Implementation of phonon dispersion with LO-TO splitting for polar materials

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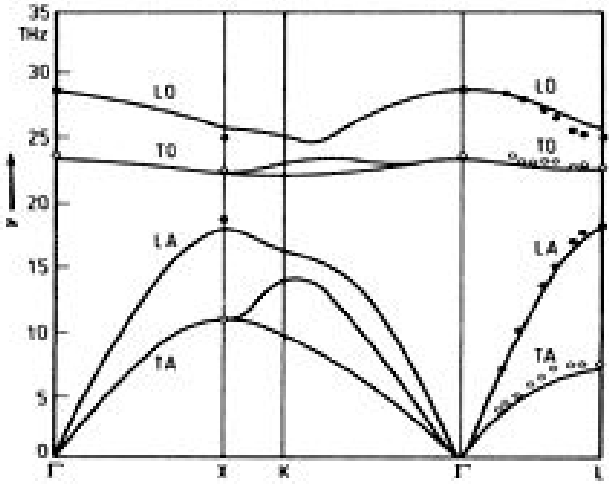
Contents

Phonon

Phonons are vibrations of the atoms in a crystal lattice, and have resonant frequencies in the infrared spectral region. The atoms in a solid are bound to their equilibrium positions by the forces that hold the crystal together. When atoms are displaced from their equilibrium positions, they experience restoring forces, and vibrate at characteristic frequencies. The relationship between frequencies and **k** is called phonon dispersion .

M. Fox, “Optical Properties of Soilds”, 2nd. Chapter 10.

Phonon's dispersion relation can be obtained directly using the quantum-mechanical approach.



Phys. Rev. Lett. ***48*** *(1982) 1846.*

Methods of calculting phonon dispersion

There are three methods to calculate phonon dispersion of solids in the First principle calculation - direct approach, linear response approach, and molecular dynamic approach.

Table 1. The linear-response approach versus the direct approach

Features	*Linear response approach*	*Direct approach*
Implementation in DFT	Calculate the dynamical matrix in the reciprocal space	Calculate the interatomic interaction force constants in the real space
Advantage	Dynamical matrix can be accurately calculated at any arbitrary **q** (wave-vector) points	Straightforward to determine the total energy as a function of atomic displacements
Disadvantage	Extensive programming required and it sometimes has special requirements for the form of pseudopotential in DFT calculations	Phonon frequencies can be accurately calculated only at **q** points that are commensurate with supercell geometry
Limitation on **k** point mesh	**k** point meshes for electronic structure and phonon calculations should be compatible	No need
Additional calculations for polar materials	Separate calculation of dynamical matrix at Γ point, Born effective charges and dielectric constants; additional calculation to separate coulombic contribution from dynamical matrix	Separate calculation of Born effective charges and dielectric constants
For accurate phonon dispersions or density of states for polar solids	Forward Fourier interpolation using the interatomic force constants followed by adding the coulombic contribution back.	Adding coulombic contribution as a constant term to the interatomic force constants followed by forward Fourier interpolation

Abbreviation: DFT, density functional theory.

Y. Wang et. al, *Comptational Material* **2**, 16006 (2016).

Computer Physics Communications 182 (2011) 2201–2207

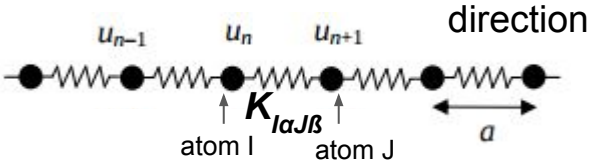
Phonon / First-principles codes for calculting phonon dispersion

Table 2. A collection of phonon/first-principles codes

Codes	*Abilities*	*Method to compute polar effects on phonons*
PWSCF/QUANTUM ESPRESSO[14]	Electronic structure; phonon	Linear-response approach
ABINIT[15]	Electronic structure; phonon	Linear-response approach
CASTEP[13]	Electronic structure; phonon	Linear-response approach
CRYSTAL[28]	Electronic structure; phonon	Mixed-space approach
VASP[11,12]	Electronic structure; phonon	Not available
YPHON[23]	Phonon	Mixed-space approach
ShengBTE[8]	Phonon; thermal conductivity; thermodynamic properties	Mixed-space approach
PhonTS[7]	Phonon; thermal conductivity; thermodynamic properties	Mixed-space approach
Phonopy[18]	Phonon; thermal conductivity; thermodynamic properties	Mixed-space approach
ALAMODE[24]	Phonon; thermal conductivity; thermodynamic properties; anharmonicity	Mixed-space approach
PHONON[17,25–27]	Phonon; thermodynamic properties	Only accurate at the Γ point
PHON[21]	Phonon; thermodynamic properties	Not available
ATAT[4,22]	Phonon; thermodynamic properties	Not available

Y. Wang et. al, *Comptational Material* **2**, 16006 (2016).

3D crystal system



Interatomic Force constants (IFCs)

$$K_{I\alpha J\beta}(R-R') = \frac{\partial^2 E_{tot}}{\partial u_{I\alpha}(R)\partial u_{J\beta}(R')} = -\frac{\partial F_{I\alpha}}{\partial u_{J\beta}(R')} \qquad (1)$$

The displacement of I-th atom along the direction α in Bravais lattice R

Dynamical matrix

$$\tilde{D}_{I\alpha J\beta}(\vec{q}) = \frac{1}{\sqrt{m_I m_J}} \sum_{\vec{R},\vec{R}'} K_{I\alpha J\beta}\left(\vec{R}'-\vec{R}\right) e^{i\vec{q}\cdot(\vec{R}'-\vec{R})} \qquad (2)$$

Mass of J-th atom

$$\omega^2(\vec{q})\vec{U}_{I\alpha}(\vec{q}) = \tilde{D}_{I\alpha J\beta}(\vec{q})\vec{U}_{J\beta}(\vec{q}) \qquad (3)$$

http://www.openmx-square.org/workshop/meeting15/index.html

Force constant

$$K_{I\alpha,J\beta}(R-R') = \frac{\partial^2 E_{tot}}{\partial \mu_{I\alpha}(R)\partial \mu_{J\beta}(R')} = -\frac{\partial F_{I\alpha}}{\partial \mu_{J\beta}(R')} \quad (1)$$

Center difference approximation

$$f'(x) = \frac{f(x+\Delta x) - f(x-\Delta x)}{2\Delta x} \quad (31)$$

Displacement

Atomic coordinate x at equilibrium state

Acoustic sum rules

2. Sum rules in the matrix of force constants

We will be concerned with satisfying two properties of the matrix of force constants [8], $\Phi_{i\alpha,j\beta}$ (where i and j label the atoms and α and β label Cartesian directions) which are difficult to impose simultaneously in *ab initio* lattice dynamics. Firstly, it should be symmetric because partial differentiation is commutative:

$$\Phi_{i\alpha,j\beta} = \Phi_{j\beta,i\alpha} \tag{2}$$

although from equation (1) we see that this explicit symmetry is missing when the element is calculated from the force. Secondly, it should obey the following sum rule which follows from Newton's third law:

$$\Phi_{i\alpha,i\beta} = -\sum_{j\neq i} \Phi_{i\alpha,j\beta}. \tag{3}$$

It follows from these two rules that:

$$\sum_{j\neq i} \Phi_{i\alpha,j\beta} = \sum_{j\neq i} \Phi_{i\beta,j\alpha}. \tag{4}$$

These three rules are true regardless of the actual symmetry of the system under consideration. If the force calculation is exact, then the rules above are automatically satisfied.

J. Phys.: Condens. Matter **9** (1997) 7861–7872.

Flow chart of phonon dispersion

For example: Graphene

1. Setup input file and keywords.
2. Displace atoms along x/y/z directions, i.e. x, -x, y, -y, z, -z.
3. Calculate total energy and atomic forces.

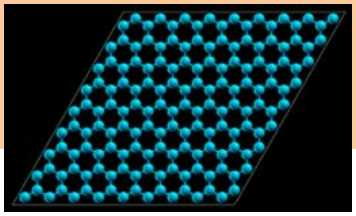
(***until iteration = 6 steps/atom x N atoms = 6N***)

12 iteration for graphene

4. Calculate force-constants and dynamical matrix (3Nx3N matrix).

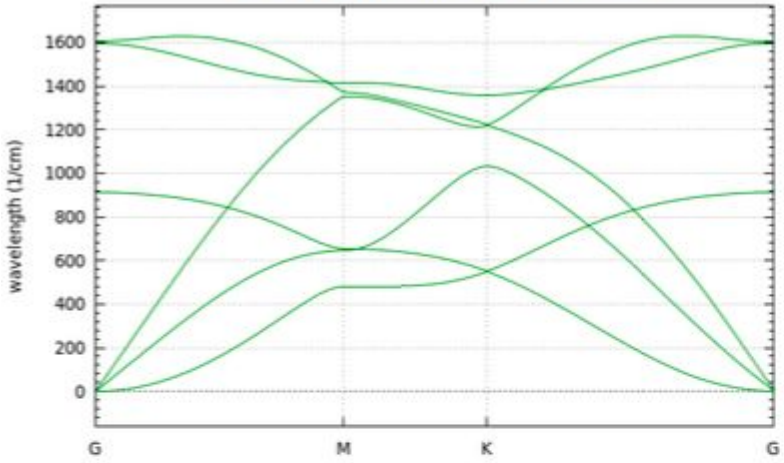
(6x6 matrix for graphene)

5. Obtain phonon dispersion and phonon density of states.
6. Write output files, i.e. *.FORCE_SETS, *.PhDis, *.PhDos

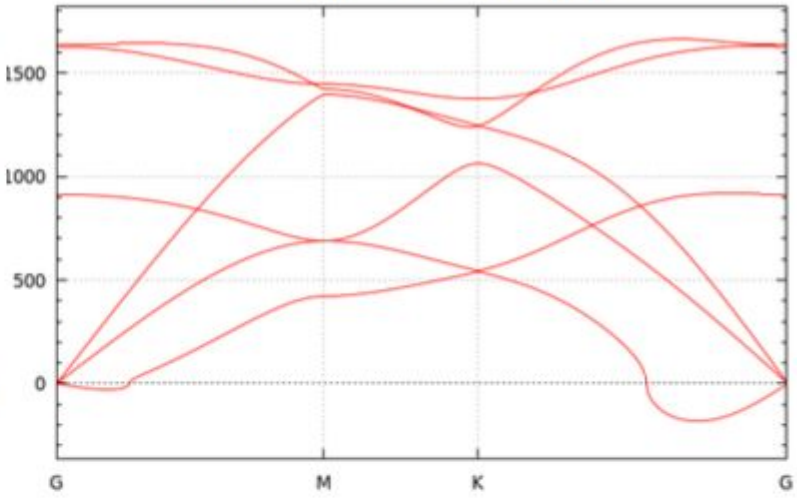


Phonon dispersion of graphene

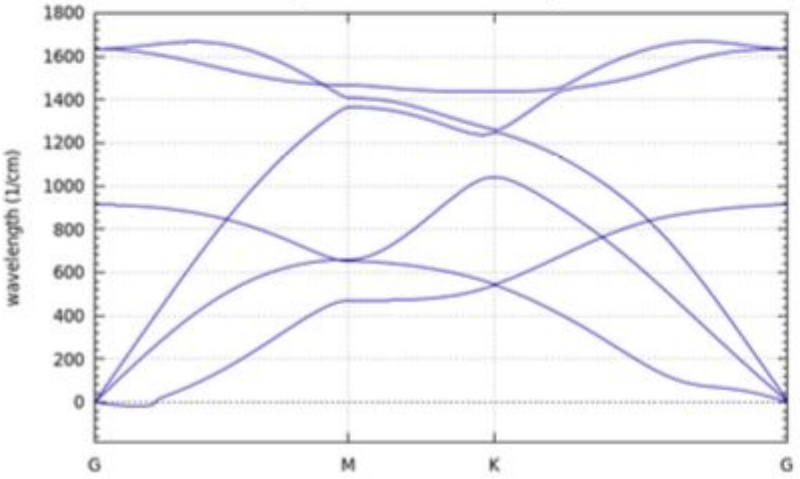
Graphene 9x9x1 supercell

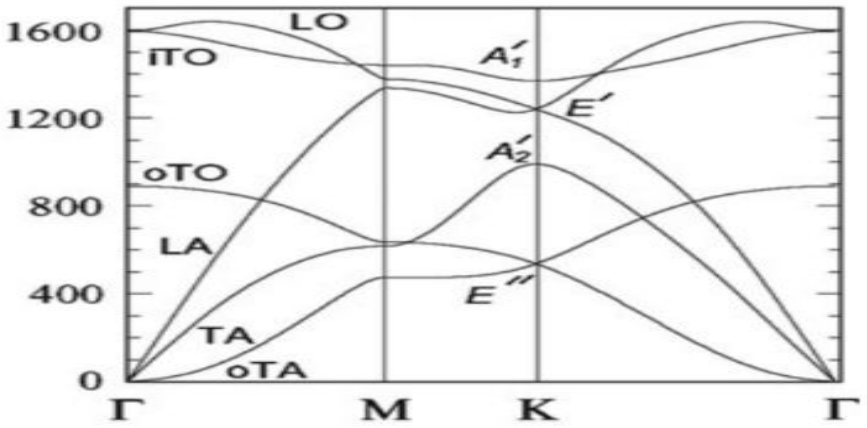


Graphene 3x3x1 supercell



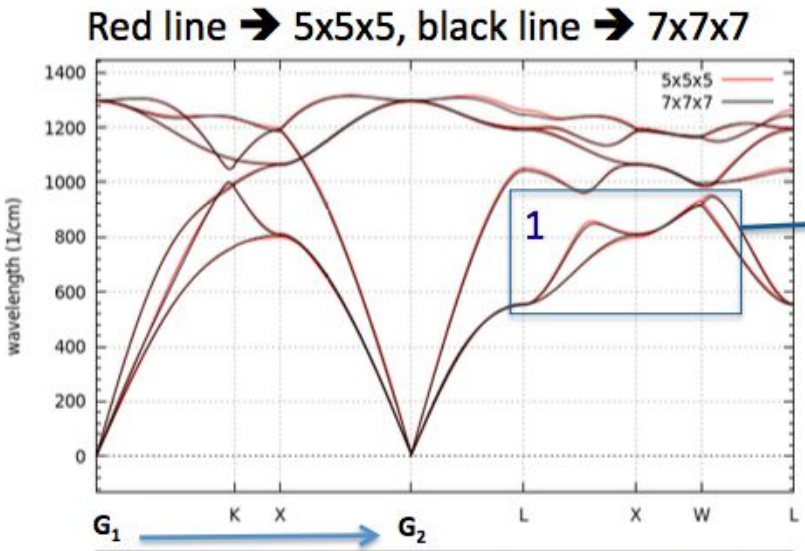
Graphene 5x5x1 supercell

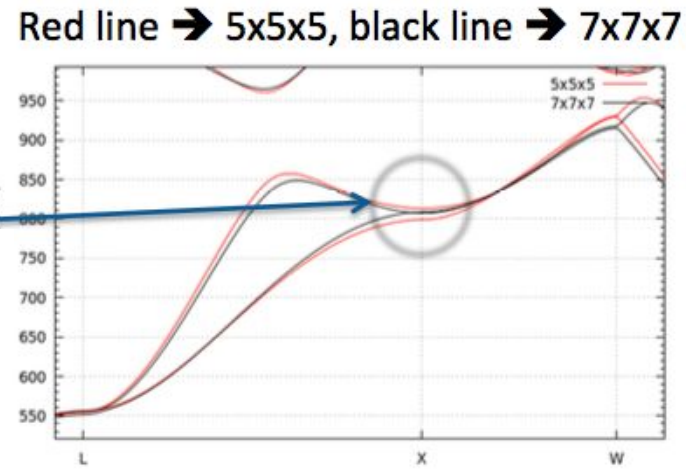


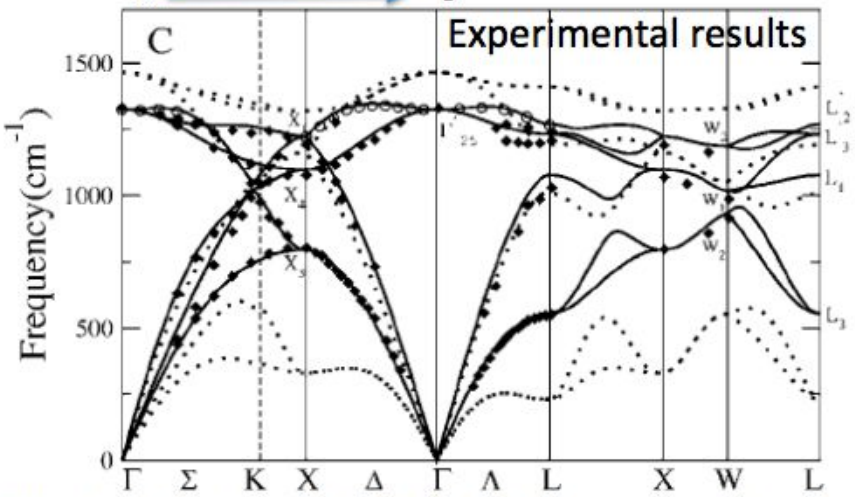


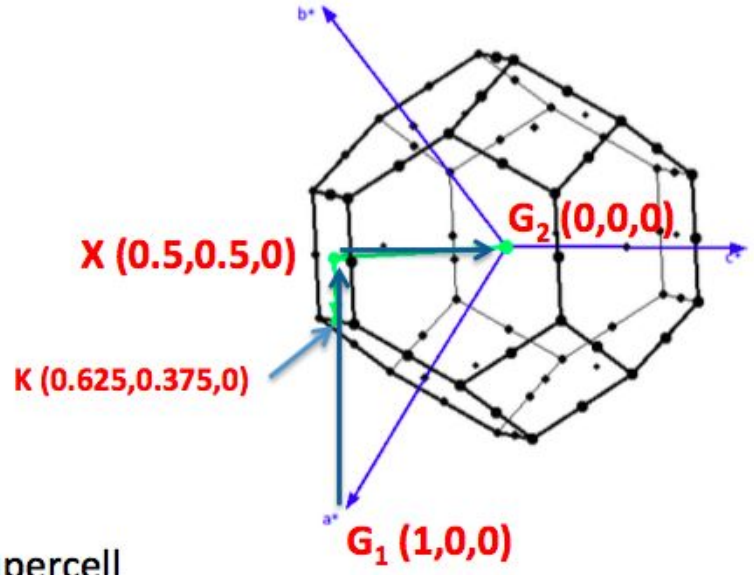
Phys. Chem. Chem. Phys., 2007, **9**, 1276–1291 | 1277

Phonon dispersion of diamond





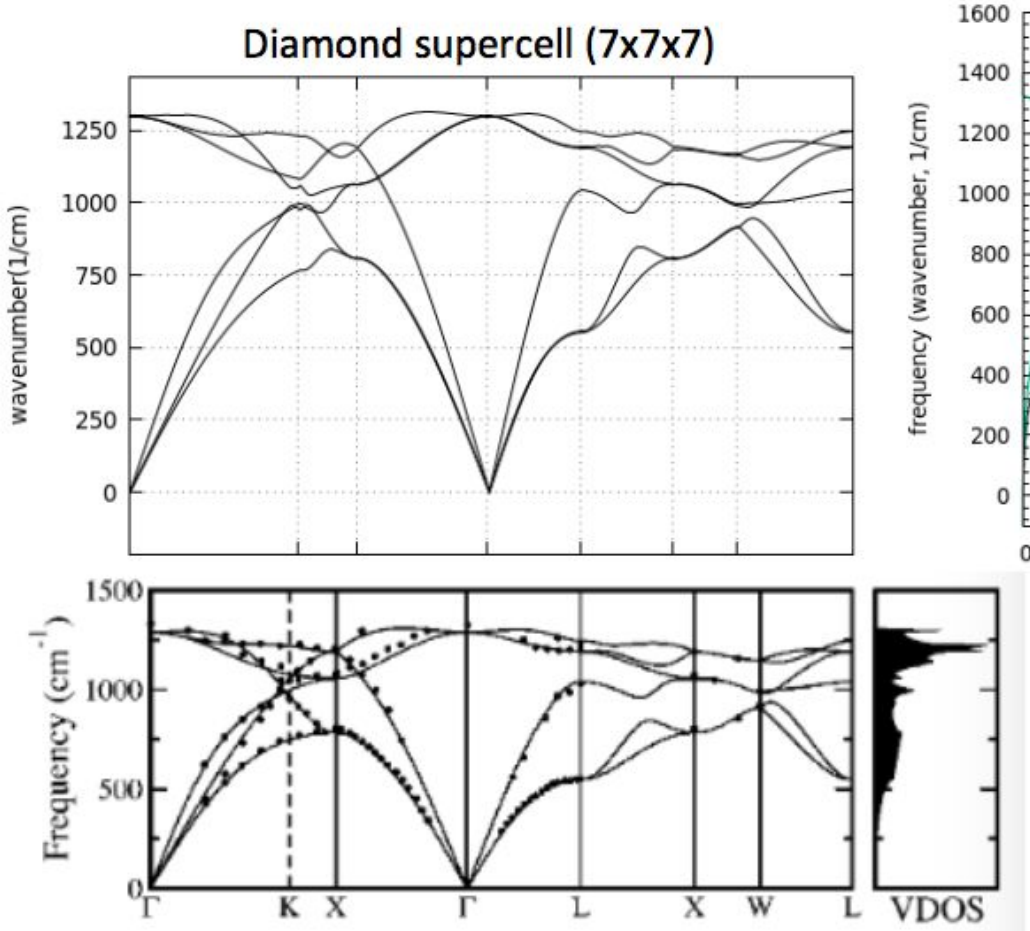


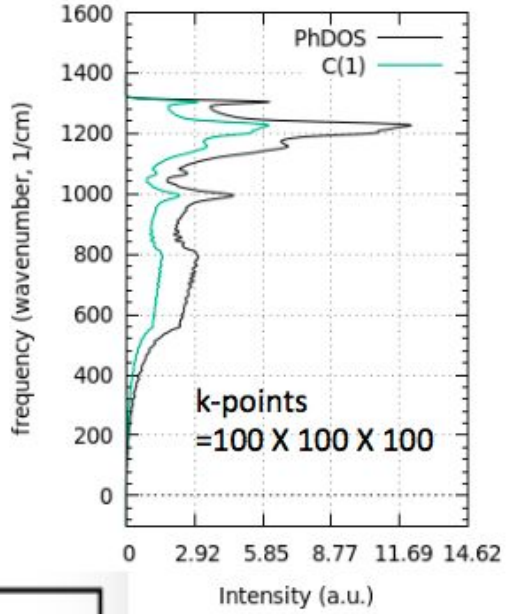


Physical Review B **71**, 205214 (2005)
Physical Review B **74**, 054302 (2006)

8x8x8 supercell in real space

Phonon density of states of diamond

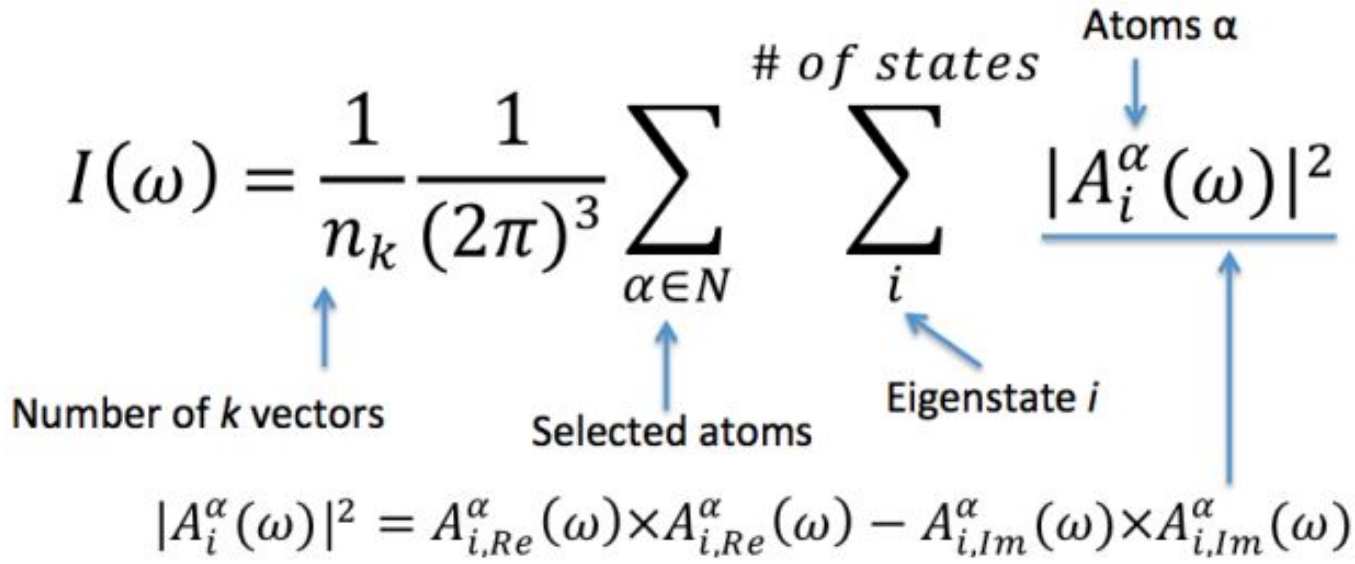




8x8x8 supercell in real space

FIG. 3. GGA *ab initio* phonon dispersions (solid lines) and vibrational density of states (VDOS) for diamond. Experimental neutron scattering data from Ref. 9 are shown for comparison (circles).

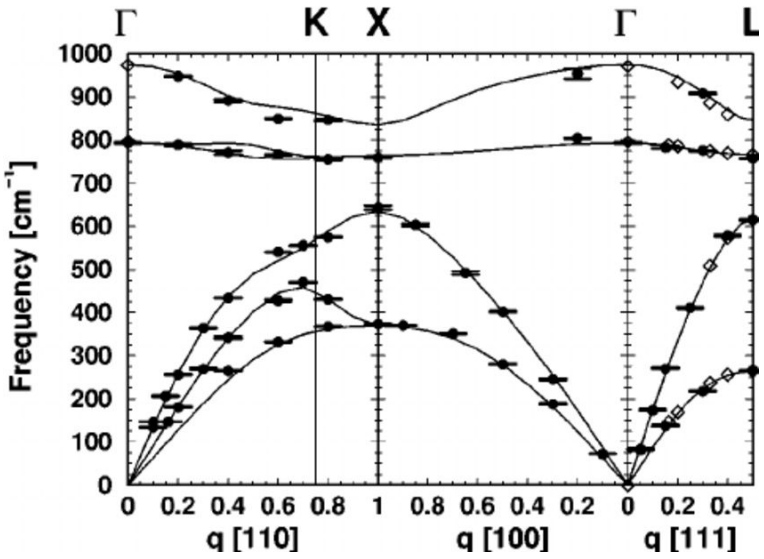
Phonon density of states



where A(ω) is the eigen-vector of atoms at a freqency ω.

The phonon density of states are broadened by Gaussian function (default FWHM = 10 cm^{-1})

LO-TO splitting for polar system



SiC phonon dispersion

Force-constants

$$ {}^{T}K_{I\alpha J\beta} = {}^{an}K_{I\alpha J\beta} + {}^{na}K_{I\alpha J\beta} $$

short-range interaction (analytic part)

long-range interaction (non-analytic part)

where I and J are atomic index and α and ß are the direction of displacement.

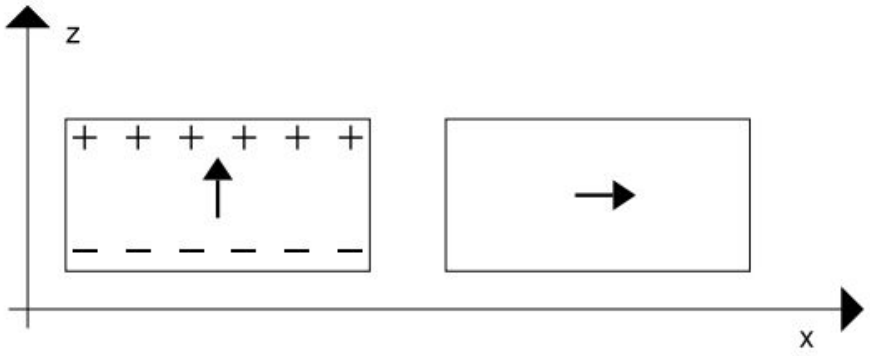


Figure 1. Electrical macroscopic polarization **P** in a slab normal to z, for a vanishing external field $\mathbf{E}^{(\mathrm{ext})}$. Left: when **P** is normal to the slab, a depolarizing field $\mathbf{E} = -4\pi\mathbf{P}$ is present inside the slab, and surface charges form, with areal density $\sigma_{\mathrm{surface}} = \mathbf{P} \cdot \mathbf{n}$. Right: when **P** is parallel to the slab, no depolarizing field and no surface charge is present.

J. Phys.: Condens. Matter **22** (2010) 123201

There is an extra polarization effect for the longitudinal optical phonon due to the long-range nature of the Coulomb interaction. This polarization effect results in an additional restoring force between the ions, yielding a higher longitudinal phonon frequency compared to the transverse optical phonon.

Analytic part and non-analytic part of force-constants

$$ {}^{T}K_{I\alpha J\beta} = {}^{an}K_{I\alpha J\beta} + {}^{na}K_{I\alpha J\beta} $$

analytic part

non-analytic part

where I and J are atomic index and α and ß are the direction of displacement.

BASIC LATTICE DYNAMICS OF POLAR SOLIDS

As phonons represent waves of collective atomic vibrations in a periodic pattern, we can choose to model a system by a repeated parallelepiped, i.e., a supercell. To formulate atomic vibrations within such a supercell, it is convenient to start from equations of motion for the atoms. For a polar solid, the forces can be divided into two additive contributions—analytic and nonanalytic.[20] The terms analytic and nonanalytic can be traced back to the mathematical definition[41] that a function is called analytic if and only if its Taylor series expansion about a reference point converges to the function at each point in some neighbourhood of the reference point, otherwise it is nonanalytic. Under the framework of first-principles calculations, the analytic contribution accounts for all the forces under the restricted periodic boundary conditions under which the averaged electric field is assumed to be zero. The nonanalytic contribution accounts the additional forces owing to a nonzero-averaged electric field.

Y. Wang et. al, *Comptational Material* **2**, 16006 (2016).

The general quadratic expression of energy

energy

displacement

dipole moment

electric field

$$T(u, \boldsymbol{E}) = \frac{1}{2} m\omega^2 u^2 - \frac{1}{4\pi}\frac{1}{2}\epsilon_\infty \int \boldsymbol{E}^2 dV - \boldsymbol{M}\cdot\boldsymbol{E} \qquad (1)$$

potential energy

electrostatic energy inside a dielectric medium

dipole-dipole interaction

$$T(u, \boldsymbol{E}) = \frac{1}{2} m\omega^2 u^2 - \frac{\Omega}{8\pi}\epsilon_\infty \boldsymbol{E}^2 - \boldsymbol{M}\cdot\boldsymbol{E} \qquad (2)$$

Born effective charge tensor

$$\vec{M} = ueZ \qquad (3)$$

$$\boldsymbol{F} \equiv -\frac{\partial T(u, \boldsymbol{E})}{\partial u} = -m\omega^2 u + eZ\cdot\boldsymbol{E} \qquad (4)$$

$$\boldsymbol{D} \equiv -\frac{4\pi}{\Omega}\frac{\partial T(\boldsymbol{u}, \boldsymbol{E})}{\partial \boldsymbol{E}} = \frac{4\pi}{\Omega}\boldsymbol{u}eZ + \epsilon_\infty \boldsymbol{E} \qquad (5)$$

Rev. Mod. Phys., Vol. 73, No. 2, April 2001

Associated with electric polatization, there will be a macroscopic electric field E and an electric displacement D, related by equation (6).

electric polarization

$$\boldsymbol{D} = \boldsymbol{E} + 4\pi\boldsymbol{P} \qquad (6)$$

electrical induction / electric displacement

electric field

$$\boldsymbol{D} - \boldsymbol{E} = 4\pi\boldsymbol{P} \qquad (7)$$

$$\boldsymbol{P} = \frac{\boldsymbol{D} - \boldsymbol{E}}{4\pi} \qquad (8)$$

In the absence of free external charges, the Maxwell equations give

$$\nabla \cdot \boldsymbol{D} = 0 \qquad (9)$$

$$\nabla \times \boldsymbol{E} = 0 \qquad (10)$$

$$\nabla \cdot \boldsymbol{D} = 0$$

$$\nabla \cdot \boldsymbol{D}_0 e^{i\vec{q}\cdot\vec{r}} = 0 \qquad (11)$$

$$i\vec{q} \cdot \boldsymbol{D}_0 e^{i\vec{q}\cdot\vec{r}} = 0 \qquad (12)$$

$$\boldsymbol{D} = 0$$

or

D, E, and P ⊥ q vector

In a longitudinal optical mode, the electric polarization P is parallel to q vector.

D_{LO} must vanish.

$$\boldsymbol{D} = 0 = \boldsymbol{E}_{LO} + 4\pi\boldsymbol{P} \qquad (13)$$

$$\boldsymbol{P} = -\frac{\boldsymbol{E}_{LO}}{4\pi} \qquad (14)$$

In the absence of free external charges, the Maxwell equations give

$$\nabla \cdot \boldsymbol{D} = 0 \qquad (15)$$

$$\nabla \times \boldsymbol{E} = 0 \qquad (16)$$

$$\nabla \times \boldsymbol{E} = \begin{vmatrix} i & j & k \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ E_x e^{i\vec{q}\cdot x} & E_x e^{i\vec{q}\cdot y} & E_x e^{i\vec{q}\cdot z} \end{vmatrix} = 0 \qquad (17)$$

$$\vec{q} \times \boldsymbol{E} = 0 \qquad (18)$$

↓

$$E_{TO} = 0 \qquad (19)$$

or

D, E, and P ∥ q vector

In a transverse optical mode, the electric polarization P is perpendicular to q vector.

E_{TO} must vanish.

Combined with eq. (5) and (8), we get eq. (20).

$$\boldsymbol{D} \equiv -\frac{4\pi}{\Omega}\frac{\partial T(\boldsymbol{u},\boldsymbol{E})}{\partial \boldsymbol{E}} = \frac{4\pi}{\Omega}\boldsymbol{u}eZ + \epsilon_\infty \boldsymbol{E} \qquad (5)$$

$$\boldsymbol{P} = \frac{\boldsymbol{D}-\boldsymbol{E}}{4\pi} \qquad (8)$$

$$\boldsymbol{P} = \frac{\boldsymbol{D}}{4\pi} - \frac{\boldsymbol{E}}{4\pi} = \frac{\boldsymbol{u}eZ}{\Omega} + \frac{\epsilon_\infty \boldsymbol{E}_{LO}}{4\pi} - \frac{\boldsymbol{E}_{LO}}{4\pi} \qquad (20)$$

After substituting eq. (14) into eq. (21), we can obtain eq. (22).

$$\boldsymbol{P} = \frac{ueZ}{\Omega} + \frac{\epsilon_\infty \boldsymbol{E}_{LO}}{4\pi} - \frac{\boldsymbol{E}_{LO}}{4\pi} \tag{21}$$

$$\boldsymbol{P} = -\frac{\boldsymbol{E}_{LO}}{4\pi} = \frac{ueZ}{\Omega} + \frac{\epsilon_\infty \boldsymbol{E}_{LO}}{4\pi} - \frac{\boldsymbol{E}_{LO}}{4\pi}$$

$$0 = \frac{ueZ}{\Omega} + \frac{\epsilon_\infty \boldsymbol{E}_{LO}}{4\pi}$$

$$\boldsymbol{E}_{LO} = -\frac{4\pi}{\Omega}\frac{ueZ}{\epsilon_\infty}$$

$$\boldsymbol{E}_{LO} \cdot \hat{q} = -\frac{4\pi}{\Omega}\frac{u_J e \sum_\nu Z_J^{\nu\beta} \cdot \hat{q}_\nu}{\epsilon_\infty} \tag{22}$$

Force-constants

$$\frac{\partial T(u,\boldsymbol{E})}{\partial u_I \partial u_J} = \frac{\partial^2 \left(\frac{1}{2} m\omega^2 u^2 - \frac{\Omega}{8\pi}\epsilon_\infty \boldsymbol{E}^2 - \boldsymbol{M}\cdot\boldsymbol{E}\right)}{\partial u_I \partial u_J} \tag{23}$$

$$^{T}K_{I\alpha J\beta} = \frac{\partial T(u,\boldsymbol{E})}{\partial u_I \partial u_J} = \quad ^{an}K_{I\alpha J\beta} + \quad ^{na}K_{I\alpha J\beta} \tag{24}$$

$$^{an}K_{I\alpha J\beta} = \frac{\partial^2 \left(\frac{1}{2} m\omega^2 u^2\right)}{\partial u_I \partial u_J} \tag{25}$$

analytic part of force constants

$$ {}^{na}K_{I\alpha J\beta} = \frac{\partial^2\left(-\frac{\Omega}{8\pi}\epsilon_\infty \boldsymbol{E}^2 - \boldsymbol{M}\cdot\boldsymbol{E}\right)}{\partial u_I \partial u_J} \tag{26} $$

$$ {}^{na}K_{I\alpha J\beta} = \frac{\partial^2(-\boldsymbol{M}\cdot\boldsymbol{E})}{\partial u_I \partial u_J} \tag{27} $$

$$ {}^{na}K_{I\alpha J\beta} = \frac{\partial^2\left((-u_I e\sum_\gamma Z_I^{\gamma\alpha})\cdot(-\frac{4\pi}{\Omega}\frac{u_J e\sum_\nu Z_J^{\nu\beta}}{\epsilon_\infty})\right)}{\partial u_I \partial u_J} \tag{28} $$

$$ {}^{na}K_{I\alpha J\beta} = \frac{4\pi}{\Omega}\frac{e^2(\sum_\gamma Z_I^{\gamma\alpha}\cdot\hat{q}_\gamma)\cdot(\sum_\nu Z_J^{\nu\beta}\cdot\hat{q}_\nu)}{\sum_\gamma\sum_\nu \hat{q}_\gamma\cdot\epsilon_\infty\cdot\hat{q}_\nu} \tag{29} $$

Born effective charge

Since the Born effective charge $Z^*_{\alpha\beta}$ is defined by a tensor:

$$Z^*_{\alpha\beta} = \frac{V_c}{|e|}\frac{\Delta P_\alpha}{\Delta u_\beta}$$

where V_c is the volume of the unit cell, e the elementary charge, Δu_β displacement along β-coordinate, ΔP_α the change of macroscopic polarization along α-coordinate, therefore we will perform the above procedures (1) and (2) at least two or three times by varying the x, y, or z-coordinate of Na atom. Then, for example, we have along x-coordinates

```
Px = 94.39497736 (Debye/unit cell) at x= -0.05 (Ang)
Px = 94.64718658 (Debye/unit cell) at x=  0.0  (Ang)
Px = 94.89939513 (Debye/unit cell) at x=  0.05 (Ang)
```

Thus,

$$\begin{aligned} Z^*_{xx} &= \frac{(94.89939513 - 94.39497736)/(2.54174776)}{0.1/0.529177} \\ &= 1.050 \end{aligned}$$

Codes:

polB.f
read_scfout.f
read_scfout.h

Data from OpenMX 3.8 manual

Born effective charge tensors

$$Z^*_{\alpha\beta} = \frac{V_c}{|e|}\frac{\Delta P_\alpha}{\Delta u_\beta}$$

Acoustic sum rule:

$$\sum_k Z^*_{k,\alpha\beta} = 0$$

For example: SiC (primitive cell)

1. Setup input file and commands
2. Do the displacement from the 1st atom to last atom
3. Calculate total energy (and print ***sic.scfout*** file)
4. CALL polB() to calculate electric polarization (P_{ij})
5. Save P_{ij} and come back to step 2 (***until iteration = 12***)
6. Calculate Born effective charge tensors at each atom
7. Apply acoustic sum rule and write ***sic.bec*** and sic.***bect*** files.

Table 1. Each element of Born effective charge tensor of SiC are listed.

Si_{ij}	x	y	z
x	2.693	0.000	0.000
y	0.000	2.693	0.000
z	0.000	0.000	2.693

Born effective charge of SiC : ***2.697*** from Raman scattering data.

C. Z. Wang, R. Yu, H. Krakauer, *Phys. Rev. B*, vol. 53, number 9, 5430-5437 (1996).

Keywords for Born effective charge tensors

MD.Type BEC

When MD.Type is specified to be BEC, the atomic Born effective charge tensors will be calculated. In BEC calculation, the number of steps are number of atoms within primitive cell times 6. For example, in the Silicon Carbide case, there are 2 atoms within primitive cell, total number of steps for displacements are 12 steps (i.e. 2 atoms X 6 steps/atom).

PolB.fileout

If you want to calculate macroscopic electric polarizations of a bulk system based on the Berry phase formalism and output to files (*.PhDos), then set the keyword 'PolB.fileout' to 'on'.

PolB.ReciVectors.NumGrids

Specify the number of grids to discretize reciprocal a-, b-, and c-vectors. For example,

PolB.ReciVectors.NumGrids 15 15 15 #default = 9 9 9

PolB.Direction

Specify the direction of polarization as reciprocal a-, b-, and c-vectors. For example,

PolB.Direction 1 1 1 #default = 1 1 1

```
MD.Type                  BEC
MD.FC.Displacement       0.05    # default=0.05

PolB.fileout on                  #default = off / 0
PolB.ReciVectors.NumGrids 9 9 9  #default = 9 9 9
PolB.Direction 1 1 1             #default = 1 1 1
```

Plot phonon dispersion - (1)

(1) We can use gcc to compile the '*FCFileReader_161023.c*' to generate an executable file (such as '*FCFileReader*').

gcc FCFileReader_161023.c -o FCFileReader -I /usr/include/x86_64-linux-gnu/sys/ -L /home/ytl/LAPACK/lapack-3.5.0 -llapack -lrefblas -lgfortran -lm

(2) After 'FCFileReader' is created, we can perform this executable file to generate phonon dispersion file (*.PhDis).

./FCFileReader

Then, we have to input some data to perform phonon dispersion, acoustic sum rules, LO-TO splitting, and phonon density of states.

Input name of *.dat file : SiC_7x7x7.dat
Input name of *.fc file : sic_7x7x7.FORCE_SETS
Does it calculate LO-TO splitting? (Yes=0/No=1) 0
Input name of *.bect file : sic.bect
Does it need to apply acoustic sum rules? (Yes=0/No=1) 0
Input name of output file : sic_7x7x7.PhDis
Input a filename of phonon density of states : sic_7x7x7.PhDos

Plot phonon dispersion - (2)

It will generate sic_7x7x7.PhDis (i.e. phonon dispersion data) and sic_7x7x7.PhDos (i.e. phonon density of states data) in the directory.

(3) There is a file 'phondisp_gnu16.c' in the 'FCReader' directory. Compile the file as follows:

gcc phondisp_gnu16.c -lm -o phondisp_gnu16

After the compile is completed correctly, one 'phondisp_gnu16' executable file can be found in the same directory. Then, we run this executable file to generate both files, sic_7x7x7.PhonDispDat1 and sic_7x7x7.GNTPhonDisp, in the directory.

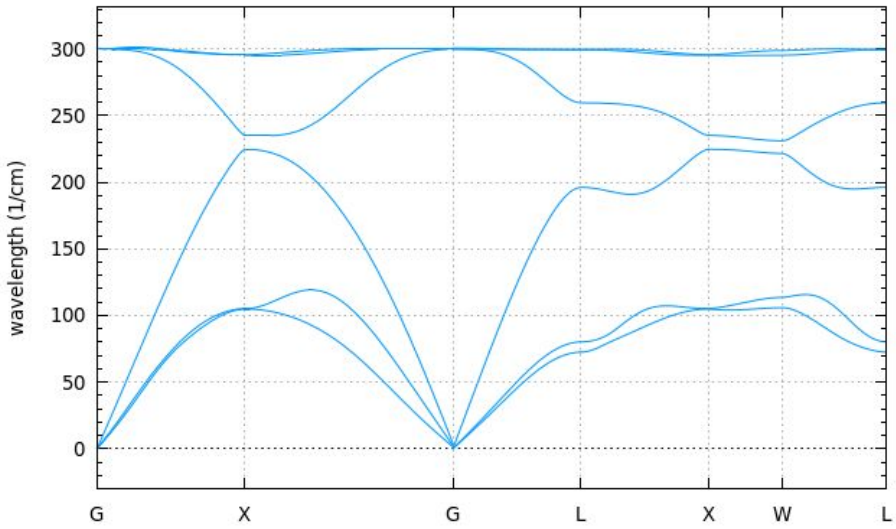
./phondisp_gnu16 sic_7x7x7.PhonDisp

Then, we input a number from 1 to 5 to select the unit we need. For example,

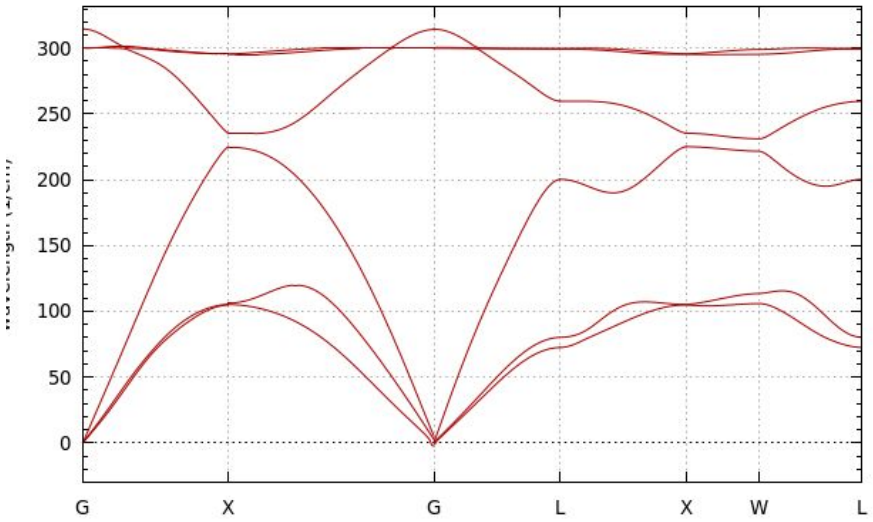
```
ytl@ytl-ubuntu14:~/Code_C_160607/IO$ ./phondisp_gnu16 sic_7x7x7.PhonDisp
Select the unit of frequency? (1) 1/cm, (2) THz, (3) eV, (4) meV, (5) mRyd. 1
sic_7x7x7.GNUPhonDisp is made
ytl@ytl-ubuntu14:~/Code_C_160607/IO$
```

(4) Finally, we use gnuplot to plot phonon dispersion, e.g. sic_7x7x7.GNUPhonDisp. For example, we type in " *gnuplot sic_7x7x7.GNUPhonDisp* ". The result is shown in Figure 3.

Phonon dispersion of GaAs crystal (1)



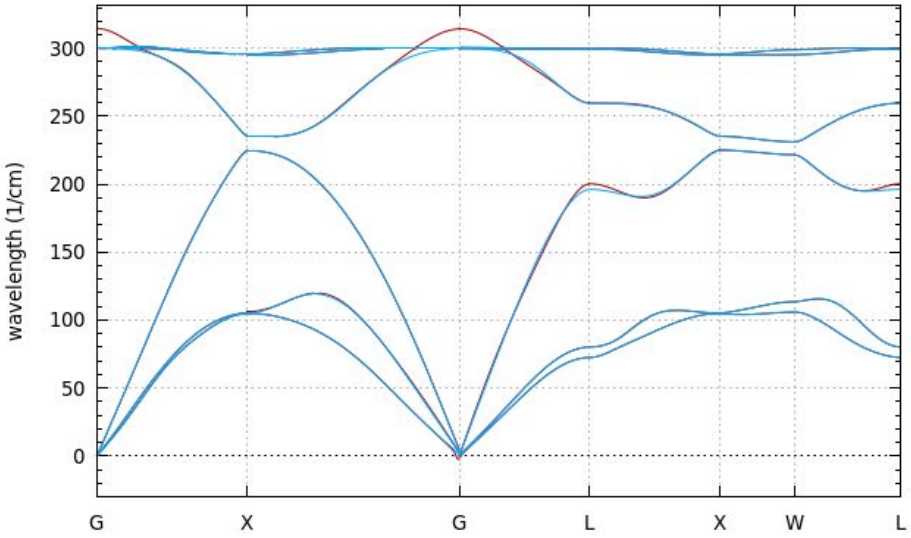
GaAs 4x4x4 phonon dispersion without LO-TO splitting

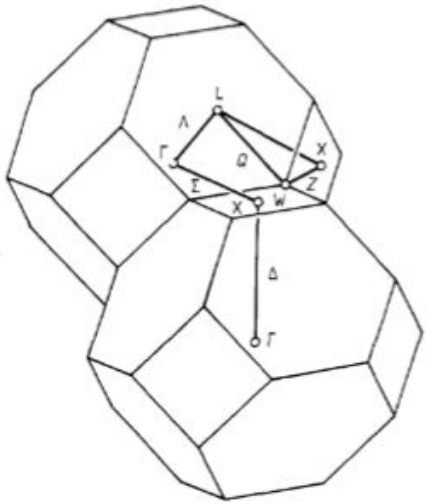


GaAs 4x4x4 phonon dispersion with LO-TO splitting

Phonon calculation

1. number of atoms = 2
2. supercell = 4x4x4
3. LDA
4. DIRECT method

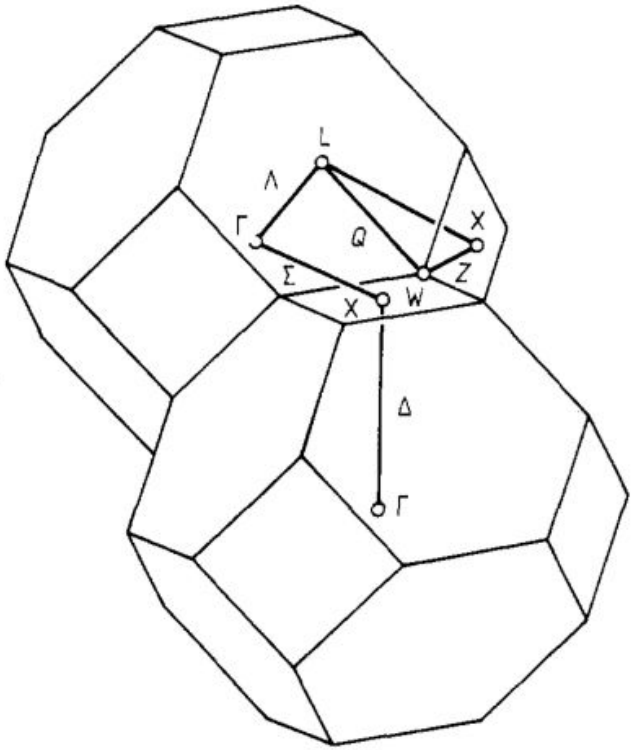


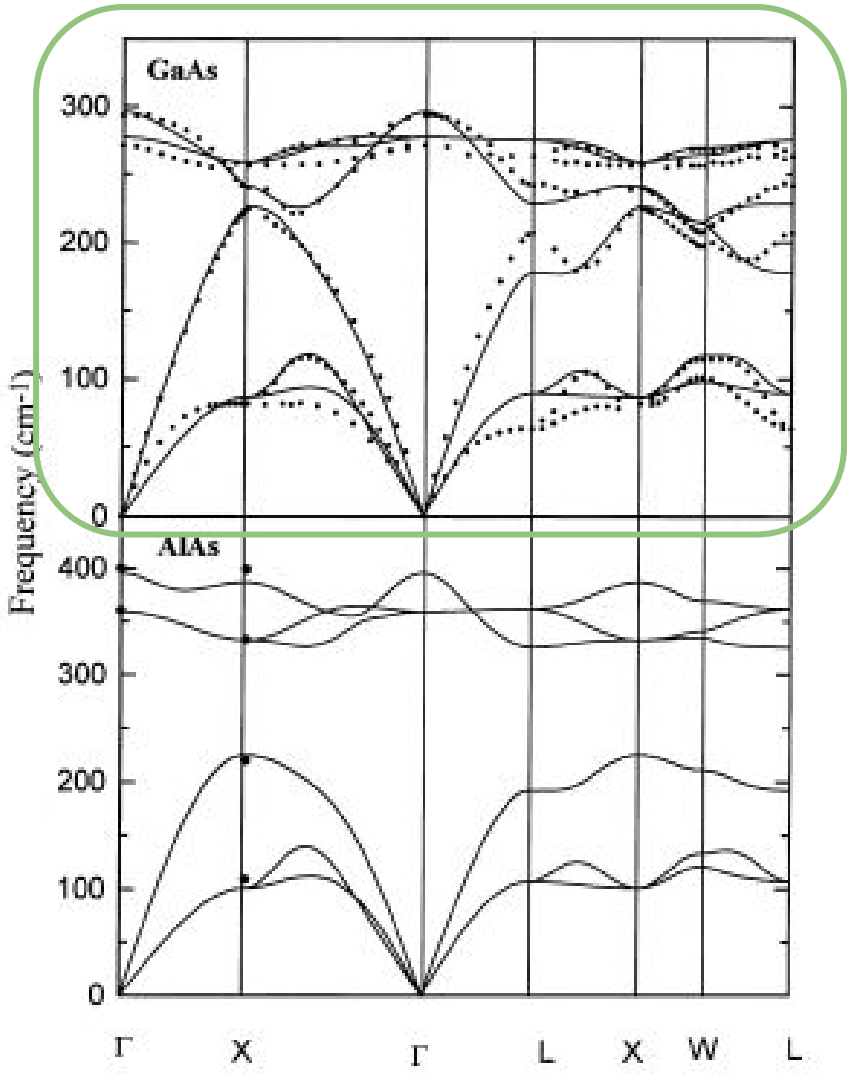


Phonon dispersion of GaAs crystal (2)

CASTEP

1. number of atoms in unit cell = 8.
2. supercell = 2x2x2
3. LDA
4. DIRECT method





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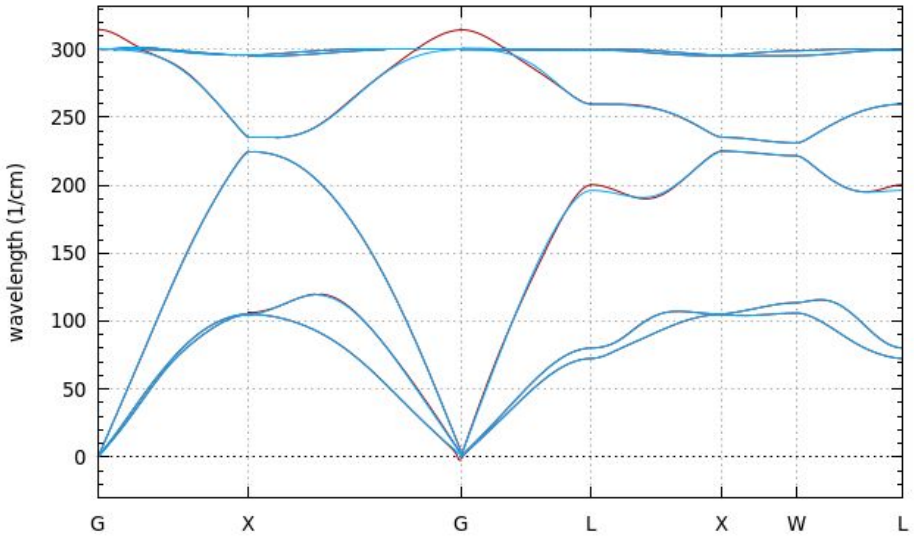
J. Phys.: Condens. Matter **2** (1990) 1457–1474.

Fig. 1. Phonon dispersions calculated for GaAs and AlAs crystals. Experimental data (dottes) are taken from Refs. [2,3].

Phonon dispersion of GaAs crystal (3)



OpenMX

1. number of atoms in unit cell = 2.
2. supercell = 4x4x4
3. LDA
4. DIRECT method

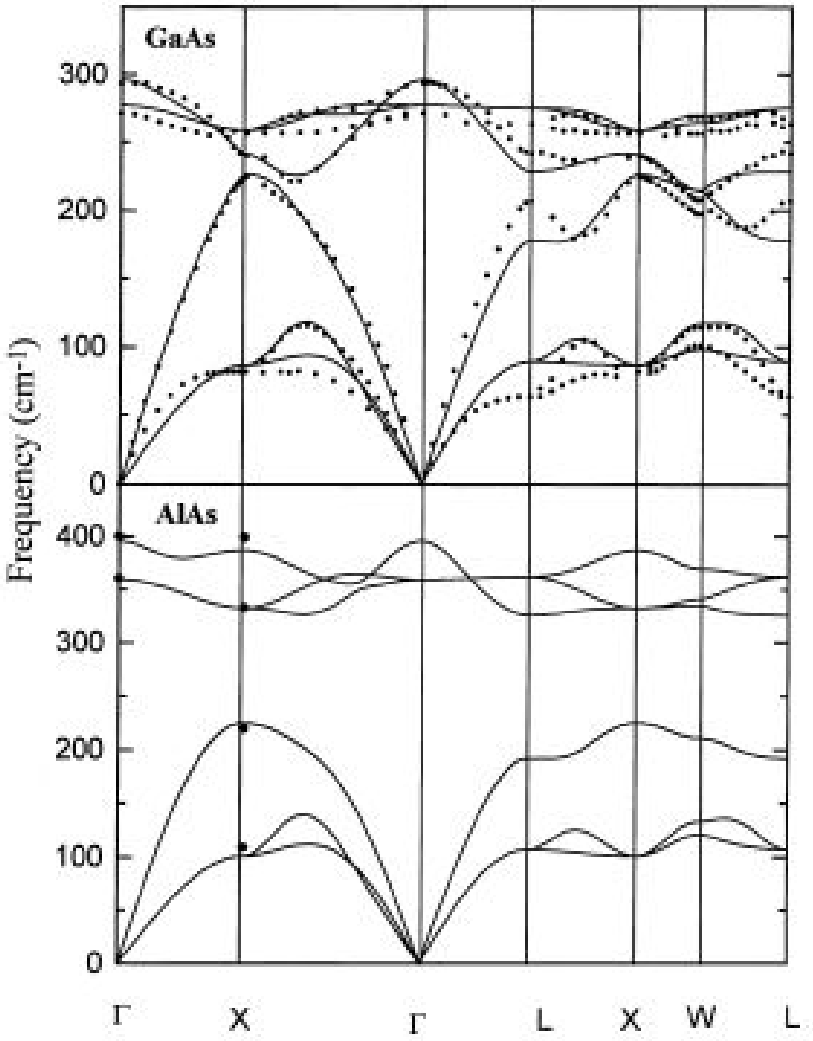


Fig. 1. Phonon dispersions calculated for GaAs and AlAs crystals. Experimental data (dottes) are taken from Refs. [2,3].

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Phonon dispersion of SiC 7x7x7 supercell

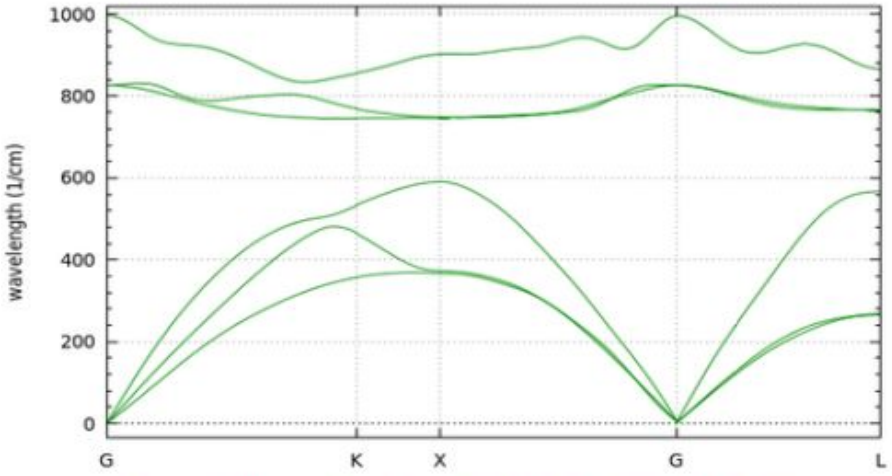


Figure 1. Phonon dispersion of SiC 7x7x7 with LO-TO splitting

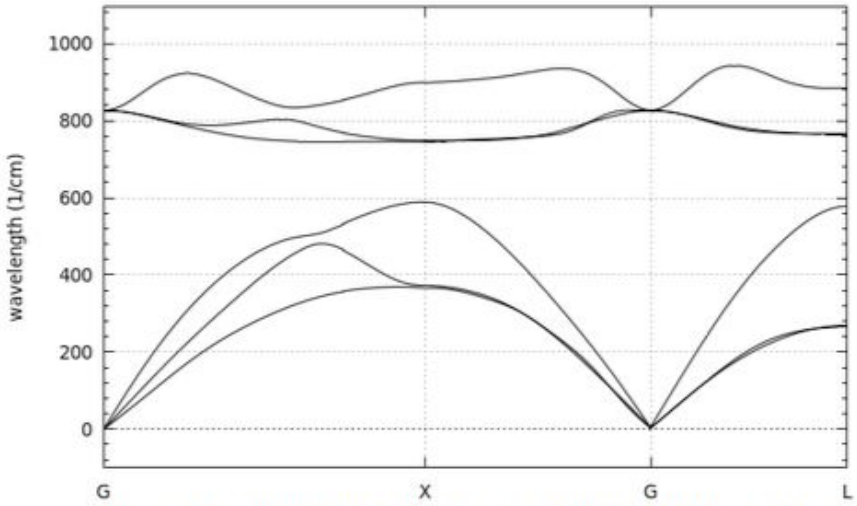


Figure 2. Phonon dispersion of SiC 7x7x7 without LO-TO splitting

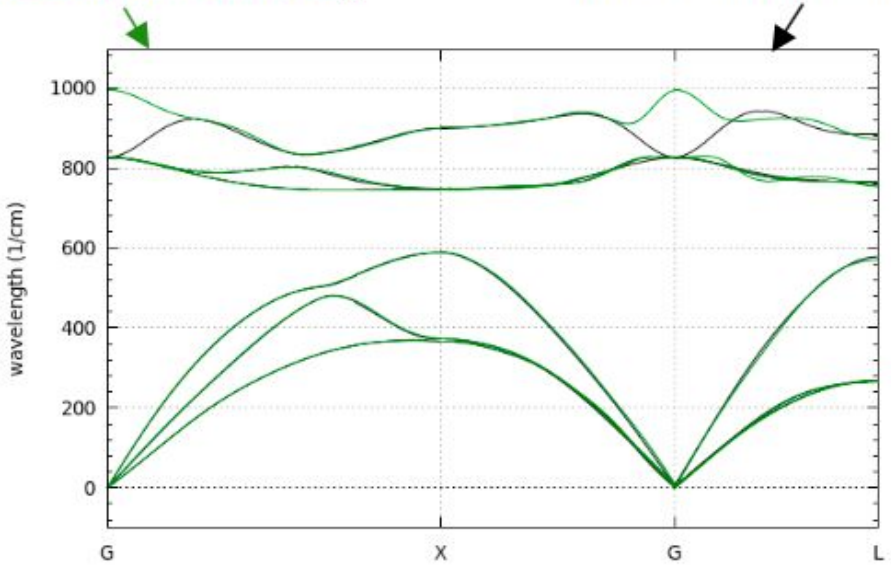
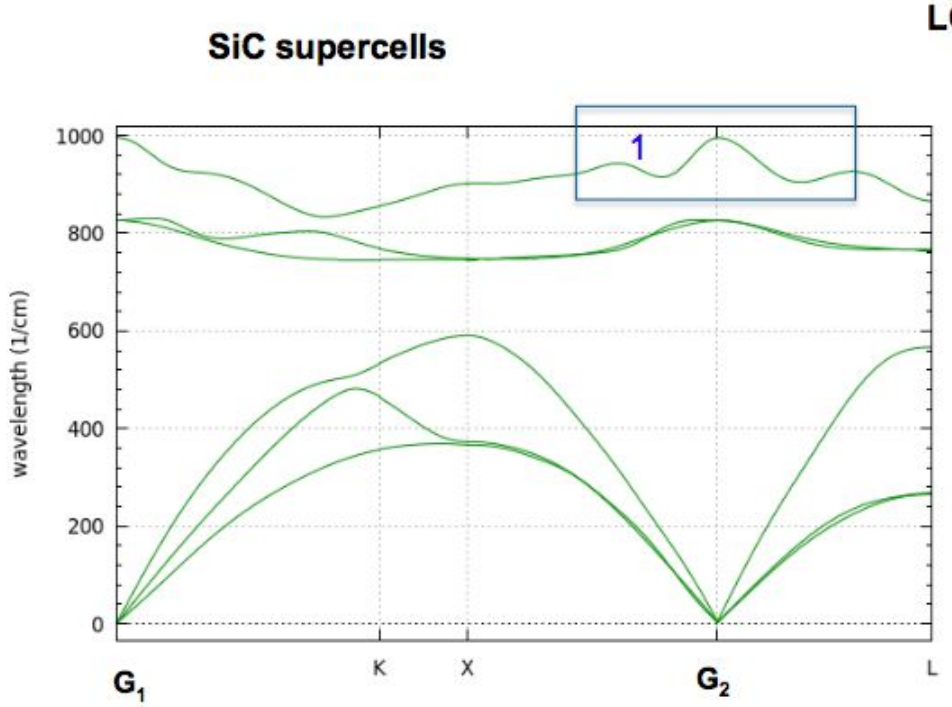
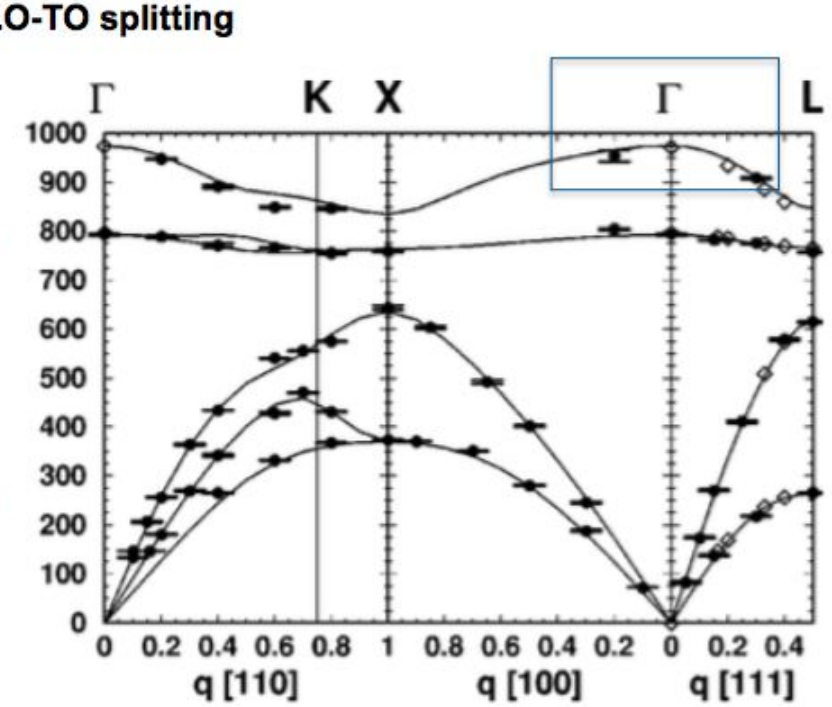
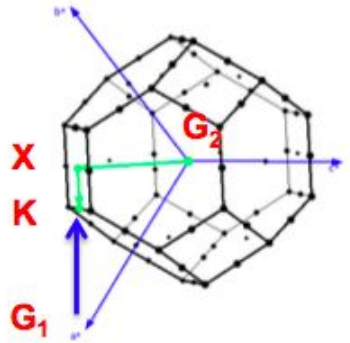


Figure 3. The **green** and **black** lines are the phonon dispersion of SiC 7x7x7 **with LO-TO splitting** and **without LO-TO splitting**, respectively.

Phonon dispersion of SiC 7x7x7 supercell







$$ {}^{na}K_{I\alpha J\beta} = \frac{4\pi}{\Omega} \frac{e^2 (\sum_\gamma Z_I^{\gamma\alpha} \cdot \hat{q}_\gamma) \cdot (\sum_\nu Z_J^{\nu\beta} \cdot \hat{q}_\nu)}{\sum_\gamma \sum_\nu \hat{q}_\gamma \cdot \epsilon_\infty \cdot \hat{q}_\nu} $$

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Keywords for phonon dispersion

The format of input file (*.dat) - (1)

Graphene 9x9x1 supercell

(1) In order to perform the force-constants calculation, we write the keywords in the input file as below:

```
MD.Type                 FC
MD.FC.Displacement      0.05   # default value is 0.05 angstrom
MD.FC.Supercell.grid    9 9 1  # default value is 3 3 3
```

```
Atoms.Number 2
Atoms.SpeciesAndCoordinates.Unit Ang # Ang|AU
<Atoms.SpeciesAndCoordinates # Unit=Ang.
1  C    1.23002520000    0.71014850000    7.50000000000  2.00  2.00
2  C    2.46007480000    1.42031150000    7.50000000000  2.00  2.00
Atoms.SpeciesAndCoordinates>
Atoms.UnitVectors.Unit Ang # Ang|AU
<Atoms.UnitVectors # unit=Ang.
   2.4600000000    0.0000000000    0.0000000000
   1.2300000000    2.1303600000    0.0000000000
   0.0000000000    0.0000000000   15.0000000000
Atoms.UnitVectors>
```

The format of input file (*.dat) - (2)

(2) And, the paths of the first Brillouin zone for constructing phonon dispersion of graphene are required. In this graphene case, we select 3 paths within the first Brillouin zone of graphene primitive cell (i.e. G->M, M->K, M->G). And, the option of applying acoustic sum rules into force-constants is turned on.

```
Phonon.Nkpath   3
<Phonon.kpath
 173  0.000000 0.000000 0.000000   0.000000 0.500000 0.000000  G M
 100  0.000000 0.500000 0.000000   0.333333 0.666666 0.000000  M K
 200  0.333333 0.666666 0.000000   0.000000 0.000000 0.000000  K G
Phonon.kpath>
PhonDisp.sumrule            0
```

(3) If the total phonon density of states and projected phonon density of states are required to calculate, the keywords will be listed as below.

```
PhDos.fileout on                        # switch on to calculate Phonon DOS.
PhDos.FreRange -100.0 1700.0 1.0  # initial Frequency, final frequency, delta frequency
PhDos.Kgrid 20 20 20

ProjectPhDos.Num.Atoms 1
<PhDos.SerialNumber.Atoms
 1
PhDos.SerialNumber.Atoms>
```

The format of input file (*.dat) - (3)

(4) Therefore, we add these keywords into input file and then perform this force-constants calculation. In the end of calculation, the *.FORCE_SETS, *.PhDis (for phonon dispersion), and *.PhDos (for phonon density of states) files will be generated. We use "phondisp_gnu16.c" code to generate a phonon dispersion file (i.e. *.PhonDispDAT1) and a *.GNUPhonDisp file for plot phonon dispersion by GNUPLOT. Then, we type in

*./phondisp_gnu16 *.GNUPLOT*

And the phonon dispersion of graphene is shown in Figure 1.

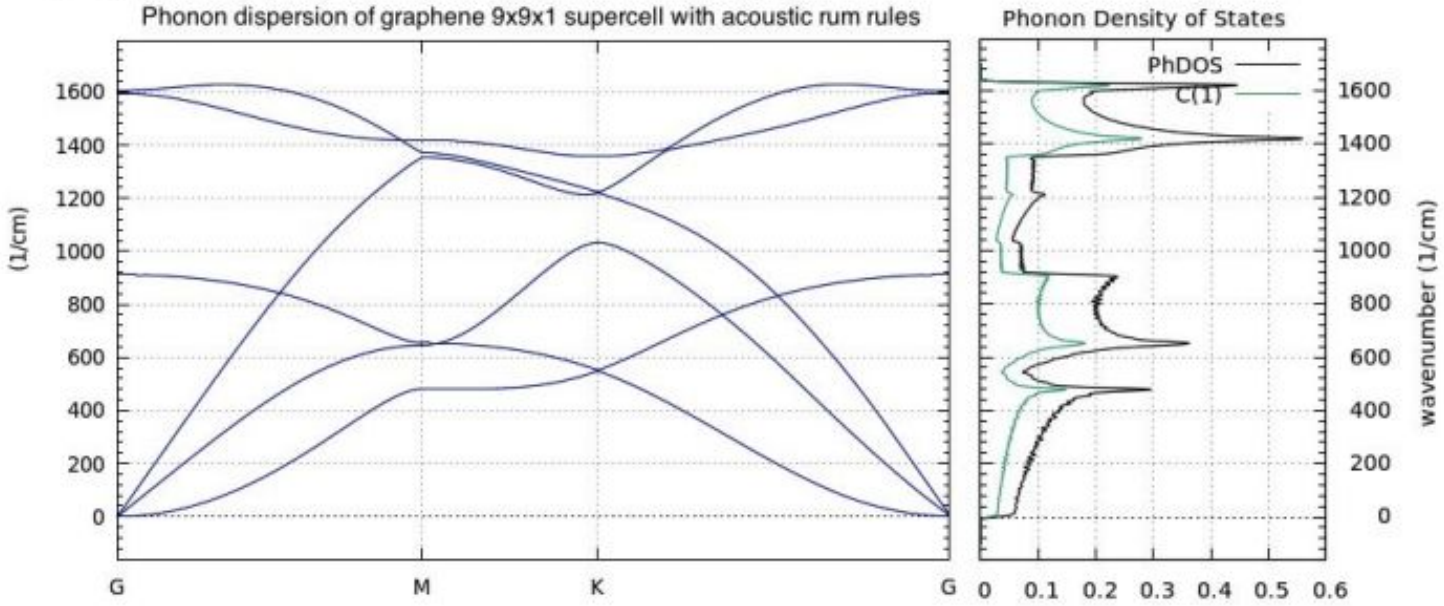


Figure 1. The phonon dispersion of graphene 9x9x1 supercell with acoustic sum rules and corresponding phonon density of states are shown. In phonon density of states, the black line and the green line are total phonon density of states and projected phonon density of states, respectively.

The format of forces (*.FORCE_SETS)

Example : Graphene 9x9x1 supercell

```
ytl@ytl-4309: ~/Code_C/IO
162
2

81
  0.0500000000000000  0.0000000000000000  0.0000000000000000
   -0.0000509455   0.0000593526  -0.0000000000
   -0.0000372433  -0.0000215178   0.0000000000
    0.0001921197   0.0002289062   0.0000000000
   -0.0002160127  -0.0000568113   0.0000000000
    0.0000330430  -0.0000397708   0.0000000000
```

# of atoms within a supercell

# of displaced atoms

displacement along a direction (x,y,z)

the first index of displaced atom

atomic forces (x,y,z) with index 1

atomic forces (x,y,z) with index 2

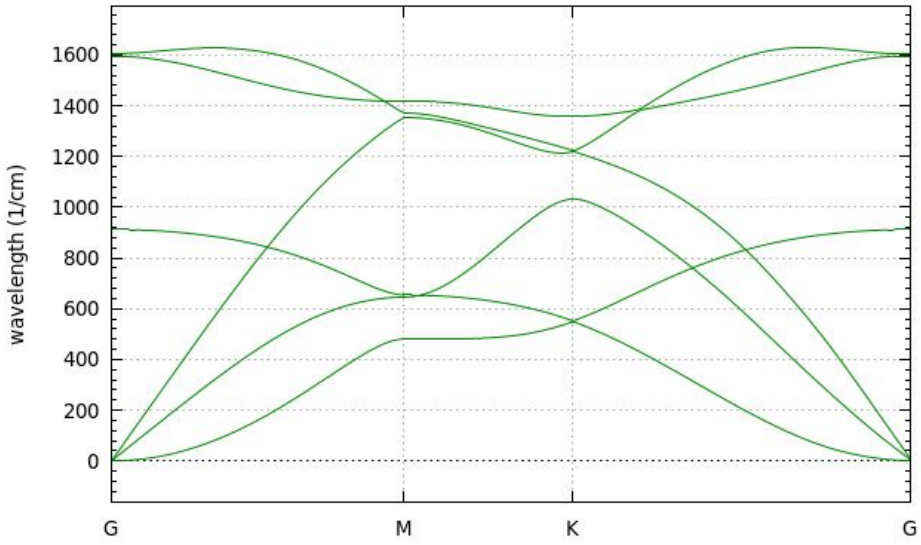
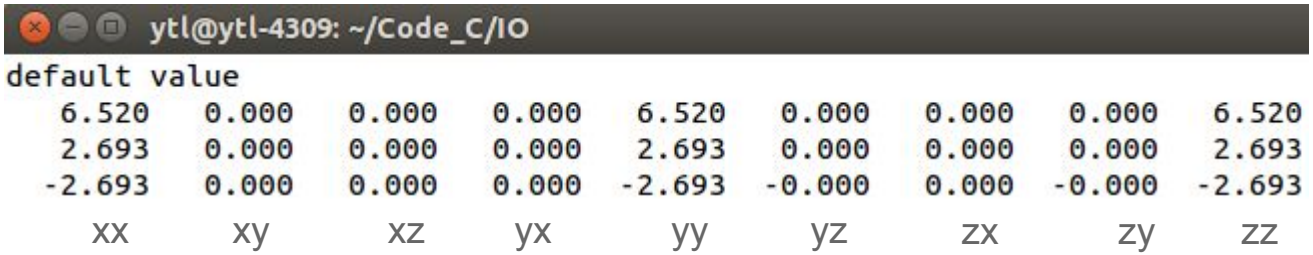


Fig 1. The phonon dispersion of graphene 9x9x1 supercell

Dielectric constant and Born effective charge tensors

Example : SiC crystal (File : sic.bect)



dielectric constant from Experiment.

BEC tensor of Si atom

BEC tensor of C atom

Experimental value of Si atom is 2.697.

C. Z. Wang, R. Yu, H. Krakauer, *Phys. Rev. B*, vol. 53, number 9, 5430-5437 (1996).

Implementation of phonon dispersion

Dynamical matrix

```
for (i=0;i<noa3;i++){
  for (j=0;j<noa3;j++){
    double sumbre=0.0,sumbim=0.0;
    for (o=0;o<fl;o++){ // unit cell R'
      double uv[3][3],rlvt[3][3],pf;
      for (ii=0;ii<3;ii++)
        for (jj=0;jj<3;jj++){
          uv[ii][jj]=unitvectors_ori[o][ii][jj]-unitvectors_ori[aa2][ii][jj]; // R(p)-R(0)
          rlvt[jj][ii]=q[t][jj]*rlv[jj][ii]; // q[3] * reciprocal lattice vectors[3][3] = rlvt
        }

      pf=two_lattices_product(uv[0],uv[1],uv[2],rlvt[0],rlvt[1],rlvt[2]); // rlvt dot R(p)-R(0)
      sumbre+=fcmatrix[i][o*noa3+j]*cos(pf);
      sumbim+=fcmatrix[i][o*noa3+j]*sin(pf);
    }

    double sqrt_mimj=sqrt(atomic_mass[i/3]*atomic_mass[j/3]); // calculate 1/sqrt(mi*mj)
    Dre[i][j]=sumbre/sqrt_mimj;
    Dim[i][j]=sumbim/sqrt_mimj; // D[q][ix3][jx3]
  }
}
```

$$\widetilde{D}_{I\alpha J\beta}(\vec{q}) = \frac{1}{\sqrt{m_I m_J}} \sum_{\vec{R},\vec{R}'} K_{I\alpha J\beta}\left(\vec{R}' - \vec{R}\right) e^{i\vec{q}\cdot(\vec{R}'-\vec{R})}$$

Mass of J-th atom

LO-TO splitting - (1)

```
if (isLOTOSplitting==0){
  // ### Non-analytic term of force constant for polar crystals ###

  // ### if q is very close to 0, non-analytic term can not be calculated ###
   // if ( |qx|+|qy|+|qz| ) is smaller than 0.000001
  if (fabs(q[t][0])+fabs(q[t][1])+fabs(q[t][2])<=0.000001){
    q[t][0]=0.0000001;
    q[t][1]=0.0000001;
    q[t][2]=0.0000001;
  }

  // q vector
  double qv[3];  // define unit vector q
  // transform q[3] to Cartesian coordinates (x,y,z).
  // It's axis will be the same as axis of Born effective charge tensor[3][3].
  // i.e. ( q x reciprocal lattice constants ).
  qv[0]=q[t][0]*rlv[0][0]+q[t][1]*rlv[0][1]+q[t][2]*rlv[0][2];
  qv[1]=q[t][0]*rlv[1][0]+q[t][1]*rlv[1][1]+q[t][2]*rlv[1][2];
  qv[2]=q[t][0]*rlv[2][0]+q[t][1]*rlv[2][1]+q[t][2]*rlv[2][2];

  // calculate qv[1][3] X dielectric constant tensor [3][3] X qv [3][1]
  double qvxdixqv=qv[0]*(di[0][0]*qv[0]+di[0][1]*qv[1]+di[0][2]*qv[2])
                 +qv[1]*(di[1][0]*qv[0]+di[1][1]*qv[1]+di[1][2]*qv[2])
                 +qv[2]*(di[2][0]*qv[0]+di[2][1]*qv[1]+di[2][2]*qv[2]);
  // get volume, define e2, and calculate 4*PI*e2/V
  double V=get_volume(tv[0],tv[1],tv[2]);
  double e2=1.0; // unit of electron
  double pix4xe2dV=PI*4*e2/V;
```

$$ {}^{na}K_{I\alpha J\beta} = \frac{4\pi}{\Omega}\frac{e^2(\sum_\gamma Z_I^{\gamma\alpha}\cdot\hat{q}_\gamma)\cdot(\sum_\nu Z_I^{\nu\beta}\cdot\hat{q}_\nu)}{\sum_\gamma\sum_\nu \hat{q}_\gamma\cdot\epsilon_\infty\cdot\hat{q}_\nu} $$

LO-TO splitting - (2)

```
// ### start to calculate non-analytic term of force constants ###
int atomi,atomi_dir,atomj,atomj_dir;
for (i=0;i<noa3;i++){
  atomi=i/3; // index of atom i
  atomi_dir=i%3;
  // index of alpha direction of Born effective charge at atom i
  // i.e. 0=x, 1=y, 2=z

  // first Z dot q
  double zq1=bect[atomi][atomi_dir][0]*qv[0]
           +bect[atomi][atomi_dir][1]*qv[1]
           +bect[atomi][atomi_dir][2]*qv[2];

  // calculate q*Za x (4PI/V) / (q x dielectic constant x q)
  double t1=zq1*(pix4xe2dV/qvxdixqv);

  for (atomj=0;atomj<number_of_atoms;atomj++){ // atomj = index of atom j
    for (atomj_dir=0;atomj_dir<3;atomj_dir++){
      // index of beta direction of Born effective charge at atom j,
      // i.e. 0=x, 1=y, 2=z

      // second Z dot q
      double zq2=all_bect[atomj][atomj_dir][0]*qv[0]
               +all_bect[atomj][atomj_dir][1]*qv[1]
               +all_bect[atomj][atomj_dir][2]*qv[2];

      fcmatrix[i][atomj*3+atomj_dir]+=zq2*t1;
      // = fcmatrix[i][j*3+k]+=zq1*zq2*(pix4xe2dV/qvxdixqv);
      // calculate q*Za x Zb*q x (4*PI/V) / (q x dielectic constant x q)
    }
  }
}
```

$$ {}^{na}K_{I\alpha J\beta} = \frac{4\pi}{\Omega}\frac{e^2\left(\sum_\gamma Z_I^{\gamma\alpha}\cdot\hat{q}_\gamma\right)\cdot\left(\sum_\nu Z_I^{\nu\beta}\cdot\hat{q}_\nu\right)}{\sum_\gamma\sum_\nu \hat{q}_\gamma\cdot\epsilon_\infty\cdot\hat{q}_\nu} $$

Acoustic sum rules

```
  // Reference : [1] G. J. Ackland, M. C. Warren, and S. J. Clark, J. Phys. Condens. Matter 9 (1997) 7861-7872.
  // rule : the acoustic sum rule
  for (k=0;k<3;k++)
    for (o=0;o<3;o++)
      for (i=0;i<noa;i++){
        double tmp=0.0;
        for (j=0;j<allatoms;j++) if (j!=primcell_index*noa+i) tmp+=fcmatrix[3*i+k][3*j+o];
        fcmatrix[3*i+k][3*(primcell_index*noa+i)+o]=-tmp;
      }

  // rule : the acoustic sum rule
  for (i=0;i<noa;i++)
    for (k=0;k<3;k++)
      for (m=0;m<3;m++){
        if (k!=m)
          for (j=0;j<allatoms;j++){
            fcmatrix[3*i+k][3*j+m]=0.5*(fcmatrix[3*i+k][3*j+m]+fcmatrix[3*i+m][3*j+k]);
            fcmatrix[3*i+m][3*j+k]=fcmatrix[3*i+k][3*j+m];
          }
      }
}
```

$$\Phi_{i\alpha,i\beta} = -\sum_{j\neq i} \Phi_{i\alpha,j\beta}.$$

$$\Phi_{i\alpha,j\beta} = \Phi_{j\beta,i\alpha}$$