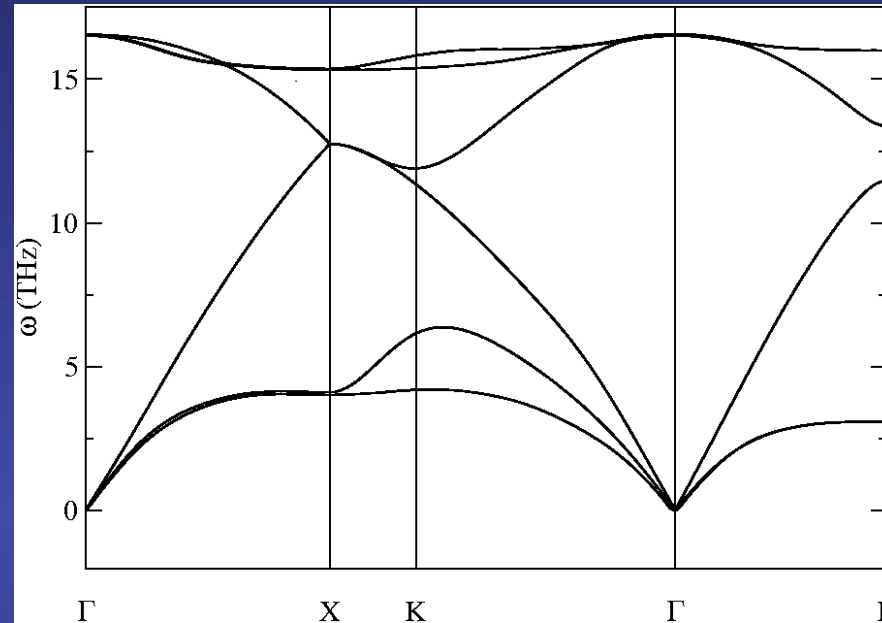# Lattice dynamics

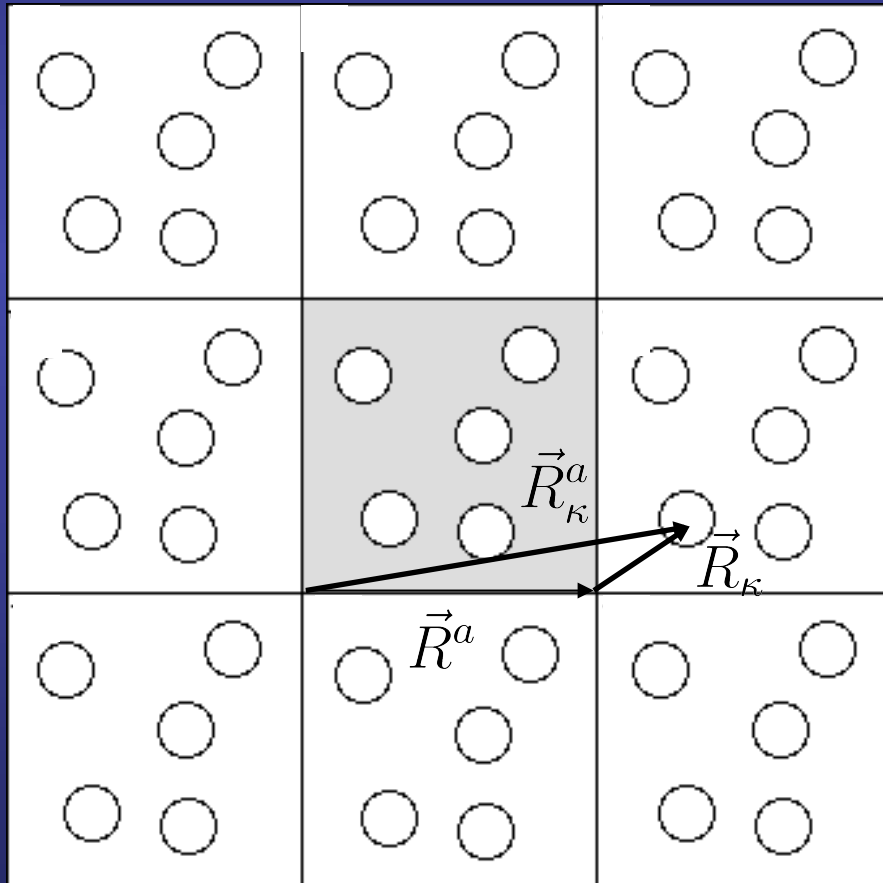**Javier Junquera**

Philippe Ghosez

Andrei Postnikov

Warm up: a little bit of notation

Greek characters (κ) refer to atoms within the unit cell

Latin characters (a) refer to the different replicas of the unit cell

Assuming periodic boundary conditions

$\vec{R}^a$ Vector defining the position of unit cell a

$\vec{R}_\kappa$ Position of atom κ within the unit cell

$\vec{R}_\kappa^a$ Position of atom κ in unit cell a

$$\vec{R}_\kappa^a = \left(\vec{R}^a + \vec{R}_\kappa \right)$$

…but the ions do not sit without moving; they oscillate around the mean equrilibrium positions

Here we shall assume that the instantaneous position of atom κ in unit cell a will deviate from its mean equilibrium position $\vec{R}^a_\kappa$ by a small deviation $\vec{u}^a_\kappa(t)$, and we may write at any given time

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

We shall assume that the typical excursions of each ion from its equilibrium position are small compared with the interionic spacing

Total energy of a periodic crystal with small lattice distortions

We shall remain in the adiabatic approximation, in which it is considered that the electrons are in their ground state for any instantaneous ionic configuration

$$E_{e+i}\left(\{\vec{R}_\kappa^\alpha(t)\}\right) = E_{e+i}\left(\{\vec{R}_\kappa^\alpha\}\right) + \sum_{a\kappa\alpha}\left(\frac{\partial E_{e+i}}{\partial u_{\kappa\alpha}^a}\right)u_{\kappa\alpha}^a(t) + \sum_{a\kappa\alpha}\sum_{b\kappa'\beta}\frac{1}{2}\left(\frac{\partial^2 E_{e+i}}{\partial u_{\kappa\alpha}^a u_{\kappa'\beta}^b}\right)u_{\kappa\alpha}^a u_{\kappa'\beta}^b + \dots$$

Some considerations

1. In principle, if we take all the orders in the expansion (see the dot, dot, dot at the right), this expression is exact.

2. All the derivatives are taken at the mean equilibrium positions. They are constants in the expansion.

3. Since, the derivatives are taken at the equilibrium positions, the first derivatives in the previous expansion vanish.

$$E_{e+i}\left(\{\vec{R}_\kappa^\alpha(t)\}\right) = E_{e+i}\left(\{\vec{R}_\kappa^\alpha\}\right) + \sum_{a\kappa\alpha}\sum_{b\kappa'\beta}\frac{1}{2}\left(\frac{\partial^2 E_{e+i}}{\partial u_{\kappa\alpha}^a u_{\kappa'\beta}^b}\right)u_{\kappa\alpha}^a u_{\kappa'\beta}^b + \dots$$

Total energy of a periodic crystal with small lattice distortions in the harmonic approximation

$$E_{e+i}\left(\{\vec{R}_\kappa^\alpha(t)\}\right) = E_{e+i}\left(\{\vec{R}_\kappa^\alpha\}\right) + \sum_{a\kappa\alpha}\sum_{b\kappa'\beta}\frac{1}{2}\left(\frac{\partial^2 E_{e+i}}{\partial u_{\kappa\alpha}^a u_{\kappa'\beta}^b}\right)u_{\kappa\alpha}^a u_{\kappa'\beta}^b + \ldots$$

We shall now consider ionic displacements that are small compared with the interatomic spacing.

Then, we can consider that all the terms beyond the quadratic one are negligible (a small number to the cube is much smaller than a small number to the square).

This approximation is called the harmonic approximation

The total energy of a periodic crystal in the harmonic approximation can be written

$$E_{e+i}^{harm}\left(\{\vec{R}_\kappa^\alpha(t)\}\right) = E_{e+i}\left(\{\vec{R}_\kappa^\alpha\}\right) + \sum_{a\kappa\alpha}\sum_{b\kappa'\beta}\frac{1}{2}\left(\frac{\partial^2 E_{e+i}}{\partial u_{\kappa\alpha}^a u_{\kappa'\beta}^b}\right)u_{\kappa\alpha}^a u_{\kappa'\beta}^b$$

Interatomic force constants in real space: definitions and symmetry properties

The second derivatives of the energy, coupling constants, are defined as the interatomic force constants in real space

$$C_{\kappa\alpha,\kappa'\beta}(a,b) = \left(\frac{\partial^2 E_{e+i}}{\partial u^a_{\kappa\alpha} u^b_{\kappa'\beta}} \right)$$

They must satisfy a number of conditions that arise from

Isotropy of space

Point group symmetry

Translation invariance **upon displacement of the lattice by an arbitrary lattice constant: the second derivative of the energy can only depend on the difference between a and b**

$$\frac{\partial^2 E_{e+i}}{\partial u^a_{\kappa\alpha} \partial u^b_{\kappa'\beta}} = \frac{\partial^2 E_{e+i}}{\partial u^0_{\kappa\alpha} \partial u^{b-a}_{\kappa'\beta}}$$

The classical equation of motion for the ions

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

Force exerted on atom κ in unit cell a by all the other ions and the electronic cloud

Acceleration of atom κ in unit cell a

By definition of force

$$\vec{F}_\kappa^a = -\nabla_{\vec{R}_\kappa^a} E_{e+i}^{harm}$$

By definition of acceleration

$$\vec{a}_\kappa^a = \frac{d^2 \vec{R}_\kappa^a(t)}{dt^2} = \frac{d^2\left(\vec{R}_\kappa^a + \vec{u}_\kappa^a(t)\right)}{dt^2} = \frac{d^2 \vec{u}_\kappa^a(t)}{dt^2}$$

In cartesian components

$$F_{\kappa\alpha}^a = -\frac{\partial E_{e+i}^{harm}}{\partial R_{\kappa\alpha}^a} = -\frac{\partial E_{e+i}^{harm}}{\partial u_{\kappa\alpha}^a}$$

In cartesian components

$$a_{\kappa\alpha}^a = \frac{d^2 u_{\kappa\alpha}^a(t)}{dt^2}$$

$$M_\kappa \frac{d^2 u_{\kappa\alpha}^a}{dt^2} = -\frac{\partial E_{e+i}^{harm}}{\partial u_{\kappa\alpha}^a}$$

The classical equation of motion for the ions

$$M_\kappa \frac{d^2 u^a_{\kappa\alpha}}{dt^2} = -\frac{\partial E^{harm}_{e+i}}{\partial u^a_{\kappa\alpha}}$$

Since

$$E^{harm}_{e+i}\left(\{\vec{R}^\alpha_\kappa(t)\}\right) = E_{e+i}\left(\{\vec{R}^\alpha_\kappa\}\right) + \sum_{a\kappa\alpha}\sum_{b\kappa'\beta} \frac{1}{2}\left(\frac{\partial^2 E_{e+i}}{\partial u^a_{\kappa\alpha} u^b_{\kappa'\beta}}\right) u^a_{\kappa\alpha} u^b_{\kappa'\beta}$$

Then

$$-\frac{\partial E^{harm}_{e+i}}{\partial u^a_{\kappa\alpha}} = -\sum_{b\kappa'\beta}\left(\frac{\partial^2 E_{e+i}}{\partial u^a_{\kappa\alpha} \partial u^b_{\kappa'\beta}}\right) u^b_{\kappa'\beta}$$

$$M_\kappa \frac{\partial^2 u^a_{\kappa\alpha}}{\partial t^2} = -\sum_{b\kappa'\beta}\left(\frac{\partial^2 E_{e+i}}{\partial u^a_{\kappa\alpha} \partial u^b_{\kappa'\beta}}\right) u^b_{\kappa'\beta}$$

For each atom, there are three equations of motion of this type (one for each cartesian direction). In total, $3 \times N_{atoms}$

The classical equation of motion for the ions: a system of coupled equations

For each atom, there are three equations of motion of this type (one for each cartesian direction). In total, $3 \times N_{atoms}$

$$M_\kappa \frac{\partial^2 u_{\kappa\alpha}^a}{\partial t^2} = -\sum_{b\kappa'\beta} \left(\frac{\partial^2 E_{e+i}}{\partial u_{\kappa\alpha}^a \partial u_{\kappa'\beta}^b} \right) u_{\kappa'\beta}^b$$

The equations of motion are coupled

To know the displacement of atom κ ,
in unit cell a ,
along cartesian direction α ,
$u_{\kappa\alpha}^a$

We require the displacement of atom κ',
in unit cell b ,
along cartesian direction β ,
$u_{\kappa'\beta}^b$

The classical equation of motion for the ions: seeking for a general solution (temporal dependency)

For each atom, there are three equations of motion of this type (one for each cartesian direction). In total, $3 \times N_{atoms}$

$$M_\kappa \frac{\partial^2 u^a_{\kappa\alpha}}{\partial t^2} = -\sum_{b\kappa'\beta} \left(\frac{\partial^2 E_{e+i}}{\partial u^a_{\kappa\alpha} \partial u^b_{\kappa'\beta}} \right) u^b_{\kappa'\beta}$$

The equations of motion are coupled

First ansatz: temporal dependency

We seek for general solutions where all the displacements have a temporal dependency of the form $e^{-i\omega_m t}$

$$u^a_{\kappa\alpha}(t) = \eta^a_m(\kappa\alpha)e^{-i\omega_m t}$$

m :index for the different solutions to the equations (index of mode)

The classical equation of motion for the ions: seeking for a general solution (spatial dependency)

For each atom, there are three equations of motion of this type (one for each cartesian direction). In total, $3 \times N_{atoms}$

$$M_\kappa \frac{\partial^2 u^a_{\kappa\alpha}}{\partial t^2} = -\sum_{b\kappa'\beta} \left(\frac{\partial^2 E_{e+i}}{\partial u^a_{\kappa\alpha} \partial u^b_{\kappa'\beta}} \right) u^b_{\kappa'\beta}$$

The equations of motion are coupled

Second ansatz: spatial dependency

For periodic structures, we can write the displacements in terms of a plane wave with respect to cell coordinates

$$u^a_{\kappa\alpha}(t) = \eta_{m\vec{q}}(\kappa\alpha) e^{i\vec{q}\cdot\vec{R}_a} e^{-i\omega_{m\vec{q}}t}$$

In contrast to a normal plane wave, this wave is only defined at the lattice point

A few properties and consequences of the ansatz

For periodic structures, we can write the displacements in terms of a plane wave with respect to cell coordinates

$$u_{\kappa\alpha}^a(t) = \eta_{m\vec{q}}(\kappa\alpha)e^{i\vec{q}\cdot\vec{R}_a}e^{-i\omega_{m\vec{q}}t}$$

The vibration of the ions have been classified according to a wave vector $\vec{q}$

- Approach equivalent to that taken for the electrons through the Bloch theorem

- If the solid is simulated by a supercell composed of N unit cells + Born-von Karman boundary conditions, then only compatible $\vec{q}$ points can be used in the previous expression.

There are as many $\vec{q}$ allowed values as unit cells there are in the supercell

In contrast to a normal plane wave, this wave is only defined at the lattice points

$\eta_{m\vec{q}}(\kappa\alpha)$ is the component along direction α of a vector called the polarization vector of the normal mode

A little bit of algebra in the equation of motion: taking the time derivatives of the ansatz equation

Now we replace the ansatz solution in the equation of motion

$$M_\kappa \frac{\partial^2 u_{\kappa\alpha}^a}{\partial t^2} = -\sum_{b\kappa'\beta} \left(\frac{\partial^2 E_{e+i}}{\partial u_{\kappa\alpha}^a \partial u_{\kappa'\beta}^b} \right) u_{\kappa'\beta}^b$$

Remember that the ansatz is

$$u_{\kappa\alpha}^a(t) = \eta_{m\vec{q}}(\kappa\alpha) e^{i\vec{q}\cdot\vec{R}_a} e^{-i\omega_{m\vec{q}}t}$$

Taking the time derivatives

$$\frac{\partial u_{\kappa\alpha}^a(t)}{\partial t} = (-i\omega_{m\vec{q}})\eta_{m\vec{q}}(\kappa\alpha) e^{i\vec{q}\cdot\vec{R}_a} e^{-i\omega_{m\vec{q}}t}$$

$$\frac{\partial^2 u_{\kappa\alpha}^a(t)}{\partial t^2} = -\omega_{m\vec{q}}^2 \eta_{m\vec{q}}(\kappa\alpha) e^{i\vec{q}\cdot\vec{R}_a} e^{-i\omega_{m\vec{q}}t}$$

A little bit of algebra in the equation of motion: replacing the ansatz in the equation

$$-M_\kappa \omega^2_{m\vec{q}} \eta_{m\vec{q}}(\kappa\alpha) e^{i\vec{q}\cdot\vec{R}_a} e^{-i\omega_{m\vec{q}}t} = -\sum_{b\kappa'\beta} \left(\frac{\partial^2 E_{e+i}}{\partial u^a_{\kappa\alpha} \partial u^b_{\kappa'\beta}} \right) \eta_{m\vec{q}}(\kappa'\beta) e^{i\vec{q}\cdot\vec{R}_b} e^{-i\omega_{m\vec{q}}t}$$

Multiplying both sides by $e^{i\omega_{m\vec{q}}t}$

$$M_\kappa \omega^2_{m\vec{q}} \eta_{m\vec{q}}(\kappa\alpha) e^{i\vec{q}\cdot\vec{R}_a} = \sum_{b\kappa'\beta} \left(\frac{\partial^2 E_{e+i}}{\partial u^a_{\kappa\alpha} \partial u^b_{\kappa'\beta}} \right) \eta_{m\vec{q}}(\kappa'\beta) e^{i\vec{q}\cdot\vec{R}_b}$$

Reordering the sums, and multiplying both sides by $e^{-i\vec{q}\cdot\vec{R}_a}$

$$M_\kappa \omega^2_{m\vec{q}} \eta_{m\vec{q}}(\kappa\alpha) = \sum_{\kappa'\beta} \left[\sum_b \left(\frac{\partial^2 E_{e+i}}{\partial u^a_{\kappa\alpha} \partial u^b_{\kappa'\beta}} \right) e^{i\vec{q}\cdot(\vec{R}_b - \vec{R}_a)} \right] \eta_{m\vec{q}}(\kappa'\beta)$$

A little bit of algebra in the equation of motion: introducing the interatomic force constant

Definition of the interatomic force constant in real space

$$C_{\kappa\alpha,\kappa'\beta}(a,b) = \left(\frac{\partial^2 E_{e+i}}{\partial u^a_{\kappa\alpha} u^b_{\kappa'\beta}} \right)$$

Then, the previous equation takes the form

$$M_\kappa \omega^2_{m\vec{q}} \eta_{m\vec{q}}(\kappa\alpha) = \sum_{\kappa'\beta} \left[\sum_b C_{\kappa\alpha,\kappa'\beta}(a,b) e^{i\vec{q}\cdot(\vec{R}_b - \vec{R}_a)} \right] \eta_{m\vec{q}}(\kappa'\beta)$$

The summation in b must be performed over all the unit cells. Since the interatomic force constants in real space depend only on the relative distance between the atoms, the origin a does not play a role anymore, and can be set to 0.

$$M_\kappa \omega^2_{m\vec{q}} \eta_{m\vec{q}}(\kappa\alpha) = \sum_{\kappa'\beta} \left[\sum_b C_{\kappa\alpha,\kappa'\beta}(0,b) e^{i\vec{q}\cdot\vec{R}_b} \right] \eta_{m\vec{q}}(\kappa'\beta)$$

A little bit of algebra in the equation of motion: the Fourier transform of the interatomic force constant

$$M_\kappa \omega^2_{m\vec{q}} \eta_{m\vec{q}}(\kappa\alpha) = \sum_{\kappa'\beta} \left[\sum_b C_{\kappa\alpha,\kappa'\beta}(0,b) e^{i\vec{q}\cdot\vec{R}_b} \right] \eta_{m\vec{q}}(\kappa'\beta)$$

The term in brackets is nothing else than the discrete Fourier transform of the interatomic force constant in real space

$$\tilde{C}_{\kappa\alpha,\kappa'\beta}(\vec{q}) = \frac{1}{N} \sum_{a,b} C_{\kappa\alpha,\kappa'\beta}(a,b) e^{-i\vec{q}\cdot(\vec{R}_a - \vec{R}_b)}$$

$$= \sum_b C_{\kappa\alpha,\kappa'\beta}(0,b) e^{i\vec{q}\cdot\vec{R}_b}$$

Therefore, the movement of the atoms can be defined in terms of the following dynamical equations

$$M_\kappa \omega^2_{m\vec{q}} \eta_{m\vec{q}}(\kappa\alpha) = \sum_{\kappa'\beta} \tilde{C}_{\kappa\alpha,\kappa'\beta}(\vec{q}) \eta_{m\vec{q}}(\kappa'\beta)$$

The equation of motion in matricial form

$$M_\kappa \omega^2_{m\vec{q}} \eta_{m\vec{q}}(\kappa\alpha) = \sum_{\kappa'\beta} \tilde{C}_{\kappa\alpha,\kappa'\beta}(\vec{q}) \eta_{m\vec{q}}(\kappa'\beta)$$

For each $\vec{q}$ vector, we have a linear homogenous system of equations, that in matrix form can be read as

$$\left(\tilde{C}(\vec{q}) \right) \left(\eta(\vec{q}) \right) = \omega^2(\vec{q}) \left(M_\kappa \delta_{\kappa\kappa'} \delta_{\alpha\beta} \right) \left(\eta(\vec{q}) \right)$$

$(3 \times N_{\text{atoms unit cell}})$ $(3 \times N_{\text{atoms unit cell}})$ $(3 \times N_{\text{atoms unit cell}})$ $(3 \times N_{\text{atoms unit cell}})$
$\times$ $\times$ $\times$ $\times$
$(3 \times N_{\text{atoms unit cell}})$ 1 $(3 \times N_{\text{atoms unit cell}})$ 1

Fourier transform of the interatomic force constants **Phonon eigendisplacements** **Phonon frequencies** **Mass matrix** **Phonon eigendisplacements**

The mass matrix: example for a system with two atoms in the unit cell

$$M_\kappa \delta_{\kappa\kappa'} \delta_{\alpha\beta}$$

	Atom 1 Direction x	Atom 1 Direction y	Atom 1 Direction z	Atom 2 Direction x	Atom 2 Direction y	Atom 2 Direction z
Atom 1 Direction x	M_1	0	0	0	0	0
Atom 1 Direction y	0	M_1	0	0	0	0
Atom 1 Direction z	0	0	M_1	0	0	0
Atom 2 Direction x	0	0	0	M_2	0	0
Atom 2 Direction y	0	0	0	0	M_2	0
Atom 2 Direction z	0	0	0	0	0	M_2

A renormalization of the displacements by the square root of the mass allows to solve a standard eigenvalue problem

$$\begin{pmatrix} \tilde{C}(\vec{q}) \end{pmatrix} \begin{pmatrix} \eta(\vec{q}) \end{pmatrix} = \omega^2(\vec{q}) \begin{pmatrix} M_\kappa \delta_{\kappa\kappa'} \delta_{\alpha\beta} \end{pmatrix} \begin{pmatrix} \eta(\vec{q}) \end{pmatrix}$$

This is not a standard eigenvalue problem due to the presence of the mass matrix (somehow the "eigenvalue" changes from one row to the other…)

We can recover an standard eigenvalue problem redefining the eigenvectors incorporating the square root of mass

$$u^a_{\kappa\alpha}(t) = \frac{1}{\sqrt{M_\kappa}} \gamma_{m\vec{q}}(\kappa\alpha) e^{i\vec{q}\cdot\vec{R}_a} e^{-i\omega_{m\vec{q}}t}$$

The dynamical equation with the renormalized displacements

Redoing previous algebra

$$\omega_{m\vec{q}}^2 \gamma_{m\vec{q}}(\kappa\alpha) = \sum_{\kappa'\beta} \frac{\tilde{C}_{\kappa\alpha,\kappa'\beta}(\vec{q})}{\sqrt{M_\kappa M_{\kappa'}}} \gamma_{m\vec{q}}(\kappa'\beta)$$

We define the dynamical matrix as

$$\tilde{D}_{\kappa\alpha,\kappa'\beta}(\vec{q}) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \tilde{C}_{\kappa\alpha,\kappa'\beta}(\vec{q})$$

So finally the dynamical equation reduces to

$$\sum_{\kappa'\beta} \tilde{D}_{\kappa\alpha,\kappa'\beta}(\vec{q}) \gamma_{m\vec{q}}(\kappa'\beta) = \omega_{m\vec{q}}^2 \gamma_{m\vec{q}}(\kappa\alpha)$$

The dynamical equation with the renormalized displacements

Redoing previous algebra

$$\sum_{\kappa'\beta} \tilde{D}_{\kappa\alpha,\kappa'\beta}(\vec{q})\gamma_{m\vec{q}}(\kappa'\beta) = \omega^2_{m\vec{q}}\gamma_{m\vec{q}}(\kappa\alpha)$$

In matrix form

$$\begin{pmatrix} \tilde{D}(\vec{q}) \end{pmatrix} \begin{pmatrix} \gamma(\vec{q}) \end{pmatrix} = \omega^2(\vec{q}) \begin{pmatrix} \gamma(\vec{q}) \end{pmatrix}$$

$$\begin{pmatrix} 3 \times N_{\text{atoms unit cell}} \end{pmatrix} \qquad \begin{pmatrix} 3 \times N_{\text{atoms unit cell}} \end{pmatrix} \qquad \begin{pmatrix} 3 \times N_{\text{atoms unit cell}} \end{pmatrix}$$
$$\times \qquad\qquad \times \qquad\qquad \times$$
$$\begin{pmatrix} 3 \times N_{\text{atoms unit cell}} \end{pmatrix} \qquad\qquad 1 \qquad\qquad\qquad 1$$

Dynamical matrix   **Phonon eigenvectors**   **Phonon frequencies**   **Phonon eigenvectors**

Units

The dynamical matrix is Hermitian

By definition

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

The transpose of the dynamical matrix is …   …and the complex conjugate of the transpose

$$\tilde{D}_{\kappa'\beta,\kappa\alpha}(\vec{q}) = \frac{\tilde{C}_{\kappa'\beta,\kappa\alpha}(\vec{q})}{\sqrt{M_{\kappa'} M_\kappa}} = \frac{1}{\sqrt{M_{\kappa'} M_\kappa}} \sum_a C_{\kappa'\beta,\kappa\alpha}(0,a) e^{i\vec{q}\cdot\vec{R}_a}$$

$$= \frac{1}{\sqrt{M_{\kappa'} M_\kappa}} \sum_a \left(\frac{\partial^2 E_{e+i}}{\partial u^0_{\kappa'\beta} \partial u^a_{\kappa\alpha}} \right) e^{i\vec{q}\cdot\vec{R}_a}$$

$$= \frac{1}{\sqrt{M_{\kappa'} M_\kappa}} \sum_a \left(\frac{\partial^2 E_{e+i}}{\partial u^{-a}_{\kappa'\beta} \partial u^0_{\kappa\alpha}} \right) e^{i\vec{q}\cdot\vec{R}_a}$$

$$= \frac{1}{\sqrt{M_{\kappa'} M_\kappa}} \sum_a \left(\frac{\partial^2 E_{e+i}}{\partial u^0_{\kappa\alpha} \partial u^{-a}_{\kappa'\beta}} \right) e^{i\vec{q}\cdot\vec{R}_a}$$

$$= \frac{1}{\sqrt{M_{\kappa'} M_\kappa}} \sum_a C_{\kappa\alpha,\kappa'\beta}(0,-a) e^{i\vec{q}\cdot\vec{R}_a}$$

$$\tilde{D}^*_{\kappa'\beta,\kappa\alpha}(\vec{q}) = \frac{1}{\sqrt{M_{\kappa'} M_\kappa}} \sum_a C_{\kappa\alpha,\kappa'\beta}(0,-a) e^{-i\vec{q}\cdot\vec{R}_a}$$

$$= \frac{1}{\sqrt{M_{\kappa'} M_\kappa}} \sum_a C_{\kappa\alpha,\kappa'\beta}(0,a) e^{i\vec{q}\cdot\vec{R}_a}$$

$$= \tilde{D}_{\kappa\alpha,\kappa'\beta}(\vec{q})$$

$$\tilde{D}_{\kappa\alpha,\kappa'\beta}(\vec{q}) = \tilde{D}^*_{\kappa'\beta,\kappa\alpha}(\vec{q})$$

Relation between phonon eigenvectors and phonon eigendisplacements

In a standard code, the dynamical matrix is diagonalized,
and the solutions are the **phonon eigenvectors**

$$\gamma_{m\vec{q}}(\kappa\alpha)$$

However, to compute many properties related with the lattice
dynamics, we require the **phonon eigendisplacements**.
For instance, the mode polarity

$$p_{m\alpha} = \sum_{\kappa\beta} Z^{*}_{\kappa,\alpha\beta}\eta_{m}(\kappa\beta)$$

Required to compute, for instance, the static dielectric constant

$$\varepsilon^{0}_{\alpha\beta} = \varepsilon^{\infty}_{\alpha\beta} + \frac{4\pi}{\Omega_0} \sum_{m} \frac{p_{m\alpha} \cdot p_{m\beta}}{\omega^{2}_{m}}$$

The phonon eigendisplacements and phonon eigenvectors are related by

$$\eta_{m\vec{q}}(\kappa\alpha) = \frac{1}{\sqrt{M_{\kappa}}}\gamma_{m\vec{q}}(\kappa\alpha)$$

Normalization of the phonon eigenvectors and phonon eigendisplacements

For the phonon eigenvectors, at a given m and $\vec{q}$

$$(\gamma_{1x}, \gamma_{1y}, \gamma_{1z}, \ldots, \gamma_{Nx}, \gamma_{Ny}, \gamma_{Nz}) \begin{pmatrix} \gamma_{1x} \\ \gamma_{1y} \\ \gamma_{1z} \\ \ldots \\ \gamma_{Nx} \\ \gamma_{Ny} \\ \gamma_{Nz} \end{pmatrix} = 1$$

For the phonon eigendisplacements, at a given m and $\vec{q}$

$$(\eta_{1x}, \eta_{1y}, \eta_{1z}, \ldots, \eta_{Nx}, \eta_{Ny}, \eta_{Nz}) \begin{pmatrix} M_1 & 0 & 0 & \ldots & 0 & 0 & 0 \\ 0 & M_1 & 0 & \ldots & 0 & 0 & 0 \\ 0 & 0 & M_1 & \ldots & 0 & 0 & 0 \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ 0 & 0 & 0 & \ldots & M_N & 0 & 0 \\ 0 & 0 & 0 & \ldots & 0 & M_N & 0 \\ 0 & 0 & 0 & \ldots & 0 & 0 & M_N \end{pmatrix} \begin{pmatrix} \eta_{1x} \\ \eta_{1y} \\ \eta_{1z} \\ \ldots \\ \eta_{Nx} \\ \eta_{Ny} \\ \eta_{Nz} \end{pmatrix} = 1$$

How to compute the force constant matrix in reciprocal space: perturbation theory

By definition

$$\tilde{D}_{\kappa\alpha,\kappa'\beta}(\vec{q}) = \frac{\tilde{C}_{\kappa\alpha,\kappa'\beta}(\vec{q})}{\sqrt{M_\kappa M_{\kappa'}}}$$

Combining density functional with first-order perturbation theory:
Density Functional Perturbation Theory (DFPT)

Advantages:

Disadvantages:

It allows to keep the simplicity of a single cell calculation, whatever q-vector which is considered, and that can even be incommensurate with the crystal lattice

Requires some additional implementation effort

How to compute the force constant matrix in real space: finite displacement technique

By definition

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

↑

…we can compute the dynamical matrix for every q-point

↑

Knowing the force constant matrix in real space…

$$C_{\kappa\alpha,\kappa'\beta}(0,a) = \frac{\partial^2 E_{e+i}}{\partial u^0_{\kappa\alpha} \partial u^a_{\kappa'\beta}} = \frac{\partial}{\partial u^0_{\kappa\alpha}}\left(\frac{\partial E_{e+i}}{\partial u^a_{\kappa'\beta}}\right) = -\frac{\partial F^a_{\kappa'\beta}}{\partial u^0_{\kappa\alpha}}$$

We displace the atom κ in the unit cell along direction α, and compute how changes the force on atom κ' in unit cell a along direction β

The derivative is computed by finite differences

How to compute the force constant matrix in real space: finite displacement technique

By definition

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

…we can compute the dynamical matrix for every q-point

Knowing the force constant matrix in real space…

In principle, we should displace the atoms in the unit cell one by one in all the three cartesian directions, and look at the force on the atom of our choice, that might be in a unit cell very far away.

From a practical point of view, the values of the force constant matrix in real space decay with the distance between the atoms… so, practically the previous sum is cut to include only a given number of distant neighbours

$$\frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \sum_b^\infty C_{\kappa\alpha,\kappa'\beta}(0,b) e^{i\vec{q}\cdot\vec{R}_b} \approx \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \sum_b^{b_{\text{cut}}} C_{\kappa\alpha,\kappa'\beta}(0,b) e^{i\vec{q}\cdot\vec{R}_b}$$
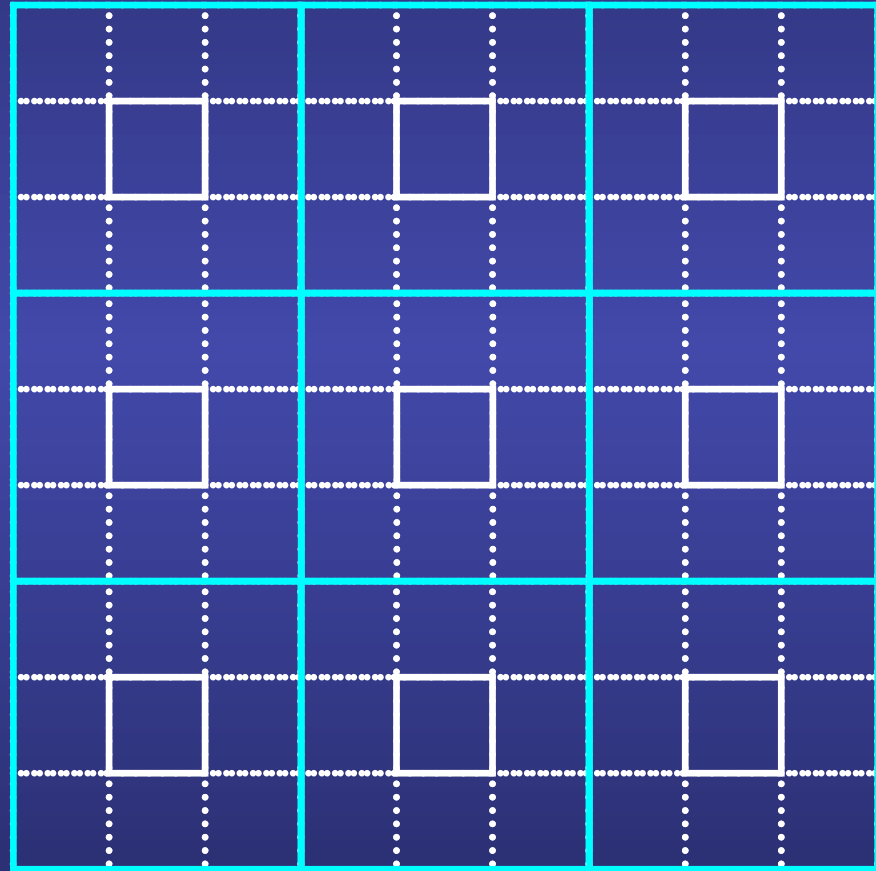
How to compute phonons in Siesta: Use of the Vibra suite.
Step 1: Build the supercell

Unit cell in real space   **Supercell in real space**

How to compute phonons in Siesta: Use of the Vibra suite. Step 1: Build the supercell

```
#
# General system descriptors
#

SystemName      Bulk Silicon in the diamond structure
#               building the supercell to compute the phonons

SystemLabel            Si
NumberOfSpecies         1
NumberOfAtoms           2
%block ChemicalSpeciesLabel
   1  14  Si
%endblock ChemicalSpeciesLabel

#
# Lattice, coordinates, k-sampling
#

LatticeConstant         5.546406 Ang     # Theor. lattice parameter of bulk Si
%block LatticeVectors
   0.00  0.50  0.50
   0.50  0.00  0.50
   0.50  0.50  0.00
%endblock LatticeVectors

AtomicCoordinatesFormat      Fractional
%block AtomicCoordinatesAndAtomicSpecies
  -0.125  -0.125  -0.125     1     28.086
   0.125   0.125   0.125     1     28.086
%endblock AtomicCoordinatesAndAtomicSpecies

kgrid_cutoff           8.0 Ang

#
# Options to generate the supercell
#

SuperCell_1    3      # number of shells in which the unit cell is
               #    repeated in the direction of the first lattice vector.
SuperCell_2    3      # Idem for the second lattice vector.
SuperCell_3    3      # Idem for the third  lattice vector.
```

We prepare an input file to run fcbuild and generate the supercell. Let´s call this input file Si.fcbuild.fdf

Variables to define the unit cell in real space

Variables to define the supercell in real space

How to compute phonons in Siesta: Use of the Vibra suite.
Step 1: Build the supercell

$siesta/Utils/Vibra/Src/fcbuild < Si.fcbuild.fdf

This will generate a file called FC.fdf with:

- The structural data of the supercell (supercell lattice vectors, atomic coordinates,…)

- The atoms that will be displaced to compute the interatomic force constants in real space

- The amount that the atoms will be displaced

The supercell should contain enough atoms so that all non-neglegeable elements of the force constant matrix are computed. The range in real space in which the force constant matrix decays to zero varies widely from system to system!!.
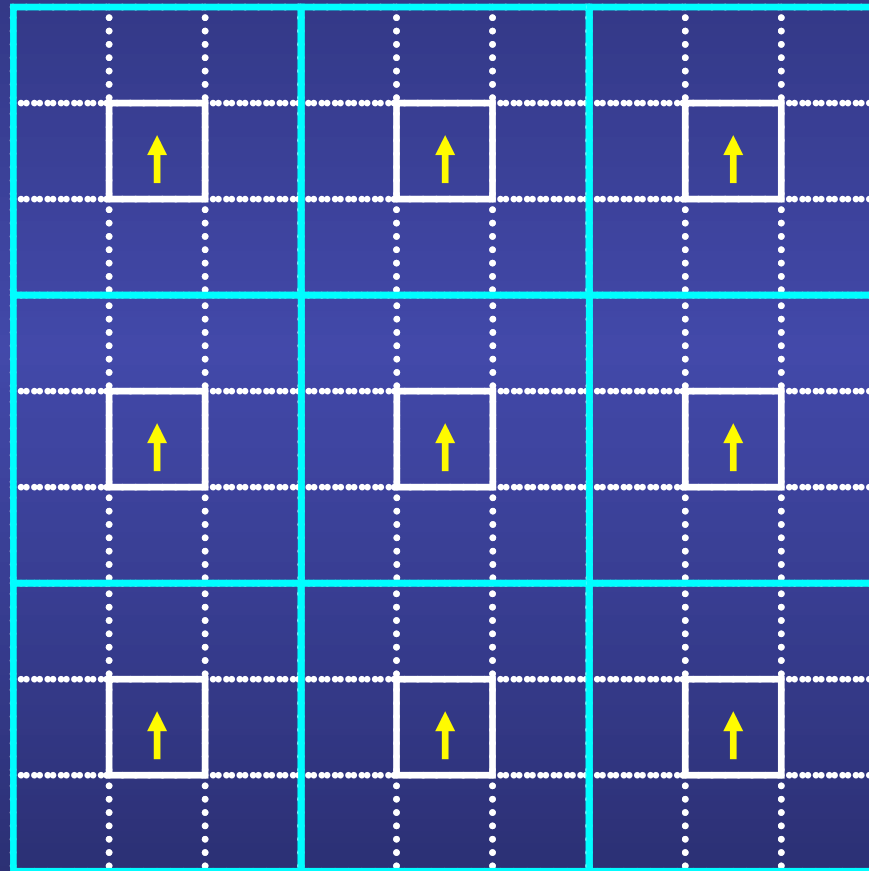
How to compute phonons in Siesta: Use of the Vibra suite.
Step 2: Displace the atoms in the unit cell and compute IFC

Unit cell in real space　　　**Supercell in real space**

**Ideally, we should displace only the atoms in the unit cell, but this
is not possible when using periodic boundary conditions… again, it
is important to converge the size of the supercell**

How to compute phonons in Siesta: Use of the Vibra suite. Step 2: Displace the atoms in the unit cell and compute IFC

```
#
# General system descriptors
#

SystemName      Bulk Silicon in the diamond structure
#               building the supercell to compute the phonons

SystemLabel            Si
NumberOfSpecies        1
NumberOfAtoms                    < FC.fdf
%block ChemicalSpeciesLabel
  1  14  Si
%endblock ChemicalSpeciesLabel

#
# Lattice, coordinates, k-sampling
#

LatticeConstant                < FC.fdf
LatticeVectors                 < FC.fdf

AtomicCoordinatesFormat        < FC.fdf
AtomicCoordinatesAndAtomicSpecies  < FC.fdf

kgrid_cutoff          8.0 Ang

#
# Grid
#

MeshCutoff            200 Ry

#
# Basis definition
#

PAO.BasisSize   SZ

#
# Options to compute the interatomic force constants in real space
#

MD.TypeOfRun    < FC.fdf    # Compute the interatomic force constants matrix
MD.FCfirst      < FC.fdf    # Index of first atom to displace
MD.FClast       < FC.fdf    # Index of the last atom to displace
MD.FCdispl      < FC.fdf    # Displacement to use for the computation of the
                            #   interatomic force constant matrix
                            #   (Remember that the second derivative of the
                            #   energy with respect the displacement of two
                            #   atoms is computed by means of a
                            #   finite difference derivative of the forces)
```

We prepare an input file to run siesta and compute the interatomic force constant matrix. Let´s call this input file Si.ifc.fdf

Many variables are taken directly from the file where the supercell is described

Only the atoms of the unit cell are displaced

How to compute phonons in Siesta: Use of the Vibra suite. Step 2: Displace the atoms in the unit cell and compute IFC

$siesta/Obj/siesta < Si.ifc.fdf > Si.ifc.out

This will generate a file called SystemLabel.FC with the interatomic force constant matrix

```
Force constants matrix
    -0.0312701       0.0482093       0.0482093
     0.0351977      -0.0006070      -0.0006070
    -0.0321113       0.0487602      -0.0469701
     0.0616160      -0.0701156       0.0616651
    -0.0423482       0.0009719      -0.0000591
     0.0529542      -0.0654082      -0.0593842
    -0.0321113      -0.0469701       0.0487602
     0.0616160       0.0616651      -0.0701156
     0.4098112      -0.1418340      -0.1418340
    -3.9652498       2.9318623       2.9318623
    -0.1379968       0.1480754       0.1571662
     0.0449045       0.0580579      -0.0614154
        . . .           . . .           . . .
```

Displace atom 1 along direction -x

As many lines as atoms in the supercell, force on the atom j in the supercell (in eV/Å)

Then loop on the directions along which the atom 1 is displaced:

-x, +x, -y, +y, -z, +z

Finally, loop on the atoms in the unit cell

How to compute phonons in Siesta: Use of the Vibra suite.
Step 3: Compute the dynamical matrix and diagonalize

Once the interatomic force constant matrix has been computed,
a Fourier transform is carried out at different k-points to
calculate the dynamical matrix

$$\tilde{D}_{\kappa\alpha,\kappa'\beta}(\vec{q}) \approx \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \sum_{b}^{b_{\text{cut}}} C_{\kappa\alpha,\kappa'\beta}(0,b) e^{i\vec{q}\cdot\vec{R}_b}$$

The k-points are defined in the same way as to compute the
electronic band structure in the same file used to define the supercell
(Si.fcbuild.fdf)

```
#
# High symmetry lines to plot the phonon band structure
#

BandLinesScale        pi/a
%block BandLines
1    0.0    0.0    0.0    \Gamma          # Begin at Gamma
45   2.0    0.0    0.0    X               # 45 points from Gamma to X
17   2.0    0.5    0.5    K               # 17 points from X to K
48   2.0    2.0    2.0    \Gamma          # 48 points from K to Gamma
41   1.0    1.0    1.0    L               # 41 points from Gamma to L
%endblock BandLines
```

How to compute phonons in Siesta: Use of the Vibra suite.
Step 3: Compute the dynamical matrix and diagonalize

$$\tilde{D}_{\kappa\alpha,\kappa'\beta}(\vec{q}) \approx \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \sum_b^{b_{\text{cut}}} C_{\kappa\alpha,\kappa'\beta}(0,b) e^{i\vec{q}\cdot\vec{R}_b}$$

$siesta/Utils/Vibra/Src/vibrator < Si.fcbuild.fdf

Output:

SystemLabel.bands: mode frequencies (in cm^{-1})
(Same structure as the electronic band structure)

SystemLabel.vectors: eigenmodes for each k-point
(format self-explained)

To plot the phonon band structure:
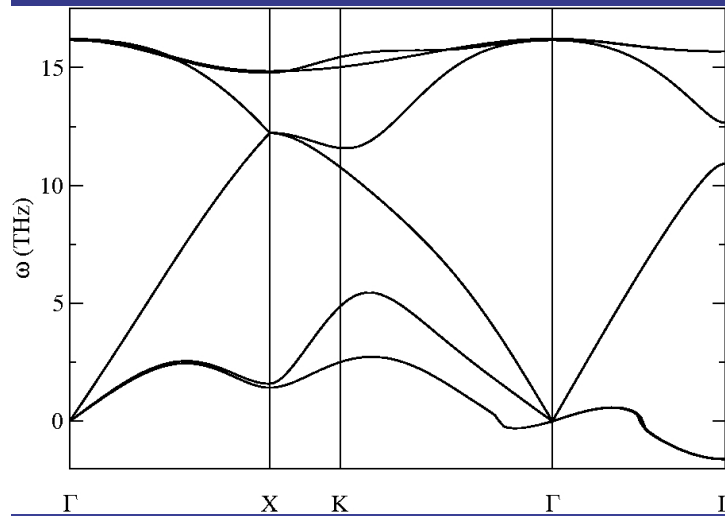
$bandline.x < Si.bands > Si.bands.dat

$gnuplot

$plot "Si.bands.dat" using 1:2 with lines
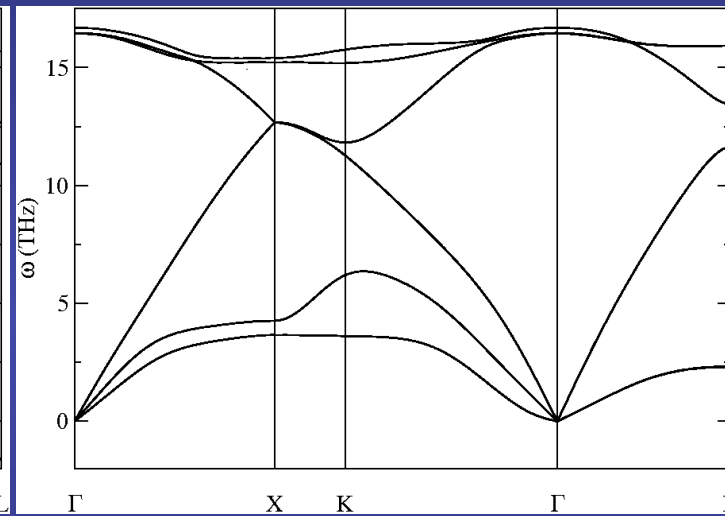
Convergence of the phonon structure with the size of the supercell

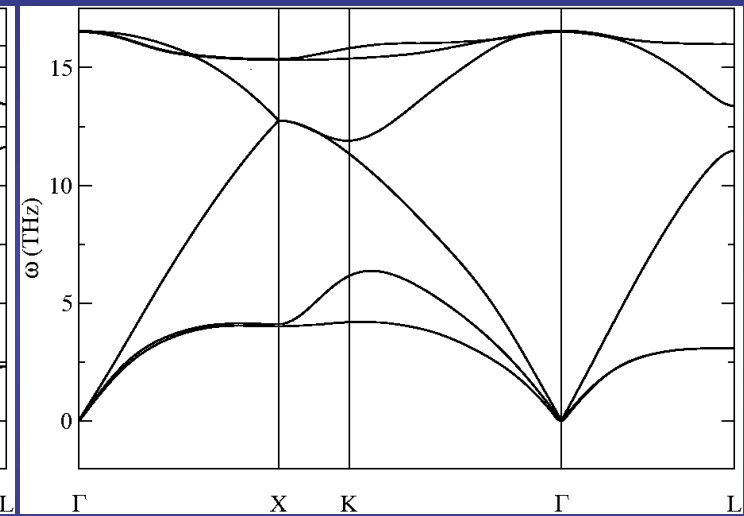**1 × 1 × 1** **2 × 2 × 2** **3 × 3 × 3**

Plane waves + pseudopotentials

Dots represent experimental points

P. E. Van Camp *et al*., Phys. Rev. B 31, 4089 (1985)