Atomic vibrations with and around SIESTA

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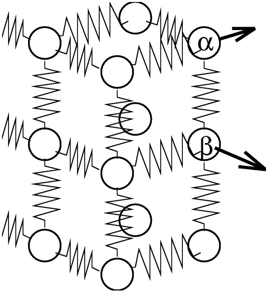
Andrei Postnikov

Outline

1. Basics: Born-Oppenheimer, dynamic equations
2. Essential about DFT in this context
3. Frozen phonon calculations, notably with SIESTA
4. Phonons in dielectric crystals (briefly)
5. Linear response (very briefly)
6. Molecular dynamics as a source of phonon information
7. Conclusions

Lattice dynamics on the Born-Oppenheimer surface

classical movement of atoms
in the electrostatic force field
from core charges
and relaxed electron density
(as an adiabatic process, different
from the Car-Parrinello approach!)



For phonons: treat the crystal
as a system of coupled oscillators,

$$\mathcal{H} = \sum_{\alpha} \frac{M_\alpha}{2} \sum_{i=1}^{3} (\dot{u}_\alpha^i)^2 + \frac{1}{2} \sum_{\alpha\beta} \sum_{i,j}^{3} F_{\alpha\beta}^{ij} u_\alpha^i u_\beta^j$$

Ways to get force constants,

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

1) frozen phonon schemes;
2) response theories.

Lattice dynamics on the Born-Oppenheimer surface

A general case (cluster, molecule, aperiodic crystal) yields $3N$ (N: number of atoms in the system) coupled equations:

$$M_\alpha \ddot{u}^i_\alpha = -\sum_\beta^N \sum_j^3 F^{ij}_{\alpha\beta} u^j_\beta$$

In case of translational invariancy,
Ansatz $\mathbf{u}_\alpha \sim \mathbf{u}_\mathbf{q}\, e^{i(\mathbf{q}\,\mathbf{r}_\alpha - \omega t)}$
and Fourier-transformation of force constants decouple the equation in $\mathbf{q}$,

$$M_s \ddot{u}^i_{s\mathbf{q}} = -\sum_{s'}^n \sum_j^3 F^{ij}_{ss'}(\mathbf{q}) u^j_{s'\mathbf{q}}$$

yielding $3n$ (n: number of atoms per unit cell) coupled equations:

$$\begin{pmatrix} & \vdots & \\ \dfrac{F^{ij}_{ss'}(\mathbf{q})}{\sqrt{M_s M_{s'}}} & - \omega^2 \delta_{ss'} \delta_{ij} & \\ & \vdots & \end{pmatrix} \begin{pmatrix} \vdots \\ u^j_{s'\mathbf{q}} \sqrt{M_{s'}} \\ \vdots \end{pmatrix} = 0$$

$det(...) = 0$ $\Rightarrow$ frequencies ω^2 ; eigenvector/$\sqrt{M}$ $\Rightarrow$ displacement pattern

Units of vibration frequencies

The vibration equations we want to solve have a form like

$$M\,\omega^2\,u = \left(\frac{\partial^2 E}{\partial u\,\partial u}\right) u$$

(omitting indices and possible "symmetrization" of force constant matrix). Therefore, in what regards units, the frequency comes out as

$$[\omega] = \sqrt{\frac{1}{[M]}\,\left[\frac{\partial^2 E}{\partial u\,\partial u}\right]}\,.$$

We'd like to have M in atomic mass units, 1.660599$\cdot 10^{-27}$ kg, energy derivatives – in "conventional" units of a DFT calculation, i.e., E in eV or Ry, and displacements – in Å or Bohr. Assume for the following that the force constants are in eV/Å^2 (otherwise 1 Ry = 13.605692 eV; 1 Bohr = 0.529177 Å). The above "frequency unit", $f.u.$, in the SI:

$$f.u. \quad = \quad \sqrt{\frac{1\,\text{eV/Å}^2}{1\,\text{a.m.u.}}} = \sqrt{\frac{\left(\frac{1.602176487\cdot 10^{-19}\,\text{J}}{10^{-20}\,\text{m}^2}\right)}{1.660599\cdot 10^{-27}\,\text{kg}}} = 9.822517\cdot 10^{13}\,\text{s}^{-1}\,.$$

Units of vibration frequencies: meV $\Leftrightarrow$ THz $\Leftrightarrow$ cm^{-1}

- meV is the measure of energy of a phonon with 1 $f.u.$:

$$\begin{aligned} f.u.{\times}\hbar &= 9.822517{\cdot}10^{13}\,\mathsf{s}^{-1}{\times}1.054572{\cdot}10^{-34}\,\mathsf{J}\cdot\mathsf{s} = 1.035855{\cdot}10^{-20}\,\mathsf{J} \\ &= 64.652976\,\mathsf{meV}\,. \end{aligned}$$

- ν, expressed in THz, is $\omega/(2\pi)$:

$$\frac{f.u.}{2\pi} = 15.6330214\,\mathsf{THz}\,.$$

- Inverse wavelength is found from $h\nu = \frac{hc}{\lambda}\,; \quad \frac{1}{\lambda} = \frac{\omega}{2\pi{\cdot}c}\,.$

$$\frac{f.u.}{2\pi{\cdot}c} = \frac{9.822517{\cdot}10^{13}\,\mathsf{s}^{-1}}{2\pi{\cdot}29979245800\,\mathsf{cm/s}} = 521.461464\,\mathsf{cm}^{-1}\,.$$

Units conversion:

1 THz $= 4.136$ meV $= 33.356$ cm^{-1};
1 meV $= 0.242$ THz $= 8.066$ cm^{-1};
1 cm^{-1} $= 0.030$ THz $= 0.124$ meV .

Density Functional Theory: total energy

The Kohn-Sham equations:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{\mathsf{SCF}}(\mathbf{r})\right]\varphi_i(\mathbf{r}) = \varepsilon_i\,\varphi_i(\mathbf{r})\,;$$

$$V_{\mathsf{SCF}}(\mathbf{r}) = e^2\sum_\alpha \frac{-Z_\alpha}{|\mathbf{r}-\mathbf{R}_\alpha|} + e^2\int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \frac{\delta E_{\mathsf{XC}}}{\delta\rho(\mathbf{r})}\,;$$

$$\rho(\mathbf{r}) = \sum_{\substack{i\\ \text{(occupied)}}} |\varphi_i(\mathbf{r})|^2$$

Total energy:

$$E^{\text{el.}}_{\text{tot}} = \sum_{(i\text{ occupied})}\varepsilon_i - \frac{e^2}{2}\int\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}' - \int V_{\mathsf{XC}}(\mathbf{r})\,\rho(\mathbf{r})\,d\mathbf{r} + E_{\mathsf{XC}}[\rho]\,.$$

Density Functional Theory: forces

For the *exact* wavefunction, $E = \langle\psi|\mathcal{H}|\psi\rangle$, the Hellmann–Feynman theorem yields:

$$E^a \equiv \frac{d}{d\mathbf{R}_a}\langle\psi|\mathcal{H}|\psi\rangle = \langle\psi|\mathcal{H}^a|\psi\rangle\,.$$

If the wavefunction contains parameters p_t dependent on displacement of ions, either implicitly or explicitly, the HF theorem is violated:

$$E^a \equiv \frac{d}{d\mathbf{R}_a}\langle\psi|\mathcal{H}|\psi\rangle = \langle\psi|\mathcal{H}^a|\psi\rangle \; + \sum_t \frac{\partial\langle\psi|\mathcal{H}|\psi\rangle}{\partial p_t}\, p_t^a\,,$$

but it can be restored

if either $\forall\, p_t^a \;=\; 0$ (basis independent on the positions of nuclei),

or $\forall \dfrac{\partial\,\langle\psi|\mathcal{H}|\psi\rangle}{\partial\, p_t} \;=\; 0\,,$ (the basis is complete).

Density Functional Theory: forces

Forces: $$\mathbf{F}_\alpha \equiv -\frac{d\,E_{\mathsf{tot}}}{d\,\mathbf{R}_\alpha} = \mathbf{F}_\alpha^{\mathsf{HF}} + \mathbf{F}_\alpha^{\mathsf{IBS}} + \cdots$$

$\mathbf{F}^{\mathsf{HF}}$: Hellmann–Feynman force,

$\mathbf{F}^{\mathsf{IBS}}$: "Pulay force", accounts for the incompleteness of basis, and/or for the dragging of basis functions with atoms (in tight-binding schemes).

Possibly futher terms, depending on practical realization.

A sufficiently good accuracy of forces is only achievable in "full-potential" schemes, i.e. those not using shape approximations (like e.g. *muffin-tin* approximation) for the potential and charge density.

Practical calculation schemes within DFT

An expansion of the Kohn-Sham functions over (fixed or variable) basis set

$$\varphi_\alpha(\mathbf{r}) = \sum_{p=1}^{Q} C_{\alpha p} \chi_p(\mathbf{r})\,;$$

yields a system of algebraic equations:

$$\sum_p C_{\alpha p} \Big[\underbrace{\int \chi_q^*(\mathbf{r}) \mathcal{H} \chi_p(\mathbf{r}) d\mathbf{r}}_{\mathcal{H}_q p} - \varepsilon_\alpha \underbrace{\int \chi_q^*(\mathbf{r})\, \chi_p(\mathbf{r})\, d\mathbf{r}}_{\mathcal{S}_q p} \Big] = 0$$

$$\rho(\mathbf{r}) = \sum_{\alpha=1}^{N} \varphi_\alpha^*(\mathbf{r})\, \varphi_\alpha(\mathbf{r}) = \sum_{pq} \underbrace{\left[\sum_{\alpha=1}^{N} C_{\alpha q}^*\, C_{\alpha p} \right]}_{\equiv D_{pq},\ \text{density matrix}} \chi_q^*(\mathbf{r})\, \chi_p(\mathbf{r})\,.$$

$\longrightarrow$ a generalized diagonalization problem, to be solved iteratively.

Technical implementations of DFT: planewave basis

- (+) Ultimately complete basis; systematic augmentation of accuracy is controlled by a single parameter (planewave cutoff);
- (+) Easy analytical manipulation, e.g., when calculating matrix elements of different observables, derivatives of the total energy etc.
- (−) Boundary conditions can be only periodic ⇒ in the course of simulating finite fragments "in the box" the spurious interactions across the box boundary are built in, and their suppression may demand for a large box size.
- (−) The number of plane waves necessary to describe fluctuations of all-electron charge density is usually beyond the reasonable computational resources. The use of pseudopotentials is *de facto* obligatory.
- (−) For a given cutoff (i.e., the largest wavevector used in the planewave expansion), the size of basis grows very rapidly with the size of simulation cell, irrespectively on whether it contains extra atoms or not (the user pays for the vacuum).

Technical implementations of DFT: localized basis sets

(+) Since all charge is physically delivered by one-electron functions centered on atoms, the basis size scales linearly with the number of atoms, irrespectively of empty space in the system. Especially important for simulations of open systems.

(+) Boundary conditions can be either periodic or strictly "vacuum-like", with no spurious interaction between repeated fragments.

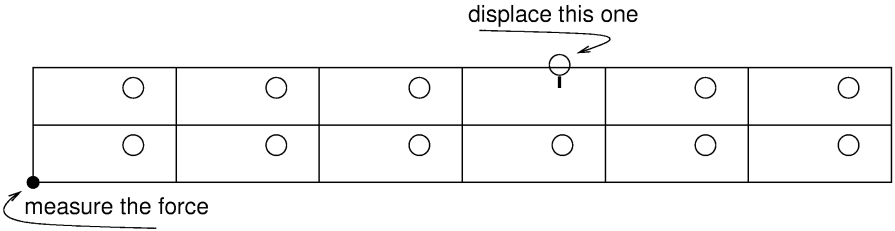
(−) The lack of systematics in gradually enhancing the completeness of basis; additional basis functions are added *ad hoc*, and no asymptotic completeness of the basis is guaranteed.

(−) Difficulties in calculating matrix elements. This is probably the most serious drawback that can be overcome by the following tricks:

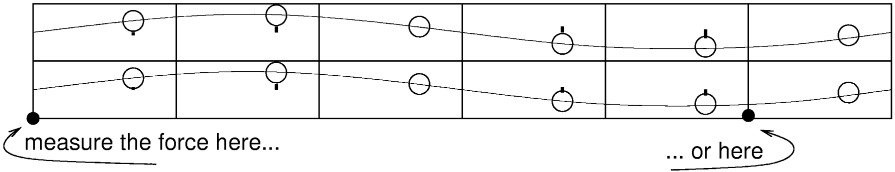
- if possible, calculate in advance and store in tables for subsequent fast interpolation (good, e.g., for dynamical simulations);
- use efficient statistical scheme rather than straightforward integration;
- use localized basis functions which allow analytical (or otherwise easy) integration (Gaussian basis sets).

Frozen phonon in a supercell

How to obtain real-space force constants $F^{ij}_{\alpha\beta}$:

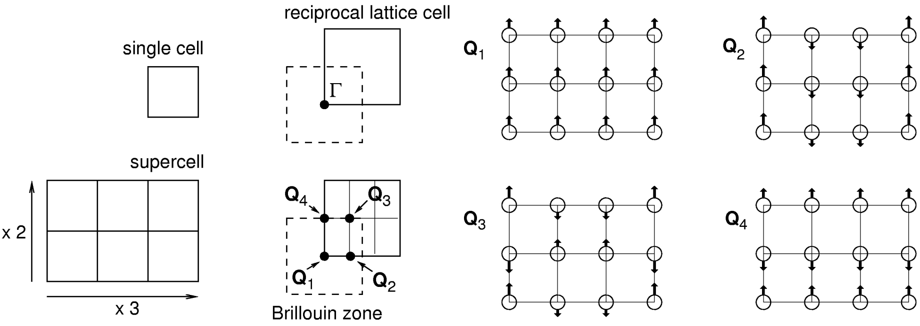


or, Fourier-transformed ones $F^{ij}_{ss'}(\mathbf{q})$:



Frozen phonon in a supercell

Γ phonon in a supercell scans different $\mathbf{q}$ values:



MD.TypeOfRun FC: SIESTA phonon trivia

- Crucial information for constructing the dynamical matrix is accumulated in the .FC file. These are forces/displacements, namely $-[F_i^\alpha(\mathbf{R}+d_j^\beta)]/d_j^\beta$: minus force induced on atom α in the direction i, as atom β is shifted by d from its equilibrium position $\mathbf{R}$ along j. The units are eV/Å^2. The default value of d (MD.FCDispl) is 0.04 Bohr.
- The writing order: external loop over N_1 atoms of the inner (single) cell; each atom undergoes 6 displacements (by the value of d), in the sequence: $-X, +X, -Y, +Y, -Z, +Z$. The forces are registered over N_2 atoms of the supercell (generated by fcbuild). After each displacement, the $-F/d$ values are written in a block, one line per atom in N_2, containing three Cartesian coordinates of the force. Hence the full number of lines in the .FC file is $N_1 \times N_2 \times 6+1$ (header line); for the calculation of Γ phonon $N_2 = N_1$.
- On crash, the calculation can be restarted from the atom whose six displacements have not been finished. This might involve re-defining the MD.FCfirst, MD.FClast parameters and removing the lines of unfinished $6 \times N_2$ block in the cumulative .FC file. Displacements of different atoms are completely independent and can be spread over machines.

Vibra input annoyances

- Different format of coordinates input in SIESTA
  `block AtomicCoordinatesAndAtomicSpecies:`
  `From ia = 1 to natoms`
  `read: xa(ix,ia), isa(ia)`
  `where xa(ix,ia) is the ix coordinate of atom iai, and isa(ia) is the species index of atom ia` (+ masses in separate block)

  and in Vibra
  `block AtomicCoordinatesAndAtomicSpecies:`
  `From ia = 1 to natoms`
  `read: xa(ix,ia), isa(ia), xmass(ia)`
  `where xa(ix,ia) is the ix coordinate of atom iai, isa(ia) is the species index of atom ia, and xmass(ia) is the atomic mass index of atom ia`.
- `AtomicCoordinatesFormat` is much more strict in Vibra.

OK, ça va...

The SIESTA way to phonons

- Γ-phonon only:
  - in the conventional unit cell, apply 6 displacements ($\pm x, y, z$) to EACH atom (consecutively or in parallel). Use block `MD.TypeOfRun FC`. Collect the force constants in the .FC file.
  - Run Vibra. Provide in its input file

```
%block BandLines
  1    0.  0.  0.
%endblock BandLines
```

  - Enjoy the results.
- $\omega(\mathbf{q})$ dispersions:
  - Construct a large enough supercell to ensure sufficient attenuation of real-space force constants within it. Use fcbuild for this.
  - Run SIESTA on thus generated supercell with `MD.TypeOfRun FC`. Collect the force constants in the .FC file.
  - Figure out which directions in the $\mathbf{q}$-space you want to explore. Add corresponding definitions in the `%block BandLines`.
    Run Vibra. Enjoy the results.

The hard SIESTA way to phonons: Γ phonon

Before doing a big calculation of phonon dispersions (on a supercell), run a Γ phonon on a single cell. It may save you some trouble. What to look at:

- There must be THREE acoustic modes with $|\omega| \leq 0.1$ cm^{-1}. If not, you have problem with insufficient MeshCutoff. Go and fix it first.
- All other modes must have POSITIVE frequencies. If some are NEGATIVE (in fact, imaginary, i.e., $\omega^2 < 0$) ones, this indicates bad initial lattice relaxation (the atoms displaced not from equilibrium). Repare as follows: Take the LOWEST (the most negative) of these modes. Displace the atoms slightly along their respective components in the eigenvector of this phonon (e.g., with the help of vib2xsf). This MUST reduce the total energy. As you don't know in which sense to displace, try both. From whichever displacement yields lower energy, start new (better) structure relaxation. Then calculate phonons anew.
- You have three zero modes and none negative. However, the "good" modes are not where they are supposed to be. As the last resort, check THE ATOMIC MASSES you provided to Vibra. If nothing helps, that's where the real work starts: was it pseudopotential? Was it basis? ... ?

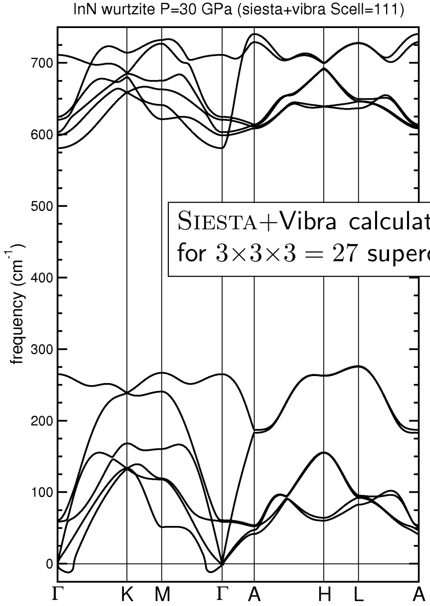
The hard SIESTA way to phonons: $\omega(\mathbf{q})$ dispersions

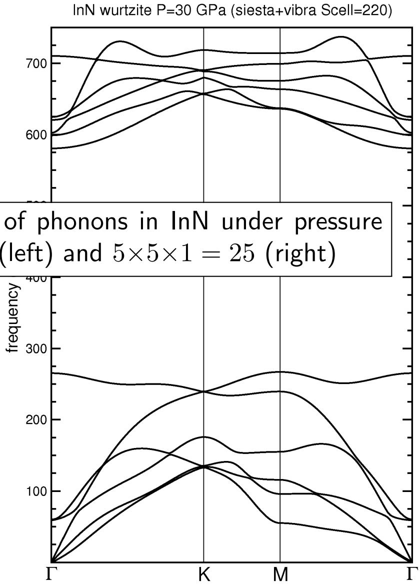
Suppose the problems described in relation with Γ phonon do not occur.

The next sensitive issue, in what regards calculating dispersions, is the localization of force constants. This is done by choosing sufficiently large supercell in fcbuild, setting `SuperCell_1,2,3`. Increasing them uniformly ultimately enforces such localization, but underway the size of the generated supercell – 1, 27, 125, ... for `SuperCell_?  = 0, 1, 2` – may explode your computer.

A suggestion:
Enlarge the supercell size only along the direction(s) along which (i.e. along whose reciprocal-space counterparts) you REALLY care about dispersion. Then you'll have a "linear scaling" in supercell size:
1, 3, 5, ... for `SuperCell_i = 0, 1, 2`.

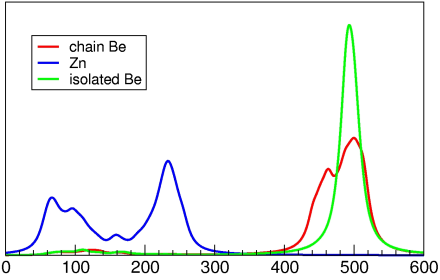
The hard SIESTA way to phonons: $\omega(\mathbf{q})$ dispersions

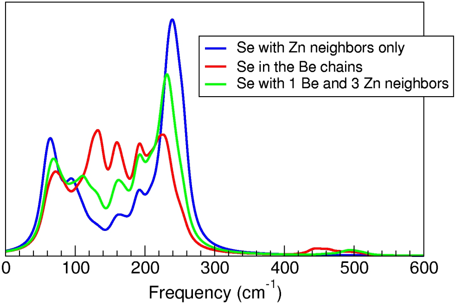




SIESTA+Vibra calculation of phonons in InN under pressure for $3{\times}3{\times}3 = 27$ supercell (left) and $5{\times}5{\times}1 = 25$ (right)

Extracting phonon density of states (case $Zn_{1-x}Be_xSe$)





Γ point only + large enough supercell $\Rightarrow$ density of modes $I(\omega)$.

How it works (use phdos):

$$I_{\aleph}(\omega) = \sum_{\alpha \in \aleph} \sum_{i} |A_i^{\alpha}(\omega)|^2 \; ;$$

$A_i^{\alpha}(\omega)$: eigenvectors,
$\aleph$: selected group of atoms.

Vibrational density of states for the $Be_6Zn_{26}Se_{32}$ supercell, resolved over different groups of atoms, calculated for q=0 of the supercell and broadened by 10 cm^{-1}. The vertical scaling for different groups is arbitrary.

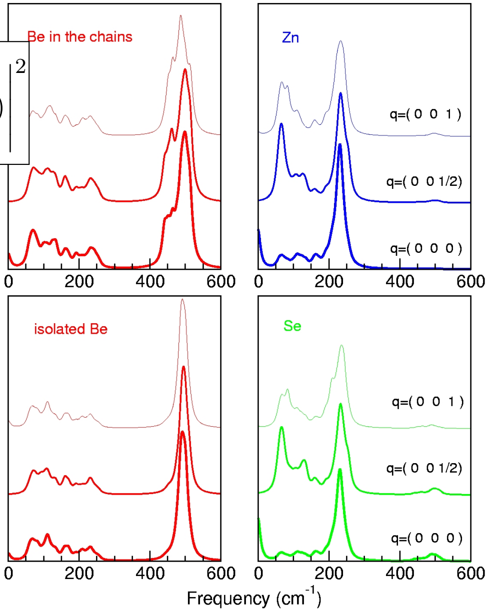
Phonon spectral function

$$I_{\aleph}(\omega, \mathbf{q}) = \sum_i \left| \sum_{\alpha \in \aleph} A_i^{\alpha}(\omega) \exp(\mathbf{q}\mathbf{R}_{\alpha}) \right|^2$$

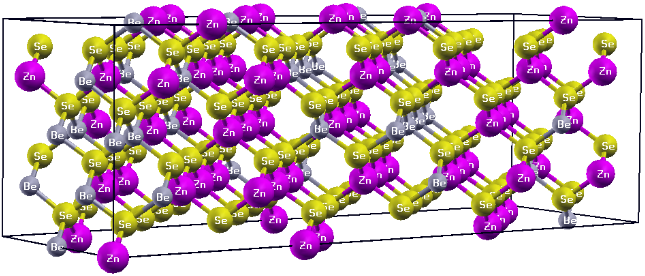
$A_i^{\alpha}(\omega)$: eigenvectors,
$\aleph$: selected group of atoms

(also implemented in phdos).

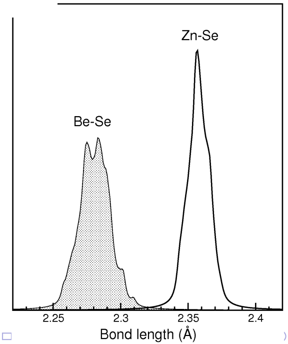
- The additional (Be-chain) mode is mostly pronounced for q=0;
- dispersion features are well seen for ZnSe sublattice.



$Be_{0.33}Zn_{0.67}Se$: phonon dispersion



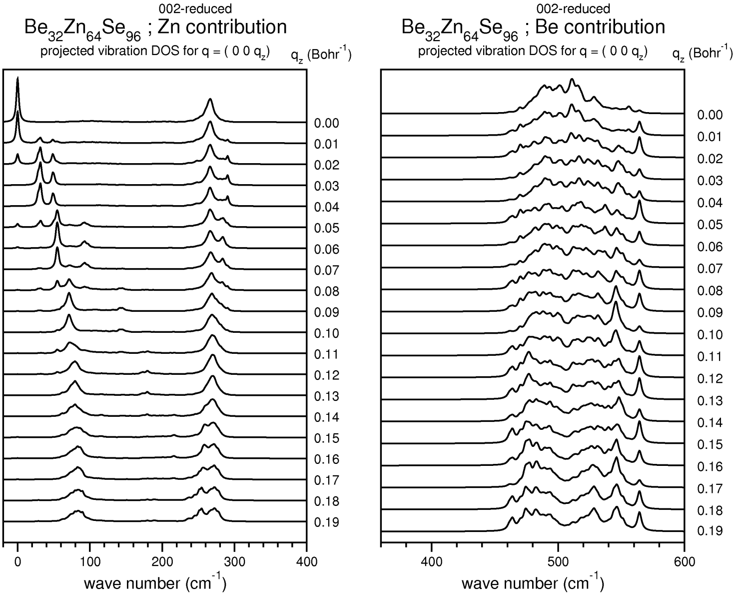
$Be_{32}Zn_{64}Se_{96}$ supercell
(002-reduced)



$Be_{32}Zn_{64}Se_{96}$ supercells

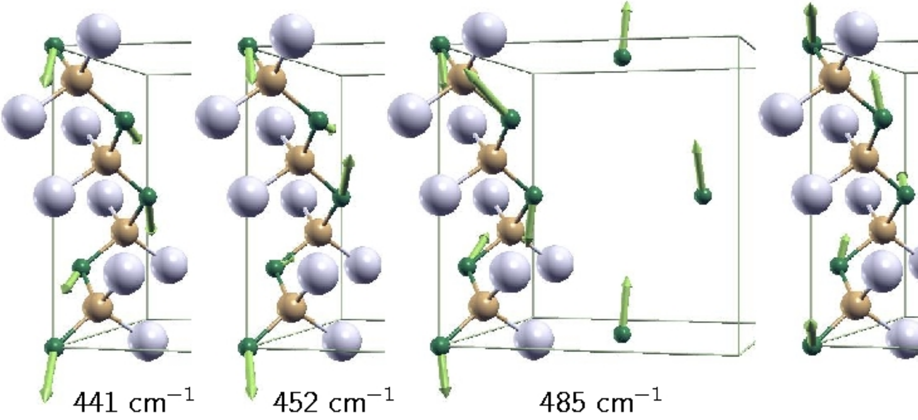
quasirandom generation

$Be_{0.33}Zn_{0.67}Se$: phonon dispersion



Vibration patterns (generated with vib2xsf)

of selected modes with substantial contribution of the chain Be atoms.

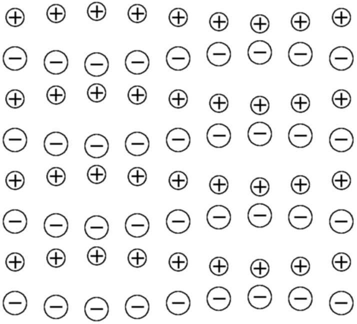


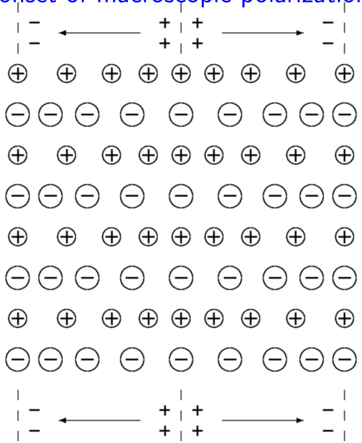
Phonons in bulk dielectics

TO phonon

LO phonon

in polar dielectrics, a difference in the force constants affecting transversal and longitudinal modes arises due to the onset of macroscopic polarization





Phonons in bulk dielectics

Dynamical matrix depends on the presence of macroscopic polarization:

$$
\begin{aligned}
D^{ij}_{\alpha\beta}(\boldsymbol{q} \to 0) &= {D^{ij}_{\alpha\beta}}^{\text{[analytical]}}(\boldsymbol{q} = 0) + {D^{ij}_{\alpha\beta}}^{\text{[non-analytical]}}(\boldsymbol{q} \to 0) \\
&= \frac{F^{ij}_{\alpha\beta}}{\sqrt{M_\alpha M_\beta}} + \frac{4\pi}{\Omega} \frac{1}{\sqrt{m_\alpha m_\beta}} \frac{\left(\sum\limits_k q_k Z^*_{\alpha,ki}\right)\left(\sum\limits_{k'} q_{k'} Z^*_{\beta,k'j}\right)}{\sum\limits_{kk'} q_k \, \epsilon^\infty_{kk'} \, q'_k} ;
\end{aligned}
$$

$$Z^*_{\alpha,ij} = \frac{\partial^2 E}{\partial \mathcal{E}_i \partial R_{\alpha j}} \; : \quad \text{Born effective (dynamical) charge (tensor).}$$

ϵ^∞: high-frequency (from the point of view of phonons) dielectric tensor, i.e. zero-frequency (from the point of view of electrons) one.

Phonons in bulk dielectics: Born effective charges

Calculated Born effective charges in SiO_2
[Umari *et* al., PRB **63**, 094305 (2001)]:

$$Z^*_{\mathrm{Si}} = \begin{pmatrix} 3.021 & 0 & 0 \\ 0 & 3.671 & -0.224 \\ 0 & 0 & 3.450 \end{pmatrix} ; \quad Z^*_{\mathrm{O}} = \begin{pmatrix} -1.413 & 0.564 & 0.505 \\ 0.519 & -1.915 & -0.615 \\ 0.447 & -0.648 & -1.715 \end{pmatrix} .$$

Anomalous Born effective charges in ferroelectrics, e.g. $KNbO_3$
[Wang *et* al., PRB **54**, 11161 (1996)]:

$$Z^*_{\mathrm{Nb}} = \begin{pmatrix} 8.16 & -0.35 & -0.35 \\ -0.35 & 8.16 & -0.35 \\ -0.35 & -0.35 & 8.16 \end{pmatrix} ; \quad Z^*_{\mathrm{O}} = \begin{pmatrix} -6.27 & 0.14 & 0.14 \\ 0.24 & -1.55 & 0.00 \\ 0.24 & 0.00 & -1.55 \end{pmatrix} .$$

reveal strong polarizability of the coresponding bonds.

Macroscopic polarization, calculation of Born effective charges are implemented in SIESTA. A corresponding private version of Vibra, designed for calculation of LO phonons, is around.

Linear response

The Kohn-Sham equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{\mathsf{SCF}}(\mathbf{r})\right]\varphi_i(\mathbf{r}) = \varepsilon_i\,\varphi_i(\mathbf{r})\,;$$

$$V_{\mathsf{SCF}}(\mathbf{r}) = e^2\sum_\alpha \frac{-Z_\alpha}{|\mathbf{r}-\mathbf{R}_\alpha|} + e^2\int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \frac{\delta E_{\mathsf{XC}}}{\delta\rho(\mathbf{r})}\,;$$

$$\rho(\mathbf{r}) = \sum_{\substack{i\\ \text{(occupied)}}} |\varphi_i(\mathbf{r})|^2$$

is linearized, introducing small parameter λ:

$$\begin{aligned}
\varphi_i(\mathbf{r}) &= \varphi_i^{(0)}(\mathbf{r}) + \lambda\,\varphi_i^{(1)}(\mathbf{r})\,;\\
V_{\mathsf{SCF}}(\mathbf{r}) &= V_{\mathsf{SCF}}^{(0)}(\mathbf{r}) + \lambda\,V_{\mathsf{SCF}}^{(1)}(\mathbf{r})\,.
\end{aligned}$$

Linear response

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V^{(0)}_{\textsf{SCF}}(\mathbf{r}) - \varepsilon_i\right]\varphi^{(1)}_i(\mathbf{r}) = -V^{(1)}_{\textsf{SCF}}(\mathbf{r})\,\varphi^{(0)}_i(\mathbf{r})\,;$$

(Sternheimer equation)

$$V^{(1)}_{\textsf{SCF}}(\mathbf{r}) = e^2\sum_\alpha \frac{Z_\alpha \mathbf{w}_\alpha(\mathbf{r}-\mathbf{R}_\alpha)}{|\mathbf{r}-\mathbf{R}_\alpha|^3} + e^2\int\frac{\rho^{(1)}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \rho^{(1)}(\mathbf{r})\left[\frac{dV_{\textsf{XC}}(\mathbf{r})}{d\rho}\right]_{\rho^{(0)}};$$

$$\rho^{(1)}(\mathbf{r}) = 2\,\mathrm{Re}\sum_{\substack{i\\ \text{(occupied)}}}\varphi^{(0)*}_i(\mathbf{r})\,\varphi^{(1)}_i(\mathbf{r})\,.$$

“Perturbation” $\lambda\mathbf{w}_\alpha$: e.g., a phonon $\mathbf{q}$ with polarization $\mathbf{A}$,

$$\mathbf{w}_\alpha = \mathbf{A}e^{i\mathbf{q}\mathbf{R}_\alpha} + \mathbf{A}^* e^{-i\mathbf{q}\mathbf{R}_\alpha}\,.$$

A good review: Baroni *et al.*, Rev. Mod. Phys. **73**, 515 (2001).

Molecular dynamics

Verlet algorithm:

$$\mathbf{r}(t+\delta t) = 2\mathbf{r}(t) - \mathbf{r}(t-\delta t) + (\delta t)^2 \frac{\mathbf{F}(t)}{M}$$

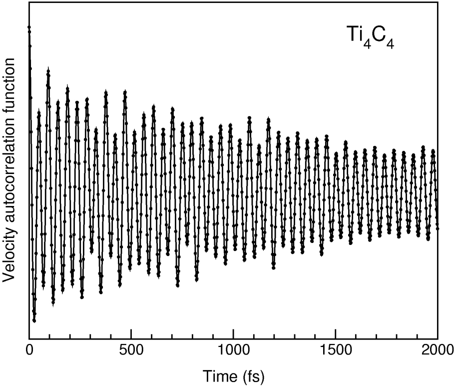
Velocity autocorrelation function:

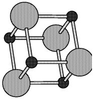
$$C_v(\tau) = \frac{1}{N}\sum_{i=1}^{N}\frac{1}{t_{\textsf{max}}}\sum_{t_0=1}^{t_{\textsf{max}}}\left[\mathbf{v}_i(t_0)\cdot\mathbf{v}_i(t_0+\tau)\right]$$

Vibrational density of states:

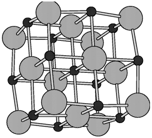
$$\begin{aligned} I(\omega) &= \left|G(\omega)\right|^2, \\ G(\omega) &= \int_{-\infty}^{\infty} d\tau\, C_v(\tau) e^{-i\omega\tau} \end{aligned}$$

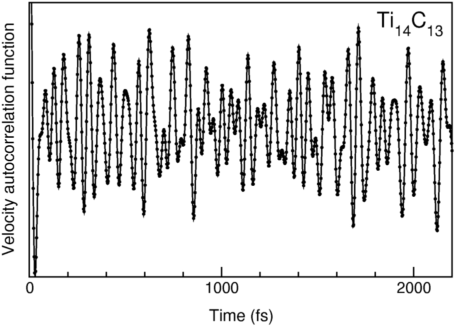
MD simulations for small clusters



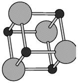


velocity autocorrelation function



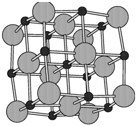


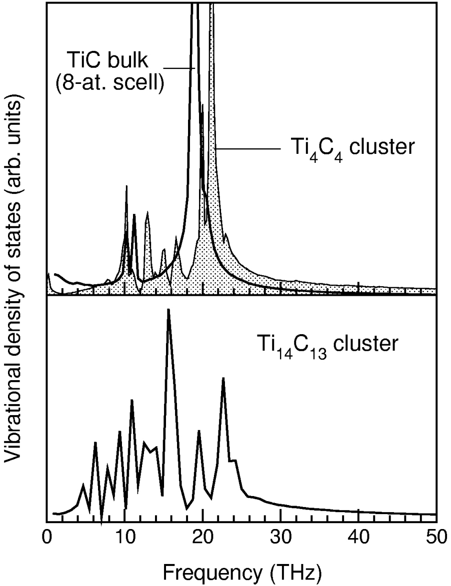
MD simulations for small clusters



Vibrational DOS extracted from MD simulations for bulk TiC (8-atom supercell, thick line in the top panel), Ti_4C_4 cluster (thin line in the top panel) and the $Ti_{14}C_{13}$ cluster (bottom panel).

Postnikov and Entel, *Phase Transitions* **77**, 149 (2004).





Molecular dynamics vs. frozen phonons

(+) anharmonic effects automatically included

(+) straightforward treatment of temperature effects (e.g., Nosé thermostat)

(±) total simulation time is limited from below by frequency resolution,

$$t_{\text{MD run}} \geq 1/(\Delta\nu)\,;$$

simulation time step is limited from above by the highest characteristic frequency,

$$\Delta t \ll 1/\nu_{\text{max.}}\,,$$

⇒ many simulation steps needed, but for large systems one may be better off than trying all displacements as in a frozen phonon calculation).

(−) at low temperatures – mostly harmonic behaviour, poor ergodicity.

Conclusions

- Be careful in checking the accuracy of calculation (cutoffs, basis, ...) before engaging in a big phonon project. Remember, you'll only get result when ALL elements of the dynamical matrix will be accumulated!
- The accumulation of force constants is the most efficiently parallelizable operation in SIESTA – unfortunately, only by hand...
- Consider molecular dynamics as a method worth consideration for getting phonons, if your system is large, and especially if you accumulate the MD trajectories anyway.
- Once you got phonons, do not be satisfied with just frequencies; get the best you can from the eigenvectors.
- If comparison with experiment desperately fails despite all efforts, it must have been anharmonicity !-)