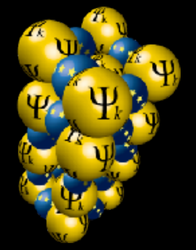
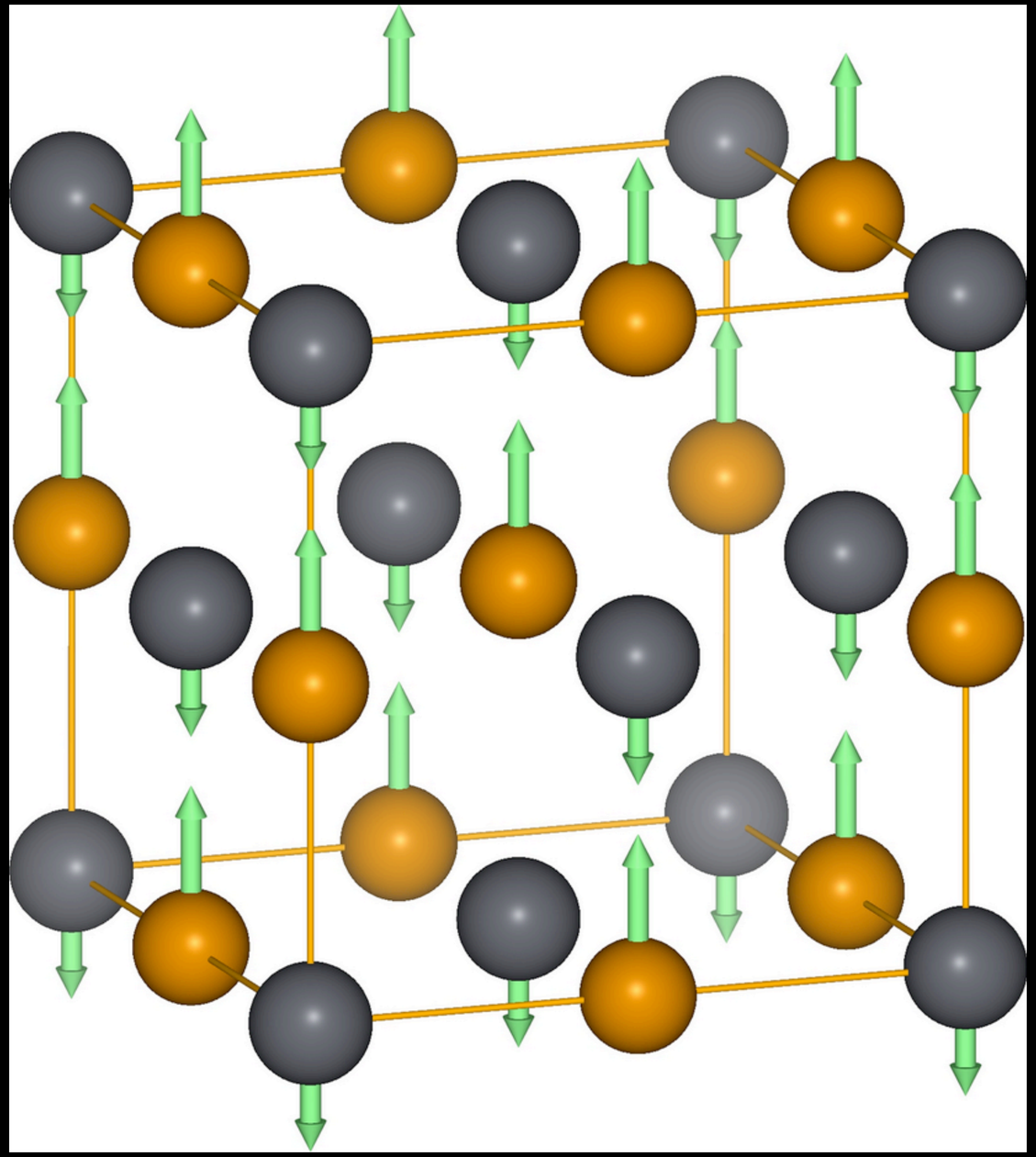


Computing Phonons in SIESTA

SIESTA School 2025
November 20th, 2025

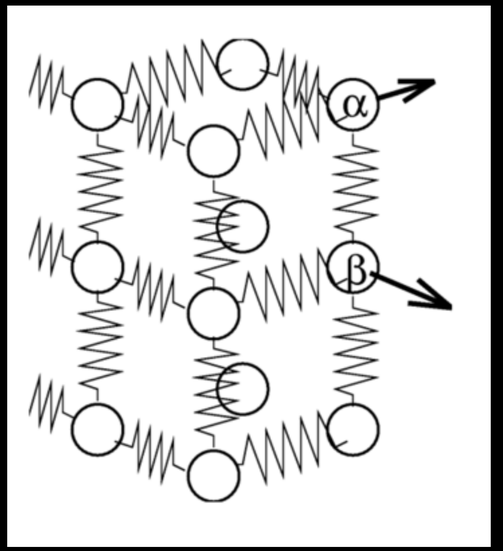
Miguel Pruneda

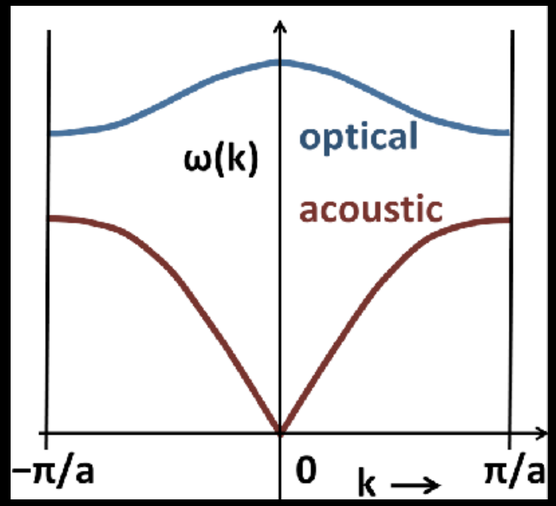
Phonons in Crystals

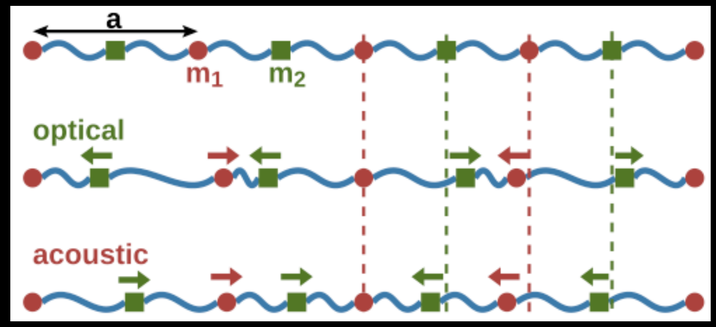


$$F_{\alpha\beta}^{ij} = \frac{\partial^2 E}{\partial u_\alpha^i \partial u_\beta^j}$$

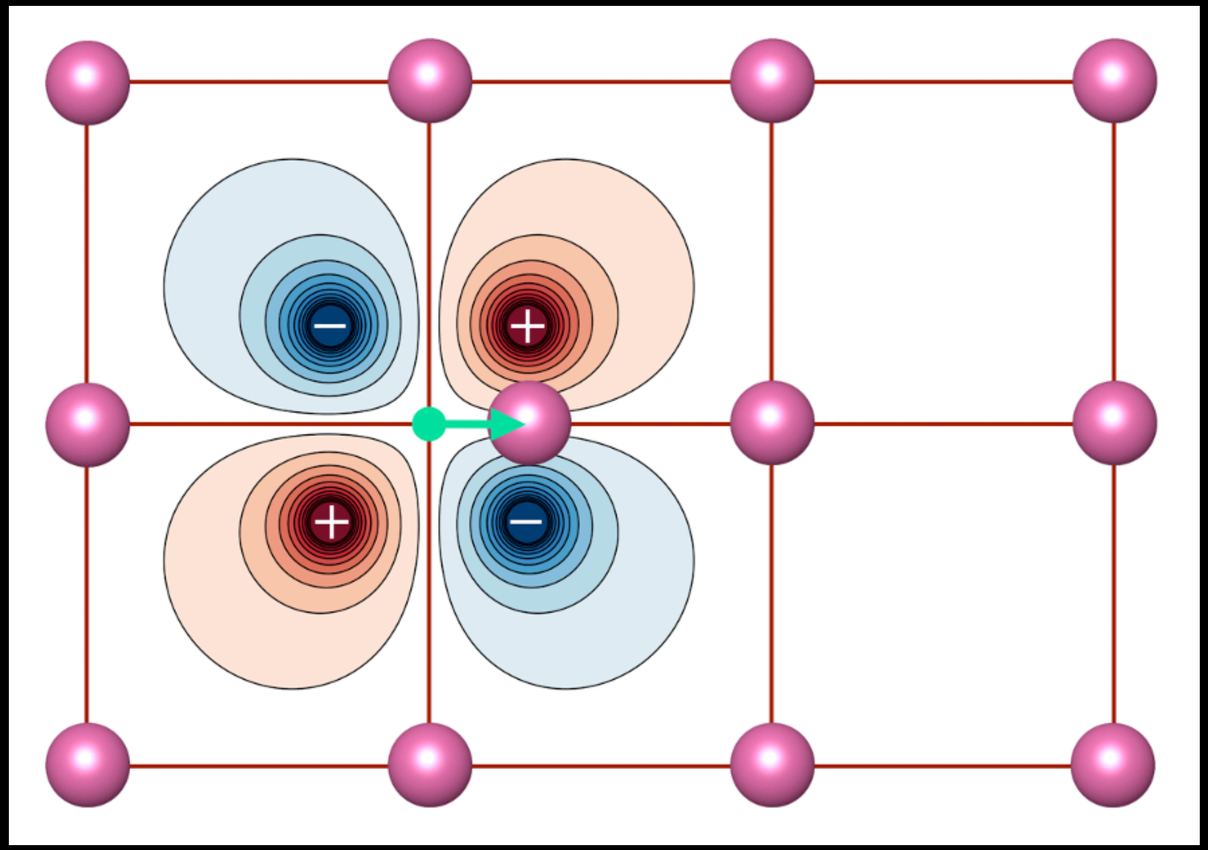
$$M_s \ddot{u}_{s\mathbf{q}}^i = -\sum_{s'}^{n} \sum_{j}^{3} F_{ss'}^{ij}(\mathbf{q}) u_{s'\mathbf{q}}^j$$

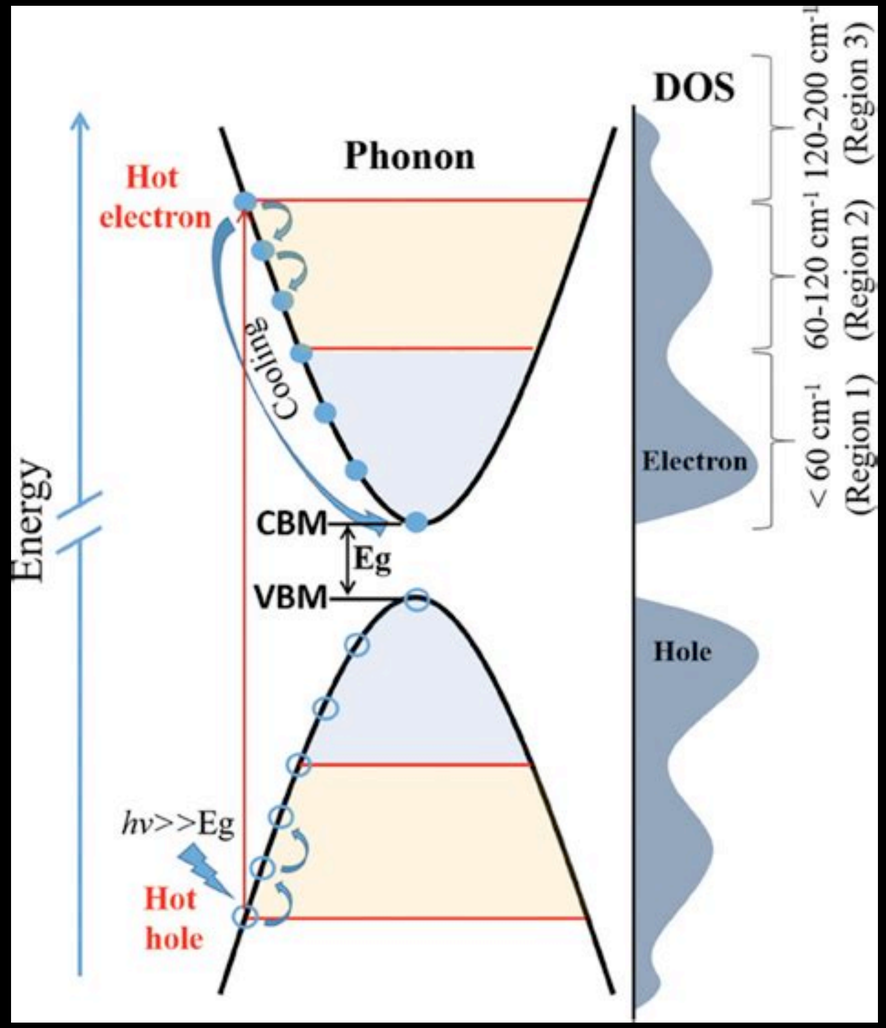






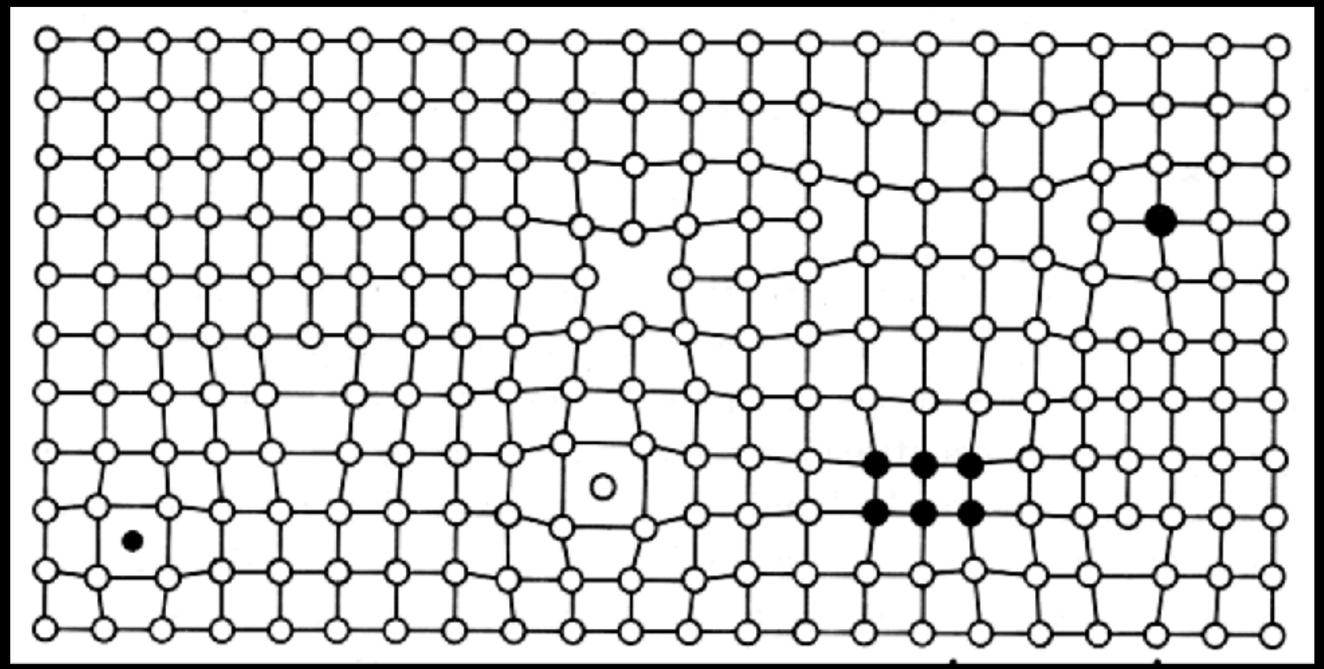
Electrons are “coupled to the lattice”





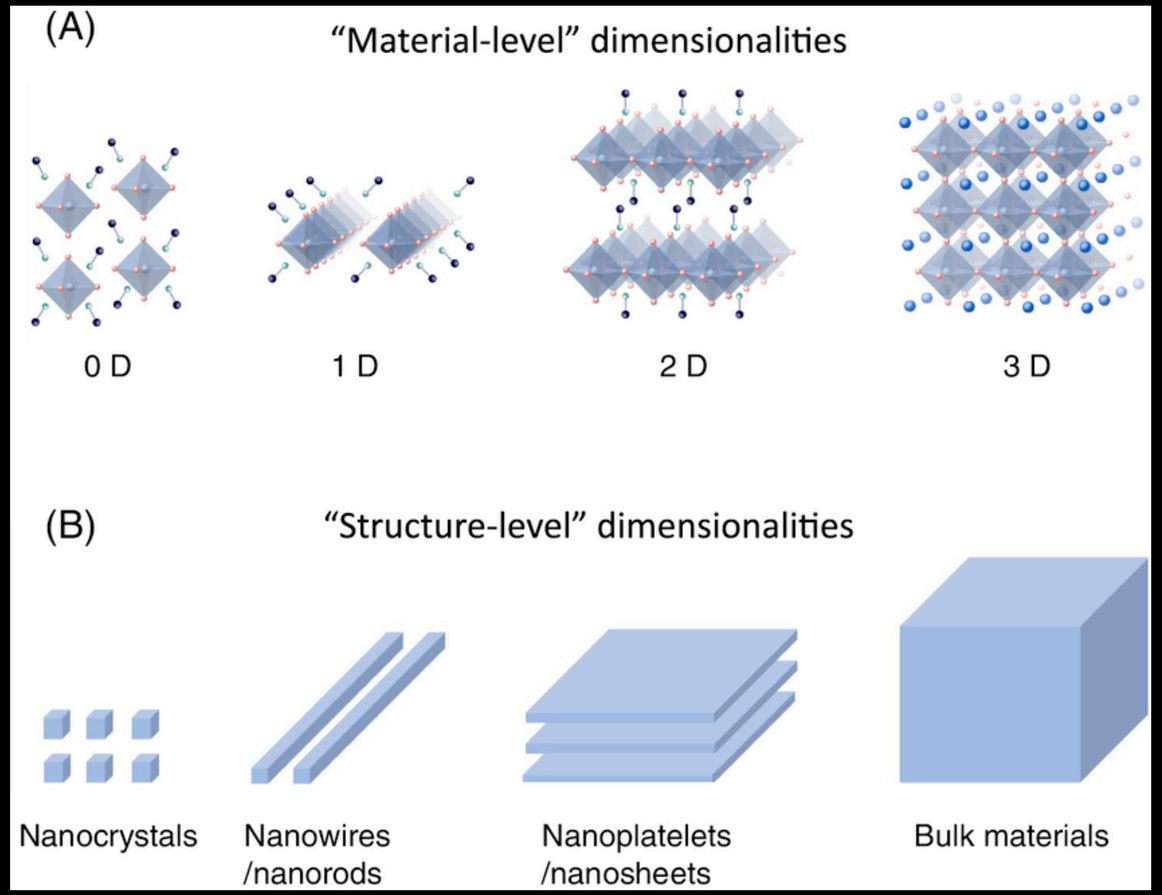
… and this has many consequences

“Crystals” are not that simple…



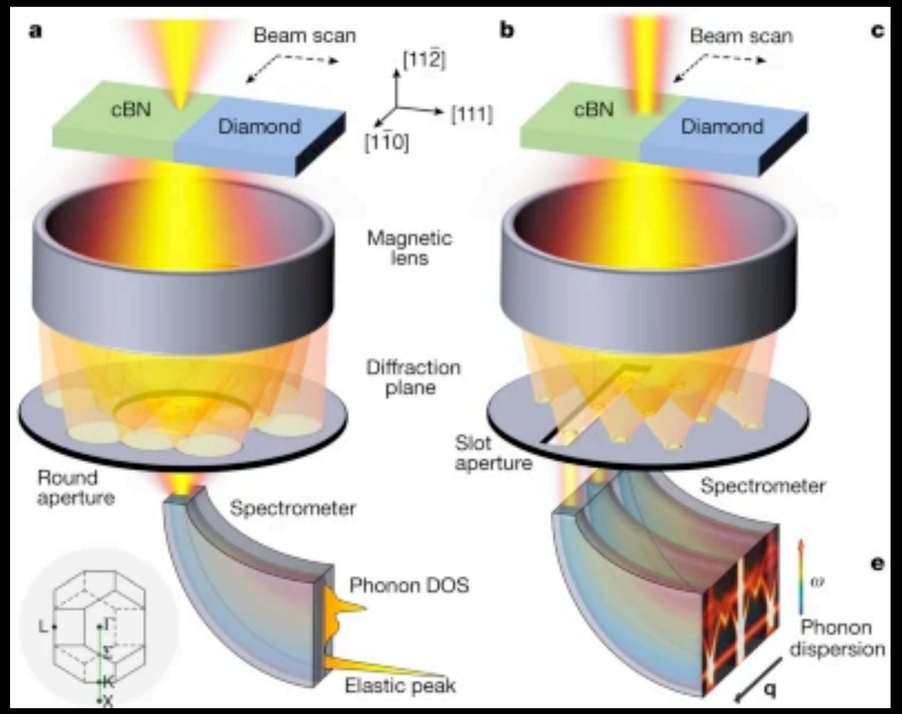
Defects

Dimensionality



Vibrational STEM-EELS

kiloelectronvolt electron beam



3D EELS (x-y-ω)

4D EELS (x-y-ω-q)

X. Yan, *et al.* Single-defect phonons imaged by electron microscopy. *Nature* 589, 65–69 (2021).

R. Qi, *et al.* Measuring phonon dispersion at an interface. *Nature* 599, 399–403 (2021).

R. Qi, *et al.* Four-dimensional vibrational spectroscopy for nanoscale mapping of phonon dispersion in BN nanotubes. *Nat Commun* 12, 1179 (2021).

Xu, M., Bao, DL., Li, A. *et al.* Single-atom vibrational spectroscopy with chemical-bonding sensitivity. *Nat. Mater.* 22, 612–618 (2023).

H. Jiang, *et al.* Atomic-scale visualization of defect-induced localized vibrations in GaN. *Nat Commun* 15, 9052 (2024).

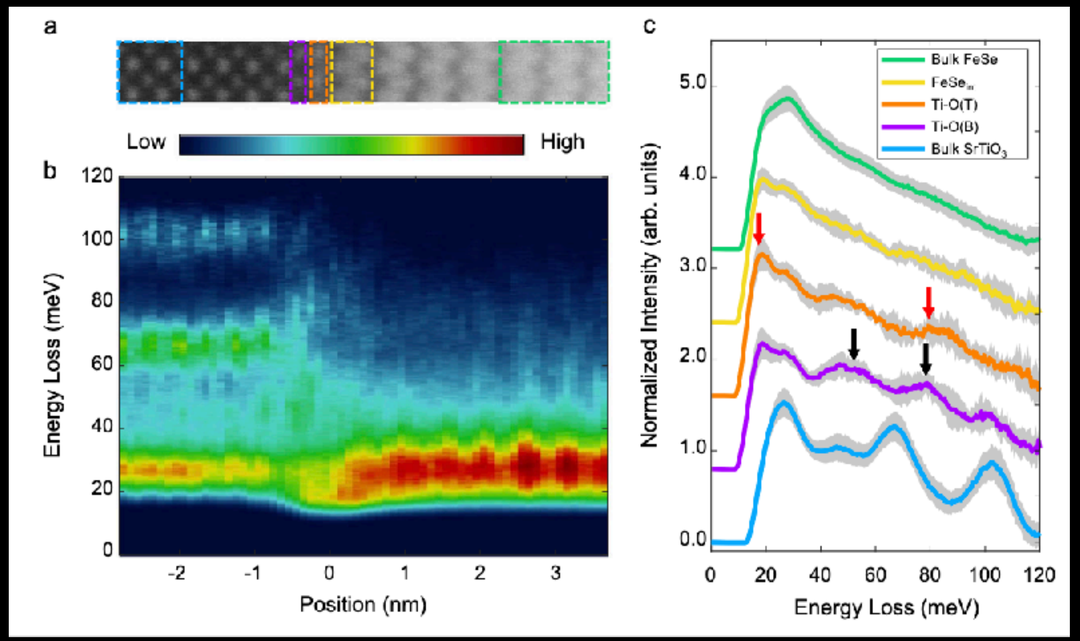
Interfacial phonons

nature communications

Article

https://doi.org/10.1038/s41467-024-47688-5

Atomic-scale observation of localized phonons at FeSe/$SrTiO_3$ interface



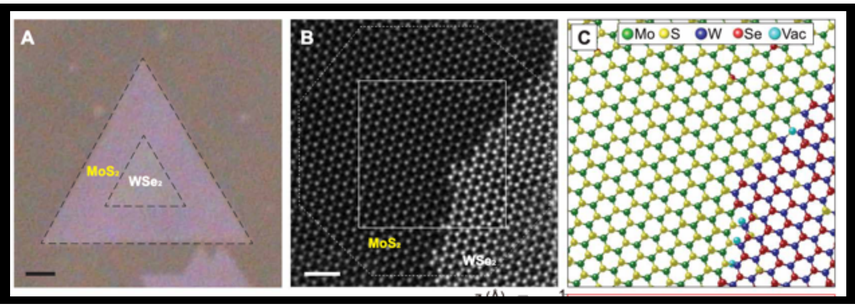
The atomically resolved phonon spectra at the FeSe/SrTiO3 interface. **a** The HAADF image showing the region where EELS spectra are acquired. **b** The map of atomically resolved off-axis EELS spectra across the interface. **c** The spectra extracted from bulk SrTiO3 (blue), Ti–O(B) (purple), Ti–O(T) (orange), FeSe layer adjacent to the interface (yellow), and bulk FeSe (green). Their spatial regions are labeled by dashed rectangles with corresponding colors in (**a**).

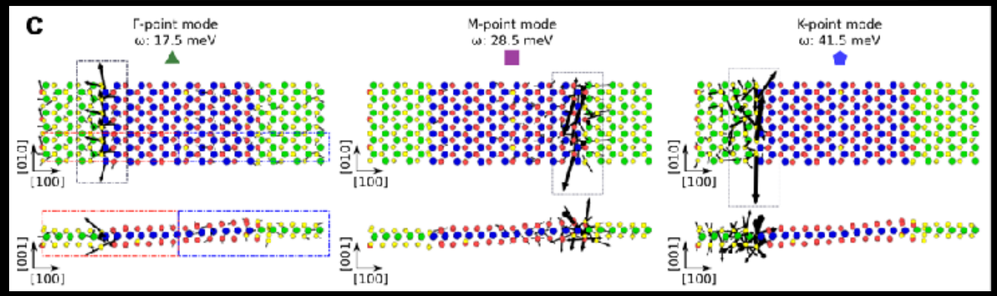
SCIENCE ADVANCES | RESEARCH ARTICLE

CONDENSED MATTER PHYSICS

Capturing 3D atomic defects and phonon localization at the 2D heterostructure interface

Xuezeng Tian[1,2†], Xingxu Yan[3,4†], Georgios Varnavides[5,6,7†], Yakun Yuan[1], Dennis S. Kim[1], Christopher J. Ciccarino[5,8], Polina Anikeeva[6,7], Ming-Yang Li[9], Lain-Jong Li[10], Prineha Narang[5]*, Xiaoqing Pan[3,4,11]*, Jianwei Miao[1]*





ACSNANO

www.acsnano.org

Strong Electron–Phonon Interaction in 2D Vertical Homovalent III–V Singularities

Lipin Chen, Oliver Skibitzki, Laurent Pedesseau, Antoine Létoublon, Julie Stervinou, Rozenn Bernard, Christophe Levallois, Rozenn Piron, Mathieu Perrin, Markus Andreas Schubert, Alain Moréac, Olivier Durand, Thomas Schroeder, Nicolas Bertru, Jacky Even, Yoan Léger, and Charles Cornet*

Cite This: ACS Nano 2020, 14, 13127−13136

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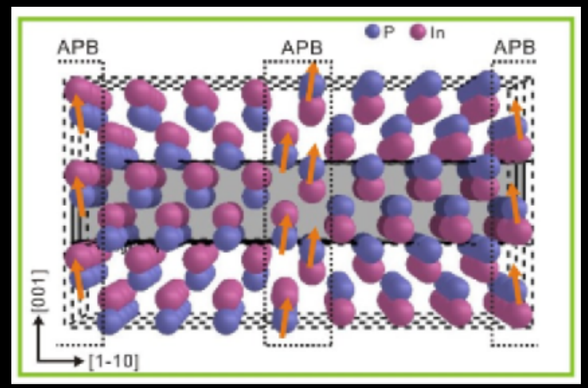


Antiphase Boundaries

Yang, H., Zhou, Y., Miao, G. *et al.* Phonon modes and electron–phonon coupling at the FeSe/$SrTiO_3$ interface. *Nature* 635, 332–336 (2024).

Hoglund, Eric R., et al. "Direct visualization of localized vibrations at complex grain boundaries." *Advanced Materials* 35.13 (2023): 2208920.

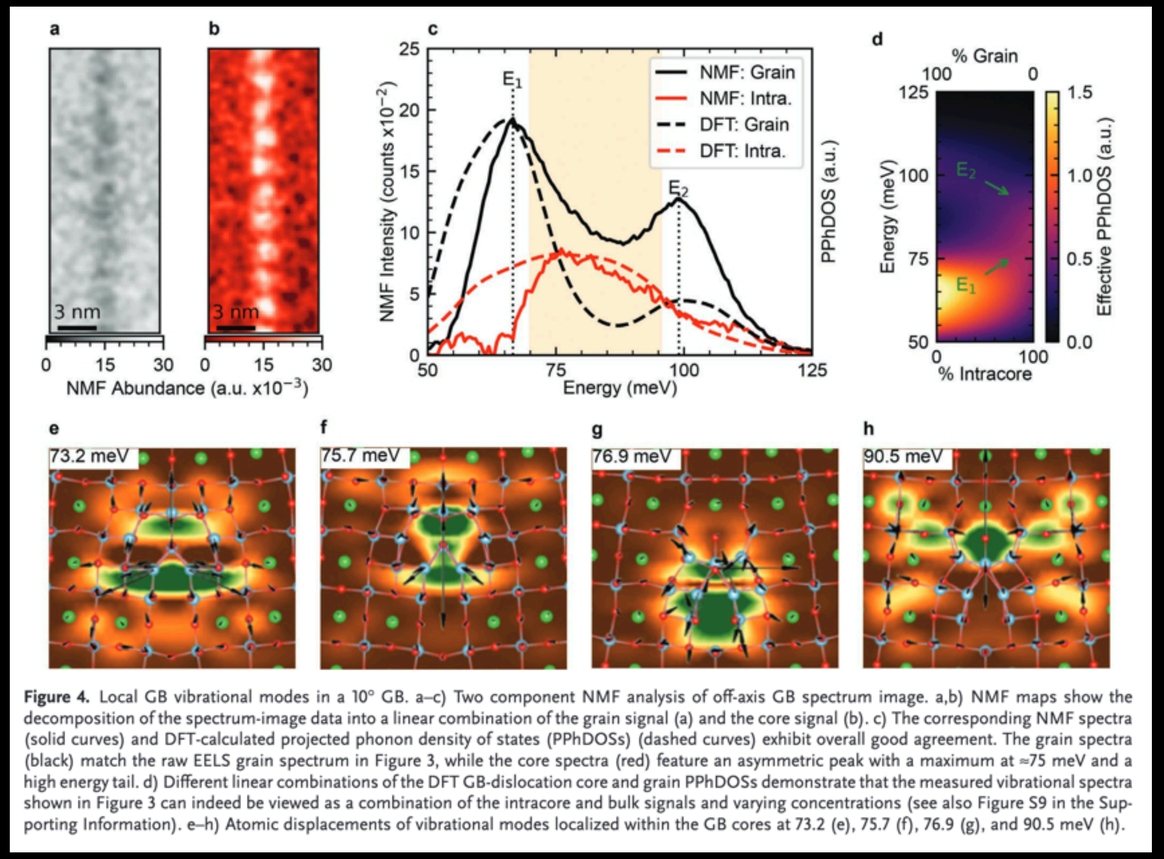
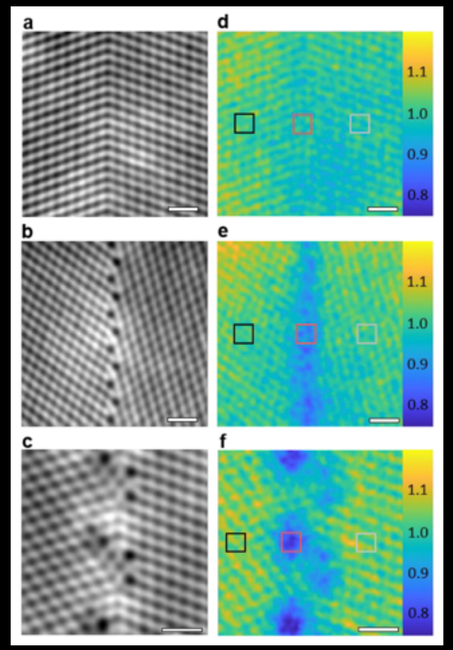


Figure 4. Local GB vibrational modes in a 10° GB. a–c) Two component NMF analysis of off-axis GB spectrum image. a,b) NMF maps show the decomposition of the spectrum-image data into a linear combination of the grain signal (a) and the core signal (b). c) The corresponding NMF spectra (solid curves) and DFT-calculated projected phonon density of states (PPhDOSs) (dashed curves) exhibit overall good agreement. The grain spectra (black) match the raw EELS grain spectrum in Figure 3, while the core spectra (red) feature an asymmetric peak with a maximum at ≈75 meV and a high energy tail. d) Different linear combinations of the DFT GB-dislocation core and grain PPhDOSs demonstrate that the measured vibrational spectra shown in Figure 3 can indeed be viewed as a combination of the intracore and bulk signals and varying concentrations (see also Figure S9 in the Supporting Information). e–h) Atomic displacements of vibrational modes localized within the GB cores at 73.2 (e), 75.7 (f), 76.9 (g), and 90.5 meV (h).



Haas, Benedikt, et al. "Atomic-resolution mapping of localized phonon modes at grain boundaries." *Nano letters* 23.13 (2023): 5975-5980.

Yan, Jingyuan, et al. "Nanoscale localized phonons at Al2O3 grain boundaries." *Nano Letters* 24.11 (2024): 3323-3330.

What are phonons?

Wikipedia

A phonon is a *quasiparticle*, collective excitation in a periodic, elastic arrangement of atoms or molecules in condensed matter, specifically in solids and some liquids.

…but we will include “molecular vibrations” in the package.

What are phonons?

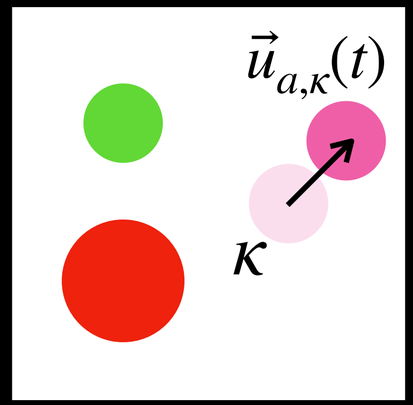
$$\vec{R}_{a,\kappa}(t) = \vec{R}^0_{a,\kappa} + \vec{u}^a_\kappa(t)$$

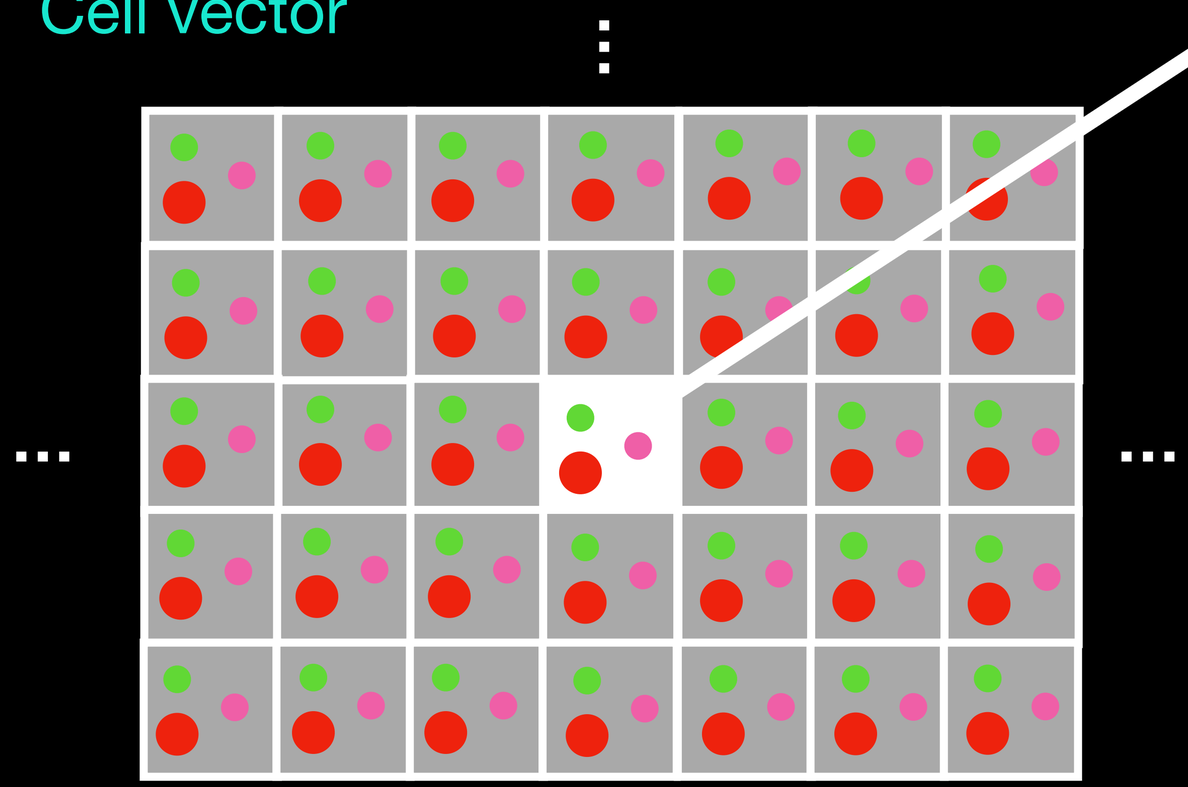
"Small" displacement from equilibrium

Atomic position within the cell

$$\vec{R}_{a,\kappa} = \vec{R}_a + \vec{\tau}_\kappa$$

Cell vector



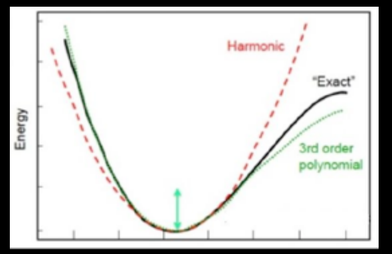


$$E_{tot}(t) = E_{tot}(\{\vec{R}^0_{a\kappa}\}) + \frac{\partial E_{tot}(\{R_{a\kappa}\})}{\partial \vec{R}_{a\kappa}} \vec{u}^a_\kappa(t) +$$

$$+\frac{1}{2}\frac{\partial^2 E_{tot}(\{R_{a\kappa}\})}{\partial \vec{R}_{a\kappa}\vec{R}_{a'\kappa'}} \vec{u}^a_\kappa(t)\vec{u}^{a'}_{\kappa'}(t) + \ldots$$

+ Adiabatic approximation

+ Harmonic approximation



What are phonons?

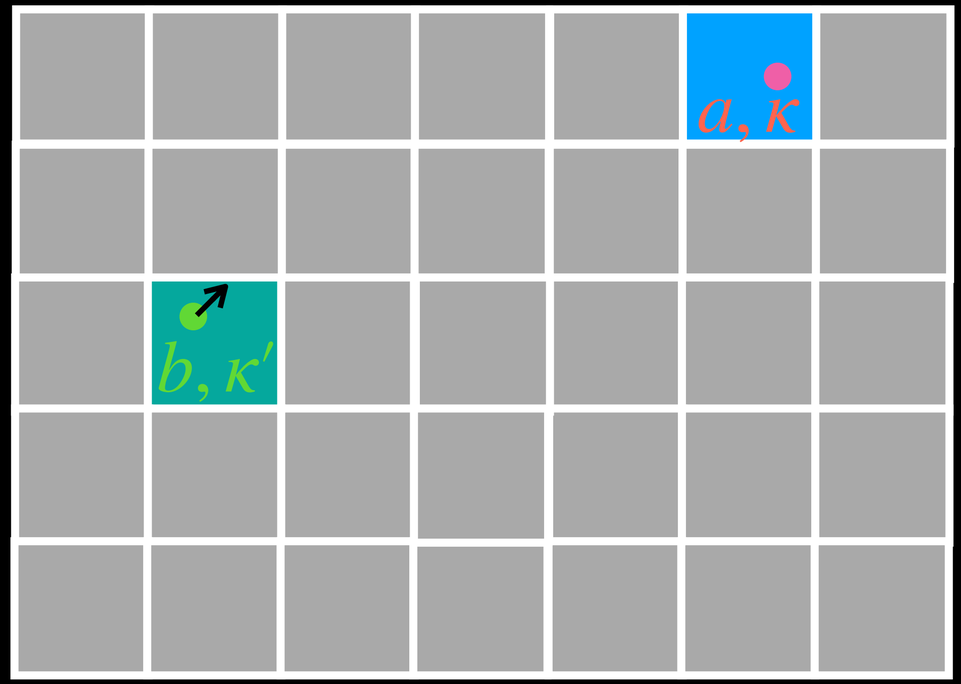
$$C_{i\kappa,j\kappa'}(a,b) = \frac{\partial^2 E_{tot}}{\partial u^a_{i\kappa} \partial u^b_{j\kappa'}} = -\frac{\partial F^b_{j\kappa'}}{\partial u^a_{i\kappa}}$$

Interatomic Force Constant matrix

(i,j) are xyz coordinate's indexes

(a,b) are cell's indexes

(κ,κ') are atom indexes within cell



What are phonons?

$$C_{i\kappa,j\kappa'}(a,b) = \frac{\partial^2 E_{tot}}{\partial u^a_{i\kappa} \partial u^b_{j\kappa'}} = -\frac{\partial F^b_{j\kappa'}}{\partial u^a_{i\kappa}}$$

Interatomic Force Constant matrix

- In the harmonic approximation, these IFC determine the lattice dynamics:

$$F^a_{i\kappa} = -\, C_{i\kappa,j\kappa'}(a,b) \cdot u^b_{j\kappa'} \qquad \vec{F}^a_{\kappa} = -\, \bar{C}_{\kappa,\kappa'}(a,b)\vec{u}^b_{\kappa'} \qquad \text{(Hooke´s law)}$$

$$\vec{F}^a_{\kappa} = M_{\kappa}\vec{a}^a_{\kappa}$$

Lattice dynamics

$$F^a_{i\kappa} = -\, C_{i\kappa,j\kappa'}(a,b)\cdot u^b_{j\kappa'} \quad \Rightarrow \quad F^a_{i\kappa} = -\sum_{j\kappa' b} C_{i\kappa,j\kappa'}(a,b)\cdot u^b_{j\kappa'}$$

(only one atomic displacement)

$$M_\kappa \frac{\partial^2 u^a_{i\kappa}}{\partial t^2} = -\sum_{j\kappa' b} \frac{\partial^2 E_{tot}}{\partial u^a_{i\kappa}\partial u^b_{j\kappa'}} u^b_{j\kappa'}$$

Harmonic displacement Ansatz

$$u^a_{i\kappa}(t) = \xi_{q\nu}(i\kappa)\, e^{i\vec{q}\cdot\vec{R}_a}\, e^{-i\omega_\nu t}$$

Periodic displacement mode

Bloch phase

Time dependence

$$M_\kappa \omega^2_{q\nu}\xi_{q\nu}(i\kappa) = \sum_{j\kappa' b} \bar{C}_{i\kappa,j\kappa'}(a,b)\, e^{i\vec{q}\cdot(\vec{R}_a-\vec{R}_b)}\, \xi_{q\nu}(j\kappa')$$

Fourier transform

Lattice dynamics

In matrix form:

dof = 3 x (# of atoms in unit cell)

$$\omega_{q\nu}^2 \left(M_\kappa \delta_{\kappa\kappa'} \delta_{ij} \right) \left(\xi_{q\nu} \right) = \left(\bar{C}(q) \right) \left(\xi_{q\nu} \right)$$

- Coordinate index
- Atom index

$$M_\kappa \omega_{q\nu}^2 \xi_{q\nu}(i\kappa) = \sum_{j\kappa' b} \bar{C}_{i\kappa, j\kappa'}(a, b)\, e^{i\vec{q}\cdot(\vec{R}_a - \vec{R}_b)}\, \xi_{q\nu}(j\kappa')$$

Fourier transform

Lattice dynamics

In matrix form:

dof = 3 x (# of atoms in unit cell)

$$\omega_{q\nu}^2 \left(M_\kappa \delta_{\kappa\kappa'} \delta_{ij}\right) \left(\xi_{q\nu}\right) = \left(\bar{C}(q)\right) \left(\xi_{q\nu}\right)$$

$$\omega_{q\nu}^2 \left(\xi_{q\nu}\right) = \left(\bar{D}(q)\right) \left(\xi_{q\nu}\right)$$

Dynamical Matrix

$$\bar{D}_{i\kappa,j\kappa'}(q) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \bar{C}_{i\kappa,j\kappa'}(q)$$

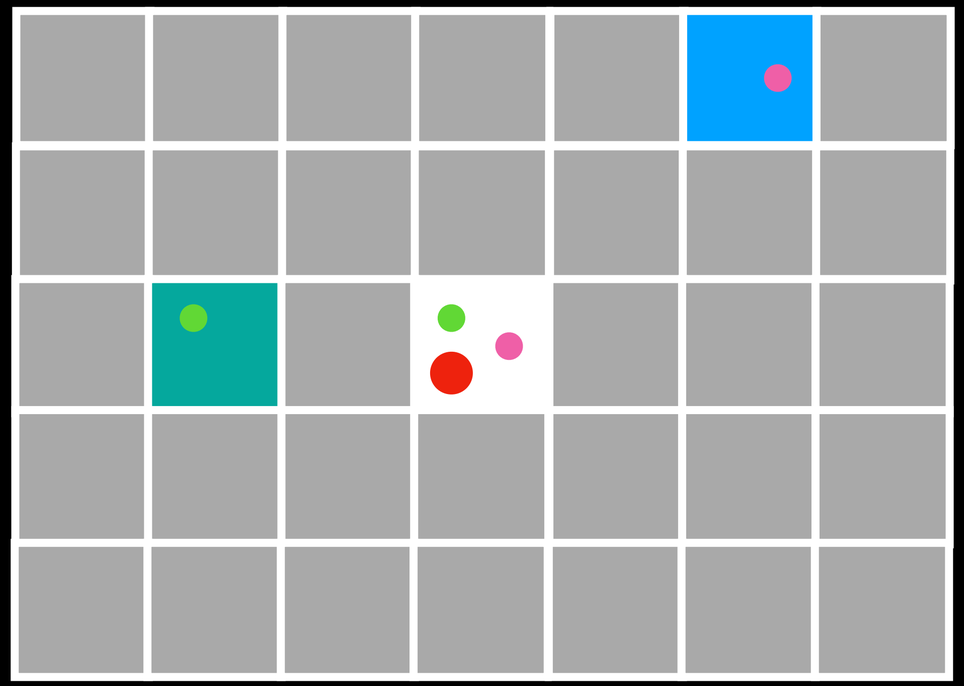
$$= \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \sum_b \bar{C}_{i\kappa,j\kappa'}(0,b)\, e^{i\vec{q}\cdot\vec{R}_b}$$

$$M_\kappa \omega_{q\nu}^2 \xi_{q\nu}(i\kappa) = \sum_{j\kappa' b} \bar{C}_{i\kappa,j\kappa'}(a,b)\, e^{i\vec{q}\cdot(\vec{R}_a - \vec{R}_b)}\, \xi_{q\nu}(j\kappa')$$

Fourier transform

How to compute phonons in SIESTA?

- Relax structure
- Build a supercell
- Displace atom “i” in cell “0”
- Compute forces over all atoms in cells R saving each row of the FC matrix
- Fourier transform the FC matrix to selected q points
- Diagonalize Dynamical Matrix and obtain frequencies and eigenmodes



$$\bar{D}_{i\kappa,j\kappa'}(q) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \sum_b \bar{C}_{i\kappa,j\kappa'}(0,b)\, e^{i\vec{q}\cdot\vec{R}_b}$$

How to compute phonons in SIESTA?

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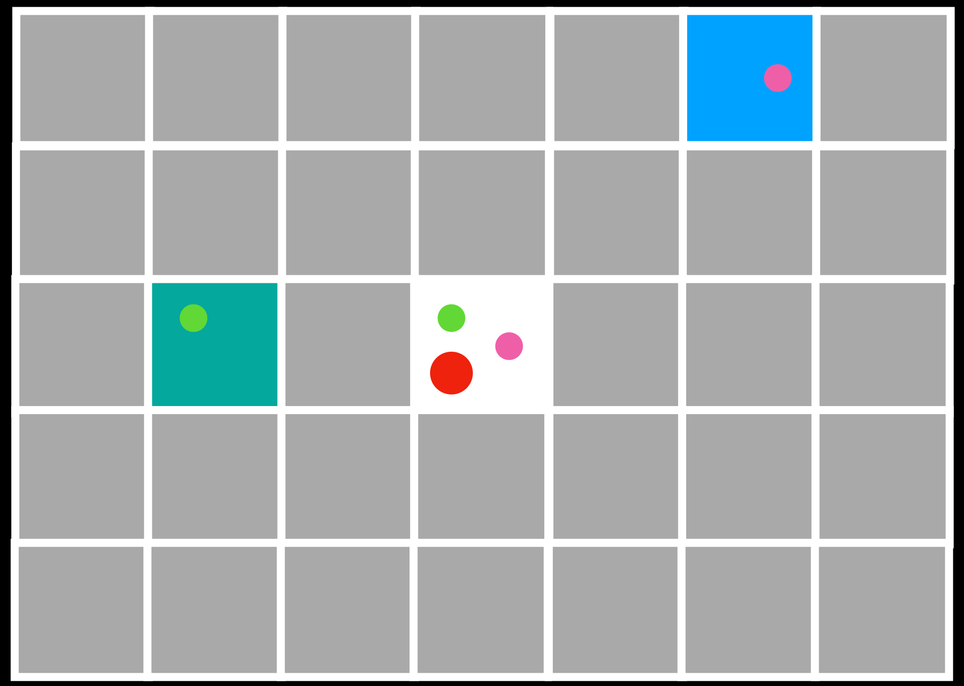
Tolerance on the forces < 0.01 eV/Å

Caution with egg box effect and grid sampling



$$\bar{D}_{i\kappa,j\kappa'}(q) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \sum_b \bar{C}_{i\kappa,j\kappa'}(0,b)\, e^{i\vec{q}\cdot\vec{R}_b}$$

How to compute phonons in SIESTA?

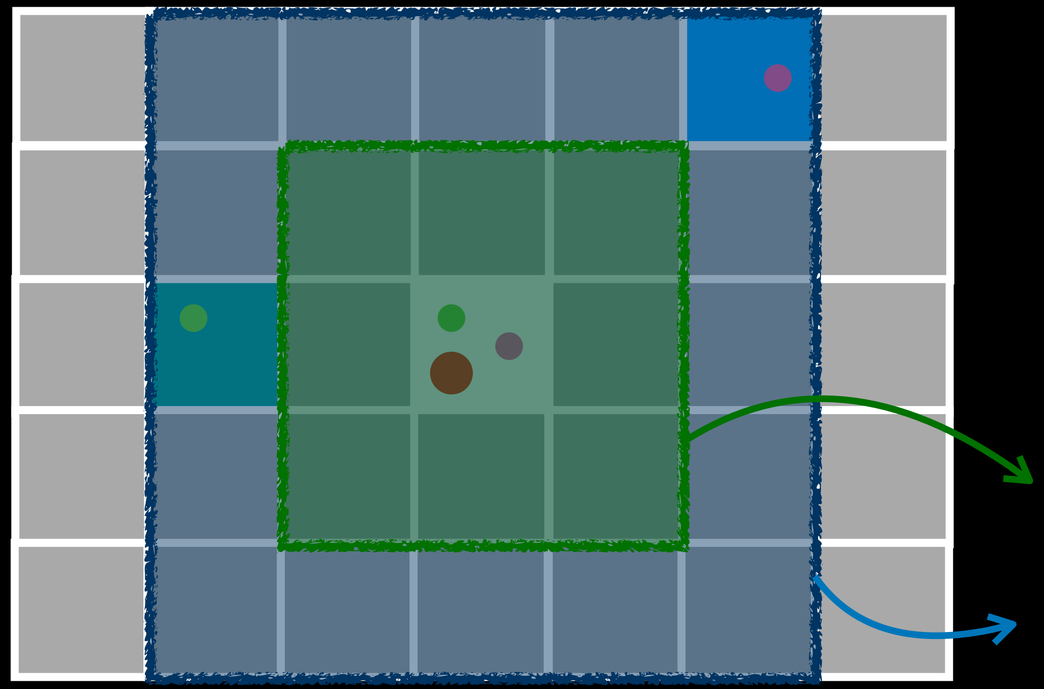
- Relax structure
- Build a supercell
- Displace atom “i” in cell “0”
- Compute forces over all atoms in cells R saving
- Fourier transform the FC matrix to selected q po
- Diagonalize Dynamical Matrix and obtain frequer

- `Fcbuild` (Utils/Vibra)

```
SuperCell_1    N
```

generates a supercell with 2N+1 unit cells along axis “1”

- Check convergence with N



$$\bar{D}_{i\kappa,j\kappa'}(q) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \sum_b \bar{C}_{i\kappa,j\kappa'}(0,b)\, e^{i\vec{q}\cdot\vec{R}_b}$$

How to compute phonons in SIESTA?

- Relax structure
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- Displace atom “i” in cell “0”
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- Fourier transform the FC matrix to selected q points
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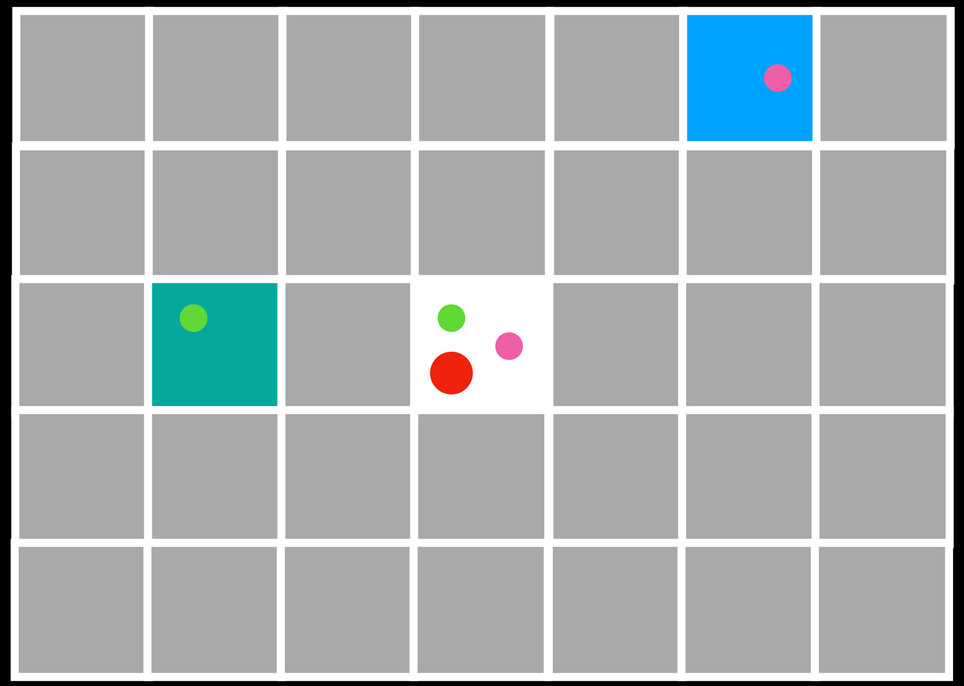

- Automatically done with FC option for MD

```
MD.TypeOfRun          FC
FC.Displacement       Δu Bohr
FC.First              1
FC.Last               N
```

- Displacements by Δu in $\pm x, \pm y, \pm z$
- Keep Δu small enough for the harmonic approximation to be valid, (but large enough to avoid numerical noise in the forces!). Frequently 0.005<Δu<0.05 Å

$$\bar{D}_{i\kappa,j\kappa'}(q) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \sum_b \bar{C}_{i\kappa,j\kappa'}(0,b)\, e^{i\vec{q}\cdot\vec{R}_b}$$

How to compute phonons in SIESTA?

- Relax structure
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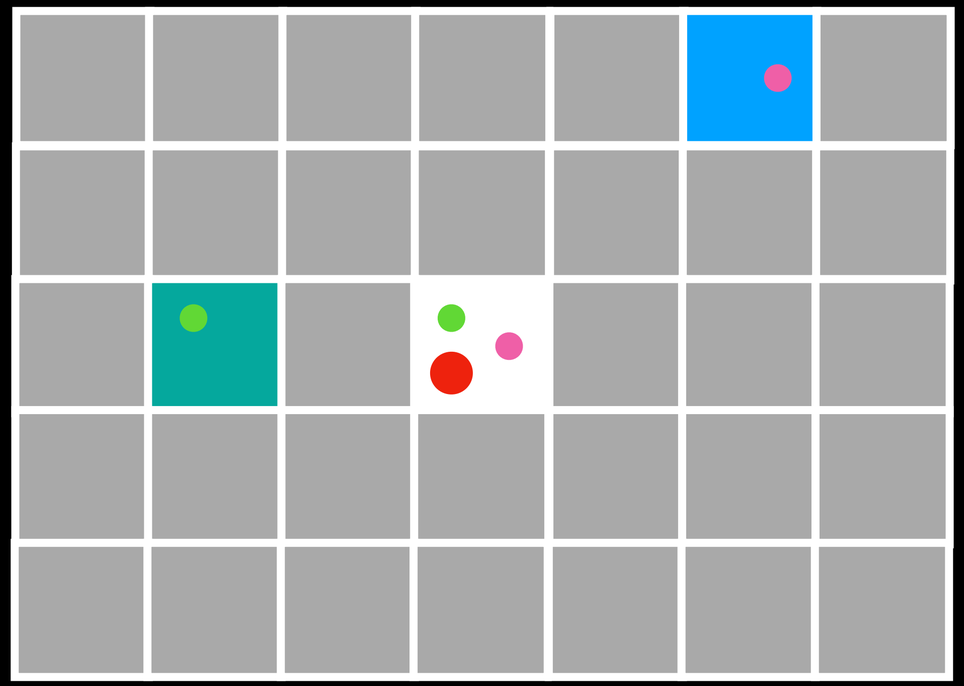
- Displace atom “i” in cell “0”
- Compute forces over all atoms in cells R saving each row of the FC matrix
- Fourier transform the FC matrix to selected q points
- Diagonalize Dynamical Matrix and obtain frequencies and eigenmodes

- Automatically stored in file `SystemLabel.FC`
- Files can be concatenated if different runs are required (caution with the first line!)



$$\bar{D}_{i\kappa,j\kappa'}(q) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \sum_b \bar{C}_{i\kappa,j\kappa'}(0,b)\, e^{i\vec{q}\cdot\vec{R}_b}$$

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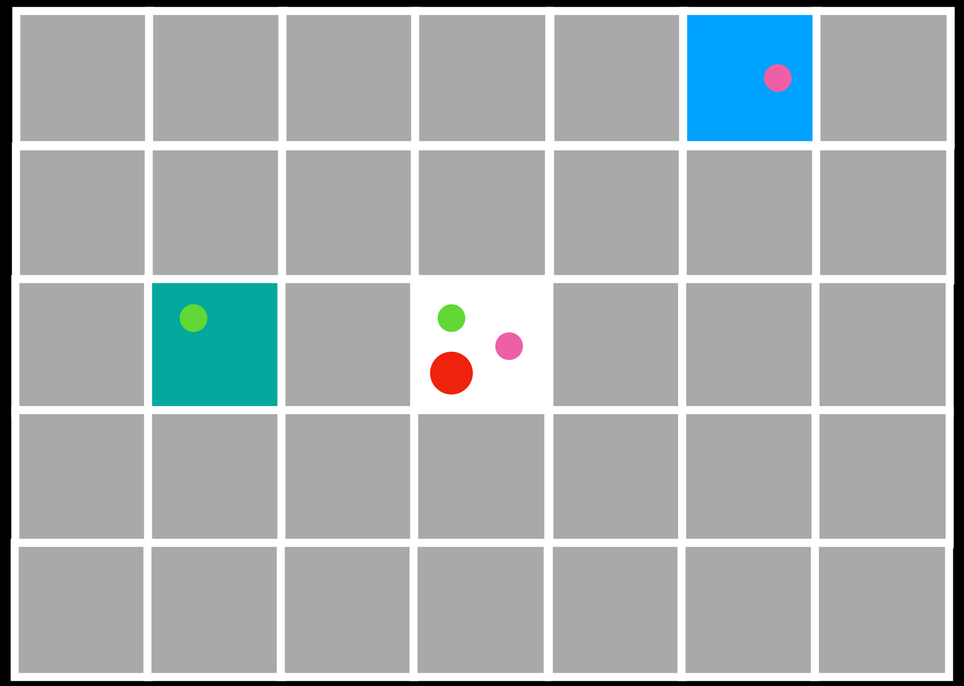
- Diagonalize Dynamical Matrix and obtain frequencies and eigenmodes

- Done by `Vibra` (Utils/Vibra)
- Reads its own input file, and `SystemLabel.FC`
- Atomic masses must be included in the AtomicCoordinates block
- Need to select q path (`BandLines`)



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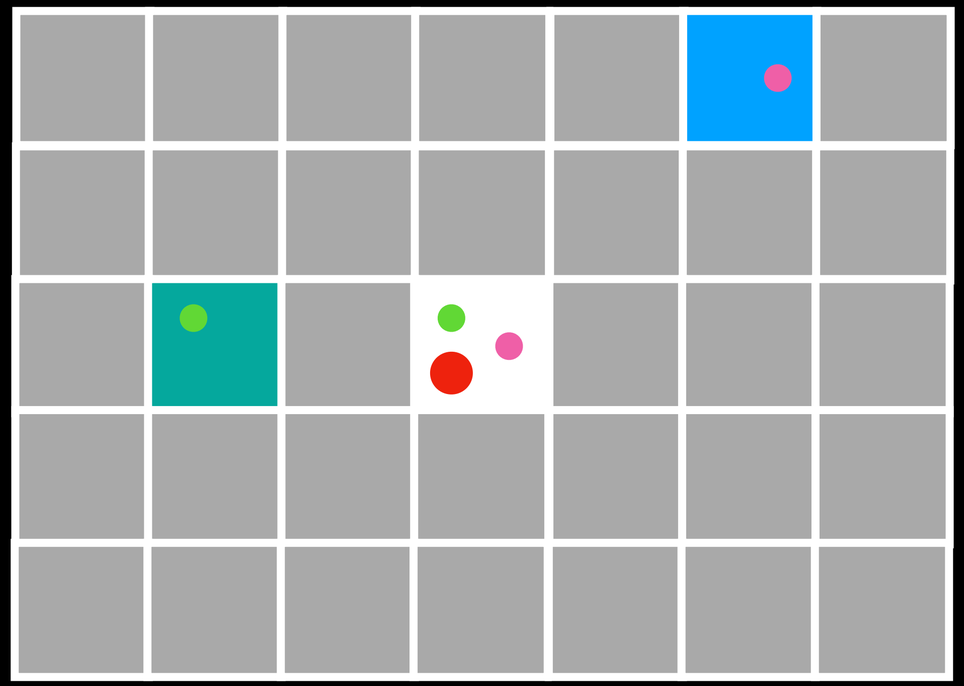

Ready for the hands-on??

How to compute phonons in SIESTA?

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- Compute forces over all atoms in cells R saving each row of the FC matrix
- Fourier transform the FC matrix to selected q points
- Diagonalize Dynamical Matrix and obtain frequencies and eigenmodes

Crystalline Silicon

- Check input files (`Si.fcbuild.fdf` & `Si.ifc.fdf`)
- `fcbuild < Si.fcbuild.fdf`
- `siesta < Si.ifc.fdf > Si.ifc.111.out`
- `vibra < Si.fcbuild.fdf`
- `gnubands -G Si.bands > bands.111.dat`
- Discuss. Check convergence with Supercell.

Benzene (molecular)

- input files (`benzene.relax.fdf`, `benzene.ifc.fdf`, `vib2xsf.dat`)
- `siesta < benzene.ifc.fdf > benzene.ifc.out`
- `vibra < benzene.ifc.fdf > vibra.out`
- Visualize eigenvectors.
- `vib2xsf < vib2xsf.dat`
- `Ovito benzene.Mode_15.AXSF (or any other)`
- Discuss.

Questions?