Density-Functional Theory for Practitioners - Lecture 4

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(Developed by Patrick Rinke and Milica Todorović)

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Revision

At your table, reflect on last week's lecture and tutorial:

- What did you learn about solids?
- What did you find difficult or easy in running the calculations?
- How did the calculations help you understand DFT better?

This lesson

Must know	Should know	Nice to know
Crystal structures	Primitive unit cell	Brillouin zone
Cohesive energy	Bulk-phase diagram	Murnaghan fit
Phonons	Phonon dispersion	Dynamical matrix
Principles of bonding	*Different bonding types*	*Bond formation*

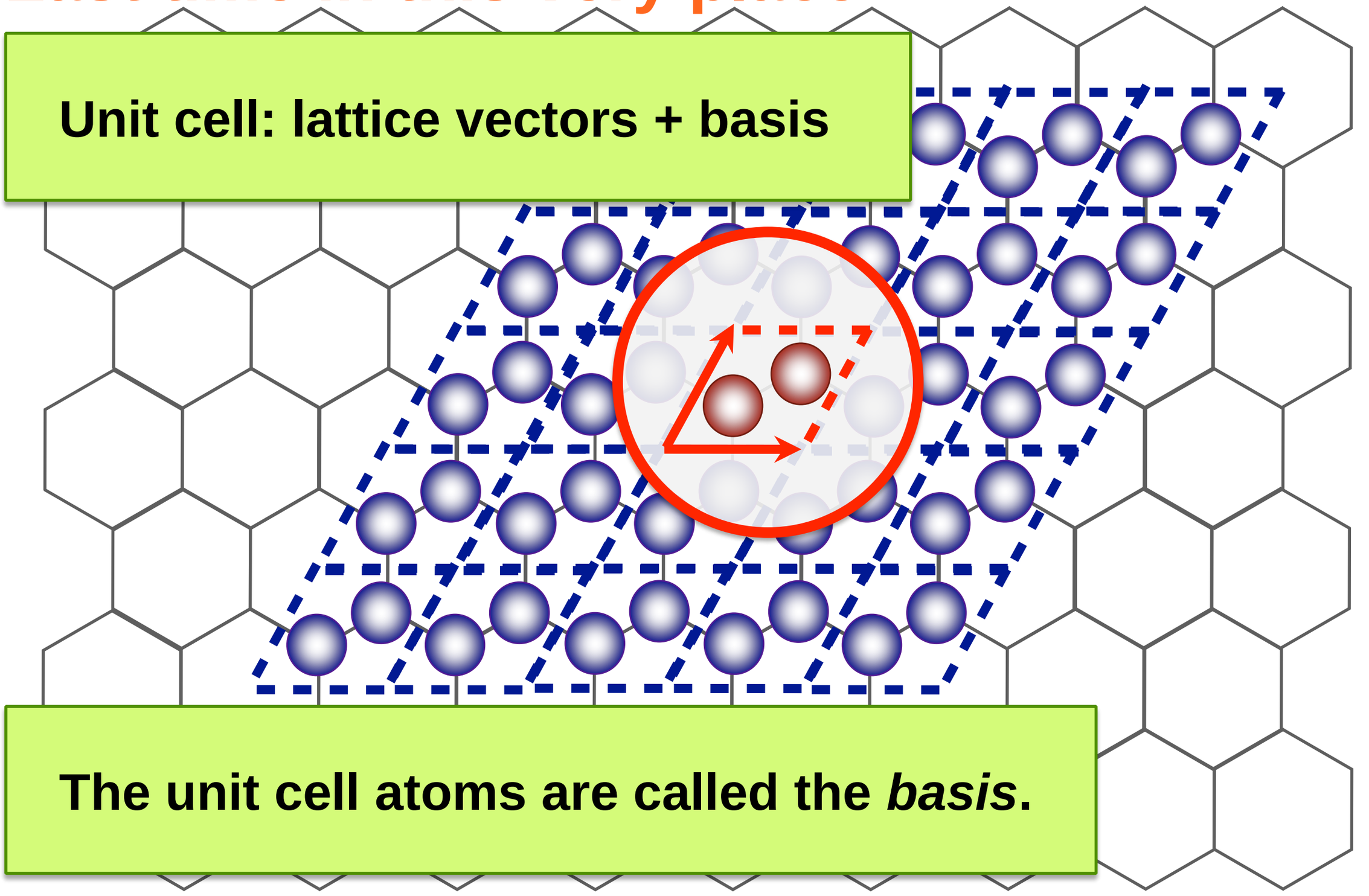
Learning outcomes

After completion of this class you

- are familiar with crystal structures and their unit cells.
- know how to calculate cohesive properties of solids.
- know how to calculate phonons with DFT.

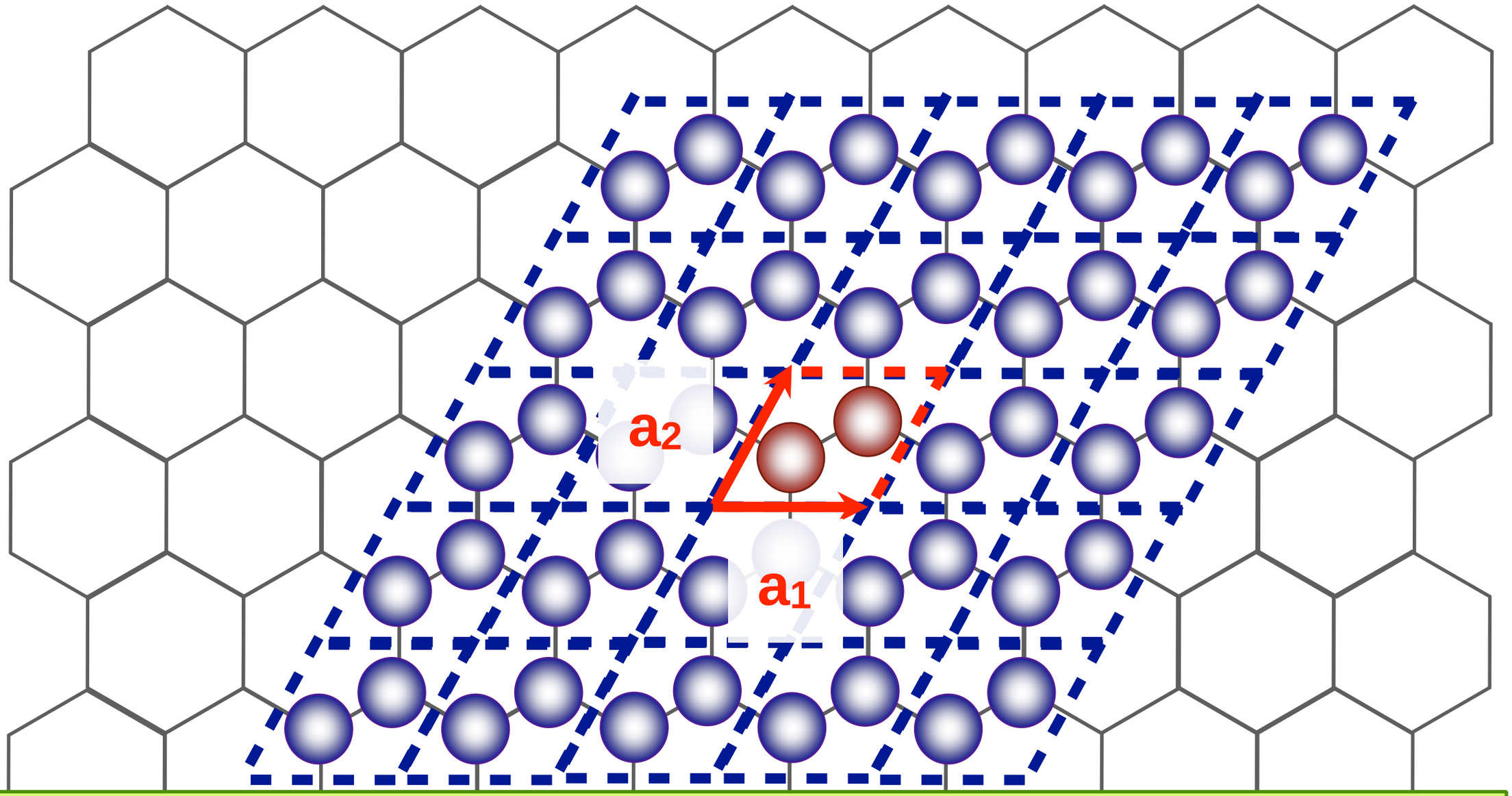
Last time in this very place

Unit cell: lattice vectors + basis



The unit cell atoms are called the *basis*.

Bravais lattice

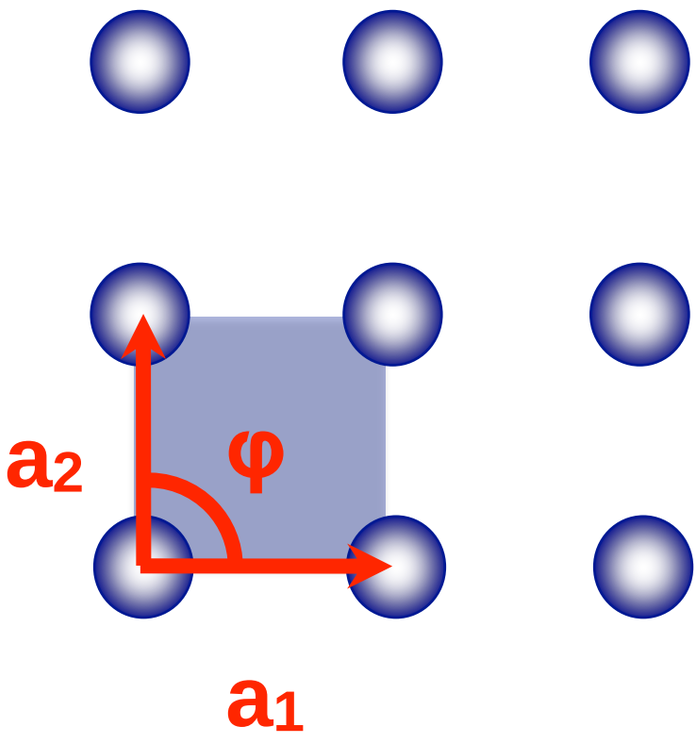


Bravais lattice: space-filling lattice of the type

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

Bravais lattices in 2D

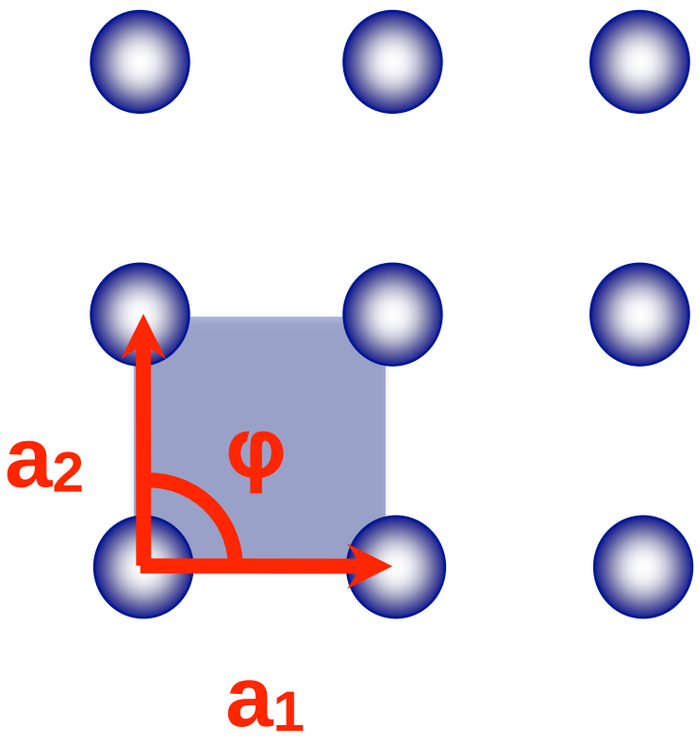
square



$|a_1|=|a_2|$, $\varphi=90°$

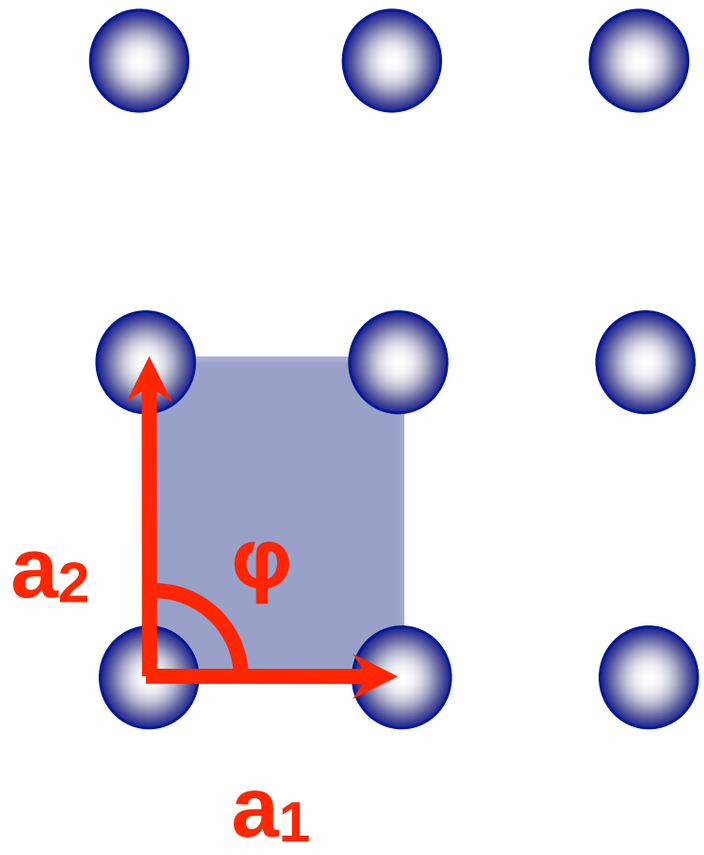
Bravais lattices in 2D

square



$|a_1|=|a_2|$, $\varphi=90°$

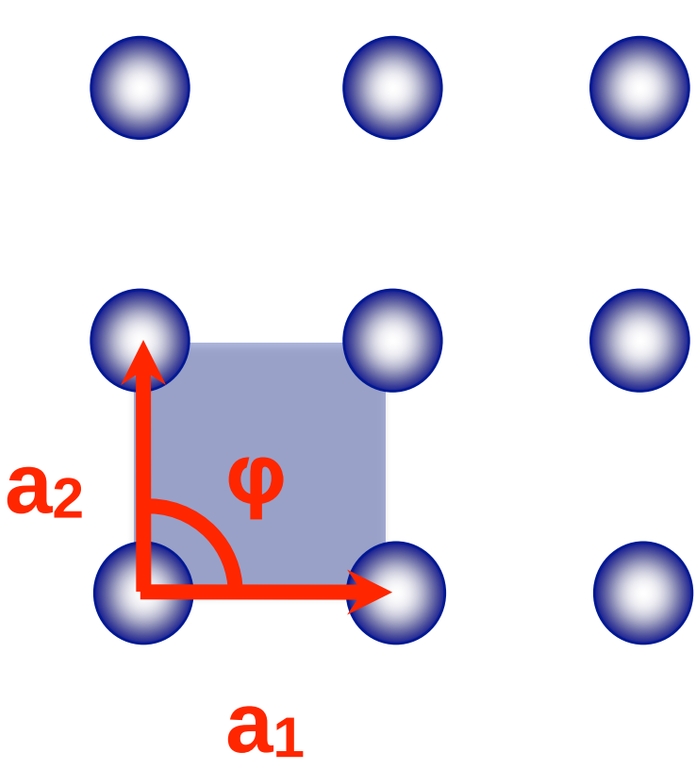
rectangular



$|a_1|\neq|a_2|$, $\varphi=90°$

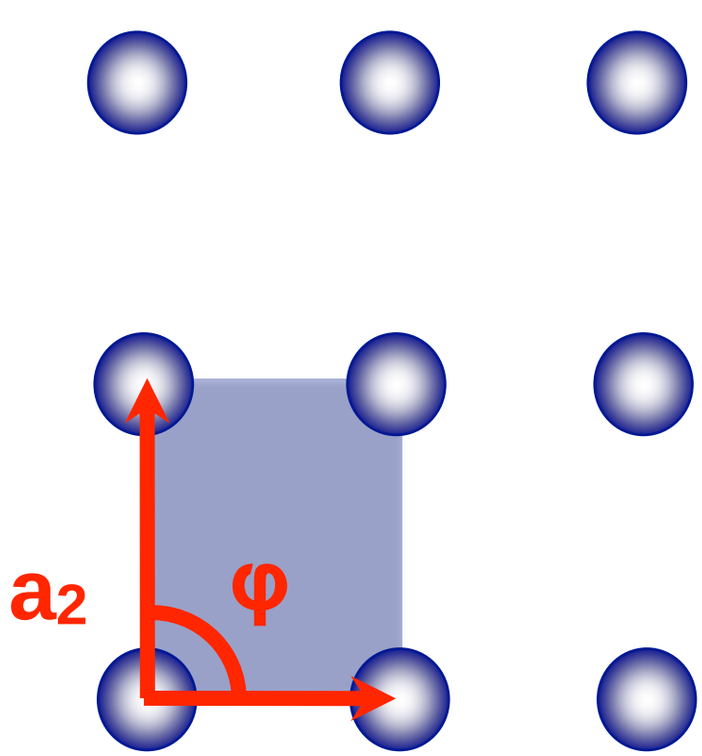
Bravais lattices in 2D

square



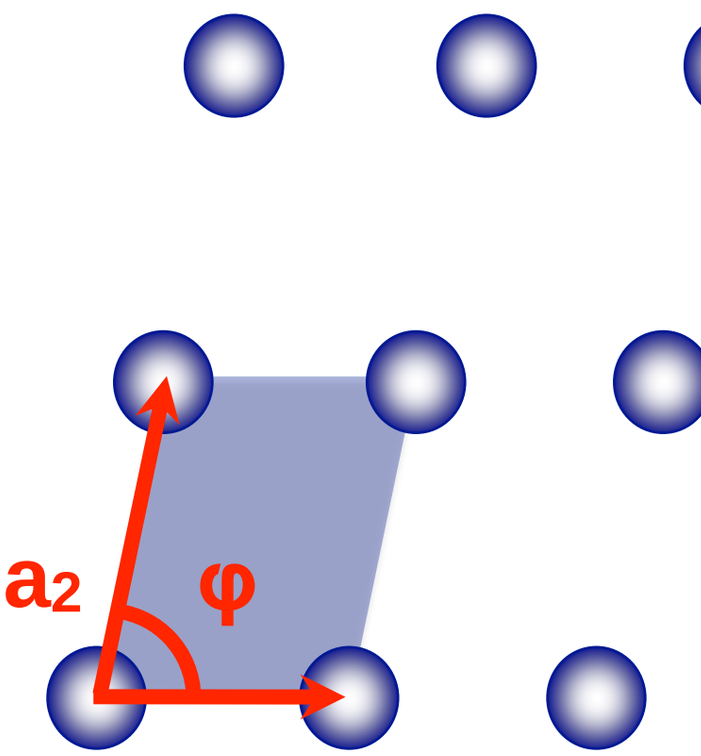
$|a_1|=|a_2|$, $\varphi=90°$

rectangular



$|a_1|\neq|a_2|$, $\varphi=90°$

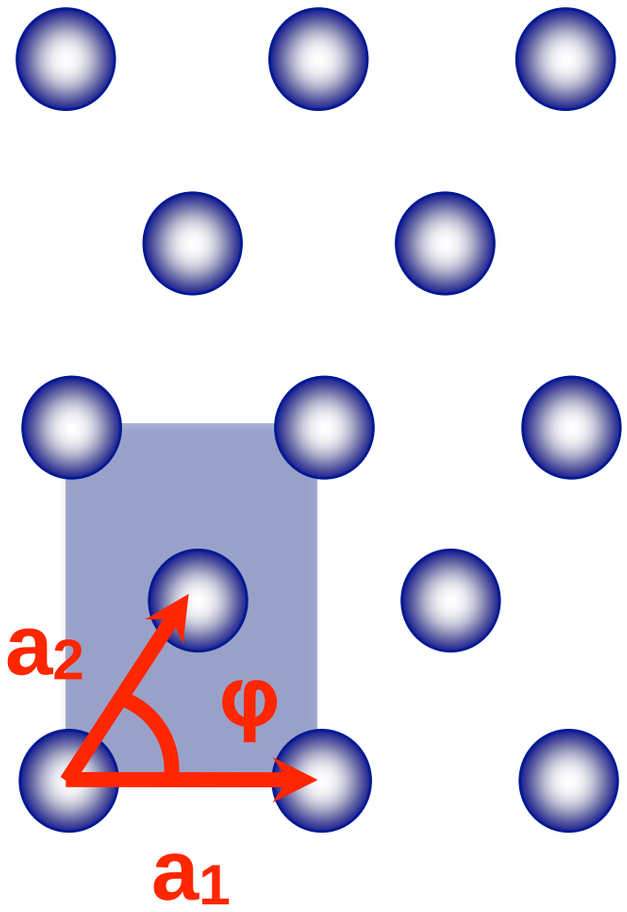
oblique



$|a_1|\neq|a_2|$, $\varphi\neq90°$

Bravais lattices in 2D

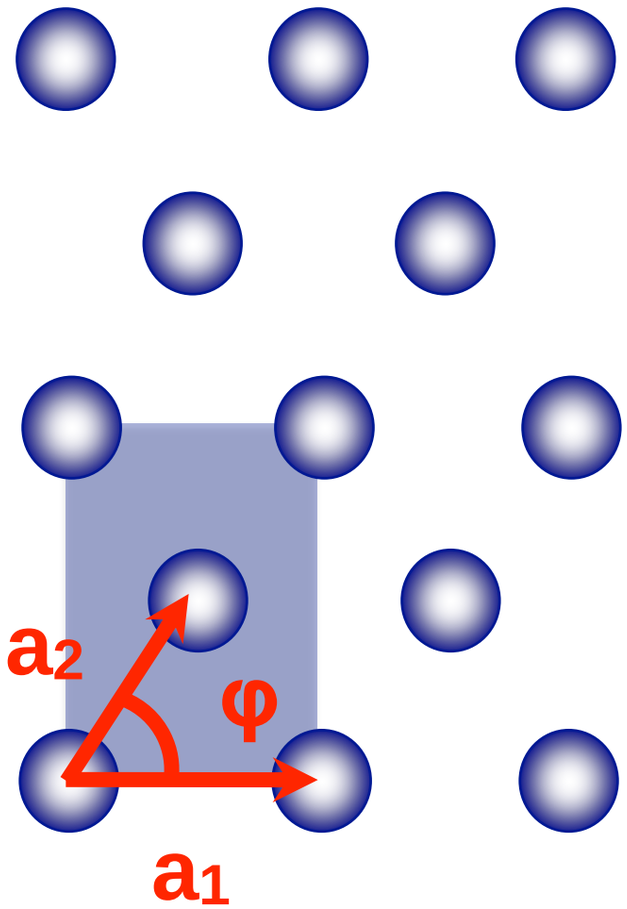
centered rectangular



$|a_1| \neq |a_2|$, $\varphi \neq 90°$

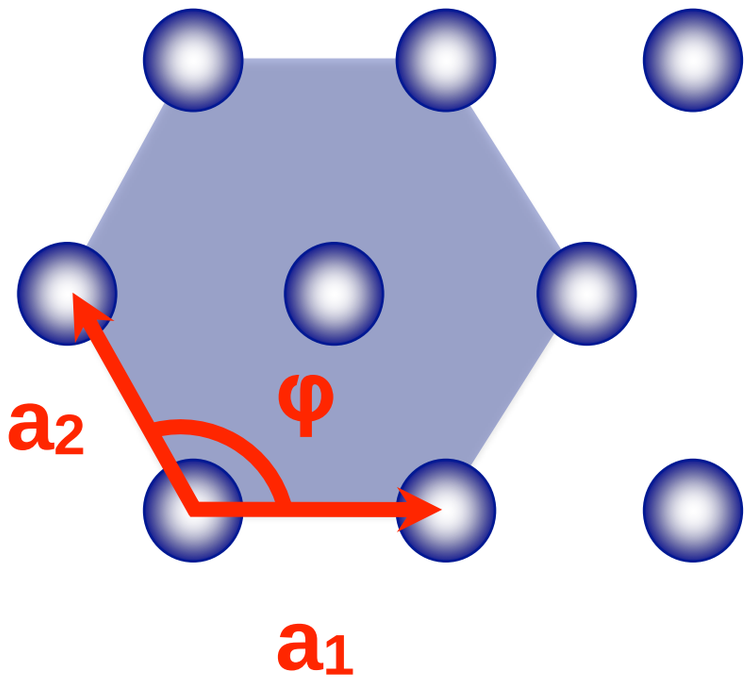
Bravais lattices in 2D

centered rectangular



$|a_1| \neq |a_2|$, $\varphi \neq 90°$

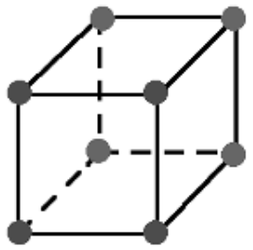
hexagonal



$|a_1| = |a_2|$, $\varphi = 120°$

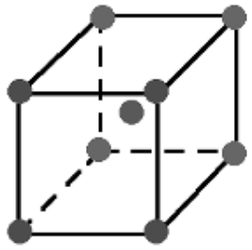
Only 5 different lattices in 2D.

Bravais lattices in 3D



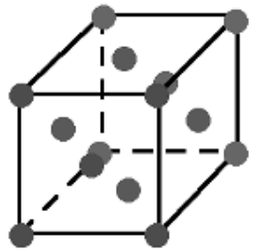
simple cubic

sc



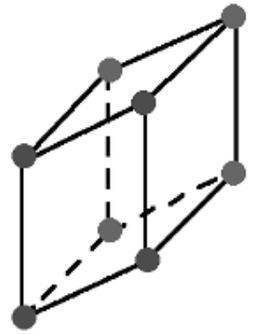
body-centered cubic

bcc

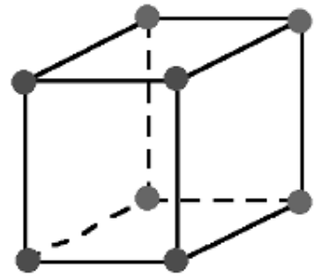


face-centered cubic

fcc/ccp

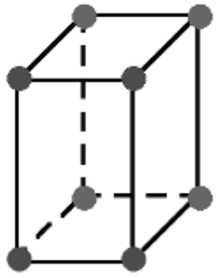


rhombohedral

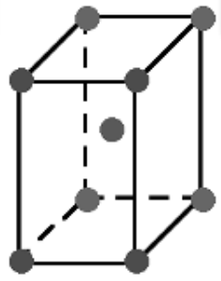


hexagonal

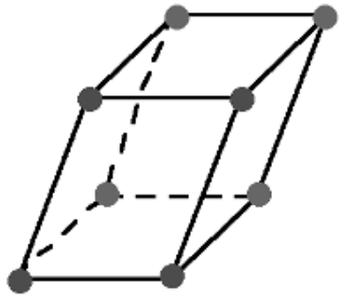
hcp



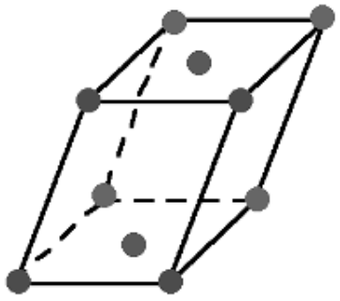
simple tetragonal



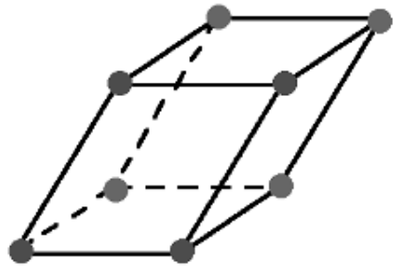
body-centered tetragonal



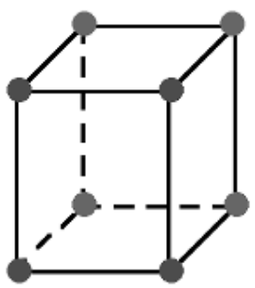
simple monoclinic



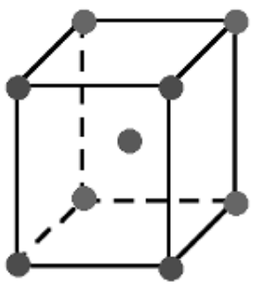
base-centered monoclinic



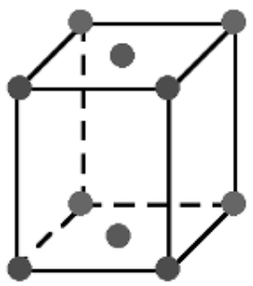
triclinic



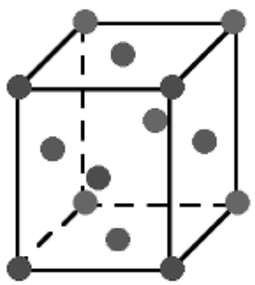
simple orthorhombic



body-centered orthorhombic



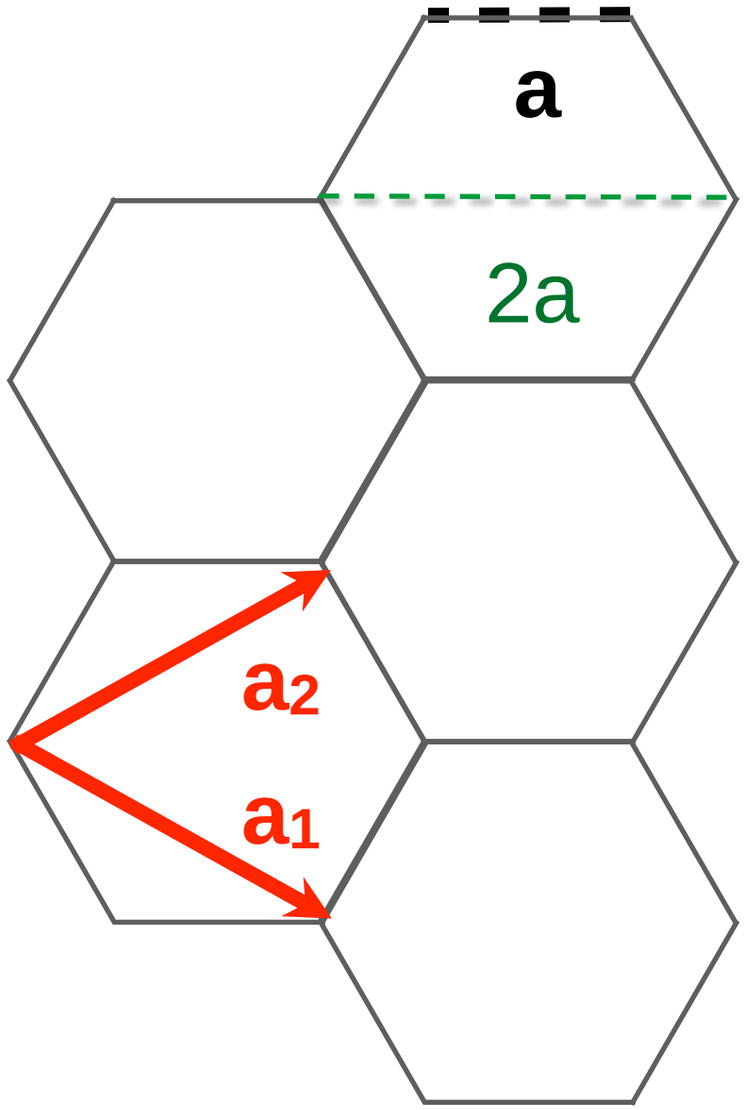
base-centered orthorhombic



face-centered orthorhombic

In 3D there are 14 different lattices.

Fractional coordinates

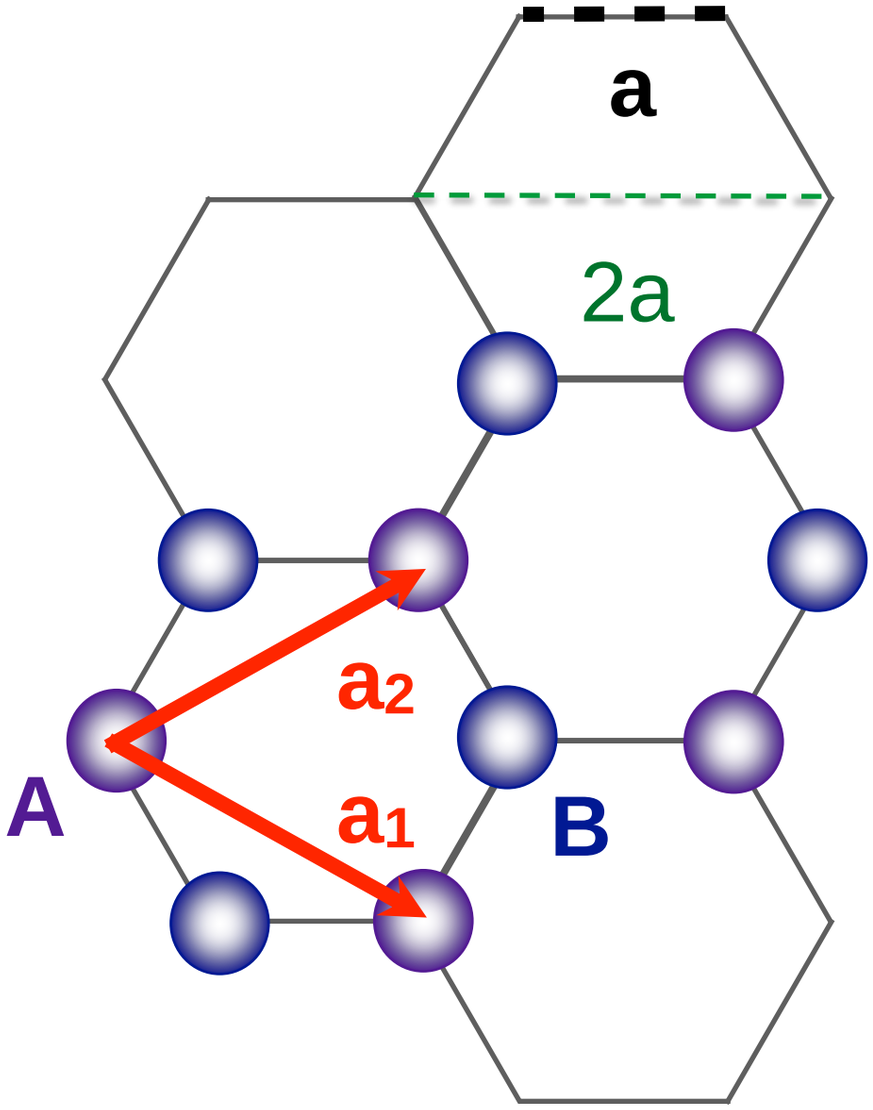


lattice vectors:

$$\boldsymbol{a_1} = \boldsymbol{a}\left(\frac{3}{2}, +\frac{\sqrt{3}}{2}\right)$$

$$\boldsymbol{a_1} = \boldsymbol{a}\left(\frac{3}{2}, -\frac{\sqrt{3}}{2}\right)$$

Fractional coordinates



lattice vectors:

$$\boldsymbol{a}_1 = \boldsymbol{a}\left(\frac{3}{2}, +\frac{\sqrt{3}}{2}\right)$$

$$\boldsymbol{a}_1 = \boldsymbol{a}\left(\frac{3}{2}, -\frac{\sqrt{3}}{2}\right)$$

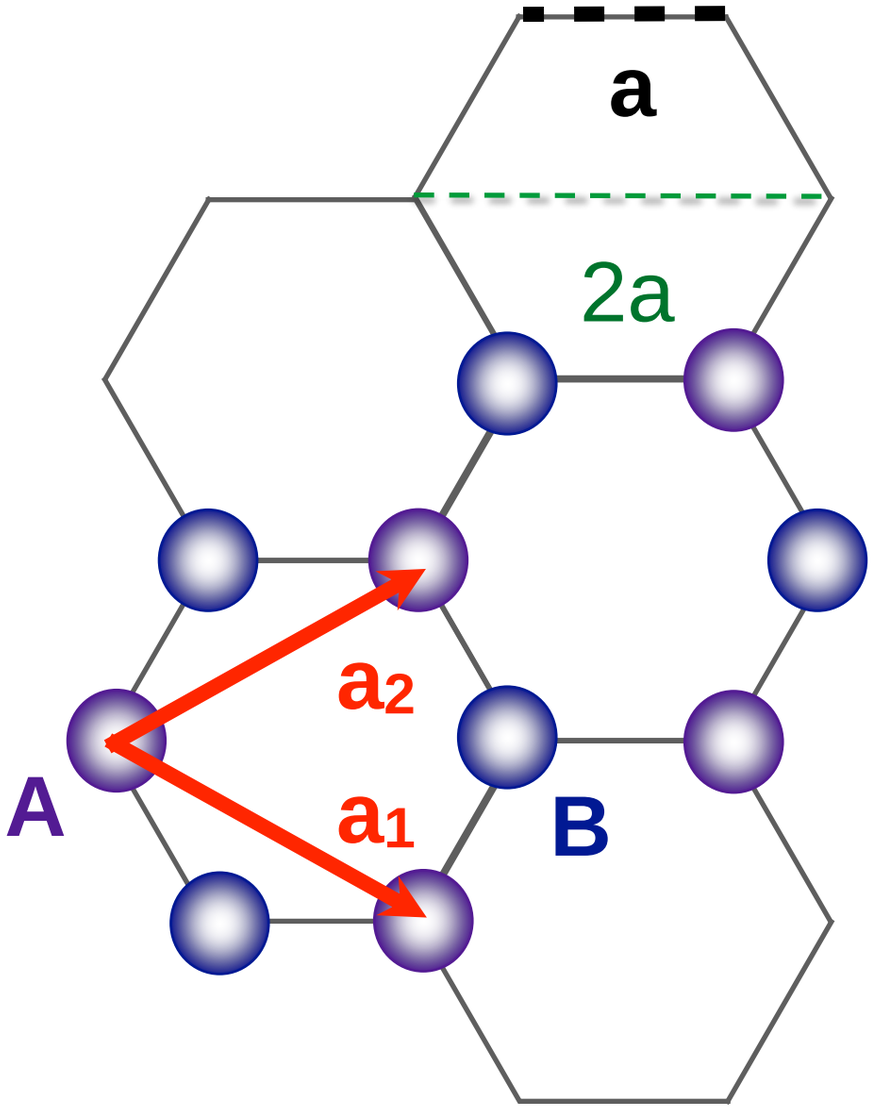
Basis (cartesian):

$$\boldsymbol{R}_a = (0,0)$$
$$\boldsymbol{R}_b = \boldsymbol{a}(2,0)$$

Basis (fractional):

$$\boldsymbol{R}_a = (0,0)$$
$$\boldsymbol{R}_b = \frac{2}{3}(\boldsymbol{a}_1 + \boldsymbol{a}_2) = \left(\frac{2}{3}, \frac{2}{3}\right)$$

Fractional coordinates



Fractional coordinates are atomic coordinates that are given in terms of the basis vectors.

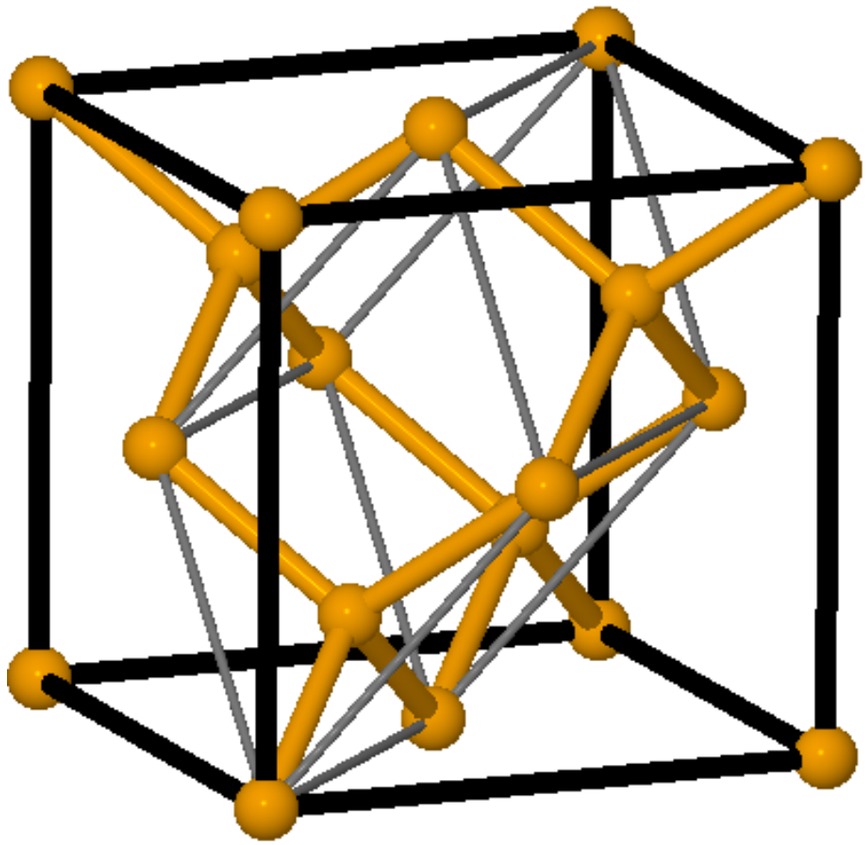
Basis (fractional):

$$\boldsymbol{R_a} = (0,0)$$

$$\boldsymbol{R_b} = \frac{2}{3}(\boldsymbol{a}_1 + \boldsymbol{a}_2)$$

$$= \left(\frac{2}{3}, \frac{2}{3}\right)$$

Fractional coordinates in 3D



a

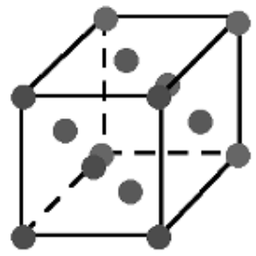
Silicon in the diamond structure

lattice vectors:

$$\mathbf{a}_1 = a/2\,(0,1,1)$$

$$\mathbf{a}_2 = a/2\,(1,0,1)$$

$$\mathbf{a}_3 = a/2\,(1,1,0)$$



face-centered cubic

fcc/ccp

basis (Fractional):

$$\mathbf{R}_A = (0,0,0)$$

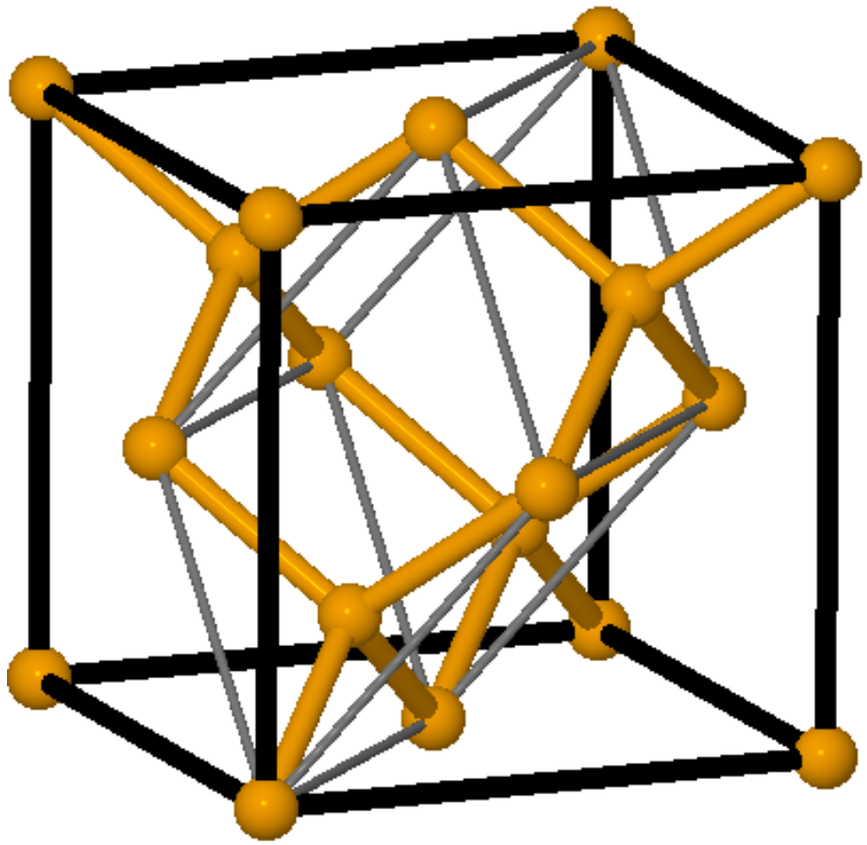
$$\mathbf{R}_B = \left(\frac{1}{4},\frac{1}{4},\frac{1}{4}\right)$$

basis (Cartesian):

$$\mathbf{R}_A = (0,0,0)$$

$$\mathbf{R}_B = a/4\,(1,1,1)$$

Cohesive energy of solids

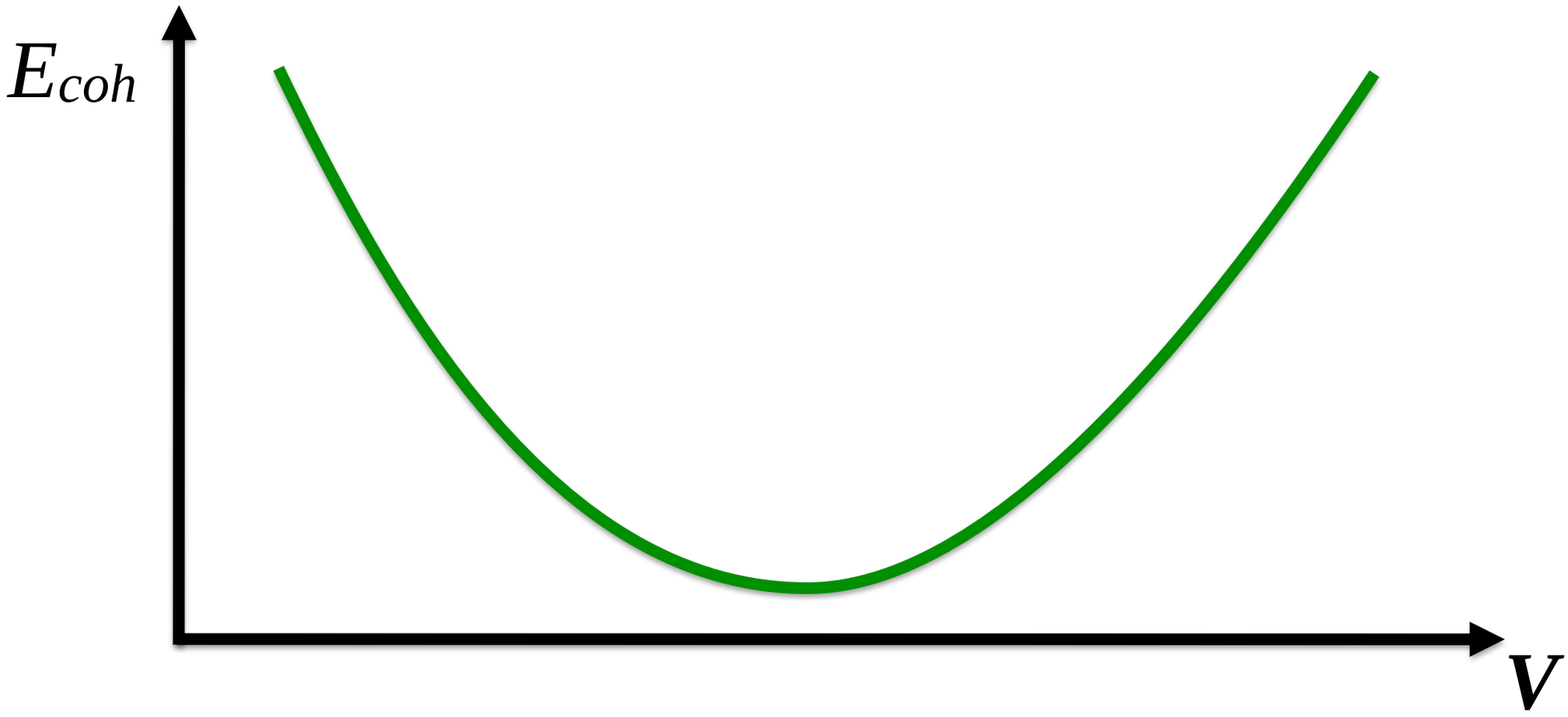


a

— 2

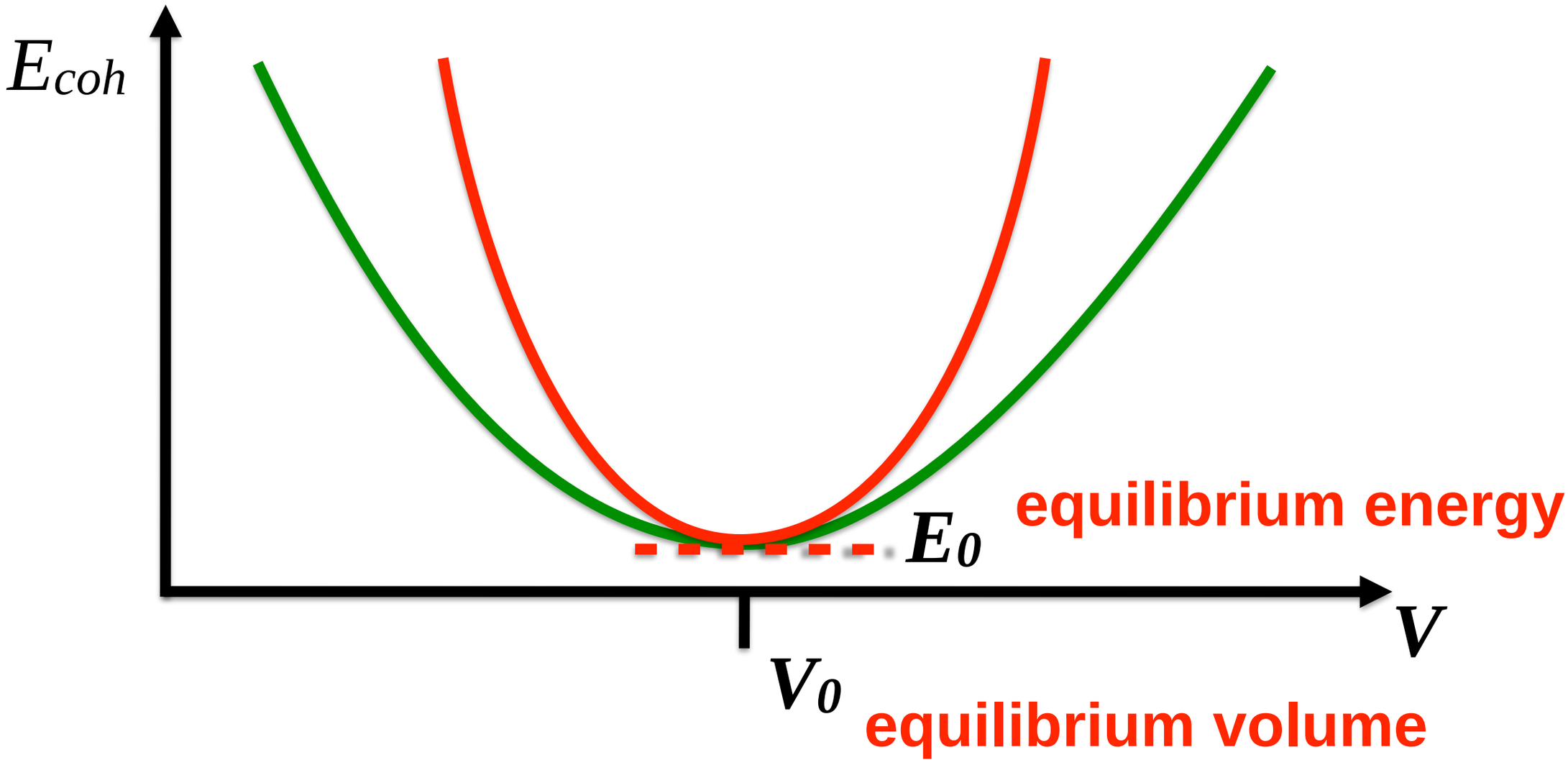
$$E_{\text{cohesive}} = E_0(\text{solid}) - \sum_{i}^{\#\ \text{atoms}} n_i E_0(\text{atom}_i)$$

Cohesive energy *vs* volume curve



In solids it is convenient to plot E_{coh} versus volume.

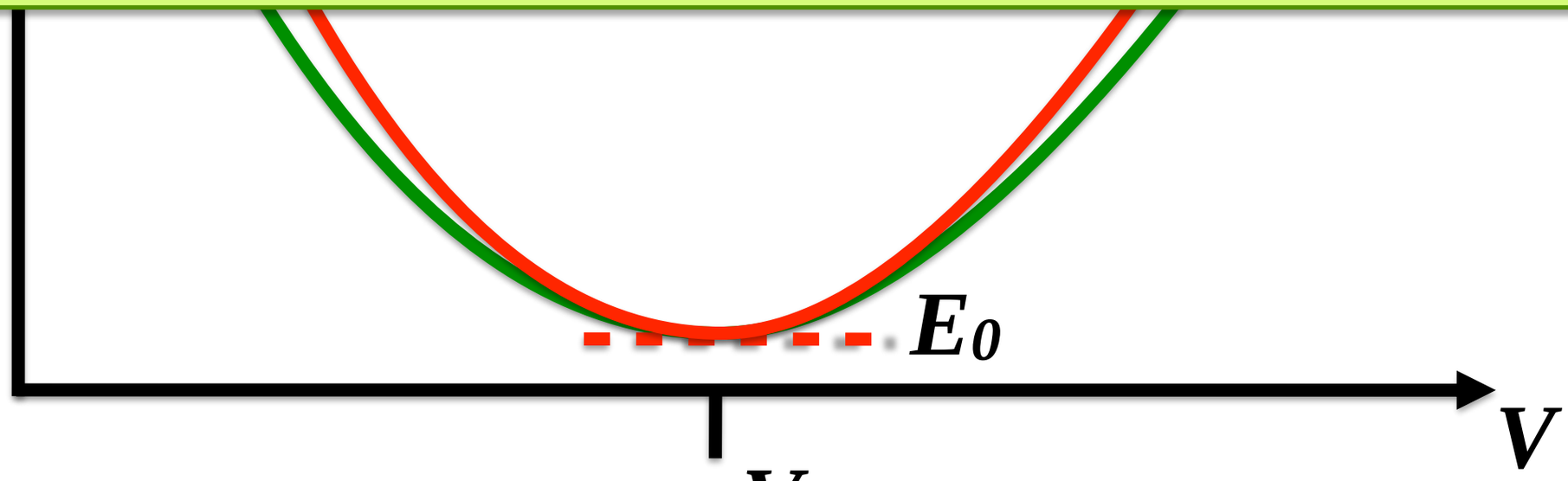
Cohesive energy *vs* volume curve



Quadratic approximation (later useful for phonons)

Birch-Murnaghan equation of state

The *bulk modulus* of a substance measures the substance's resistance to uniform compression.



bulk modulus **bulk modulus derivative**

$$E(V) = E_0 + \frac{B_0 V}{B_0'}\left[\frac{(V_0/V)^{B_0'}}{B_0' - 1} + 1\right] - \frac{B_0 V_0}{B_0' - 1}$$

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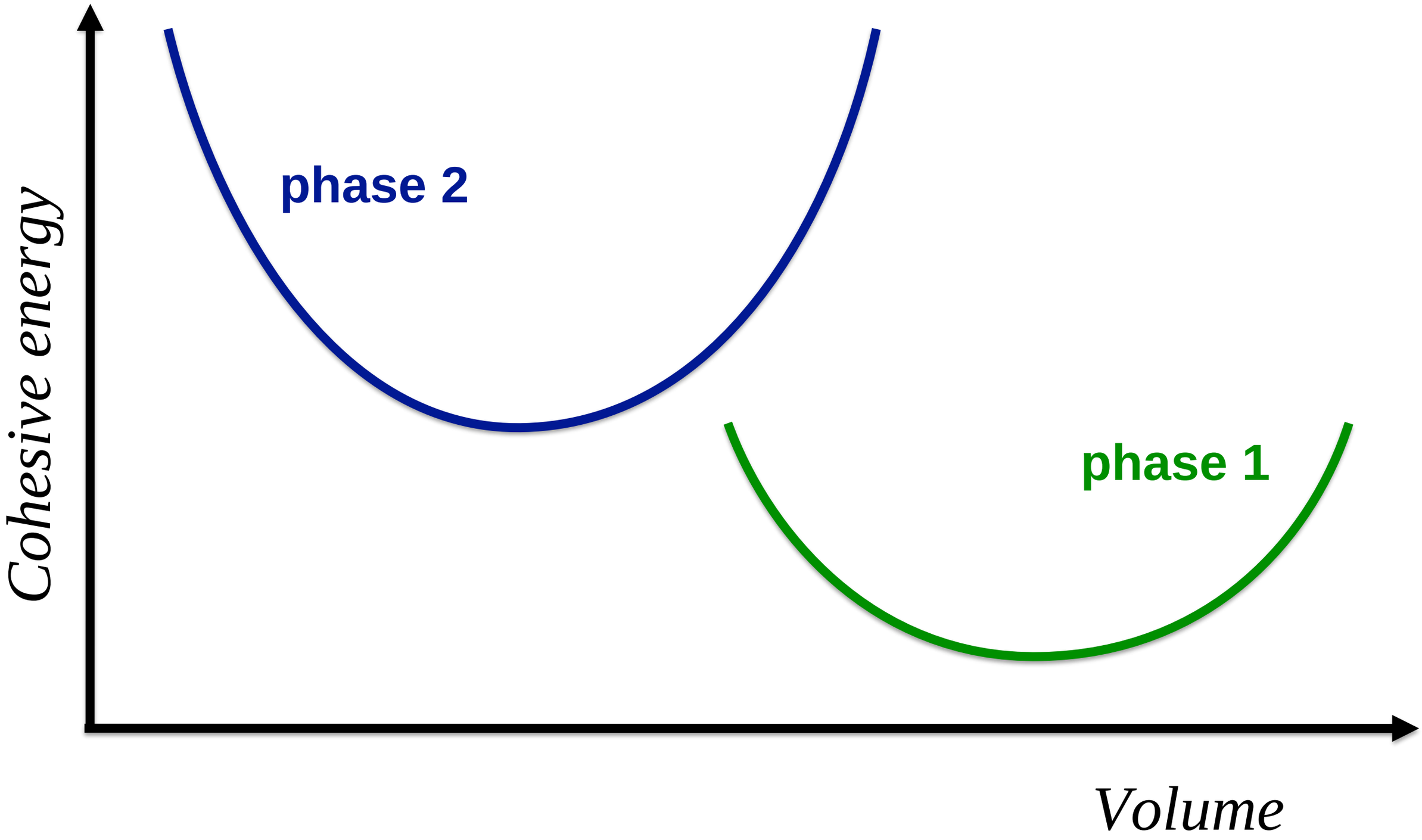
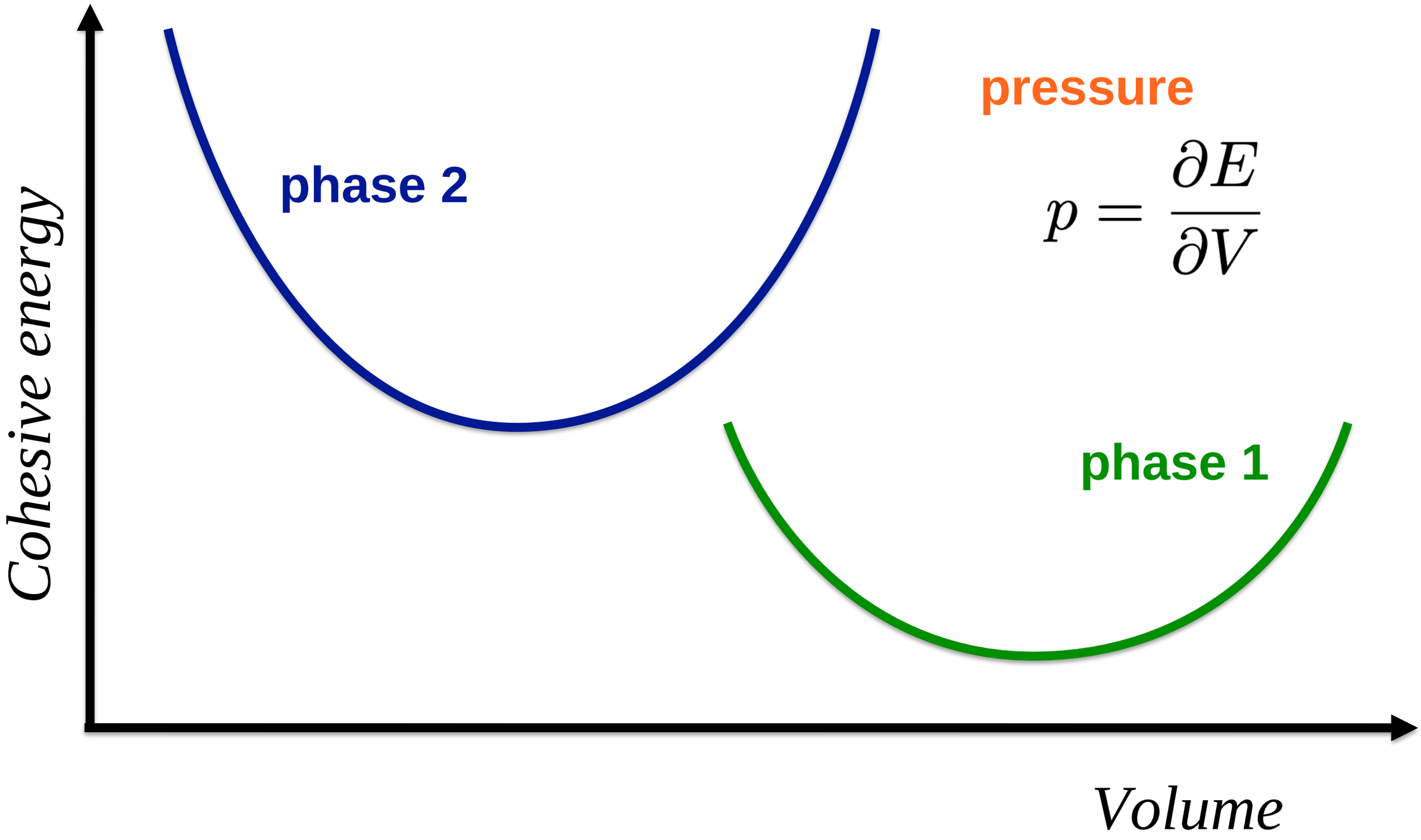
F. D. Murnaghan, Proc. Natl. Acad. Sci. 30, 244 (1944)
F. Birch, Phys. Rev. 71, 809 (1947)

Simple phase diagrams



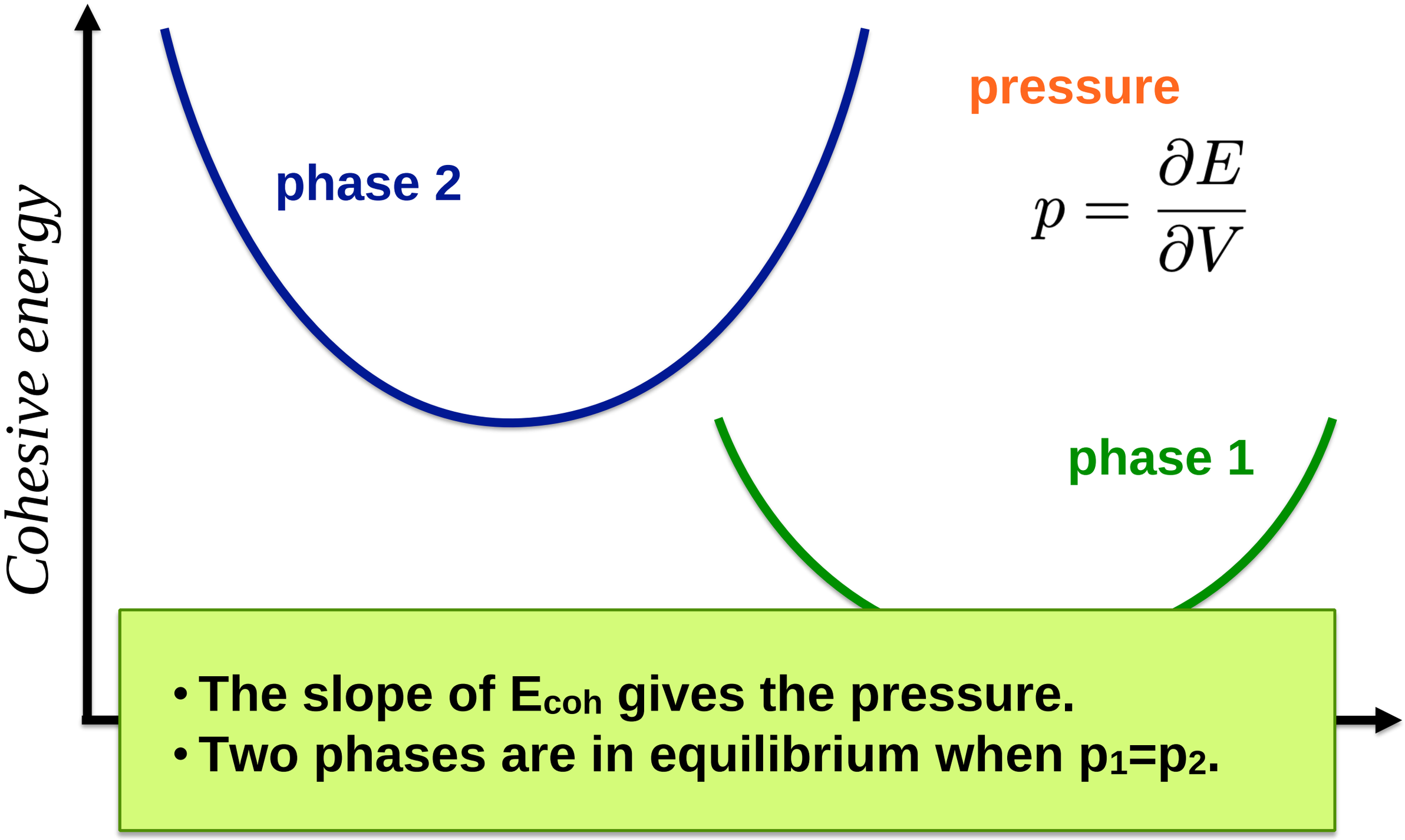
Simple phase diagrams



pressure

$$p = \frac{\partial E}{\partial V}$$

Simple phase diagrams

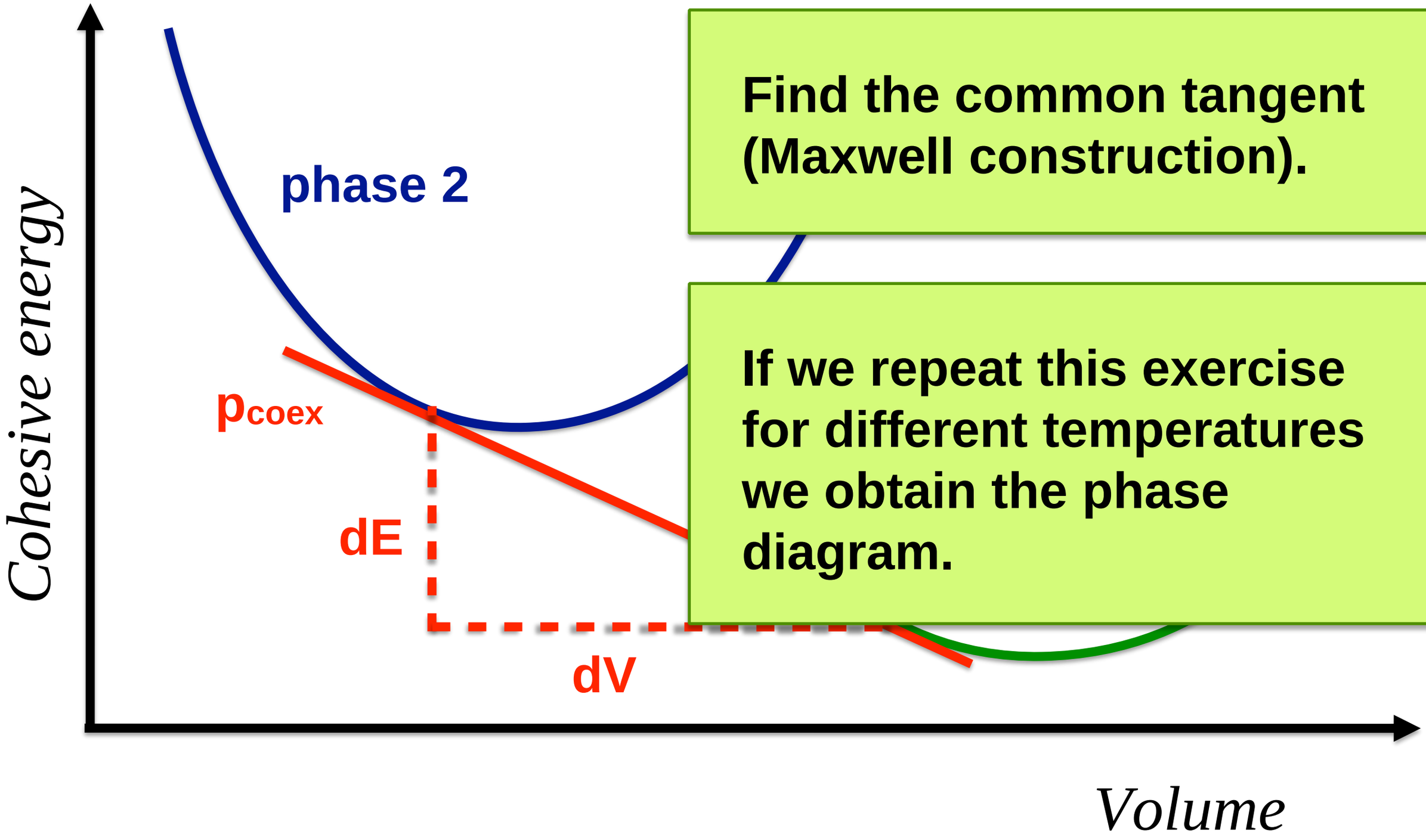


pressure

$$p = \frac{\partial E}{\partial V}$$

- **The slope of E_{coh} gives the pressure.**
- **Two phases are in equilibrium when $p_1 = p_2$.**

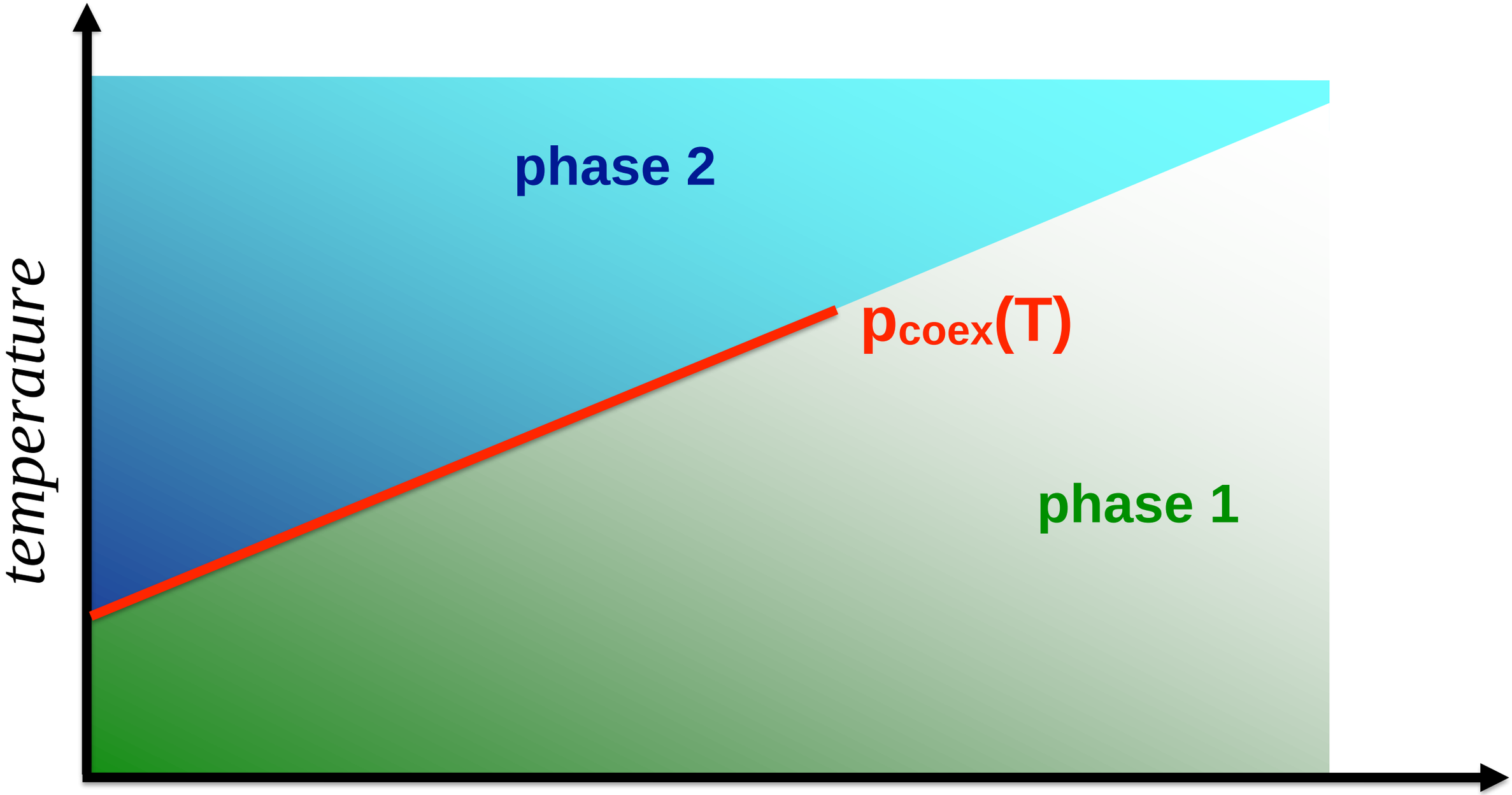
Simple phase diagrams



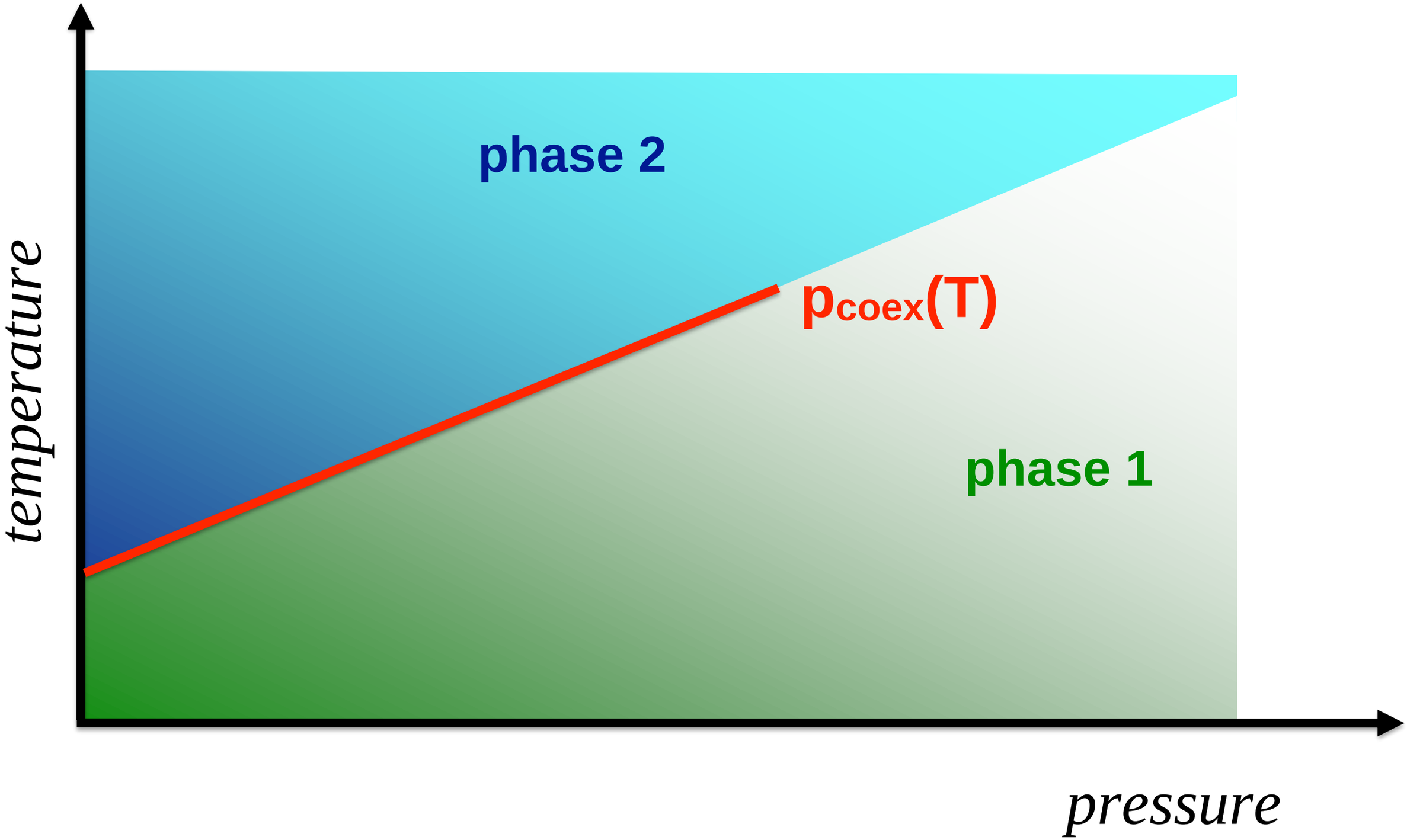
Find the common tangent (Maxwell construction).

If we repeat this exercise for different temperatures we obtain the phase diagram.

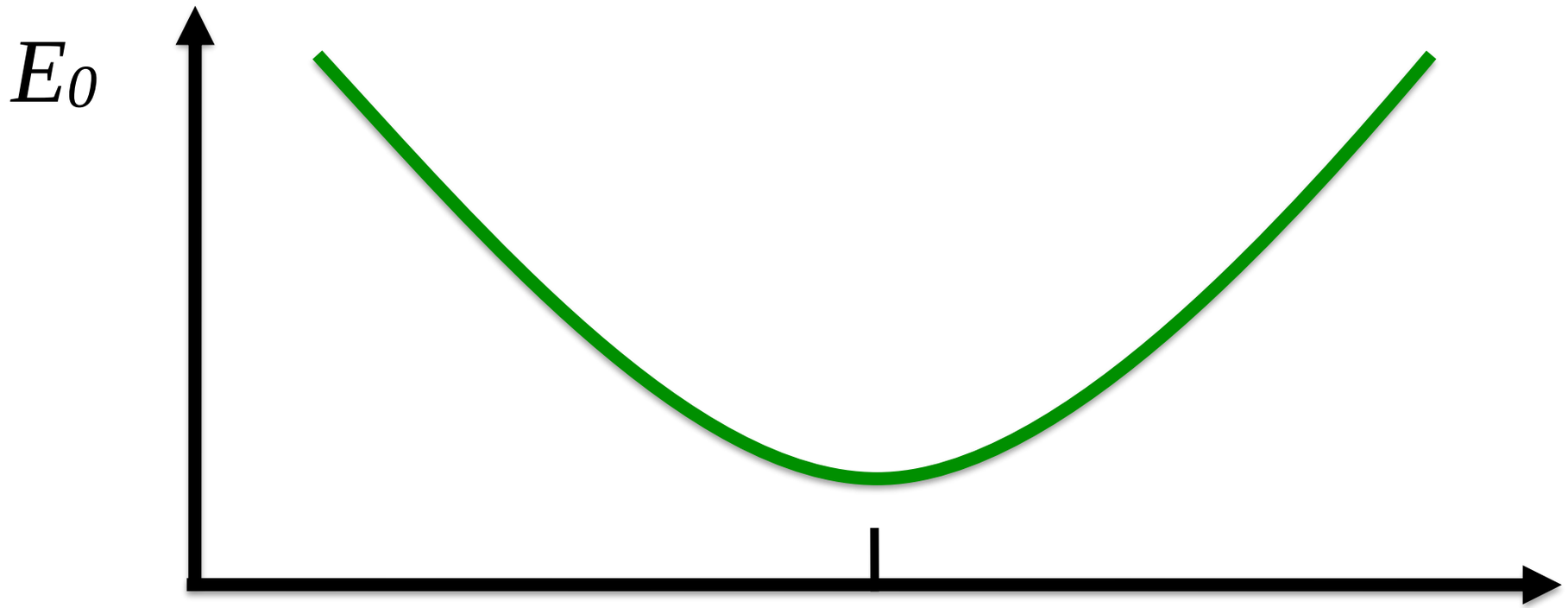
Simple phase diagrams



Questions on phases?



Phonons — Harmonic approximation



harmonic oscillator:

$$E_0(\mathbf{R}) = E_0(\mathbf{R}_0) + \frac{1}{2}\underbrace{\left.\frac{\partial^2 E_0(\mathbf{R})}{\partial \mathbf{R}^2}\right|_{\mathbf{R}_0}}_{k}(\mathbf{R}-\mathbf{R}_0)^2$$

vibrational frequency

atomic mass

Hessian matrix

$$\Phi_{ij} = \frac{\partial^2 E_0}{\partial \mathbf{R}_i \partial \mathbf{R}_j}$$

Hessian matrix (or atomic force constants)

Can be calculated with density-functional perturbation theory (DFPT).

S. Baroni, et al., Rev. Mod. Phys. 73, 515 (2001)

Hessian matrix

$$\Phi_{ij} = \frac{\partial^2 E_0}{\partial \mathbf{R}_i \partial \mathbf{R}_j} = -\frac{\partial}{\partial \mathbf{R}_i}\mathbf{F}_j \approx \frac{\mathbf{F}_j(\mathbf{R}_i^0 + \epsilon \mathbf{d}_i)}{\epsilon}$$

Hessian matrix (or atomic force constants)

Or it can be calculated with DFT and finite differences.

K. Kunc, and R. M. Martin, Phys. Rev. Lett. 48, 406 (1982)
K. Parlinski, Z. Q. Li, and Y. Kawazoe, Phys. Rev. Lett. 78, 4063 (1997)

Hessian matrix

$$\Phi_{ij} = \frac{\partial^2 E_0}{\partial \mathbf{R}_i \partial \mathbf{R}_j} = -\frac{\partial}{\partial \mathbf{R}_i}\mathbf{F}_j \approx \frac{\mathbf{F}_j(\mathbf{R}_i^0 + \epsilon \mathbf{d}_i)}{\epsilon}$$

Hessian matrix (or atomic force constants)

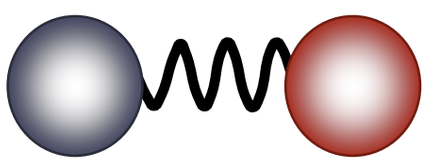
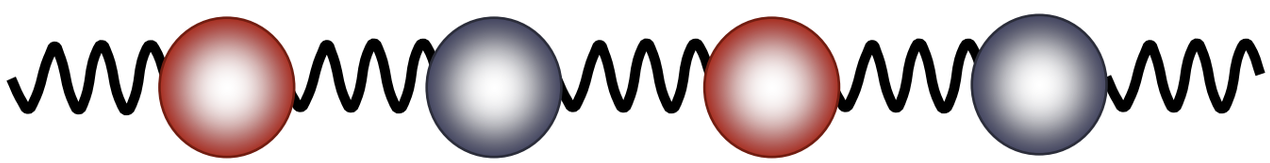
Or it can be calculated with DFT and finite differences.

For example with the phonopy **code.**

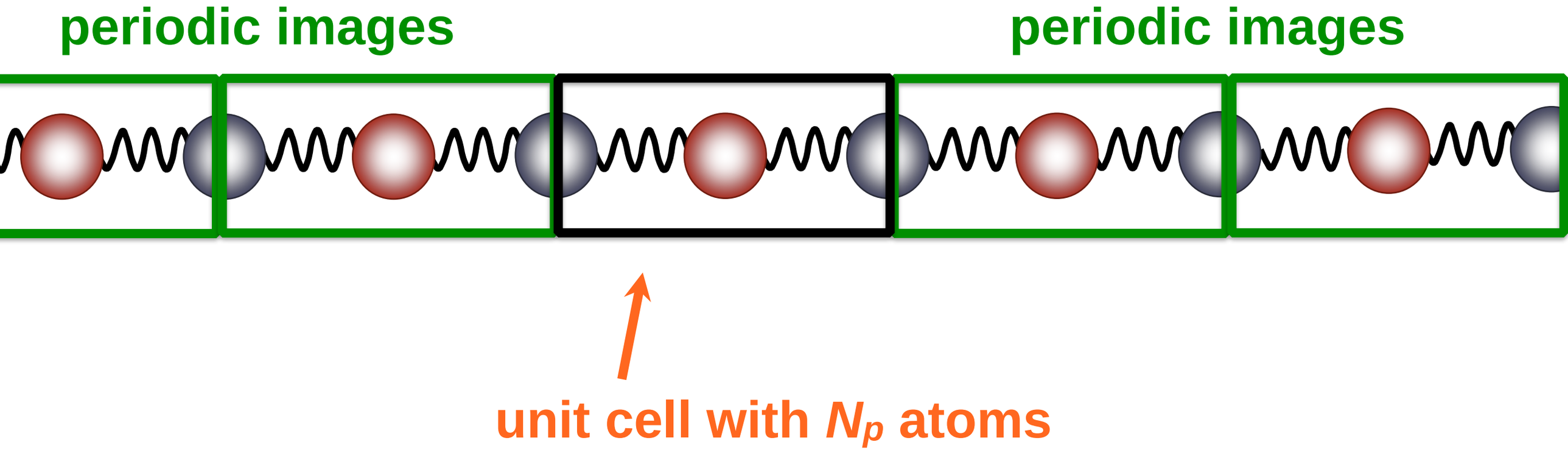
A.Togo, F. Oba, and I.Tanaka, Phys. Rev. B 78, 134106 (2008)

Hessian matrix — molecules vs solids

But *N* goes to infinity…

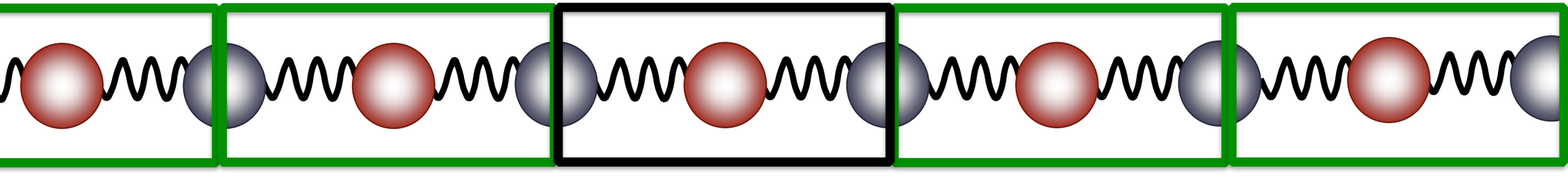
molecules	solids
	
number of atoms : ***N***	number of atoms : ***N***
degrees of freedom : ***3N***	degrees of freedom : ***3N***
dimension of Hessian : ***9N²***	dimension of Hessian : ***9N²***

Periodic boundary conditions



Periodic boundary conditions

periodic images **unit cell - N_p atoms** **periodic images**



real-space

reciprocal-space

Hessian Φ_{ij}

$$i, j \to \infty$$

dynamical matrix $D_{i'j'}(\mathbf{q})$

$$i', j' \leq N_p$$

Fourier transform

$$D_{i'j'}(\mathbf{q}) = \sum_j \frac{e^{i\left(\mathbf{q}(\mathbf{R}_j^0 - \mathbf{R}_{j'}^0)\right)}}{\sqrt{M_{i'} M_{j'}}} \Phi_{i'j}$$

K. Parlinski, Z. Q. Li, and Y. Kawazoe, Phys. Rev. Lett. 78, 4063 (1997)

Periodic boundary conditions

real-space

reciprocal-space

$$D_{i'j'}(\mathbf{q}) = \sum_j \frac{e^{i\left(\mathbf{q}(\mathbf{R}^0_j - \mathbf{R}^0_{j'})\right)}}{\sqrt{M_{i'} M_{j'}}} \Phi_{i'j}$$

Fourier transform can be truncated since

$$\Phi_{ij} = 0 \quad \textbf{for large} \quad \left|\mathbf{R}^0_j - \mathbf{R}^0_{j'}\right|$$

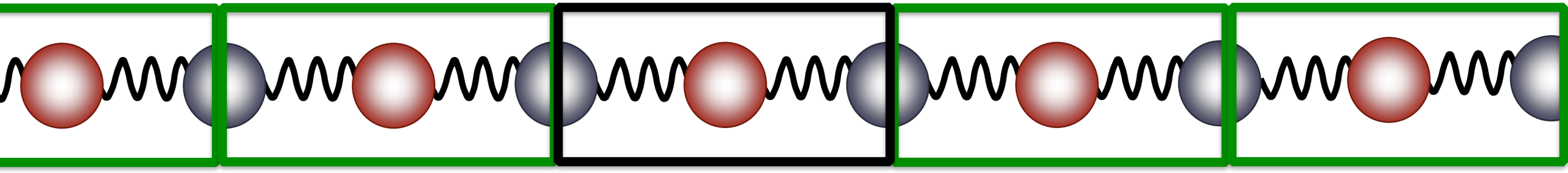
Hessian Φ_{ij} with finite number of entries

dynamical matrix $D_{i'j'}(\mathbf{q})$ for whole reciprocal space

Aalto University
School of Science

K. Parlinski, Z. Q. Li, and Y. Kawazoe, Phys. Rev. Lett. 78, 4063 (1997)

Phonon band structure



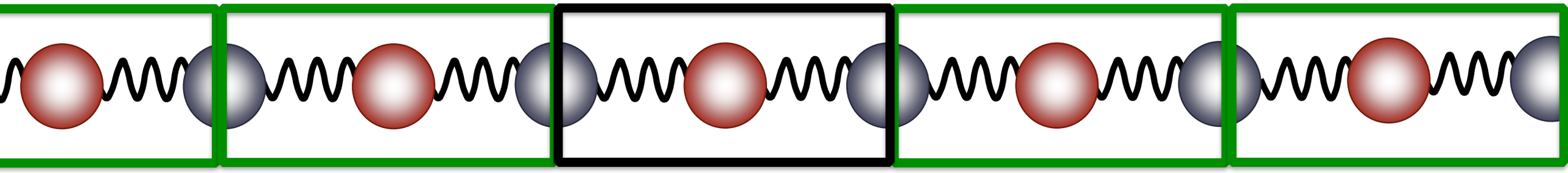
Eigenvalue problem:

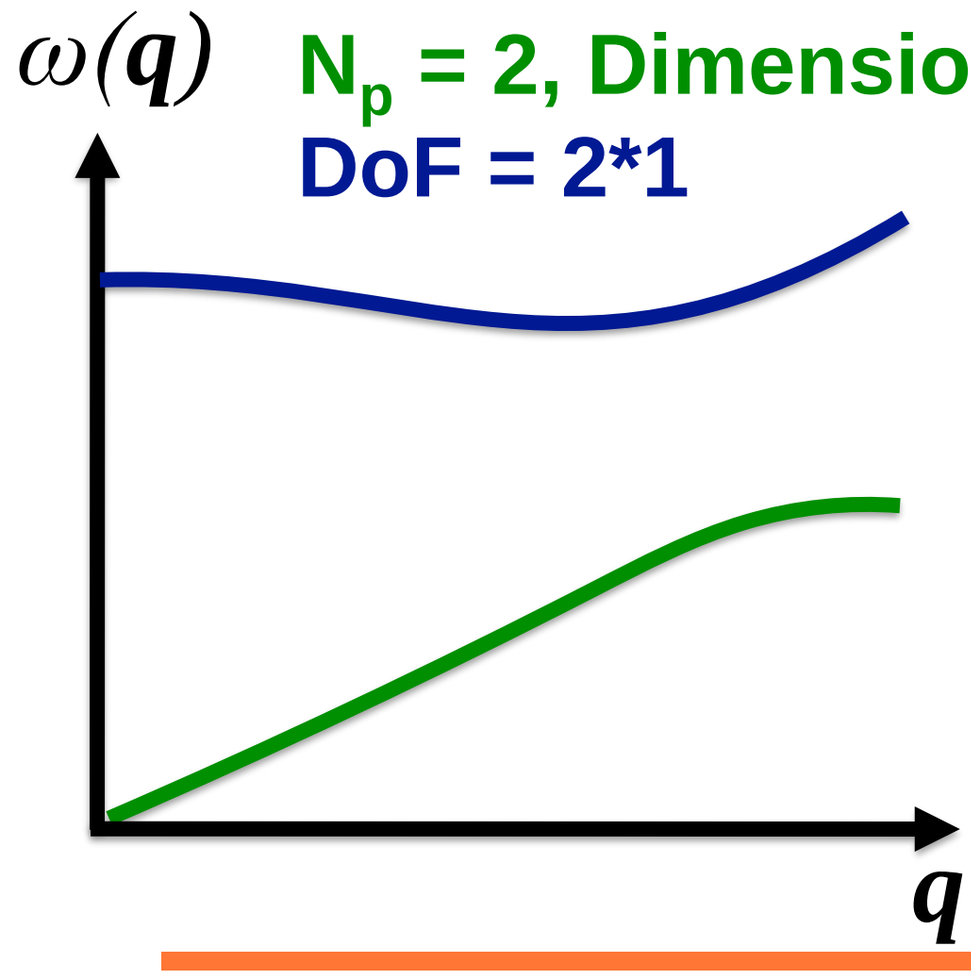
phonon frequencies

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

phonon modes

Phonon band structure





N_p = 2, Dimensionality = 1

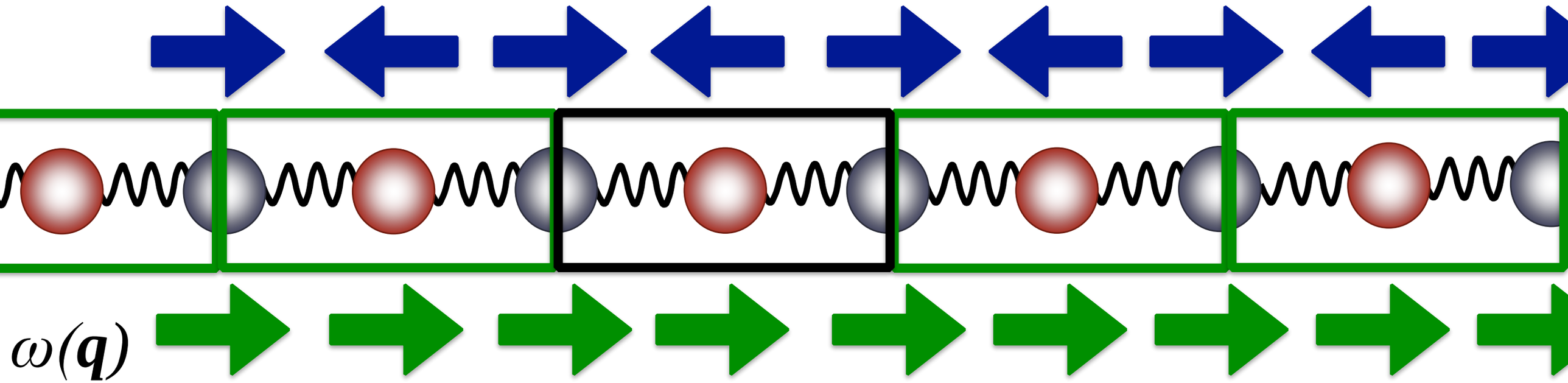
DoF = 2*1

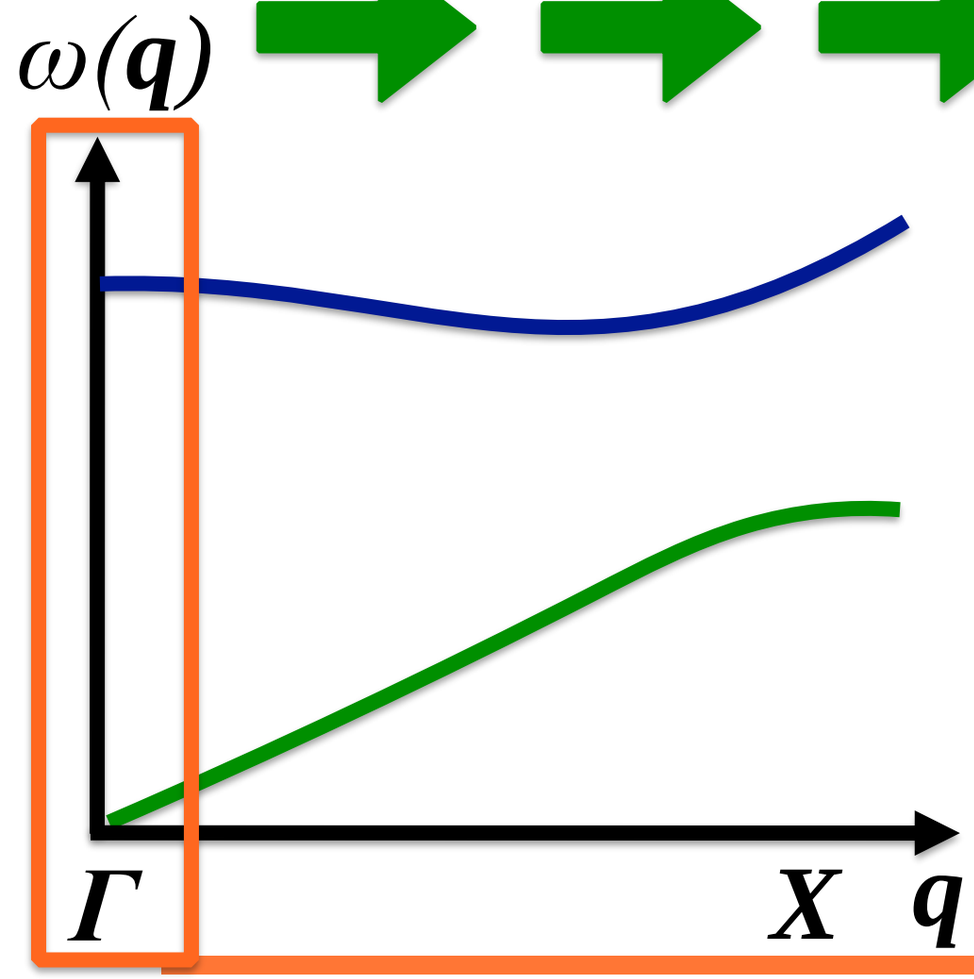
$$\mathbf{D}(\mathbf{q})\nu(\mathbf{q}) = \omega^2(\mathbf{q})\nu(\mathbf{q})$$

Dependency on where we are in the reciprocal space

How these modes look like?

Phonon band structure

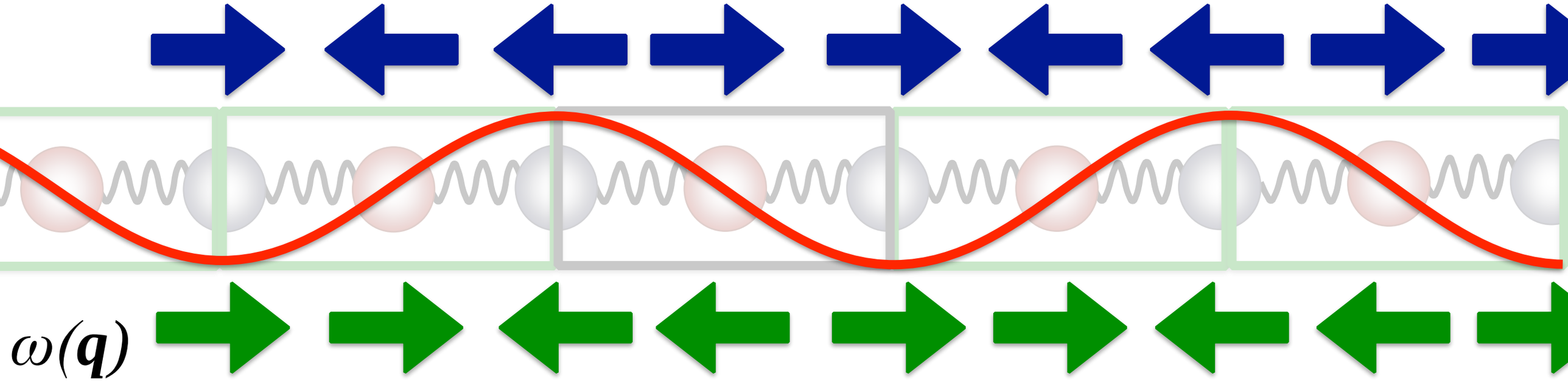


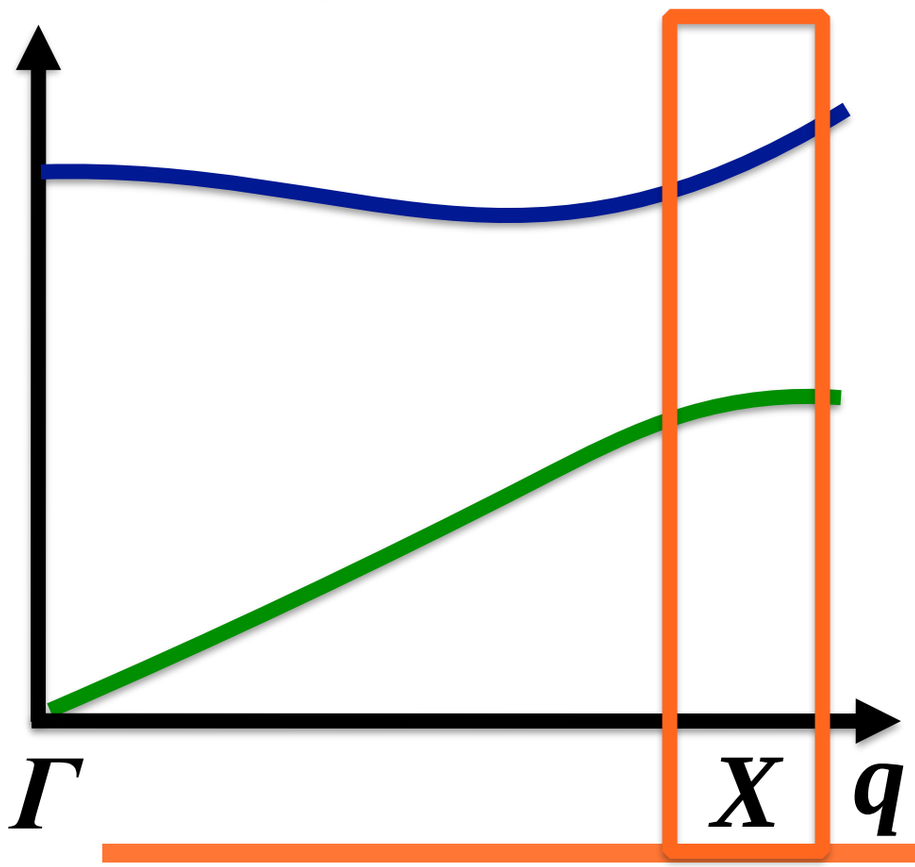


$$\mathbf{D}(\mathbf{q})\nu(\mathbf{q}) = \omega^2(\mathbf{q})\nu(\mathbf{q})$$

$$D_{i'j'}(\mathbf{q}) = \sum_j \frac{e^{i\left(\mathbf{q}(\mathbf{R}^0_j - \mathbf{R}^0_{j'})\right)}}{\sqrt{M_{i'}M_{j'}}}\Phi_{i'j} \quad =1$$

Phonon band structure

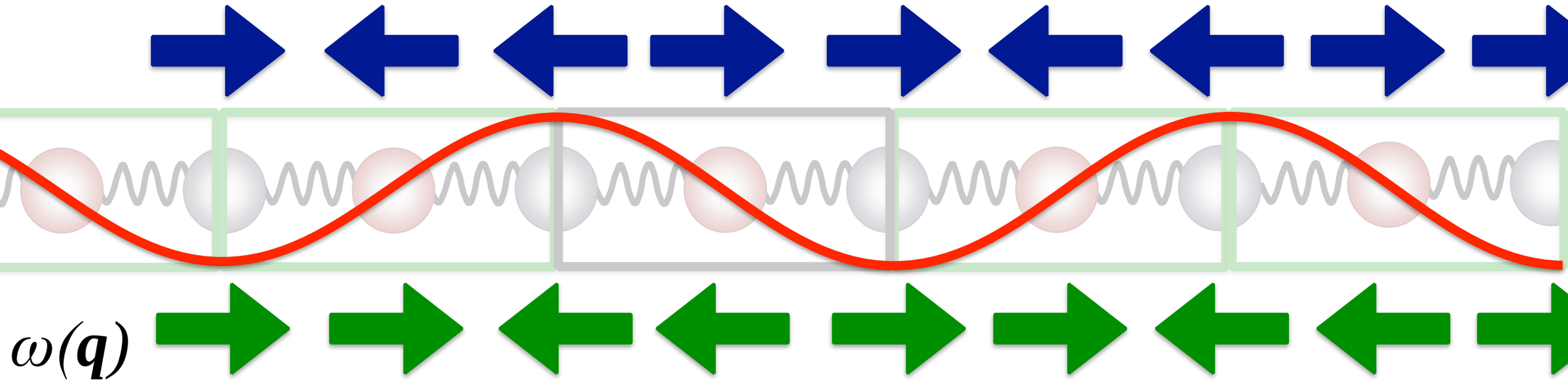


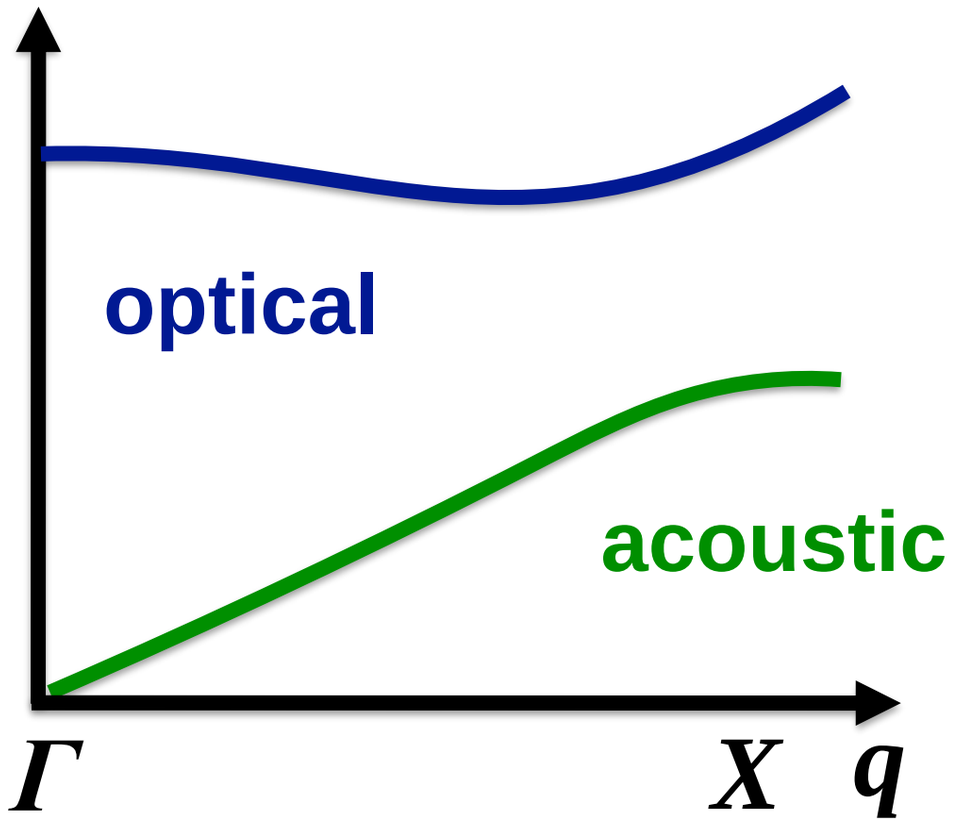


$$\mathbf{D}(\mathbf{q})\nu(\mathbf{q}) = \omega^2(\mathbf{q})\nu(\mathbf{q})$$

$$D_{i'j'}(\mathbf{q}) = \sum_j \frac{e^{i\left(\mathbf{q}(\mathbf{R}^0_j - \mathbf{R}^0_{j'})\right)}}{\sqrt{M_{i'}M_{j'}}}\Phi_{i'j}$$

Phonon band structure – back in 3D

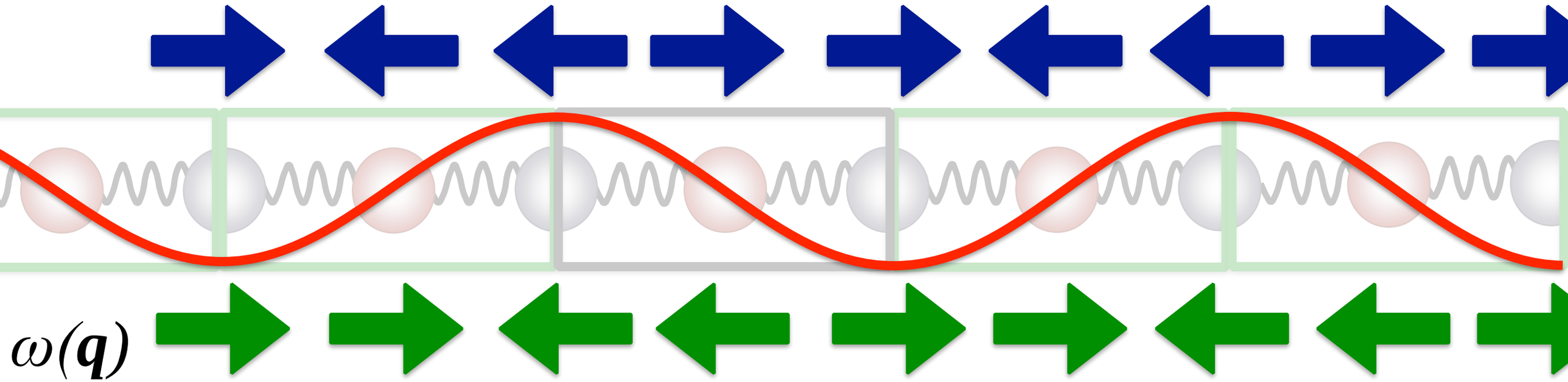


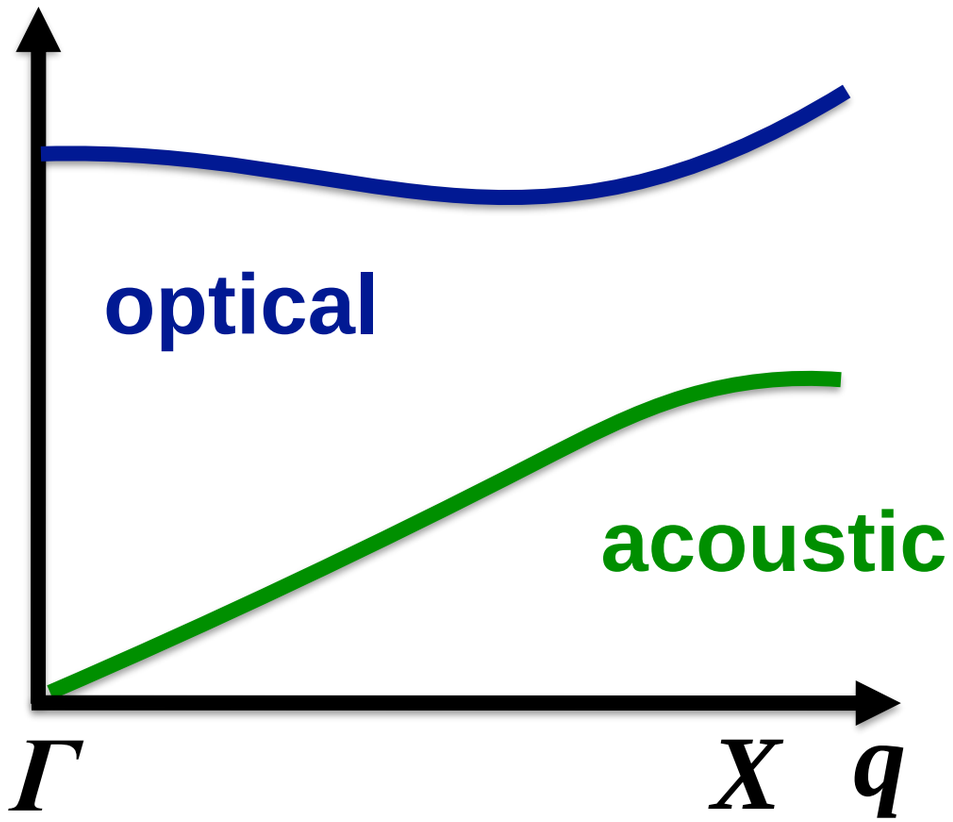


3 acoustic modes

- **atoms in unit cell in phase**
- **vanish at Γ**
- **strong linear dispersion at Γ**

Phonon band structure – back in 3D

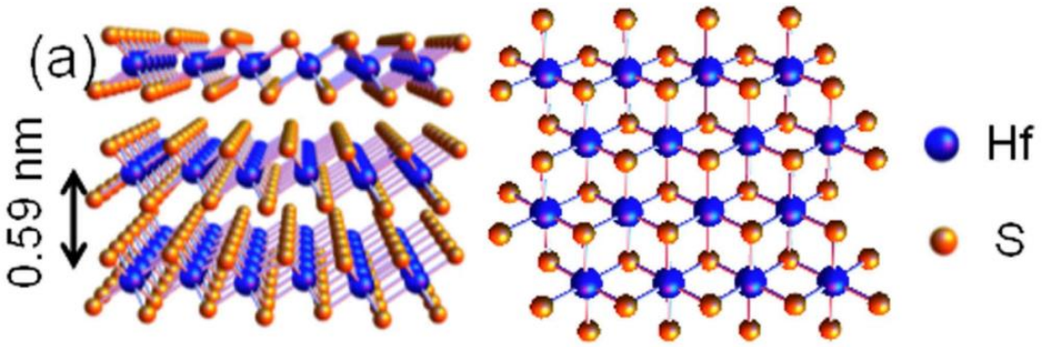


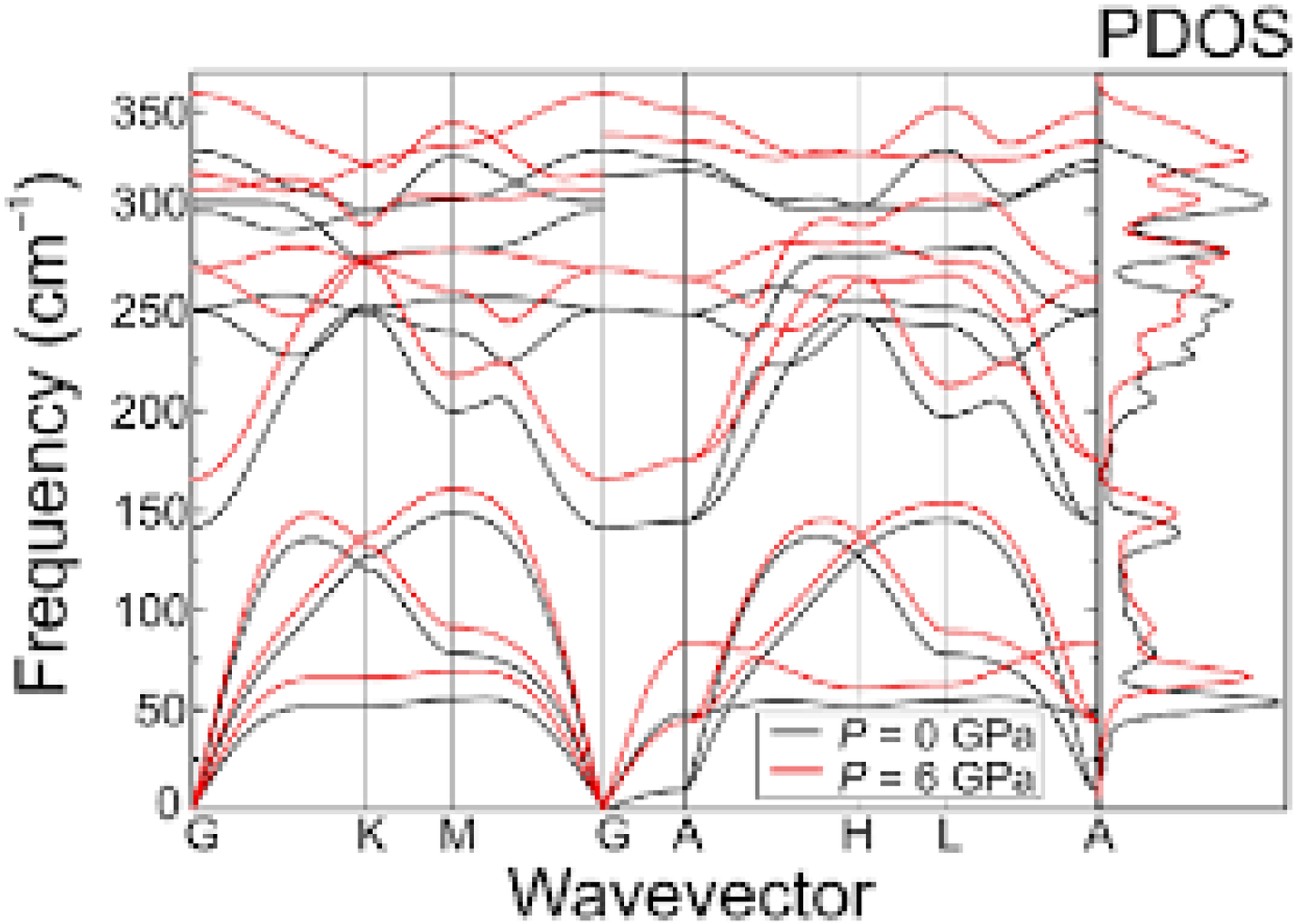


$3N_p$-3 optical modes

- **atoms in unit cell out of phase**
- **frequency always > 0**
- **weak dispersion**

Phonon band structure – back in 3D





HfS_2

3 acoustic modes

- atoms in unit cell in phase
- vanish at Γ
- strong linear dispersion at Γ

$3N_p$-3 optical modes

- atoms in unit cell out of phase
- frequency always > 0
- weak dispersion

J. Ibáñez *et al*. Sci Rep 8, 12757, (2018)

Questions?

Interesting links:

FHI-vibes: different types of vibrations and phonon calculations
https://vibes-developers.gitlab.io/vibes/

All your FHI-aims calculations and preparing workflows on one website:
https://gims.ms1p.org/static/index.html

Building a molecule/monocrystalic structure/monocrystalic surface through python (Atomic Simulation Environment):
https://wiki.fysik.dtu.dk/ase/ase/build/build.html