Practical exercices on frozen phonon calculations with SIESTA

MAX training: SIESTA school
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Outline

1. Au chain
   - Relaxation of bulk (fcc)
   - Phonon in rigid linear chain
   - Relaxation in linear chain + Γ phonons
   - Phonon dispersion in relaxed chain
2. BN monolayer
   - Relaxation of periodic layer
   - Brillouin zone, symmetry points and supercells
   - FC calculation on a $(2\sqrt{3} \times 2\sqrt{3})$ supercell
   - Phonon dispersion in relaxed monolayer

Phonons/Au-chain. Structure of exercise

Please read the EXERCISE file in the exercise directory.
Executables to be used:
($SIESTA_ROOT)/Obj/siesta
($SIESTA_ROOT)/Util/... (from standard Siesta distribution);

my tools in http://www.home.uni-osnabrueck.de/apostnik/download.html

– look for Sies2vesta/..., Sies2LD/..., vibq0 .

Specific tasks are explained below for each Directory/Input_file.fdf :

Bulk_relax/Bulk_relax.fdf : Find out the equilibrium lattice constant of fcc Au.

Chain_2at_fixed/chain_2at_fixed.fdf : Calcuate frozen zone-boundary phonon for a linear chain of Au atoms placed at nearest-neighbour distances like those in bulk fcc Au. Identify and discuss the dynamical intability.

Chain_2at_relax/chain_2at_relax.fdf : Structure optimization of zigzag-type distorted chain.

Chain_2at_phonon/chain_2at_phonon.fdf : Calculate frozen Gamma phonon in a zigzag-distorted linear chain (2 atoms / unit cell).

Chain_2at_vibra/ ... .fdf : Calculate phonon dispersion using the Vibra suite (construction of supercell - FC calculation within a supercell - calculation of phonon dispersions).

Au-chain/Bulk_relax

```
...
Number_of_atoms     1
Number_of_species   1
Lattice_constant 4.08 Ang #
%block Lattice_vectors
  0.    0.5   0.5   #
  0.5   0.    0.5   #
  0.5   0.5   0.    #
%endblock Lattice_vectors

%block Chemical_species_label
  1   79    Au
%endblock Chemical_species_label
Atomic_coordinates_format    Fractional
%block Atomic_Coordinates_and_Atomic_Species
     0.000     0.000     0.000     1
%endblock Atomic_Coordinates_and_Atomic_Species
...
```

Pseudoptential and basis settings from the SIESTA database

Au-chain/Bulk_relax

```
...
MD.TypeOfRun     CG
MD.VariableCell   T
MD.NumCGsteps    50
#
MeshCutoff              250.0 Ry
XC.functional   LDA
XC.authors      CA
...
```

Calculation result :

```
outcell: Unit cell vectors (Ang):
       -0.000032    2.036251    2.036251
        2.036251   -0.000032    2.036251
        2.036251    2.036251   -0.000032

outcell: Cell vector modules (Ang)   :    2.879693    2.879693    2.879693
outcell: Cell angles (23,13,12) (deg):     60.0010     60.0010     60.0010
```

Equilibrium
lattice parameter :
4.0725 Å
(exp. value: 4.078 Å).

Au-chain/Chain_2at_fixed

```
...
Lattice_constant   1.000 Ang
%block Lattice_vectors
      10.000000000       0.000000000       0.000000000
       0.000000000      10.000000000       0.000000000
       0.000000000       0.000000000       5.759386000
%endblock Lattice_vectors

Atomic_coordinates_format     Fractional
%block Atomic_Coordinates_and_Atomic_Species
       0.0    0.0   -0.25   1   196.97   Au    1
       0.0    0.0    0.25   1   196.97   Au    2
%endblock Atomic_Coordinates_and_Atomic_Species
...
MD.TypeOfRun  FC
MD.VariableCell   F
MD.FCfirst     1
MD.FClast      2
```

We need (at least) 2 atoms / unit cell, otherwise the result for Γ phonon is trivial

Au-chain/Chain_2at_fixed : the FC file

```
Force constants matrix
      0.4099901     -0.0000000     -0.0000000
     -0.3972756     -0.0000000     -0.0000000
      0.4099901      0.0000000     -0.0000000
     -0.3972756      0.0000000      0.0000000
      0.0000000      0.4099901      0.0000000
     -0.0000000     -0.3972756     -0.0000000
     -0.0000000      0.4099901     -0.0000000
      0.0000000     -0.3972756      0.0000000
      0.0000000      0.0000000     -1.0140798
      0.0000000     -0.0000000      1.0258146
     -0.0000000      0.0000000     -1.0140798
     -0.0000000      0.0000000      1.0258146
     -0.3972752     -0.0000000     -0.0000000
      0.4099898     -0.0000000     -0.0000000
     -0.3972752     -0.0000000      0.0000000
      0.4099898      0.0000000     -0.0000000
      0.0000000     -0.3972752     -0.0000000
     -0.0000000      0.4099898      0.0000000
     -0.0000000     -0.3972752      0.0000000
      0.0000000      0.4099898     -0.0000000
     -0.0000000     -0.0000000      1.0258136
      0.0000000     -0.0000000     -1.0140787
      0.0000000      0.0000000      1.0258136
     -0.0000000      0.0000000     -1.0140787
```

Note the (approximate) symmetry
(atom 1) $\leftrightarrow$ (atom 2);
the returning (?) force maximal along [001].

Au-chain/Chain_2at_fixed : Γ-phonon

`vibq0` creates two files:

`siesta.bands` :

```
  0.000000000000000000000000000000000
  0.000000000000000000000000000000000          0.000000000000000000000000000000000
-52.877733418928400253770980625533167          33.264213225158894019519392005000967
         6           1           1
  0.000000    -52.8777     -0.0000      0.0000      0.0000     33.2642     33.2642
         1
   0.000000   'G'
```

`siesta.vectors` :

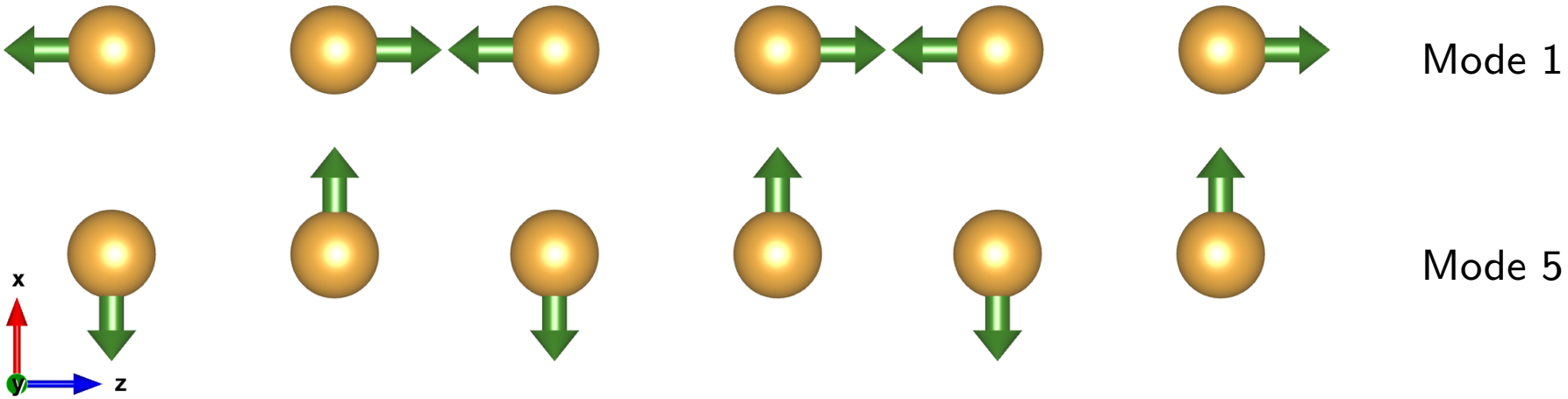
```
k            =     0.000000    0.000000    0.000000
Eigenvector  =     1
Frequency    =   -52.877733
Eigenmode (real part)
  0.0000E+00  0.0000E+00 -0.7071E+00
  0.0000E+00  0.0000E+00  0.7071E+00
...
Eigenvector  =     5
Frequency    =    33.264213
Eigenmode (real part)
 -0.7071E+00  0.0000E+00  0.0000E+00
  0.7071E+00  0.0000E+00  0.0000E+00
...
Eigenvector  =     6
Frequency    =    33.264213
Eigenmode (real part)
 -0.4815E-34 -0.7071E+00 -0.0000E+00
 -0.4815E-34  0.7071E+00 -0.0000E+00
```

Note the "Peierls-type instability" (at shorter interatomic distance replaced by zigzag-type instability)

Au-chain/Chain_2at_fixed : visualize the Γ-phonon

`vib2vesta < vib2vesta.inp`

creates six files, a `Vesta` input file for each mode:



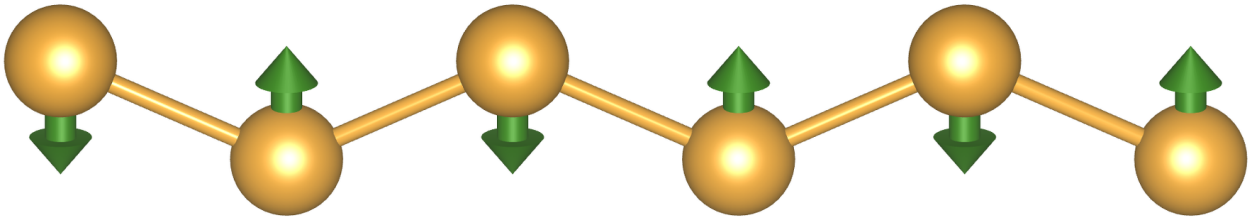
run `vib2vesta` in interactive mode
to get more control over parameters,
then modify the preset "responses" in the input file `vib2vesta.inp`

Au-chain/Chain_2at_relax and Chain_2at_phonon

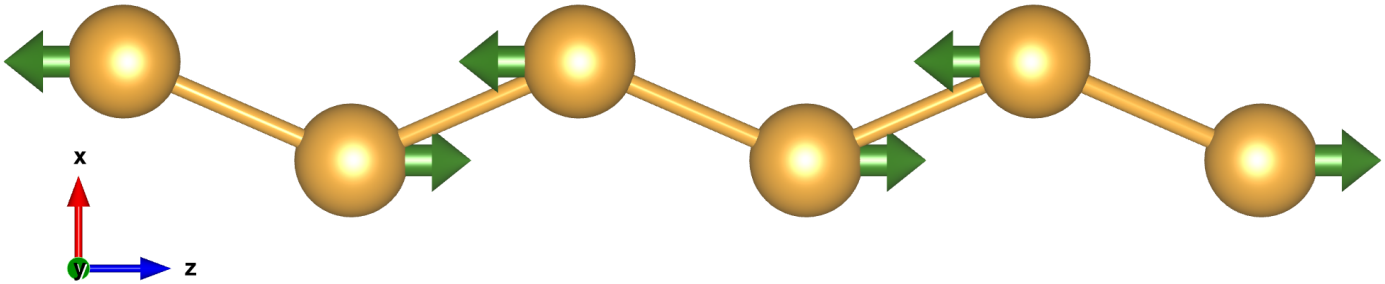
The relaxed structure transferred from the .XV file (after relaxation) into the .fdf format using the xv2fdf tool, to "freeze" the structure for frozen phonon calculations:

```
...
Lattice_constant   1.000 Bohr
%block Lattice_vectors
      18.897268778       0.000000000       0.000000000
       0.000000000      18.897268778       0.000000000
       0.000000000       0.000000000       8.710043059
%endblock Lattice_vectors
Atomic_coordinates_format     NotScaledCartesianBohr
%block Atomic_Coordinates_and_Atomic_Species
       0.944931112       0.316058546      -2.177510774    1    196.97    Au
      -0.944931116      -0.316058552       2.177510761    1    196.97    Au
%endblock Atomic_Coordinates_and_Atomic_Species
```

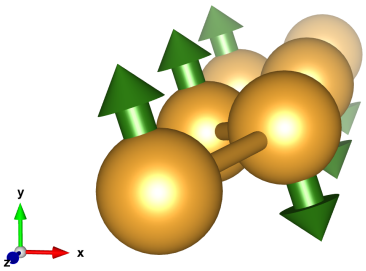
Au-chain/Chain_2at_relax and Chain_2at_phonon



mode 5 (114 cm^{-1})



mode 6 (212 cm^{-1})



mode 1 ($i4$ cm^{-1}; must be zero)

The vibration of an isolated chain along its direction shouldn't cost any energy! – if it does it is due to numerical errors (mesh etc.)

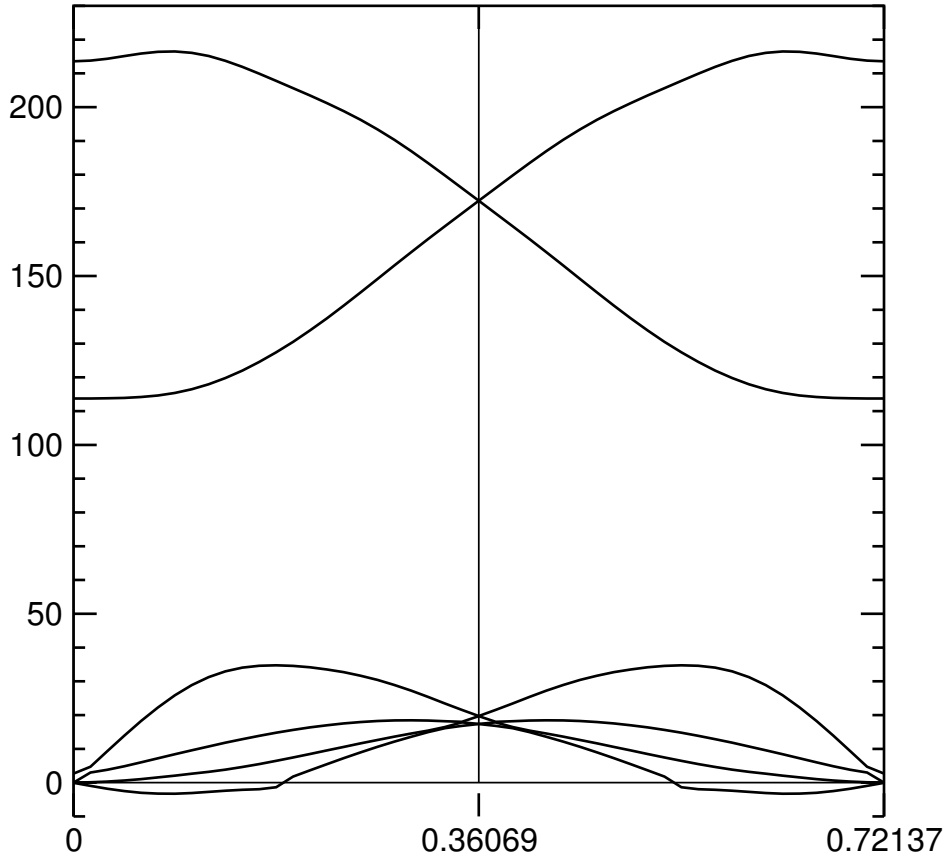
Au-chain/Chain_2at_vibra : phonon dispersion

```
Lattice_constant   1.000 Bohr
%block Lattice_vectors
      18.897268778       0.000000000       0.000000000
       0.000000000      18.897268778       0.000000000
       0.000000000       0.000000000       8.710043059
%endblock Lattice_vectors
Atomic_coordinates_format     NotScaledCartesianBohr
%block Atomic_Coordinates_and_Atomic_Species
    0.944931112     0.316058546    -2.177510774    1    196.97    Au     1
   -0.944931116    -0.316058552     2.177510761    1    196.97    Au     2
%endblock Atomic_Coordinates_and_Atomic_Species
SuperCell_1          0
SuperCell_2          0
SuperCell_3          4
Vibra.FC   siesta.FC
BandLinesScale  ReciprocalLatticeVectors
%block BandLines
  1  0.  0.  0.  \Gamma
 48  0.  0.  1.  \Gamma
%endblock BandLines
Eigenvectors  T
```

To set up a $\omega(\mathbf{q})$ calculation:
run `fcbuild`;
run `siesta`
on the constructed supercell;
run `vibra`
with the corresponding `.fdf` files.

Au-chain/Chain_2at_vibra : phonon dispersion

The dispersion.bands file comes with "absolute" distances along the $\mathbf{q}$ path, i.e., in Bohr^{-1} and 2π factor included:
$2\pi/8.710043059 = 0.7213724$.




```
 0.0000000000000000
 0.0000000000000000        0.72137247366271440
-3.2631873169647871         216.50267537115403
         6           1           49
0.000000     -0.0634     -0.0056      0.0008      2.6703    113.7370    213.5780
...
0.721372     -0.0634     -0.0056      0.0008      2.6703    113.7370    213.5780
         2
  0.000000   'Gamma'
  0.721372   'Gamma'
```

BN-monolayer. Structure of exercise

Please read the EXERCISE file in the exercise directory.
Executables to be used:
($SIESTA_ROOT)/Obj/siesta
($SIESTA_ROOT)/Util/... (from standard Siesta distribution);
my tools in http://www.home.uni-osnabrueck.de/apostnik/download.html

– look for Sies2vesta/..., Sies2LD/..., vibq0 .

Specific tasks are explained below for each Directory/Input_file.fdf :

Relax/BN_relax.fdf : Calculation of equilibrium structure (lattice parameter) of isolated BN layer.

Phonon_G/phonon_G.fdf : Calculation of Gamma-phonon for an isolated BN layer.

Phonon_GMK/phonon_GMK.fdf : Construction of supercell that would have Γ, M and K points of the modified crystal structure onto Γ of the supercell. Calculate frozen Γ phonon in such supercell.

Phonon_Q/phonon_Q.fdf : Calculate phonon dispersions using the Vibra suite (construction of supercell – FC calculation within a supercell – calculation of phonon dispersions) along the $\Gamma - M - K - \Gamma$ path.

BN-monolayer/Relax

Unconstrained structure relaxation of a periodic BN-monolayer (2 atoms / unit cell). Start with a guess for lattice parameter and approximate atom coordinates...

```
PAO.EnergyShift       50 meV
PAO.BasisSize         DZP
Atomic_coordinates_format   Fractional
LatticeConstant       1.00 Ang
%block LatticeParameters
  2.40  2.40  10.00   90.  90.  120.
%endblock LatticeParameters
AtomicCoordinatesFormat     Fractional
%block AtomicCoordinatesAndAtomicSpecies
  0.67  0.33  0.10  1
  0.33  0.67  0.90  2
%endblock AtomicCoordinatesAndAtomicSpecies
```

... allow sufficiently dense $\mathbf{k}$-mesh and sufficiently high Energy Cutoff in order to get accurate and stable forces:

```
%block kgrid_Monkhorst_Pack
 10  0  0  0.   #
  0 10  0  0.   #
  0  0  1  0.   #
%endblock kgrid_Monkhorst_Pack
MeshCutoff            250. Ry
```

Note that the lattice remains hexagonal, the atom coordinates converge to $(\frac{2}{3},\ \frac{1}{3},\ 0)$ and $(\frac{1}{3},\ \frac{2}{3},\ 0)$, the BN sheet remains flat. The variation of the c parameter has no meaning and can be ignored.

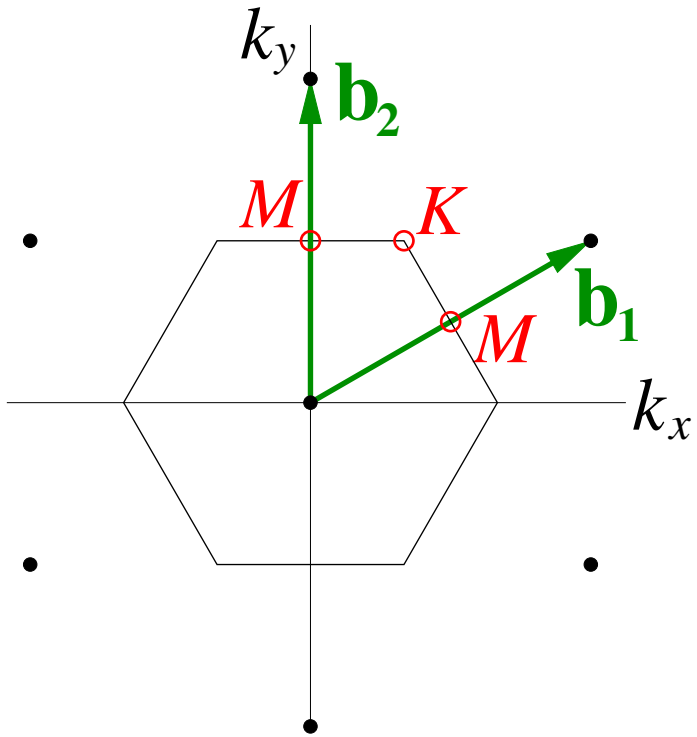
BN-monolayer: supercells and the Brillouin zone

The "standard" Hex lattice vectors:

$$\mathbf{a}_1 = \begin{bmatrix} a \\ 0 \\ 0 \end{bmatrix}; \quad \mathbf{a}_2 = \begin{bmatrix} -\frac{a}{2} \\ \frac{a\sqrt{3}}{2} \\ 0 \end{bmatrix}; \quad \mathbf{a}_3 = \begin{bmatrix} 0 \\ 0 \\ c \end{bmatrix}$$

Reciprocal lattice vectors:

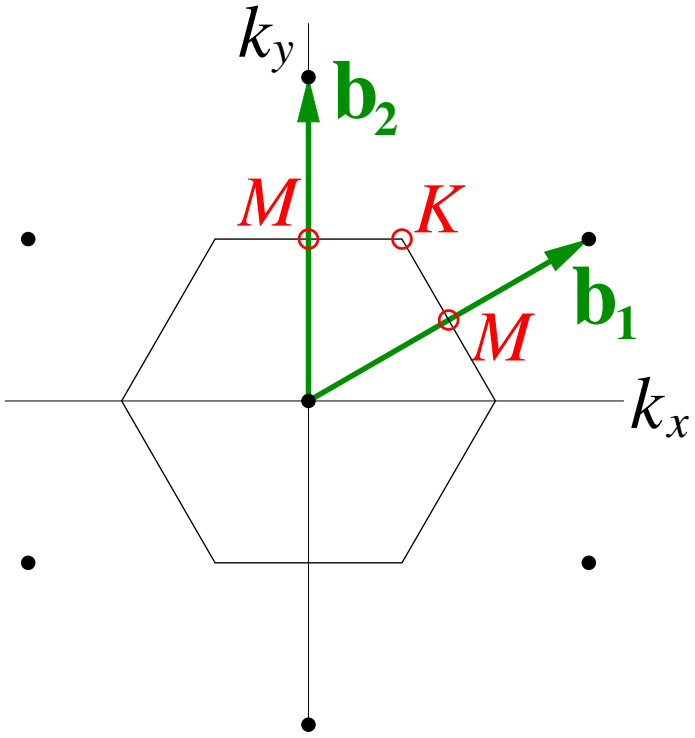
$$\mathbf{b}_1 = \begin{bmatrix} \frac{2\pi}{a} \\ \frac{2\pi}{a\sqrt{3}} \\ 0 \end{bmatrix}; \quad \mathbf{b}_2 = \begin{bmatrix} 0 \\ \frac{4\pi}{a\sqrt{3}} \\ 0 \end{bmatrix}; \quad \mathbf{b}_3 = \begin{bmatrix} 0 \\ 0 \\ \frac{2\pi}{c} \end{bmatrix}$$

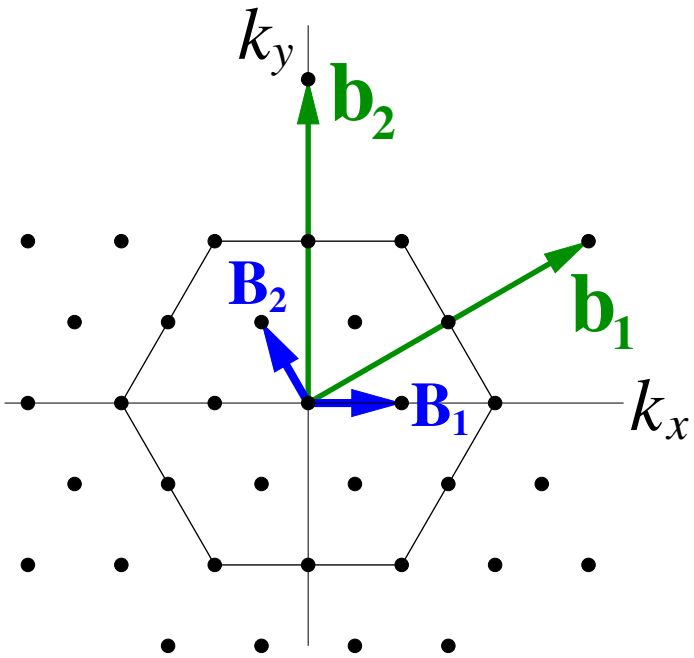


BN-monolayer: supercells and the Brillouin zone

Reciprocal lattice vectors:

$$\mathbf{b}_1 = \begin{bmatrix} \frac{2\pi}{a} \\ \frac{2\pi}{a\sqrt{3}} \\ 0 \end{bmatrix}; \quad \mathbf{b}_2 = \begin{bmatrix} 0 \\ \frac{4\pi}{a\sqrt{3}} \\ 0 \end{bmatrix}; \quad \mathbf{b}_3 = \begin{bmatrix} 0 \\ 0 \\ \frac{2\pi}{c} \end{bmatrix}$$



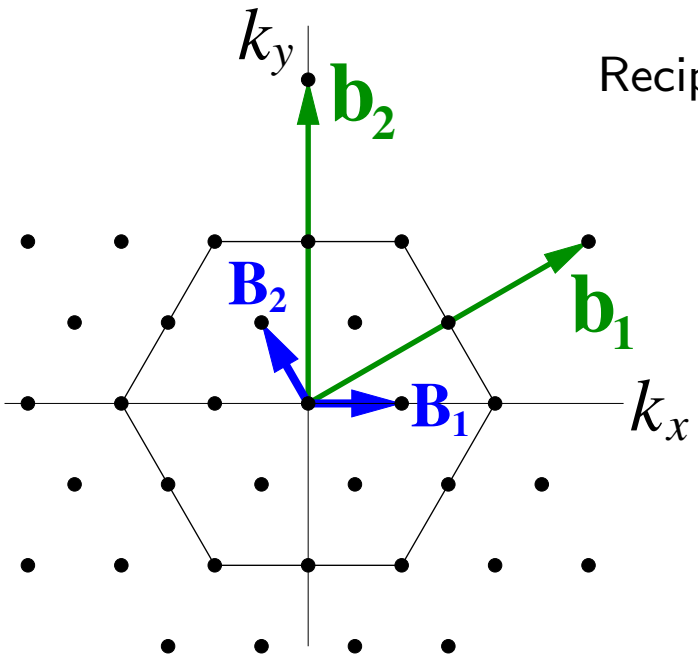


We look for a supercell that would map all M and K points onto Γ.

Reciprocal lattice vectors of this supercell:

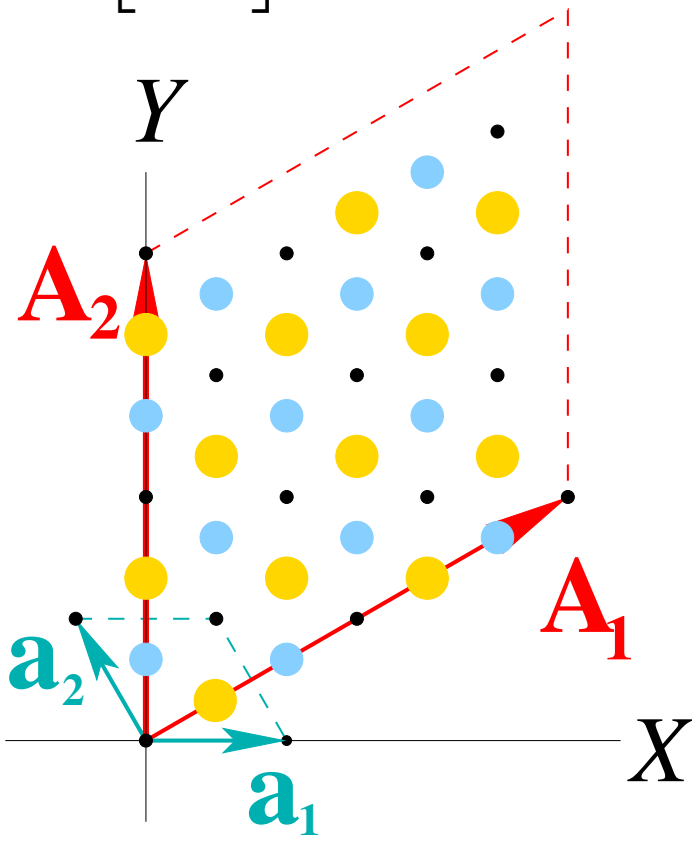
$$\mathbf{B}_1 = \begin{bmatrix} \frac{2\pi}{3a} \\ 0 \\ 0 \end{bmatrix}; \quad \mathbf{B}_2 = \begin{bmatrix} -\frac{\pi}{3a} \\ \frac{\pi}{a\sqrt{3}} \\ 0 \end{bmatrix}$$

BN-monolayer: supercells and the Brillouin zone



Reciprocal lattice vectors of the supercell:

$$\mathbf{B}_1 = \begin{bmatrix} \frac{2\pi}{3a} \\ 0 \\ 0 \end{bmatrix}; \quad \mathbf{B}_2 = \begin{bmatrix} -\frac{\pi}{3a} \\ \frac{\pi}{a\sqrt{3}} \\ 0 \end{bmatrix}$$



Lattice vectors of the $(2\sqrt{3} \times 2\sqrt{3})$ supercell:

$$\mathbf{A}_1 = \begin{bmatrix} 3a \\ a\sqrt{3} \\ 0 \end{bmatrix}; \quad \mathbf{A}_2 = \begin{bmatrix} 0 \\ 2a\sqrt{3} \\ 0 \end{bmatrix}$$

BN-monolayer/Phonon_GMK

See pre-calculated `.FC` file (along with `.XV`, renamed with the `_save` extension).

```
...
NumberOfSpecies        2
NumberOfAtoms         24
Lattice_constant 8.64293 Ang #  2*sqrt(3)*2.495 (initial lattice parameter)
%block Lattice_vectors
 0.8660254  0.5   0.0
 0.0        1.0   0.0
 0.0        0.0   1.157  #  --> 10 Ang, as for the simple cell
%endblock Lattice_vectors
...
AtomicCoordinatesFormat     Fractional
%block AtomicCoordinatesAndAtomicSpecies
  0.166666666667    0.0               0.0    1
  0.333333333333    0.0               0.0    2
  0.666666666667    0.0               0.0    1
  0.833333333333    0.0               0.0    2
 ...
  0.0               0.833333333333    0.0    1
  0.166666666667    0.833333333333    0.0    2
  0.5               0.833333333333    0.0    1
  0.666666666667    0.833333333333    0.0    2
%endblock AtomicCoordinatesAndAtomicSpecies
```

Results of vibq0 (or vibra calculation: 72 frequencies at the supercell Γ,

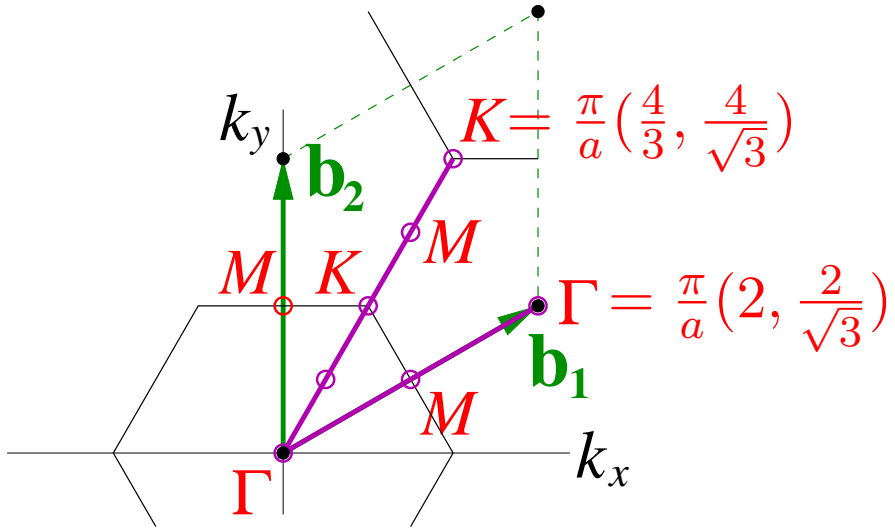
degener.	ω (cm^{-1})
3	0
6	127
...	
4	1478

The eigenvectors of these modes can be projected onto different $\mathbf{q}$ values (with the help of `phdos`), thus revealing Γ, M and K-type vibrations.

BN-monolayer/Phonon_Q : phonon dispersion

The relaxed structure transferred from the .XV file (after relaxation) into the `.fdf` format using `xv2fdf`, to "freeze" the structure for FC calcs:

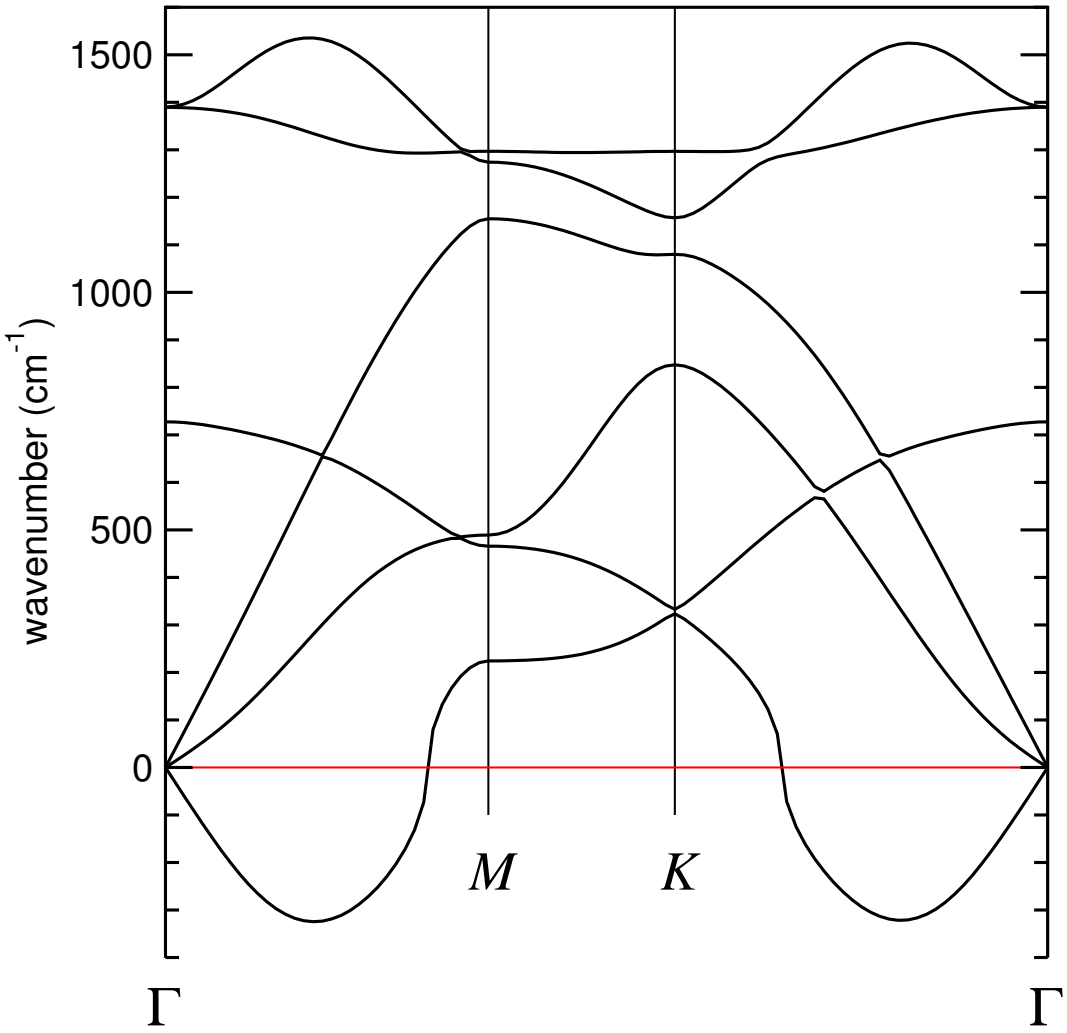
```
...
LatticeConstant       2.495 Ang
%block LatticeParameters
  1.000  1.000  4.008   90.  90.  120.
%endblock LatticeParameters
AtomicCoordinatesFormat     Fractional
%block AtomicCoordinatesAndAtomicSpecies
  0.666666666667    0.333333333333    0.0  1   10.81
  0.333333333333    0.666666666667    0.0  2   14.01
%endblock AtomicCoordinatesAndAtomicSpecies
SuperCell_1           2
SuperCell_2           2
SuperCell_3           0
...
BandLinesScale        pi/a
#%block BandLines
#  1  2.0       1.154701  0.0  \Gamma
#  2  0.0       0.0       0.0  \Gamma
#  4  1.333333  2.309401  0.0  K
#%endblock BandLines
%block BandLines
  1  0.0       0.0       0.0  \Gamma
 35  0.0       1.154701  0.0  M
 20  0.666667  1.154701  0.0  K
 40  0.0       0.0       0.0  \Gamma
%endblock BandLines
Eigenvectors          True
```



NB: two `BandLines` blocks are provided; the first (commented) is intended to check high-symmetry points (those included in `Phonon_GMK`, the path in the Fig. above);

the second is short $\Gamma - M - K - \Gamma$ path.

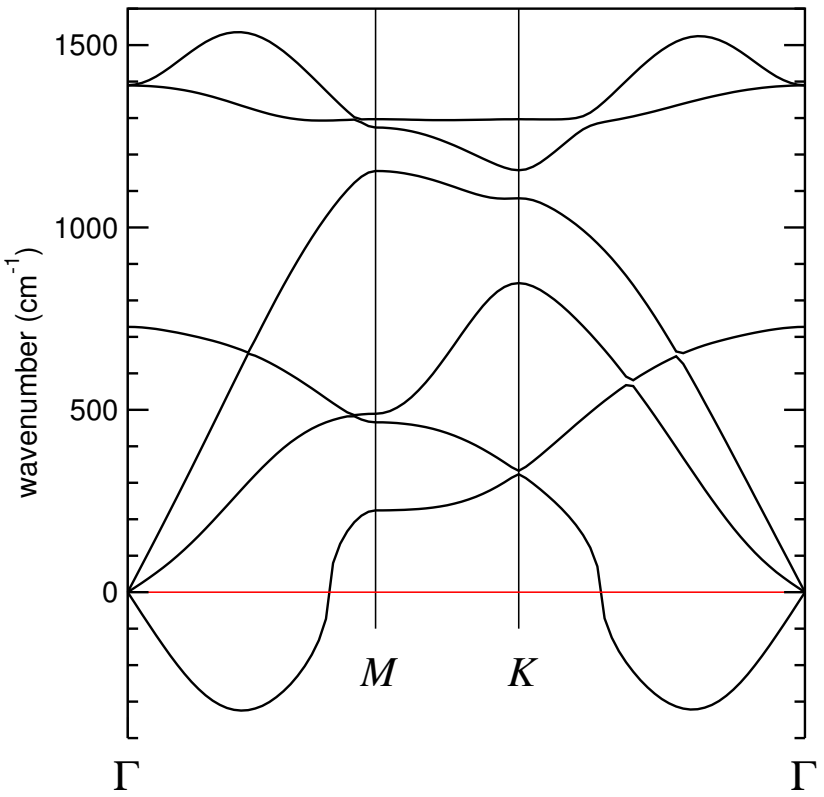
BN-monolayer/Phonon_Q : phonon dispersion



⇐ The LO branch is not split off from TO at Γ (since non-analytic contributions to the FC were not added)

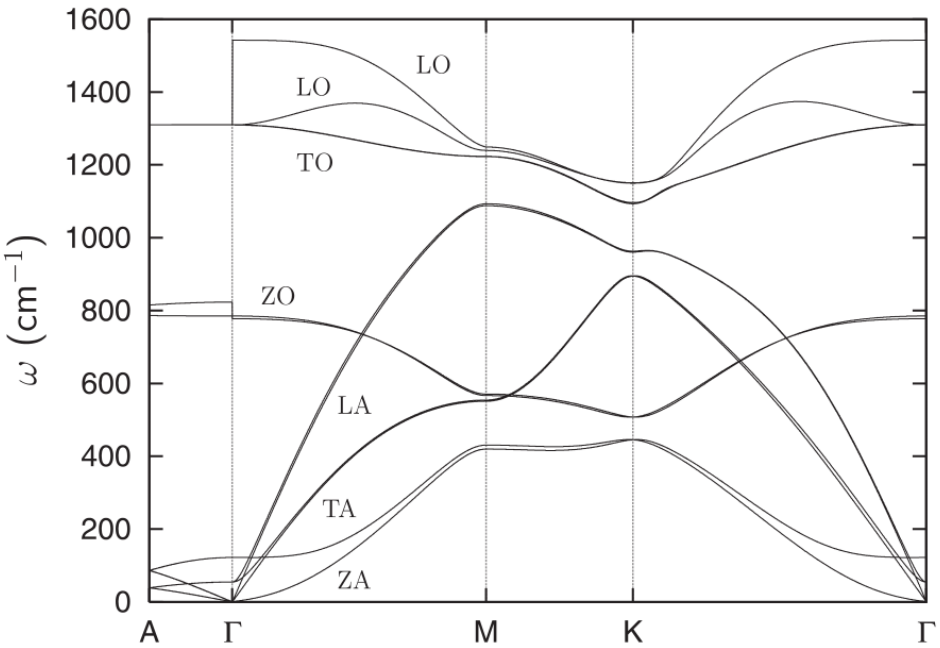
⇐ The (spurious) instability around Γ (but *not* in Γ) is due to insufficient supercell size (long-wavelength phonons are badly mapped)

BN-monolayer/Phonon_Q : phonon dispersion



cf. results for 3-dim. BN:

Michel+Verberck, PRB**83**, 115328 (2011);
Serrano *et al.*, PRL **98**, 095503 (2007).



Phonon dispersions of 3D h-BN with Coulomb forces included.