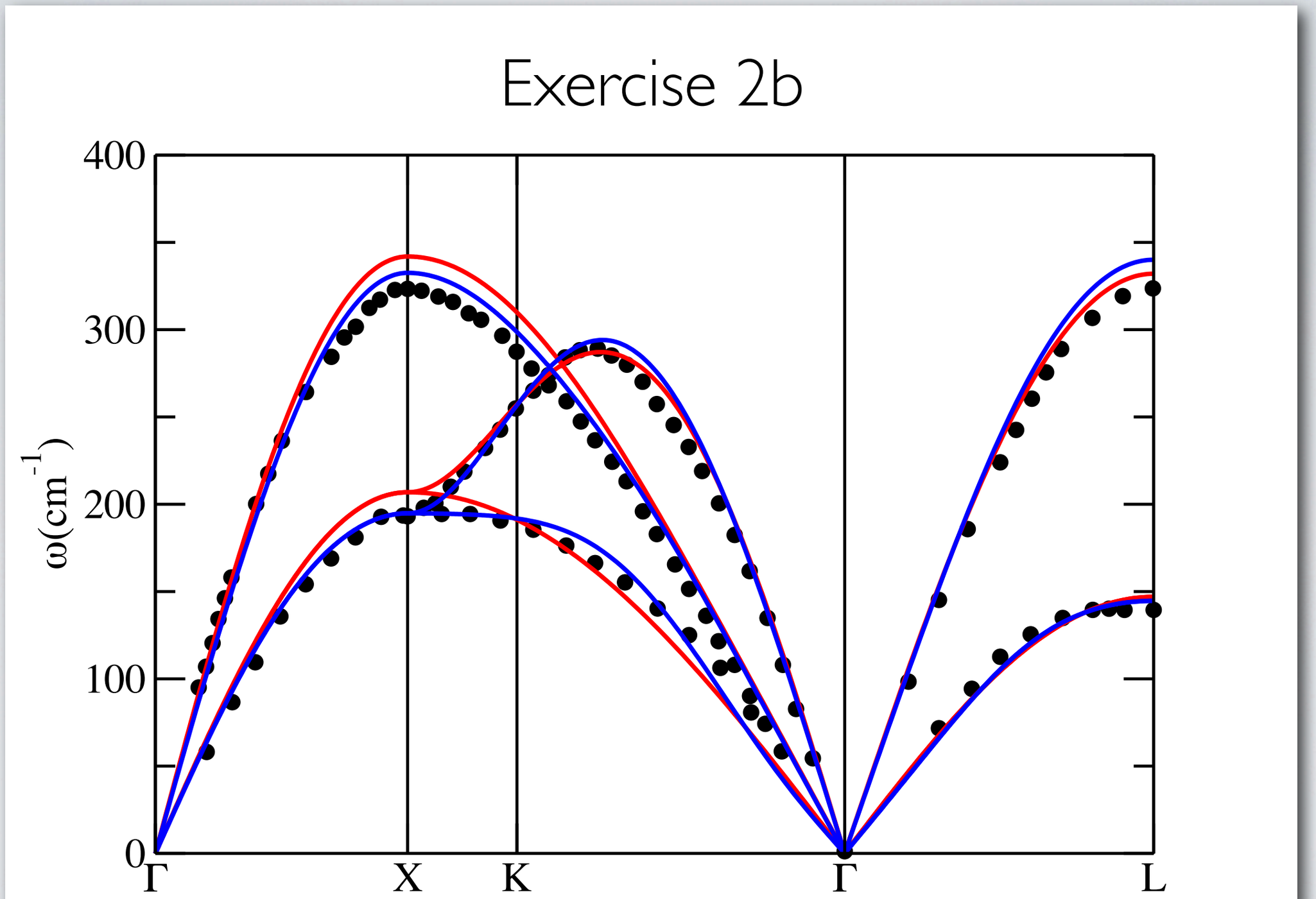
(b) Change into the directory *phonopy-FHI-aims-displacement-01* and run *FHI-aims*:

```
cd phonopy-FHI-aims-displacement-01
mpirun -np 4 aims.x > phonopy-FHI-aims-displacement-01.out
```

(c) Change into parent directory and run *phonopy-FHI-aims* again

```
cd ..
phonopy-FHI-aims
```

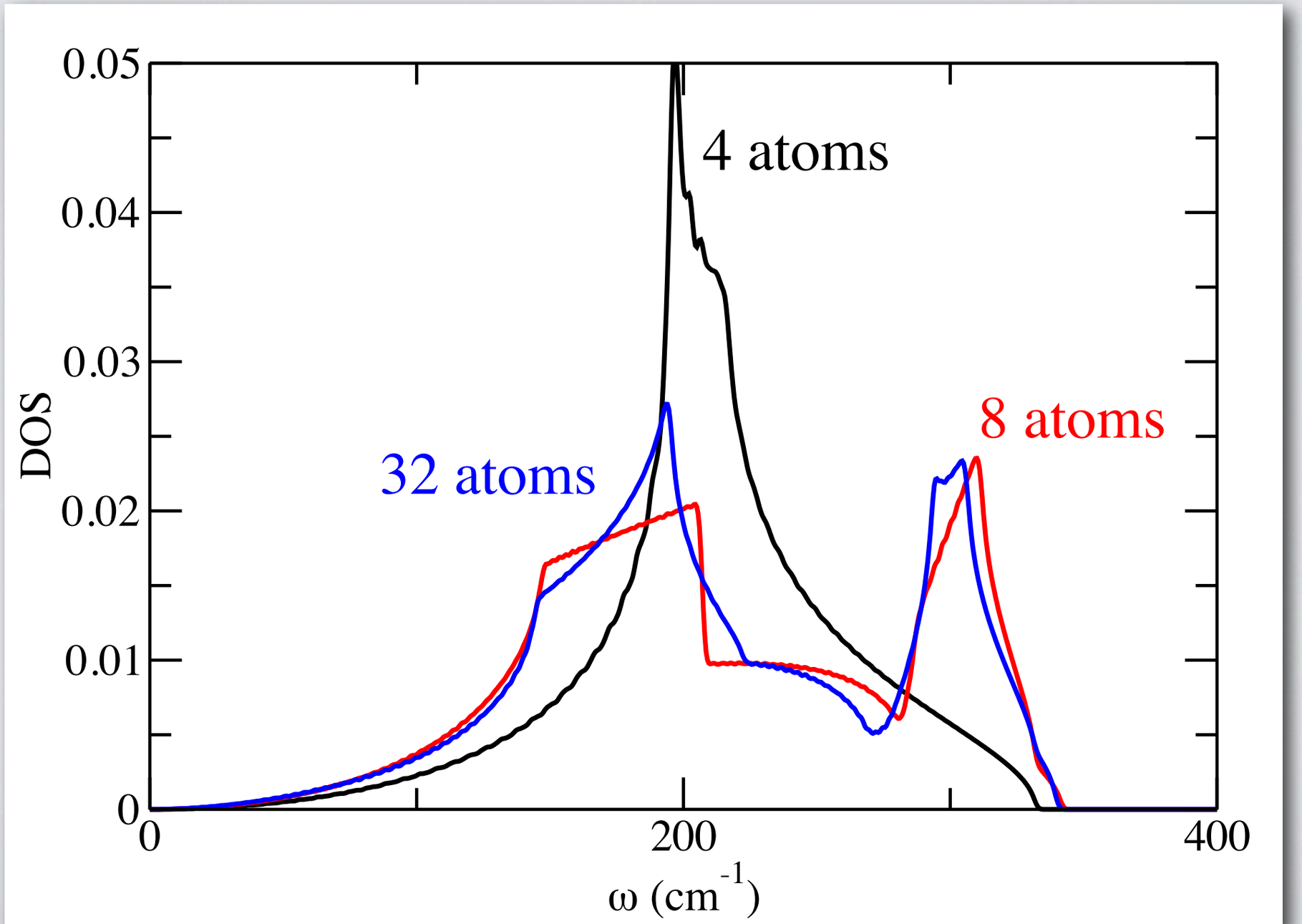
BAND STRUCTURE



Exp.: R. Stedman and G. Nilsson, *Phys Rev* **145**, 492 (1966).

DENSITY OF STATES

$$g(\omega) = \sum_s \int \frac{d\mathbf{q}}{(2\pi)^3} \delta(\omega - \omega(\mathbf{q})) = \sum_s \int_{\omega(\mathbf{q})=\omega} \frac{dS}{(2\pi)^3} \frac{1}{|\nabla\omega(\mathbf{q})|}$$



THE HARMONIC FREE ENERGY

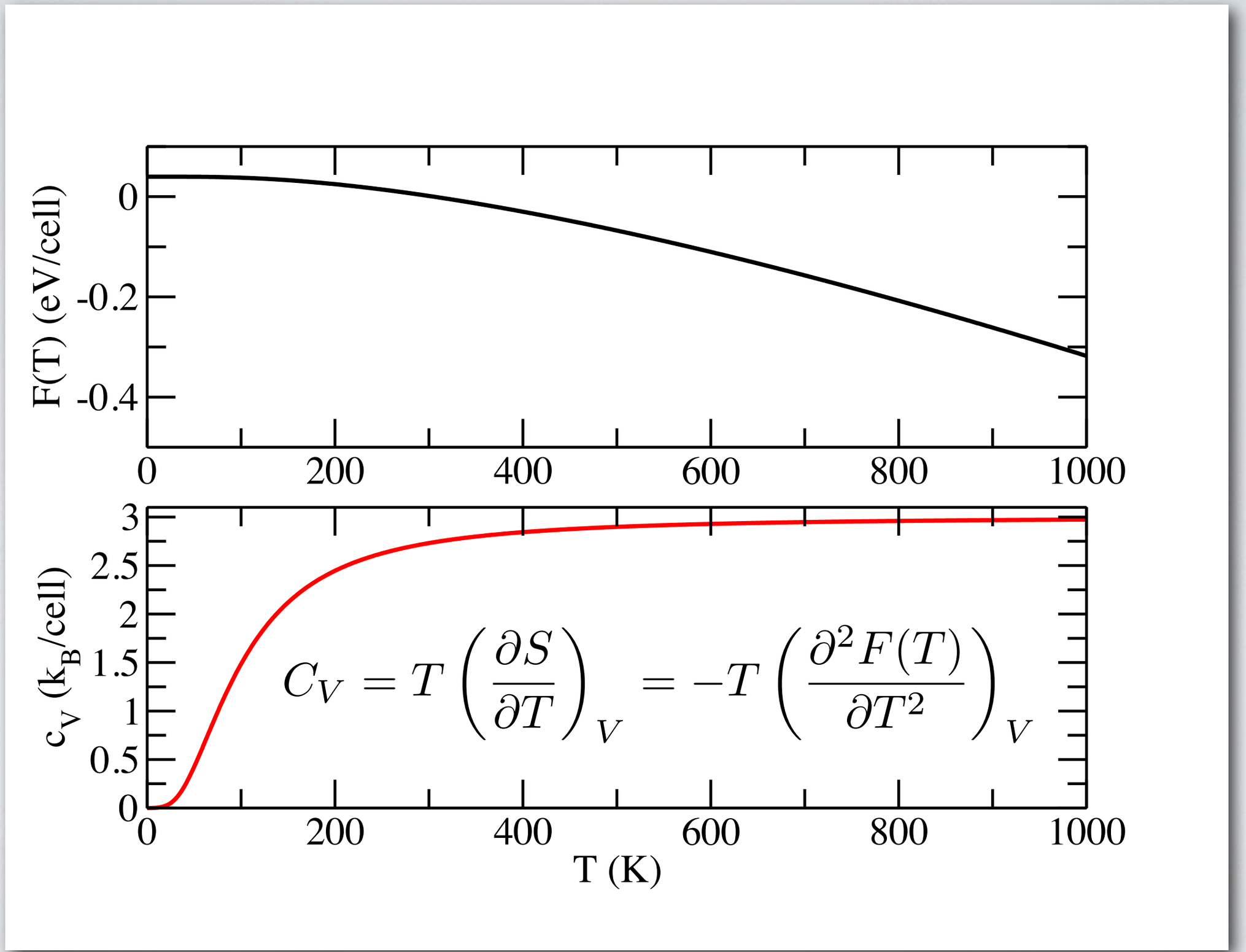
$$F^{ha}(T) = E(\{\mathbf{R}_0\}) + \int d\omega\ g(\omega)\frac{\hbar\omega}{2} + \int d\omega\ g(\omega)\ k_B T \ln\left(1 - e^{\left(-\frac{\hbar\omega}{k_B T}\right)}\right)$$

Static Equilibrium Energy

Zero-point vibration

Thermally induced vibrations

FREE ENERGY AND HEAT CAPACITY



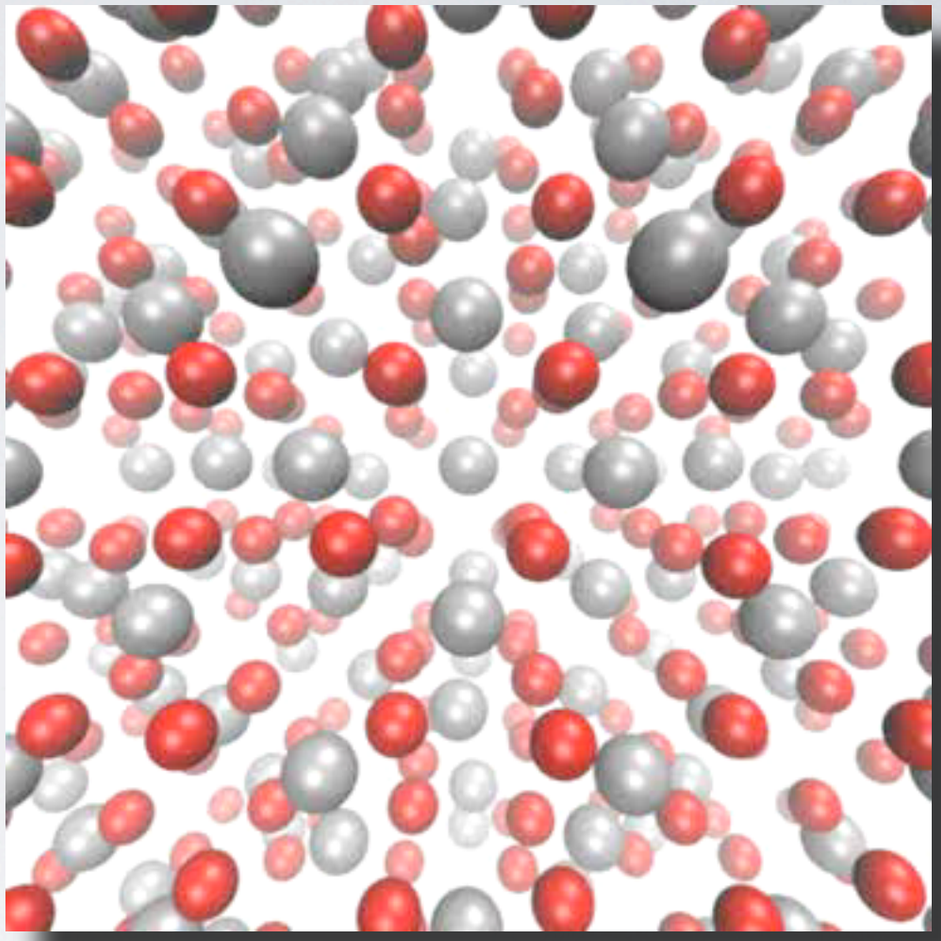
EXERCISE III

HARMONIC MOLECULAR DYNAMICS

Numerical Integration
of the **equations of motion**

L. Verlet, *Phys. Rev.* **159**, 98 (1967).

$$M_I \, \ddot{\mathbf{R}}_I(t) = \mathbf{F}_I(\mathbf{R}_1(t), \cdots, \mathbf{R}_N(t))$$



Harmonic potential orders of magnitude faster,
but **the more inaccurate the higher the temperature**!

```
cp exercise_1/phonopy-FHI-aims-force_constants.dat exercise_3/
```

exercise_3/control.in

```
MD_MB_init    300.0
MD_time_step 0.001
MD_clean_rotations .false.
MD_schedule
  MD_segment  5.0 NVT_parrinello 300.0     0.050
    harmonic_potential_only phonopy-FHI-aims-force_constants.dat
  MD_segment 20.0 NVT_parrinello 300.0     0.050
    harmonic_potential_only phonopy-FHI-aims-force_constants.dat
```

```
mpirun -np 4 aims.x > aims.out
```

Exercise 4 and 5 - electronic conductivity of Al

tutorial4 files are located in:

```
/afs/ictp.it/public/shared/smr2475/tutorials/tutorial4/skeleton
```

Exercise 4 and 5 - electronic conductivity of Al

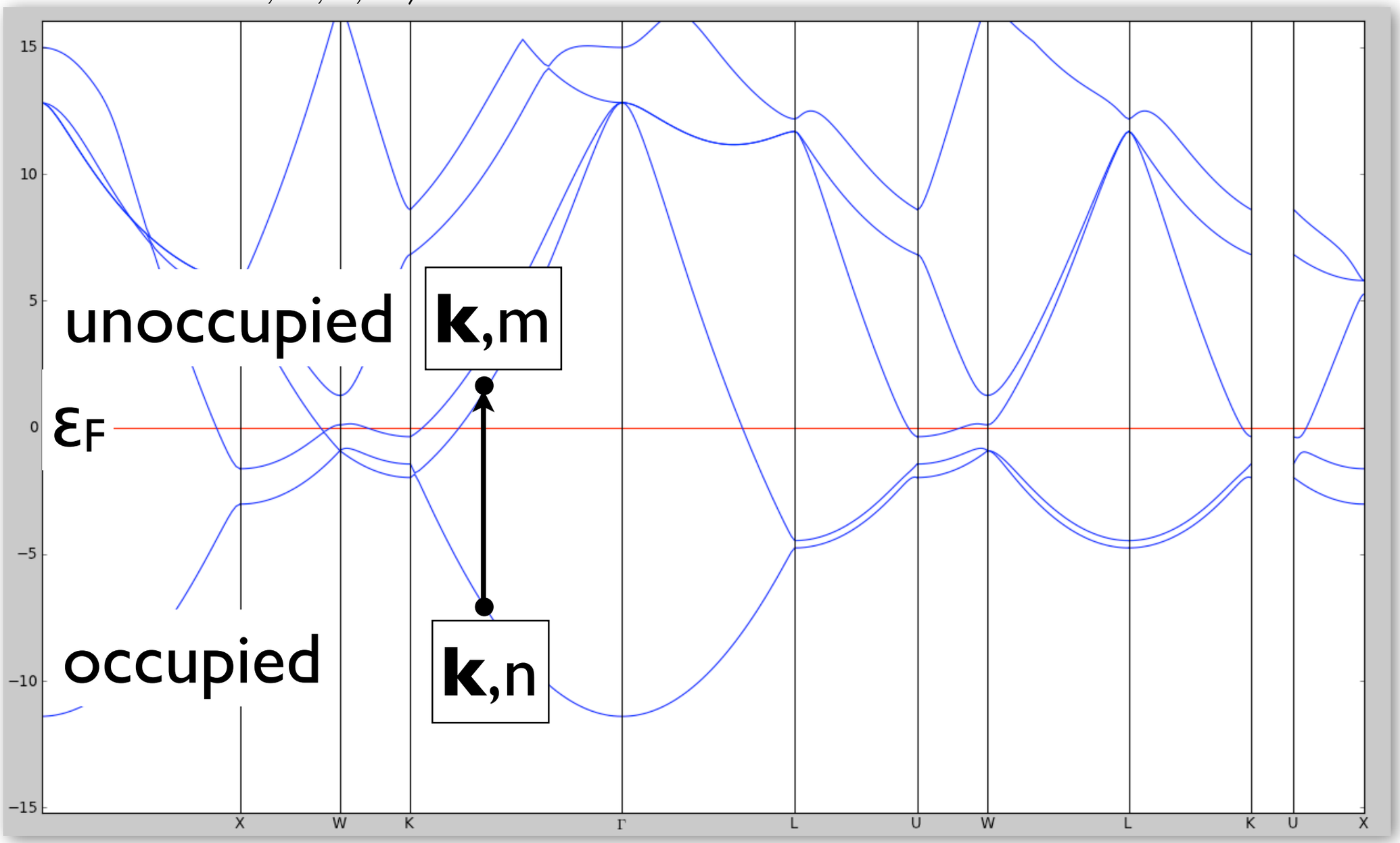
Central equation: *Kubo-Greenwood* optical conductivity

$$\sigma(\omega) = \frac{2\pi e^2}{3Vm_e^2\omega} \sum_{\mathbf{k},m,n,m\neq n} \left|\langle\Psi_{\mathbf{k}n}|\hat{\mathbf{p}}|\Psi_{\mathbf{k}m}\rangle\right|^2 \cdot (f_{\mathbf{k}n} - f_{\mathbf{k}m})\,\delta\left(\epsilon_{\mathbf{k}n} - \epsilon_{\mathbf{k}m} - \hbar\omega\right)$$

summation over all k-points and states (i.e. entire band-structure)	interband (m,n) momentum-matrix transition elements	Fermi-occupation number difference

Exercise 4 and 5 - electronic conductivity of Al

$$\sigma(\omega) = \frac{2\pi e^2}{3Vm_e^2\omega} \sum_{\mathbf{k},m,n,m\neq n} \left|\langle \Psi_{\mathbf{k}n}|\hat{\mathbf{p}}|\Psi_{\mathbf{k}m}\rangle\right|^2 \cdot (f_{\mathbf{k}n} - f_{\mathbf{k}m})\,\delta\left(\epsilon_{\mathbf{k}n} - \epsilon_{\mathbf{k}m} - \hbar\omega\right)$$



Exercise 4: optical conductivity of Al

- Calculation of σ(ω) for a primitive Al unit-cell (1 atom)

`geometry.in`

```
lattice_vector 1.9943 1.9943 0.0000
lattice_vector 0.0000 1.9943 1.9943
lattice_vector 1.9943 0.0000 1.9943

atom_frac 0.00 0.00 0.00 Al
```

`control.in (to be added)`

```
compute_kubo_greenwood 0.1   0.025   -11   -1   0.0   2.0   1000   a a
```

Exercise 5: electronic conductivity of Al

- Calculation of $\sigma(\omega)$ for a thermodynamic average at temperature T in an Al supercell

Exercise 5: electronic conductivity of Al

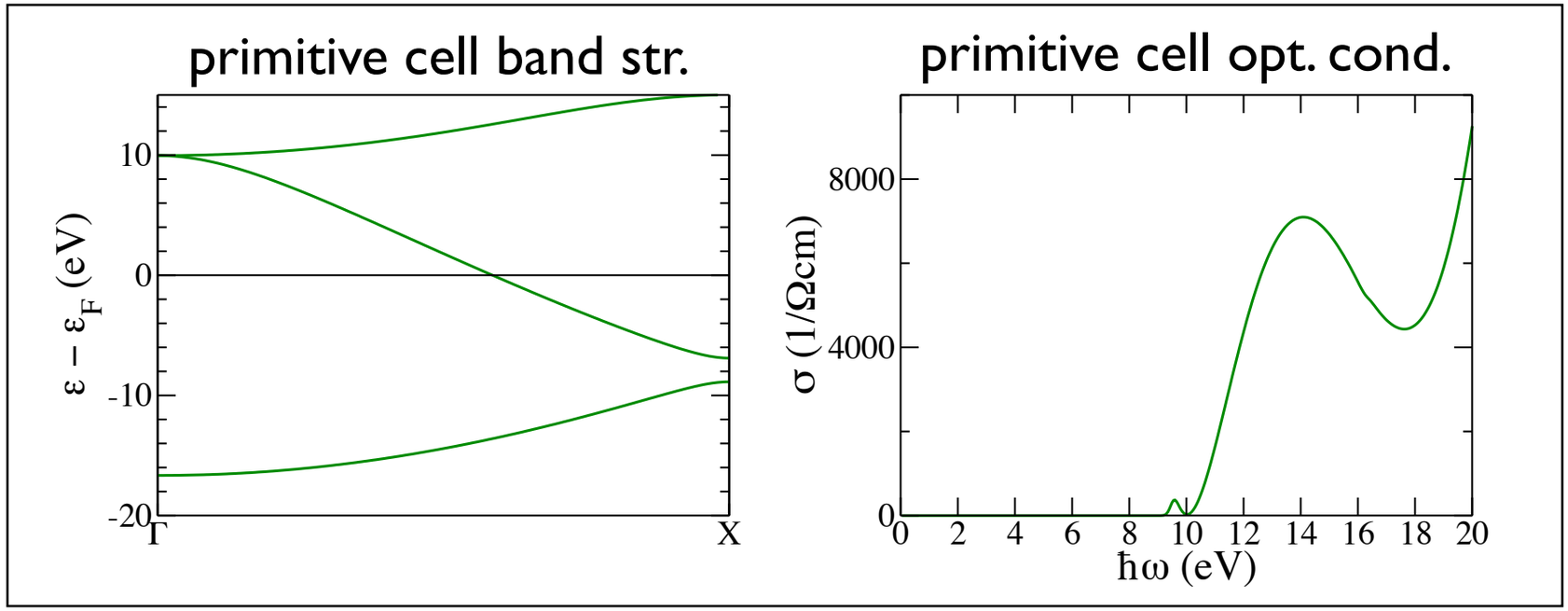
- Calculation of σ(ω) for a thermodynamic average at temperature T in an Al supercell

$$\sigma(\omega) = \frac{2\pi e^2}{3Vm_e^2\omega} \sum_{\mathbf{k},m,n,m\neq n} \left|\langle \Psi_{\mathbf{k}n}|\hat{\mathbf{p}}|\Psi_{\mathbf{k}m}\rangle\right|^2 \cdot (f_{\mathbf{k}n} - f_{\mathbf{k}m})\, \delta\left(\epsilon_{\mathbf{k}n} - \epsilon_{\mathbf{k}m} - \hbar\omega\right)$$

$$\sigma(\omega) = \frac{2\pi e^2}{3Vm_e^2\omega} \left\langle \sum_{\mathbf{k},m,n,m\neq n} \left|\langle \Psi_{\mathbf{k}n}|\hat{\mathbf{p}}|\Psi_{\mathbf{k}m}\rangle\right|^2 \cdot (f_{\mathbf{k}n} - f_{\mathbf{k}m})\, \delta\left(\epsilon_{\mathbf{k}n} - \epsilon_{\mathbf{k}m} - \hbar\omega\right) \right\rangle_{\mathbf{T}}$$

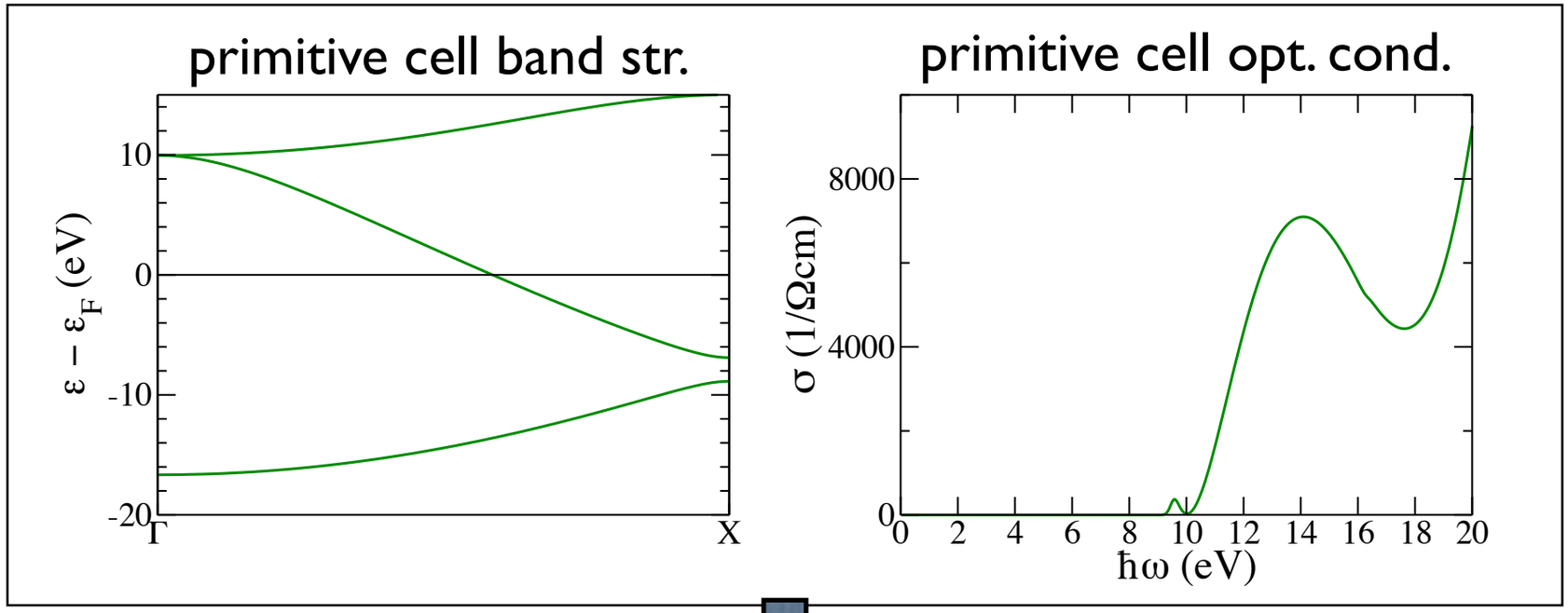
Exercise 5: electronic conductivity of Al

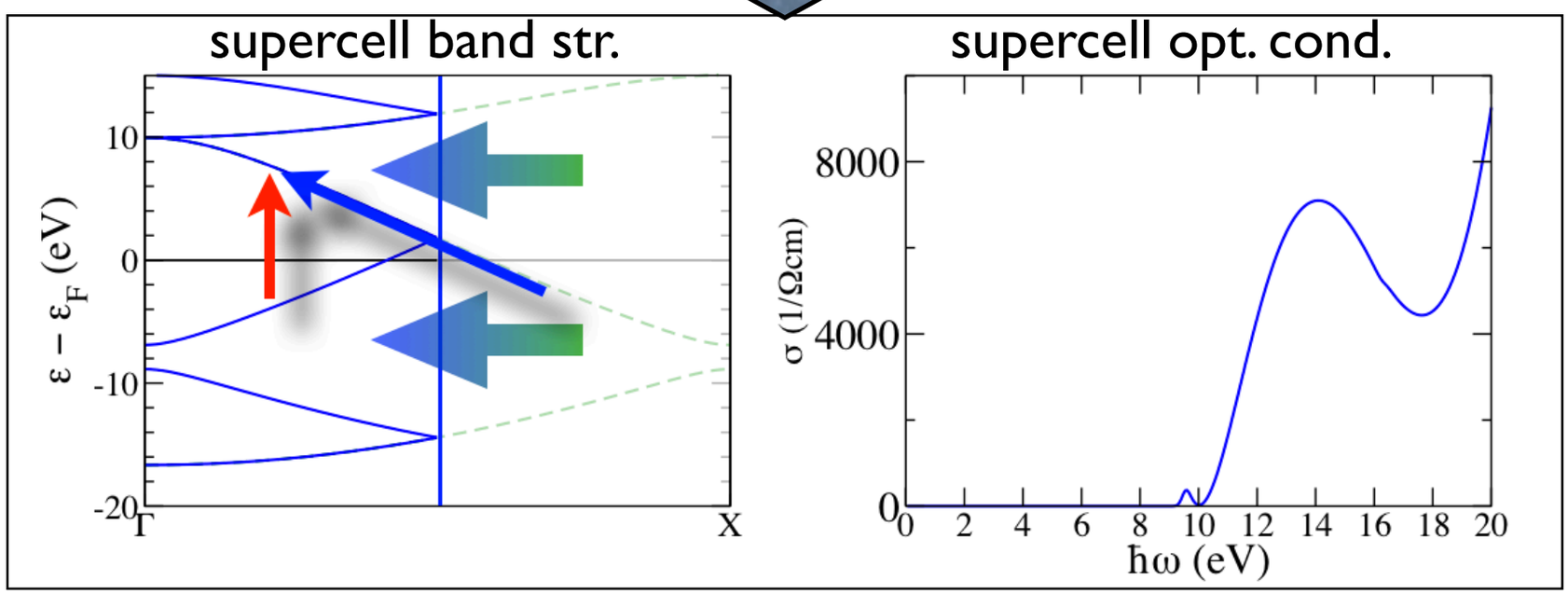
- Calculation of σ(ω) for a thermodynamic average at temperature T in an Al supercell



Exercise 5: electronic conductivity of Al

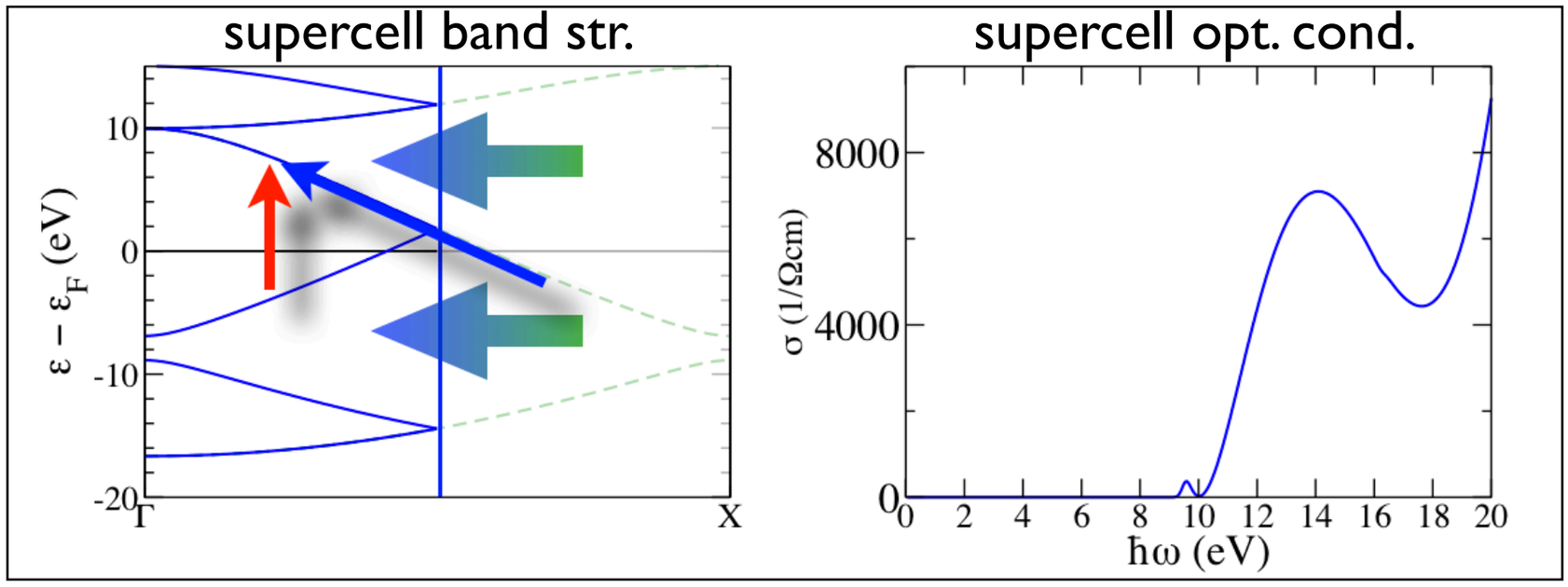
- Calculation of σ(ω) for a thermodynamic average at temperature T in an Al supercell





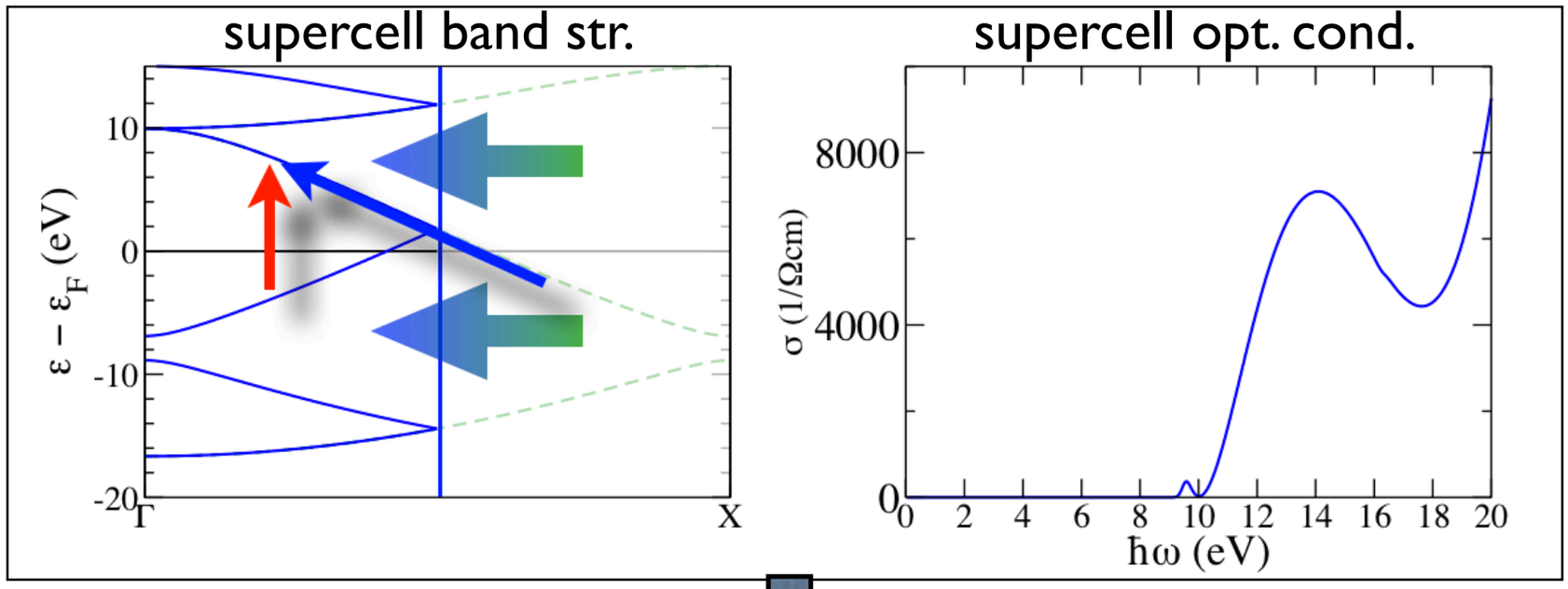
Exercise 5: electronic conductivity of Al

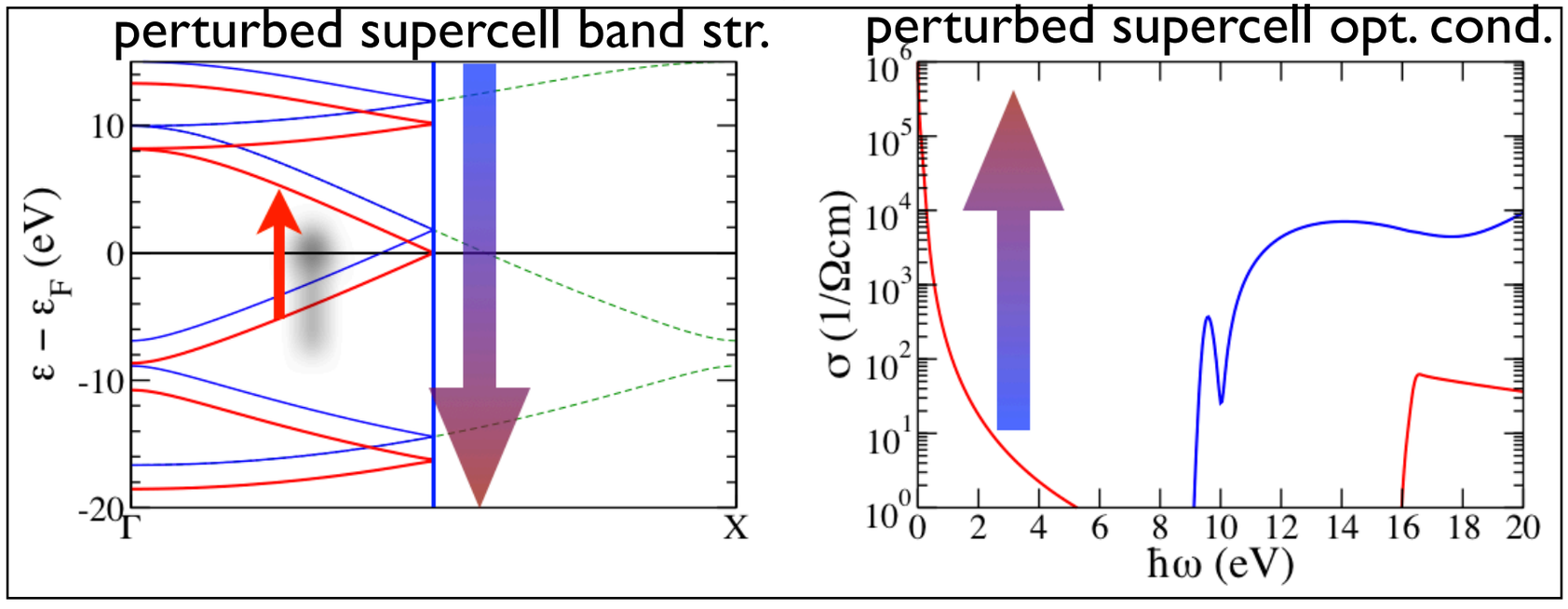
- Calculation of σ(ω) for a thermodynamic average at temperature T in an Al supercell



Exercise 5: electronic conductivity of Al

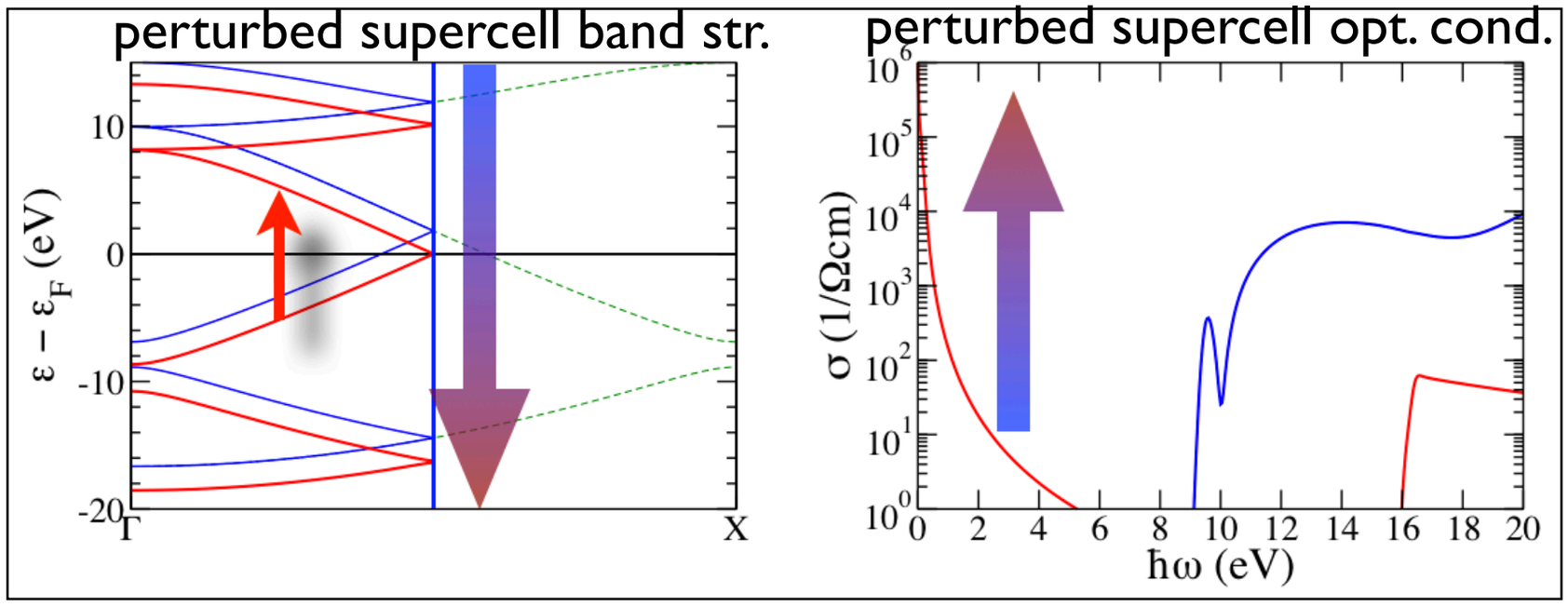
- Calculation of σ(ω) for a thermodynamic average at temperature T in an Al supercell





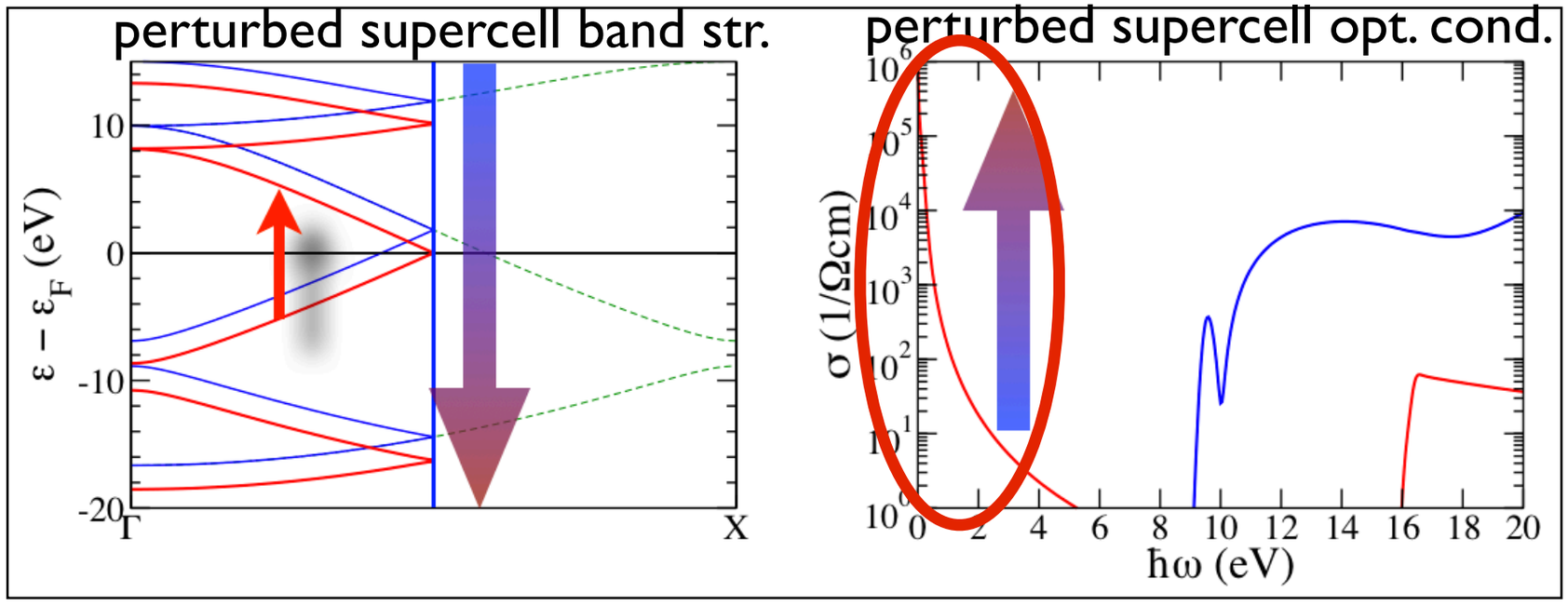
Exercise 5: electronic conductivity of Al

- Calculation of σ(ω) for a thermodynamic average at temperature T in an Al supercell



Exercise 5: electronic conductivity of Al

- Calculation of σ(ω) for a thermodynamic average at temperature T in an Al supercell



- low-ω contributions ⟶ information on σ_{DC}
- many different perturbed supercell spectra from MD ⟶ thermodynamic averaged spectra including electron-phonon interaction

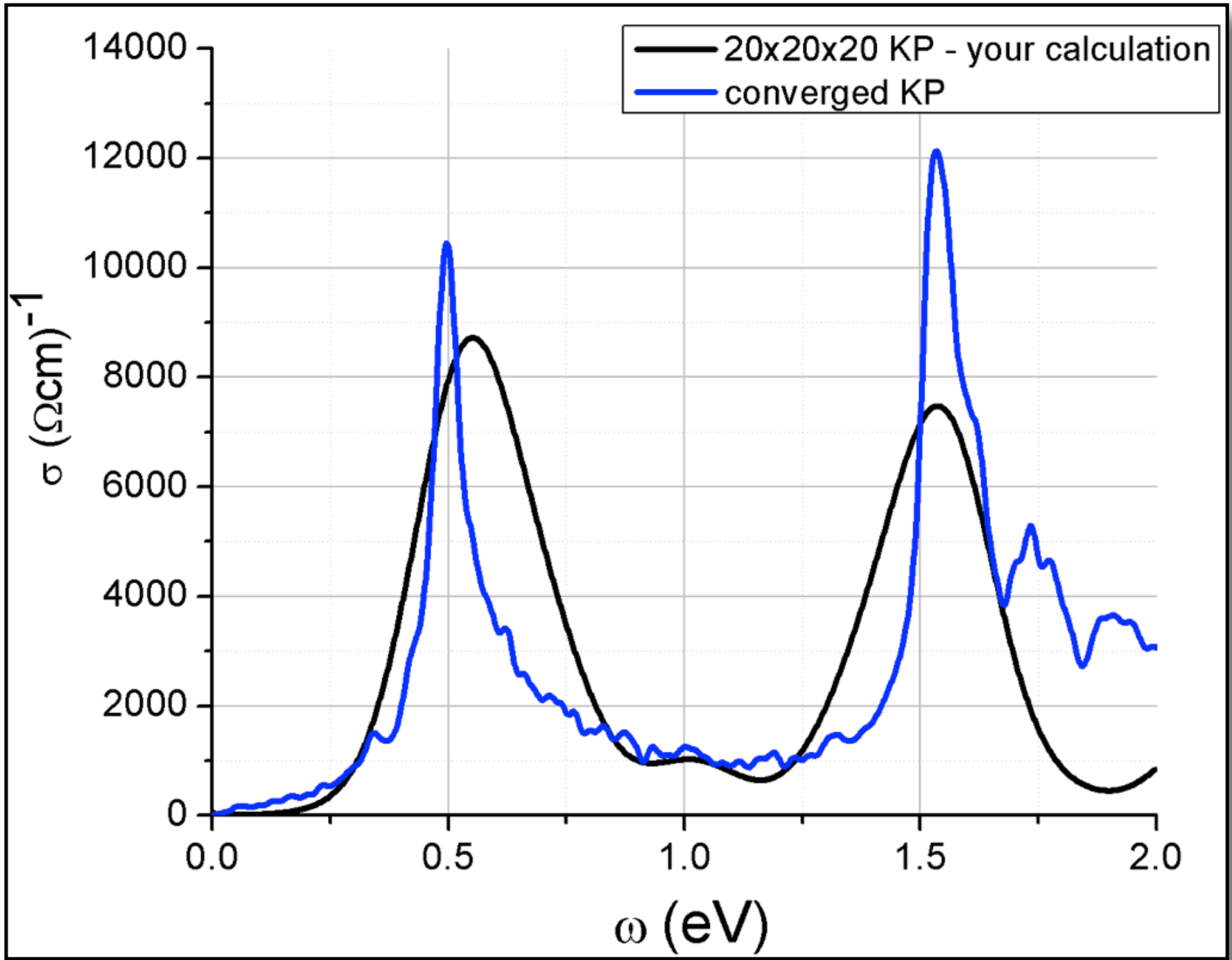
Exercise 4 and 5: electronic conductivity of

- Exercise 4:
  - calculate $\sigma(\omega)$ spectrum for a primitive Al unit-cell (1 atom)

- Exercise 5.a:
  - calculate $\sigma(\omega)$ of 16 perturbed configurations (snapshots) of an 8-atom supercell from the MD-run of exercise 3! (one or two different temperatures)

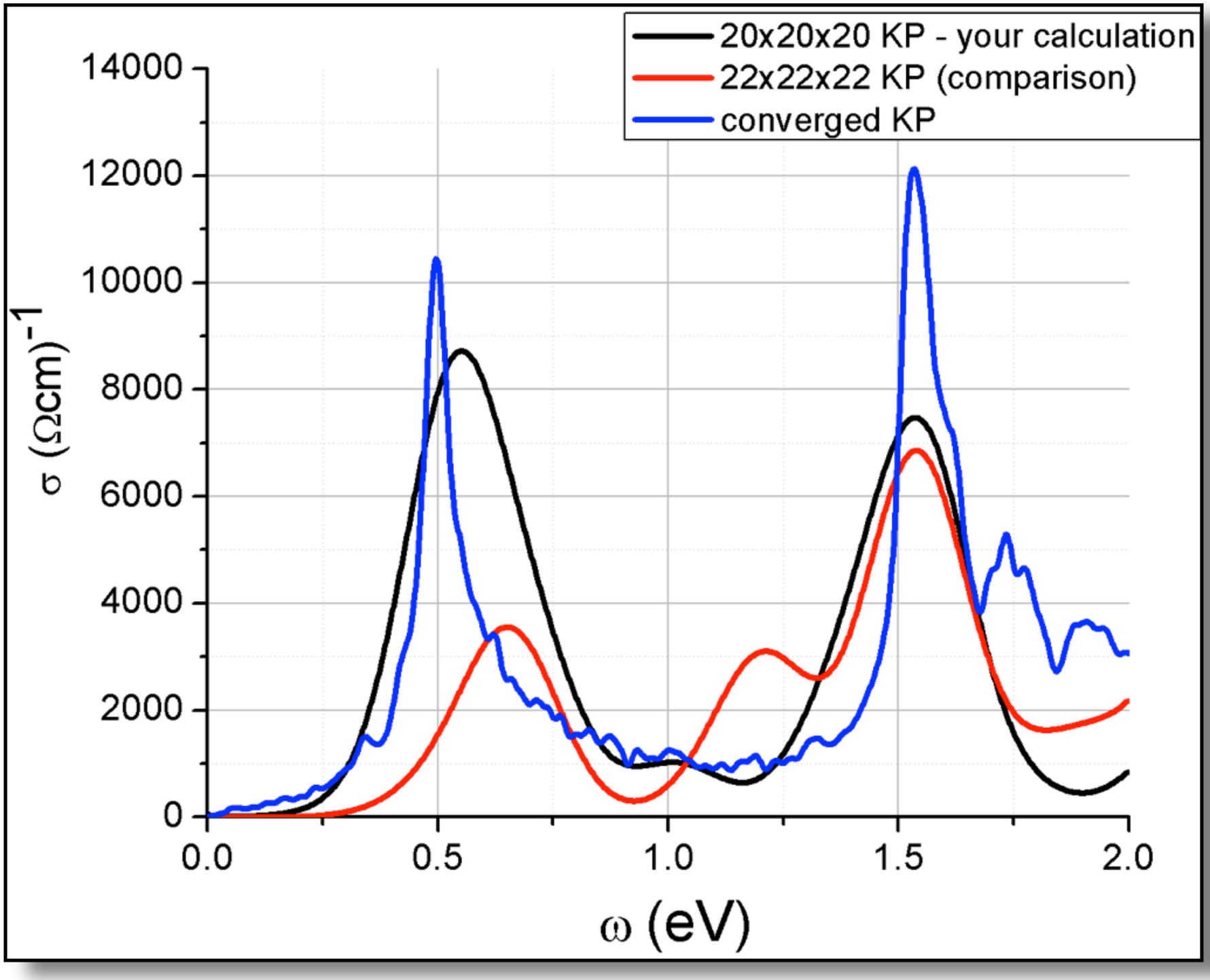
- Exercise 5.b:
  - take the average of 240 snapshots (provided by us) for 4 temperatures
  - extrapolate the spectra to $\omega \rightarrow 0$ (i.e. obtain σ_{DC})
  - study the temperature behaviour: $\sigma_{DC}(T)$

Results ex. 4: optical conductivity of Al



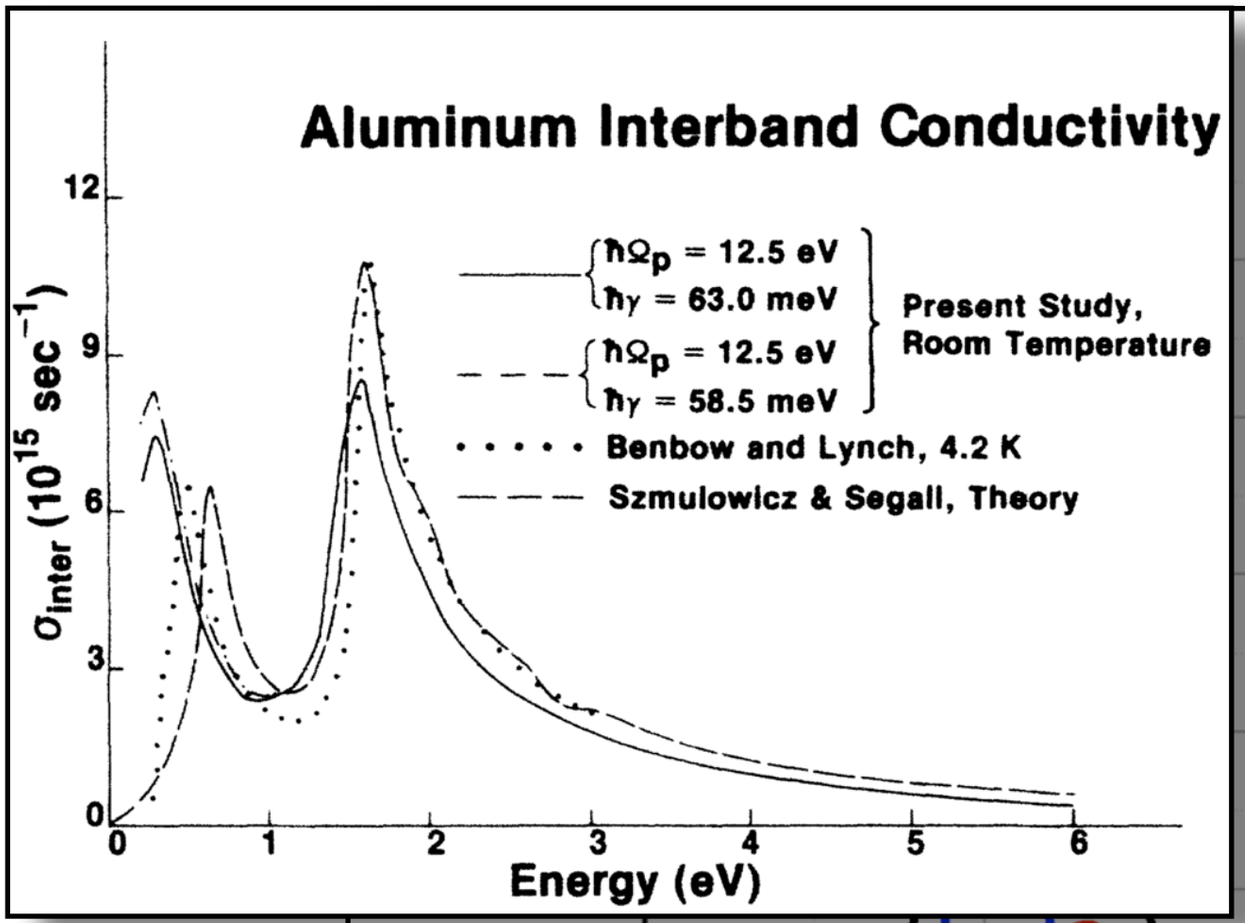
Qualitative agreement of peak-positions for 20^3 KP and converged spectrum ...

Results ex. 4: optical conductivity of Al



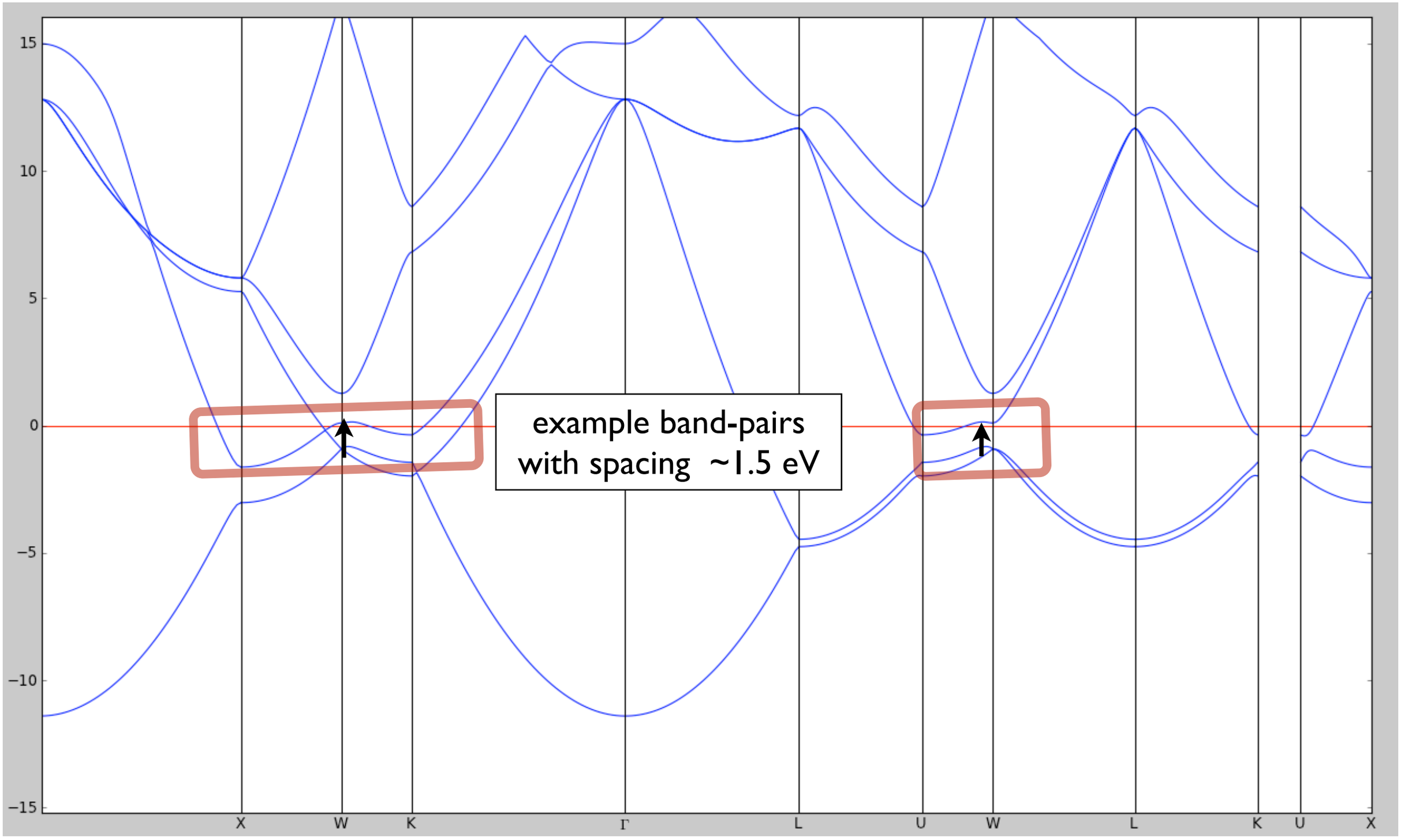
...is only coincidental

Results ex. 4: optical conductivity of Al



Comparison to experiment holds well

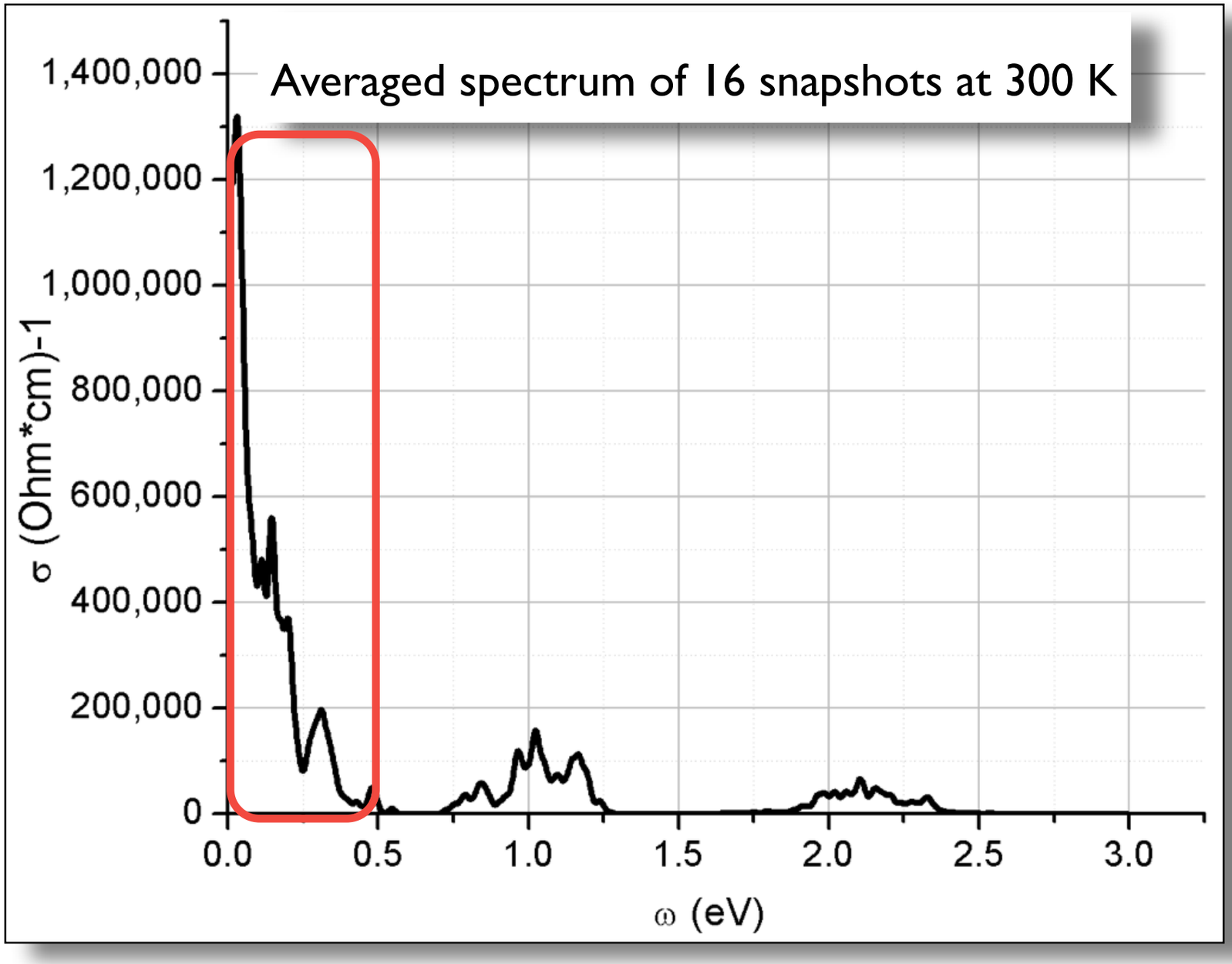
Results ex. 4: optical conductivity of Al



Origin of peaks: particular, parallel transition regions in the BS

Results ex. 5.a: electronic conductivity of Al

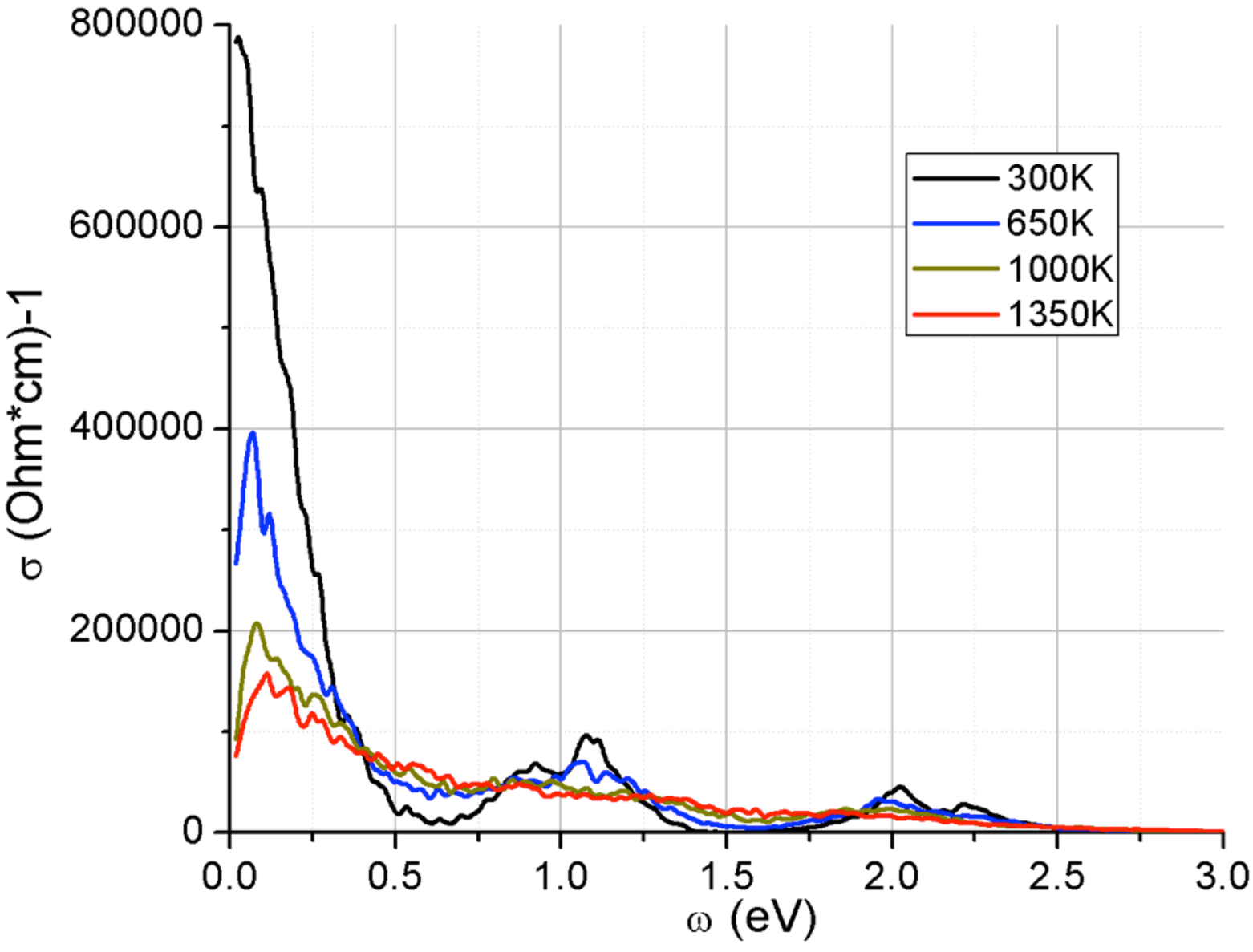
First look at the results:



Low ω-peak due to perturbed supercell

Results ex. 5.b: electronic conductivity of Al

Snapshot-converged spectra

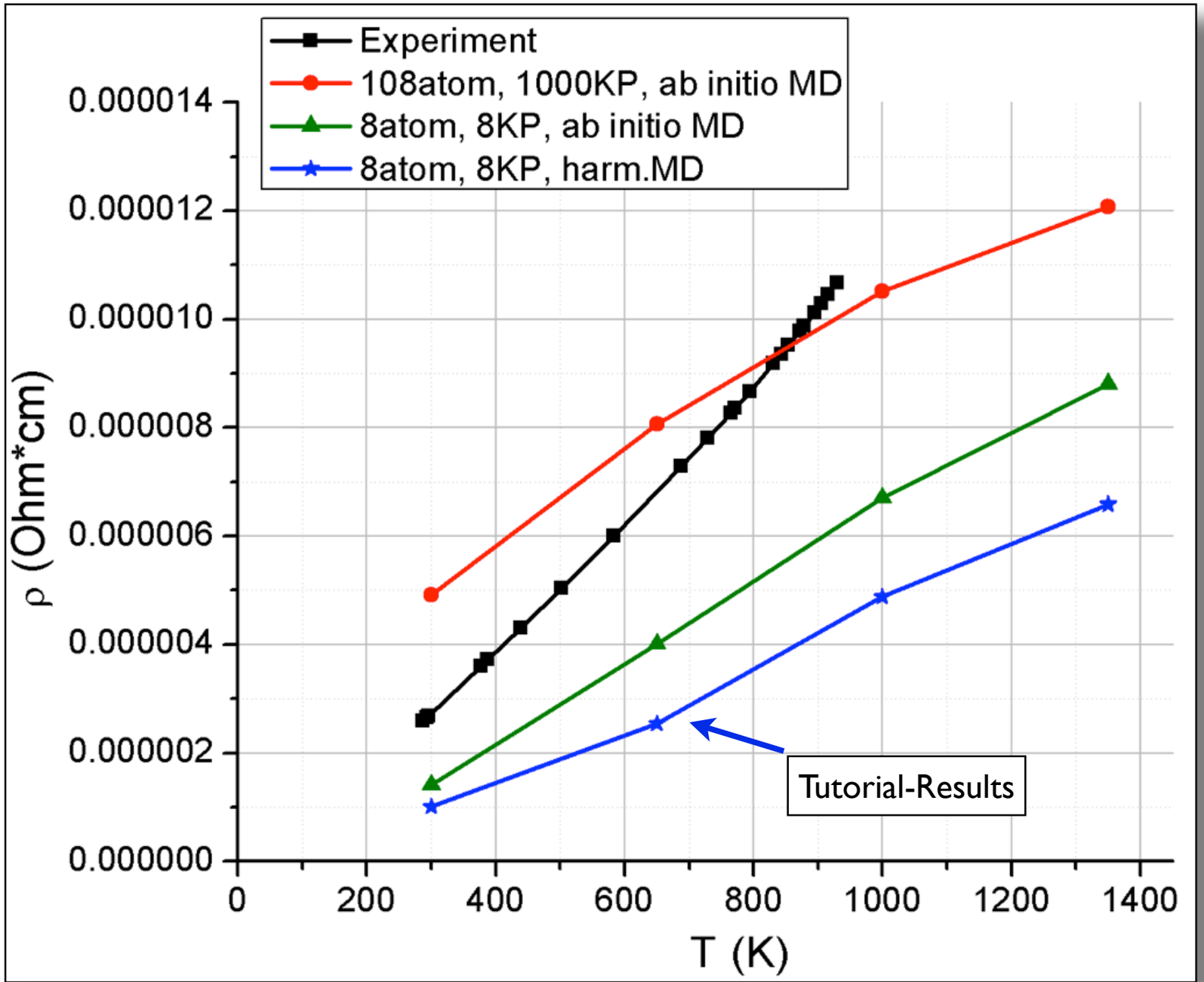


Lowering of Drude peak with temperature

Results ex. 5.b: electronic conductivity of Al

- Linear resistivity ✓
- Increase with T ✓
- Order of magn. of experiment ✓

T-dependence of ρ



Results ex. 5.b: electronic conductivity of Al

T-dependence of ρ

•Lin

•Inc

•Or

exp

However ... things not considered:

•volume expansion

•(low temperature) quantum effects

• electron-electron scattering