

Calculation of lattice vibrations:
frozen phonons and molecular dynamics
(with SIESTA)

MAX training: SIESTA school
by the European centre of excellence MAX,
Barcelona, May 26, 2017

Andrei Postnikov
(Metz, France)



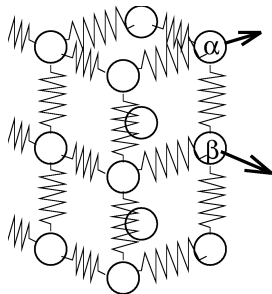
Outline

- 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 Molecular dynamics as a source of phonon information

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,



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

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:

$$M_\alpha \ddot{u}_\alpha^i = - \sum_\beta^N \sum_j^3 F_{\alpha\beta}^{ij} u_\beta^j$$

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} ,

$$M_s \ddot{u}_{s\mathbf{q}}^i = - \sum_{s'}^n \sum_j^3 F_{ss'}^{ij}(\mathbf{q}) u_{s'\mathbf{q}}^j$$

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

$$\begin{pmatrix} \vdots \\ \frac{F_{ss'}^{ij}(\mathbf{q})}{\sqrt{M_s M_{s'}}} - \omega^2 \delta_{ss'} \delta_{ij} \\ \vdots \end{pmatrix} \begin{pmatrix} \vdots \\ u_{s'\mathbf{q}}^j \sqrt{M_{s'}} \\ \vdots \end{pmatrix} = 0$$

$\det(\dots) = 0 \Rightarrow$ 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/Å² (otherwise 1 Ry = 13.605692 eV; 1 Bohr = 0.529177 Å). The above “frequency unit”, *f.u.*, in the SI:

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

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

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

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

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

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

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

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

Units conversion:

$$1 \text{ THz} = 4.136 \text{ meV} = 33.356 \text{ cm}^{-1};$$

$$1 \text{ meV} = 0.242 \text{ THz} = 8.066 \text{ cm}^{-1};$$

$$1 \text{ cm}^{-1} = 0.030 \text{ THz} = 0.124 \text{ meV}.$$

Density Functional Theory: total energy

The Kohn-Sham equations:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{SCF}}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r});$$
$$V_{\text{SCF}}(\mathbf{r}) = e^2 \sum_{\alpha} \frac{-Z_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha}|} + e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{\text{XC}}}{\delta \rho(\mathbf{r})};$$
$$\rho(\mathbf{r}) = \sum_{\substack{i \\ \text{(occupied)}}} |\varphi_i(\mathbf{r})|^2$$

Total energy:

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

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

Density Functional Theory: forces

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

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

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

Possibly further 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:

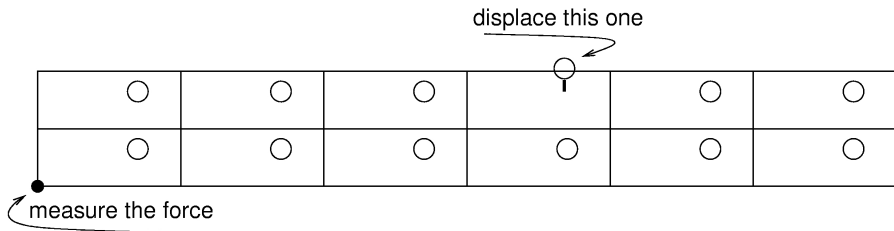
$$\sum_p C_{\alpha p} \left[\underbrace{\int \chi_q^*(\mathbf{r}) \mathcal{H} \chi_p(\mathbf{r}) d\mathbf{r}}_{\mathcal{H}_{qp}} - \varepsilon_{\alpha} \underbrace{\int \chi_q^*(\mathbf{r}) \chi_p(\mathbf{r}) d\mathbf{r}}_{S_{qp}} \right] = 0$$

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

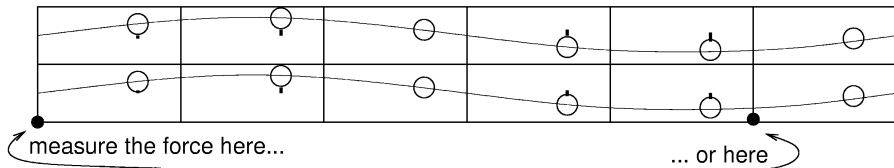
→ a generalized diagonalization problem, to be solved iteratively.

Frozen phonon in a supercell

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

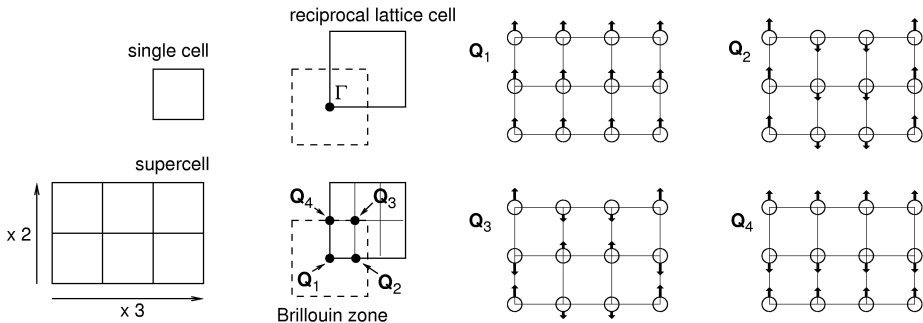


or, Fourier-transformed ones $F_{ss'}^{ij}(\mathbf{q})$:



Frozen phonon in a supercell

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



- 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/Å². 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 ia , 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 ia , $isa(ia)$ 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
```

...or, use my tool `Sies2LD/vibq0`

- ▶ 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 $|\omega| \leq 0.1 \text{ cm}^{-1}$. 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? ... ?

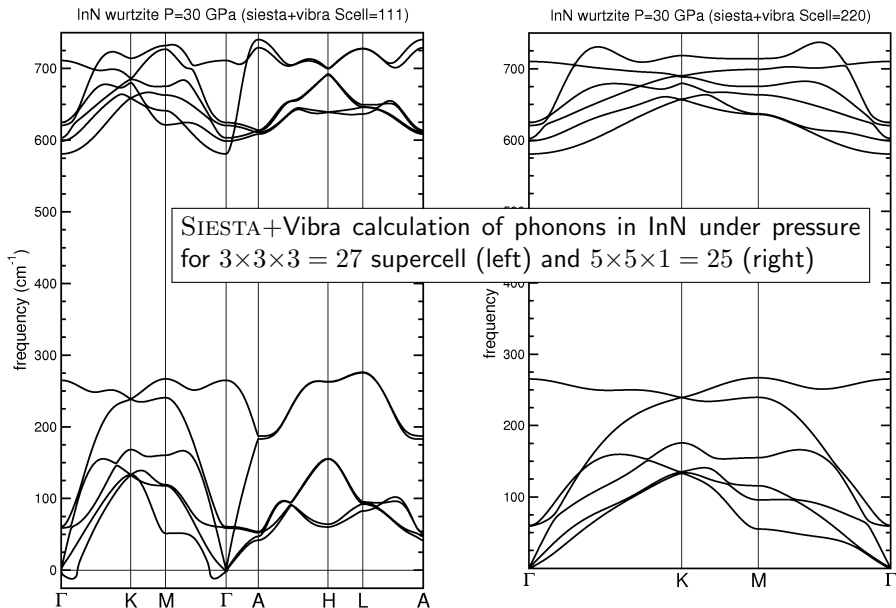
The hard SIESTA way to phonons: $\omega(\mathbf{q})$ dispersions

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



Density of modes and spectral function

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

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

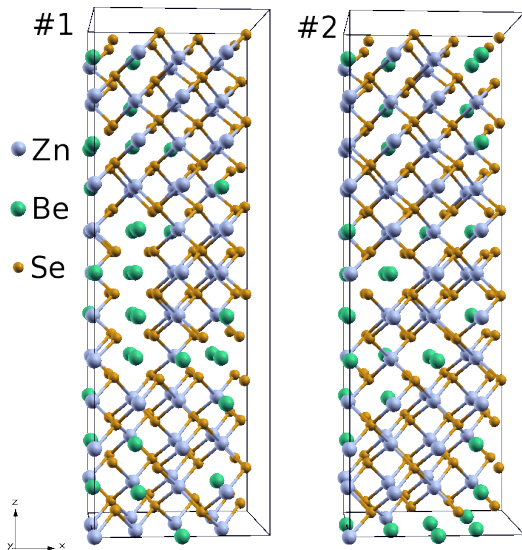
$A_i^\alpha(\omega)$: eigenvectors, \aleph : selected group of atoms.

Phonon spectral function

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

(implemented in [Sies2LD/phdos](#)). Moreover, the separation of Longitudinal and Transversal modes...

q-resolved modes density: an example of (Zn,Be)Se



- **Motivation / setup:**

probing the “1-bond – 2-mode” behaviour away from the Brillouin zone center.

- Solid solution is simulated by **S**pecial **Q**uasirandom **S**upercells.

- Two different ones of 192 atoms were tried ($\text{Be}_{32}\text{Zn}_{64}\text{Se}_{96}$, long in one dimension, in order to well probe the dispersion).

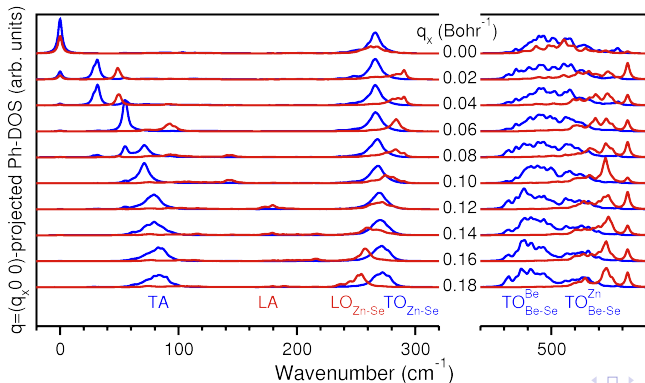
- **Experimental insight:**

inelastic neutron scattering and Raman spectroscopy; see details in PRB**89**, 155201 (2013).

Revealing q -dispersion: L- and T- spectral functions

$$I_{\mathbb{N}}^L(\omega, \mathbf{q}) = \sum_i \left| \sum_{\alpha \in \mathbb{N}} \left(\frac{\mathbf{q}}{|\mathbf{q}|} \cdot \mathbf{A}_i^\alpha e^{i\mathbf{q}\mathbf{R}_\alpha} \right) \right|^2 \delta(\omega - \omega_i);$$

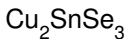
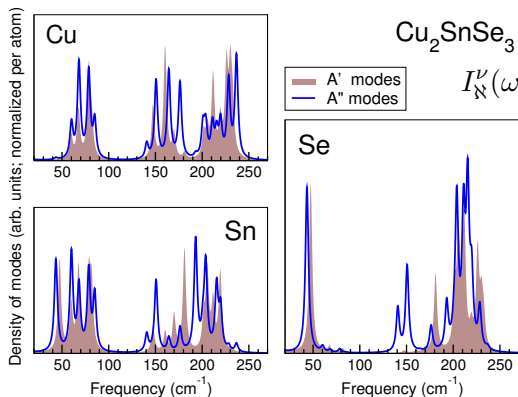
$$I_{\mathbb{N}}^T(\omega, \mathbf{q}) = \sum_i \left| \sum_{\alpha \in \mathbb{N}} \left[\mathbf{A}_i^\alpha - \frac{(\mathbf{q} \cdot \mathbf{A}_i^\alpha)}{|\mathbf{q}|} \right] e^{i\mathbf{q}\mathbf{R}_\alpha} \right|^2 \delta(\omega - \omega_i).$$



An example of (Zn,Be)Se:

q -dispersion in the acoustic branch, bimodal behaviour in the $\text{TO}_{\text{Be-Se}}$ (getting more pronounced along $\Gamma \rightarrow X$), the crossing of LO and TO branches with q in the Zn-Se domain.

Projecting vibrations according to irred. representations



$$I_{\mathbb{N}}^{\nu}(\omega) = \sum_i \left| \sum_{\alpha \in \mathbb{N}} \mathbf{A}_i^{\alpha} \mathbf{S}_i^{\alpha\nu} \right|^2 \delta(\omega - \omega_i).$$

Contribution of chemical species in vibration modes of CTSe (24 at./cell), according to projections corresponding to A' and A'' IrReps.

Symmetry coordinates constructed from individual cartesian displacements of atoms in CTSe according to A' , A'' IrReps of the Cc space group.

Sites	A' modes			A'' modes		
	#1	#2	#3	#1	#2	#3
(x, y, z)	Z	Y	X	$-Z$	Y	$-X$
$(x, -y, z+1/2)$	Z	$-Y$	X	Z	Y	X

Vibration contributions to energy

In a system of harmonic oscillators $\{\omega_k\}$, the partition function:

$$Z = \sum_{\{n_k\}} e^{-\frac{1}{k_B T} \sum_k \hbar \omega_k (n_k + \frac{1}{2})} = \sum_{\{n_k\}} \prod_k e^{-\frac{\hbar \omega_k}{k_B T} (n_k + \frac{1}{2})} = \prod_k e^{-\frac{\hbar \omega_k}{2k_B T}} \left(1 - e^{-\frac{\hbar \omega_k}{k_B T}}\right)^{-1}.$$

The free energy and entropy:

$$F = -k_B T \ln Z = \sum_k \left[\frac{\hbar \omega_k}{2} + k_B T \ln \left(1 - e^{-\frac{\hbar \omega_k}{k_B T}}\right) \right], \quad \text{or, via mode density } g(\omega):$$

$$F = k_B T \int_0^{\omega_{\max}} \left[\ln(e^x - 1) - \frac{x}{2} \right] g(\omega) d\omega \quad \text{with } x = \frac{\hbar \omega}{k_B T};$$

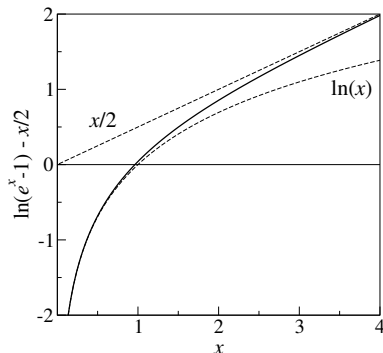
$$S = -\frac{\partial F}{\partial T} = k_B \int_0^{\omega_{\max}} \left[\frac{x}{e^x - 1} - \ln(1 - e^{-x}) \right] g(\omega) d\omega.$$

In a large supercell, $\mathbf{q} = 0$ discrete spectrum samples the continuous density of modes:

$$g(\omega) \approx \sum_{\alpha} \delta(\omega - \omega_{\alpha}).$$

Vibration contributions to energy

$$F = k_B T \int_0^{\omega_{\max}} \left[\ln(e^x - 1) - \frac{x}{2} \right] g(\omega) d\omega; \quad \text{integrand in the figure:}$$



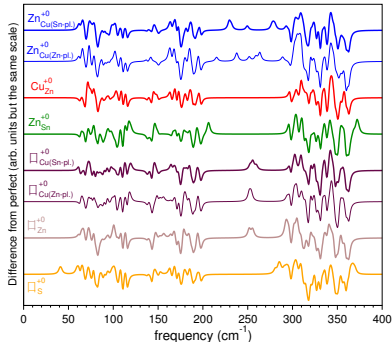
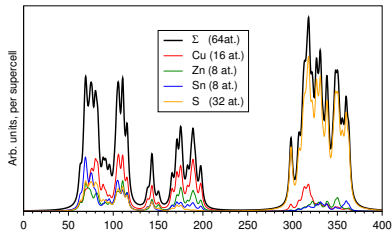
$$x = \frac{\hbar\omega}{k_B T} \text{ for some values of } \omega \text{ and } T.$$

ω (cm^{-1})	T (K)		
	50	300	400
50	1.44	0.24	0.18
250	7.20	1.20	0.90
400	11.51	1.92	1.44

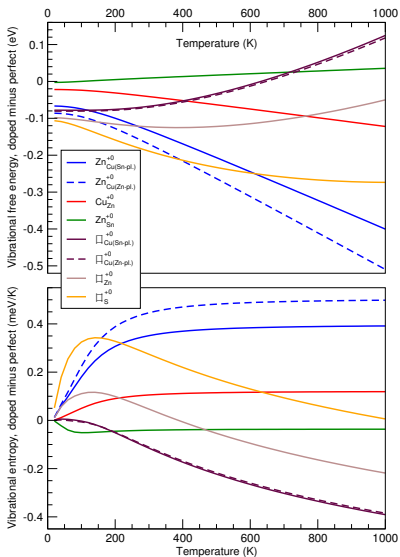
→ the resulting F either positive or negative; large negative contribution results from low-frequency modes.

Vibration entropy calculations: $\text{Cu}_2\text{ZnSnS}_4$ with point defects

$\text{Cu}_2\text{ZnSnS}_4$: 64-at. supercell, total density of modes



Vibrational properties of point defects in CZTS



Vibration entropy calculations: $\text{Cu}_2\text{ZnSnS}_4$ with point defects

Parameters of point defect formation.

\square_{Cu} : vacancy at Cu site, Zn_{Sn} – substitutional Zn at the Sn site etc.

Defect	Formation energy of a neutral defect ΔE (eV)*	Modification of the free energy due to vibrations, ΔF_{vib} (eV) at $T=550$ °C
\square_{Cu}	0,76	0,058
\square_{Zn}	2,14	-0,084
Cu_{Zn}	1,04	-0,101
Zn_{Sn}	-0,04	0,029
\square_{S}	1,71	-0,27
Zn_{Cu}	1,4	-0,42

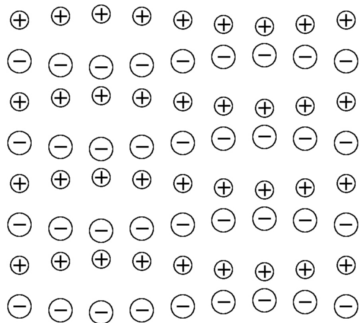
* Calculations of Chen *et al.*, *PRB***81**, 245204 (2010)

Observation: the energy lowering is important in cases where spectral weight is redistributed into lower frequencies (\square_{S} , Zn_{Cu}).

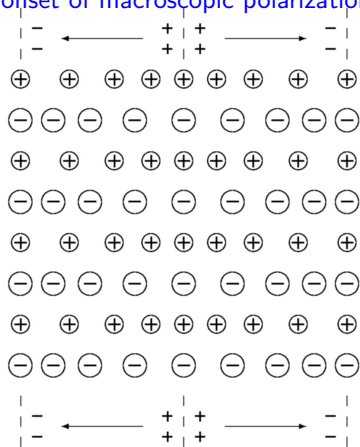
Phonons in bulk dielectrics

TO phonon

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



LO phonon



Phonons in bulk dielectrics

Dynamical matrix depends on the presence of macroscopic polarization:

$$\begin{aligned} D_{\alpha\beta}^{ij}(\mathbf{q} \rightarrow 0) &= D_{\alpha\beta}^{ij} \text{ [analytical]}(\mathbf{q} = 0) + D_{\alpha\beta}^{ij} \text{ [non-analytical]}(\mathbf{q} \rightarrow 0) \\ &= \frac{F_{\alpha\beta}^{ij}}{\sqrt{M_{\alpha}M_{\beta}}} + \frac{4\pi}{\Omega} \frac{1}{\sqrt{m_{\alpha}m_{\beta}}} \frac{\left(\sum_k q_k Z_{\alpha,ki}^*\right) \left(\sum_{k'} q_{k'} Z_{\beta,k'j}^*\right)}{\sum_{kk'} q_k \epsilon_{kk'}^{\infty} q_{k'}}; \end{aligned}$$

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

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 dielectrics: Born effective charges

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

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

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

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

reveal strong polarizability of the corresponding 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.

Verlet algorithm:

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

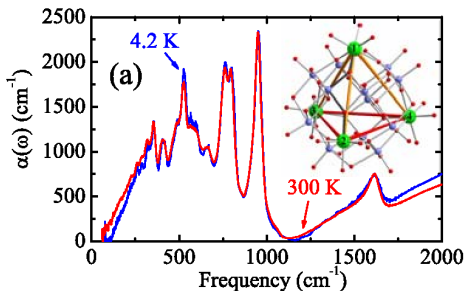
Velocity autocorrelation function:

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

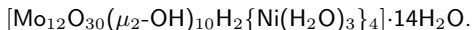
Vibrational density of states:

$$I(\omega) = |G(\omega)|^2,$$
$$G(\omega) = \int_{-\infty}^{\infty} d\tau C_v(\tau) e^{-i\omega\tau}$$

MD vs frozen phonons for Ni₄ molecular magnet

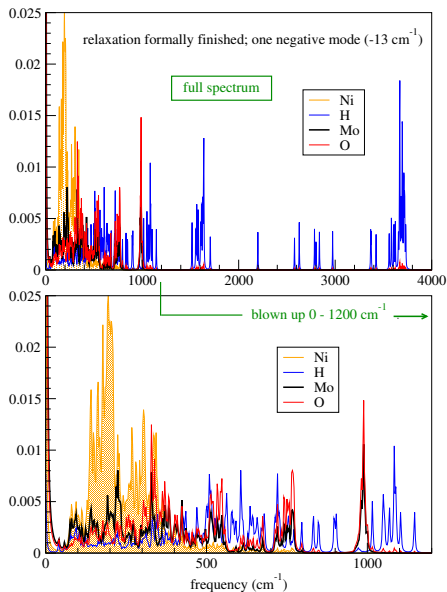


Ni₄, alias



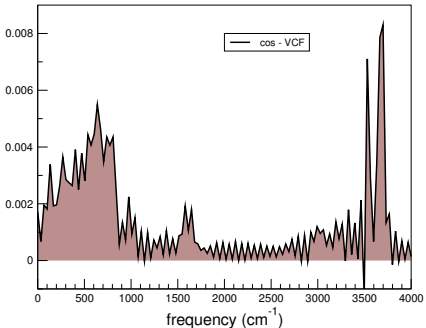
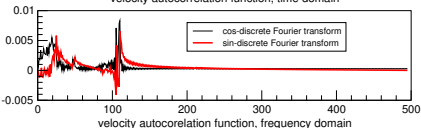
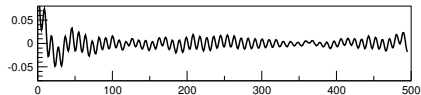
Infrared absorption spectrum

by K.J. Cao and J.L. Musfeldt

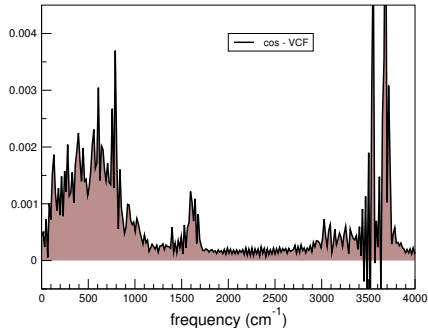
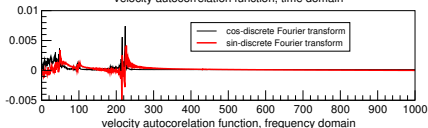
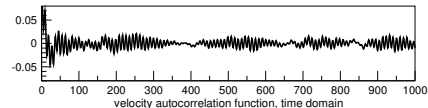


MD vs frozen phonons for Ni₄ molecular magnet

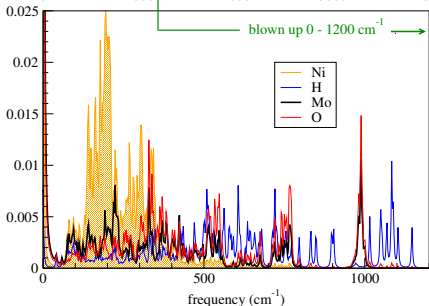
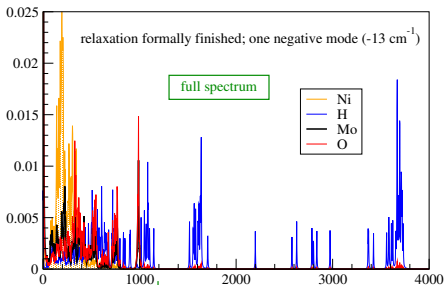
Steps 0-495 (July 16, 2010)



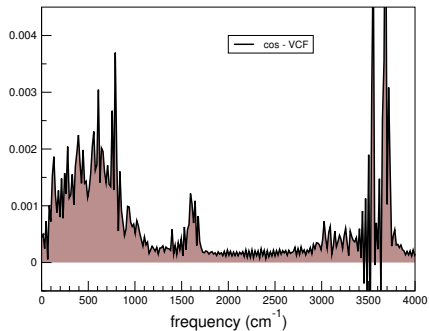
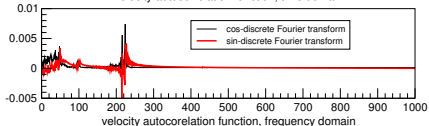
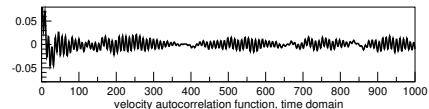
Steps 0-1013 (Sep 9, 2010)



MD vs frozen phonons for Ni₄ molecular magnet



Steps 0-1013 (Sep 9, 2010)



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.