

Post-processing tools for analysis of lattice dynamics following SIESTA + Vibra calculation

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3. Other post-processing and visualization utilities

The tools concerning the lattice dynamics have been developed having in mind the Γ phonons calculated for a large enough supercell, that is a typical case in a simulation of molecular crystals or disordered substitutional alloys.

The phdos tool is designed for analyzing the zone-center vibration results. As the system is supposed to be large (e.g., a supercell chosen for a periodic crystal), the (artificially broadened, for convenience) discrete spectrum may serve as a fair approximation to the total density of modes, and if weighted with (squared) components of eigenvectors at different atoms, it provides a decomposition into contributions of different atoms in the total density of vibration modes.

A more sophisticated option is the *projection* of different eigenvectors according to various criteria. The typical system under study is a supercell in which, e.g., an alloying, or some kind of deformation, breaks the underlying perfect periodicity. Still, some trends related to the latter can be revealed by appropriate projections. The two obvious cases are the projections onto (1) \mathbf{q} -vectors of the underlying lattice and (2) irreducible representations of the space group of the underlying lattice; the corresponding formulas and some results

can be found in Ref. 136. The first type of projection, if done for a sequence of \mathbf{q} values, helps to reveal “phonon dispersions,” obviously blurred by the broken periodicity, also making distinction between transversal and longitudinal modes (see Ref. 137 for an example of use). To make the trends more pronounced, the supercell needs to be sufficiently long in the direction concerned (see, e.g., Fig. 16). The simplest case, a projection onto a single $\mathbf{q} = 0$ value, may also be of interest, since it enhances the modes that are expected to dominate the infrared or Raman spectra and thus facilitates their comparison with the experiment.

The symmetry projection may help to isolate in a possibly complex spectrum those modes which are expected to dominate according to a given selection rule, again in view of their verification against the experiments. The group-symmetry information needed for the projections is available, e.g., from the Bilbao Crystallographic Server,¹³⁸ and the technical details are explained in the documentation included in the tools.

The vibent tool performs a straightforward calculation (see, e.g., Sec. II.C in Ref. 139 or Sec. 5.3 in Ref. 140) of temperature-dependent vibration contributions to the free energy and entropy (see Fig. 17 as an example). The necessary input information is the vibration spectrum, originating from the Vibra frozen phonon calculation on a sufficiently large system.

The velcf tool calculates the velocity autocorrelation function and its Fourier transform from a (presumably sufficiently long) molecular dynamics (MD) history, recorded in the .MD or .ANI file. This technique¹⁴¹ can be used to obtain phonon frequencies and was applied along with a SIESTA calculation in Ref. 142. An example of such simulation (1000 MD steps at 600 K) is shown in Fig. 18 in comparison with frozen phonon results, revealing similarities of the spectra obtained.

Sies2LD suite

Tool	Calculates	Needs
<code>phdos</code>	density of modes, in different projections	<code>.XV</code> , <code>.vectors</code> (from Vibra)
<code>vibent</code>	vibrational entropy	<code>.XV</code> , <code>.bands</code> (from Vibra)
<code>velcf</code>	velocity auto-correlation function	<code>.XV</code> , (<code>.MD</code> <code>.ANI</code>)

`phdos` and `vibent` may only address results of lattice dynamics calculations for Gamma. For these calculations to make sense, they have to be done on large enough supercell. A typical case under study is that of a mixed system (alloy), represented by a special quasirandom (or, otherwise mixed) supercell. `velcf` post-processes a standard MD run.

phdos: \mathbf{q} -resolved density of modes

In solid solutions, where topological disorder destroys an exact crystal periodicity, the projection of phonon eigenvectors taken along with a $\exp(i\mathbf{q}\mathbf{R})$ plane wave may help to reveal somehow a smeared $\omega(\mathbf{q})$ dispersion trends in a form of “spectral function”:

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

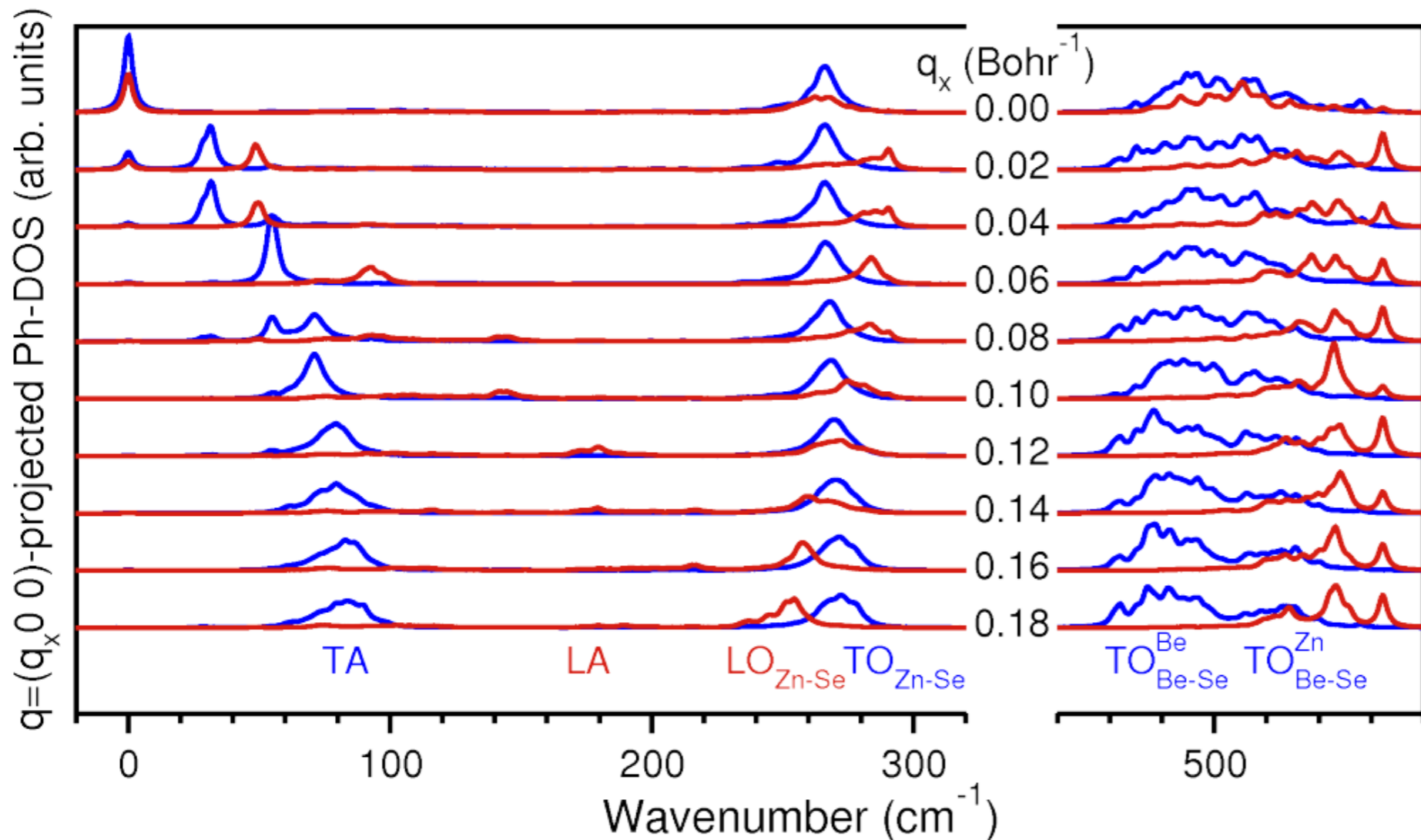
It amplifies the weights of vibrations in which similar atoms move in phase with a given \mathbf{q} -wave throughout the crystal, and suppresses the movements whose phase are at random with such wave. In particular, the $\mathbf{q}=0$ projection amplifies the “prototype” zone-center TO mode of zincblende crystal, the quasi rigid movement of the cation sublattice against the anion one:

$$I_{\mathcal{N}}(\omega, \mathbf{q}=0) = \sum_i \left| \sum_{\alpha \in \mathcal{N}} \mathbf{A}_i^\alpha(\omega) \right|^2 \delta(\omega - \omega_i).$$

Projecting into **L**ongitudinal and **T**ransversal components

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

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



An example
of (Zn,Be)Se:

note the crossing of
LO and TO branches
with q
in the ZnSe domain.

vibent : Vibration contributions to entropy

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:

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

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

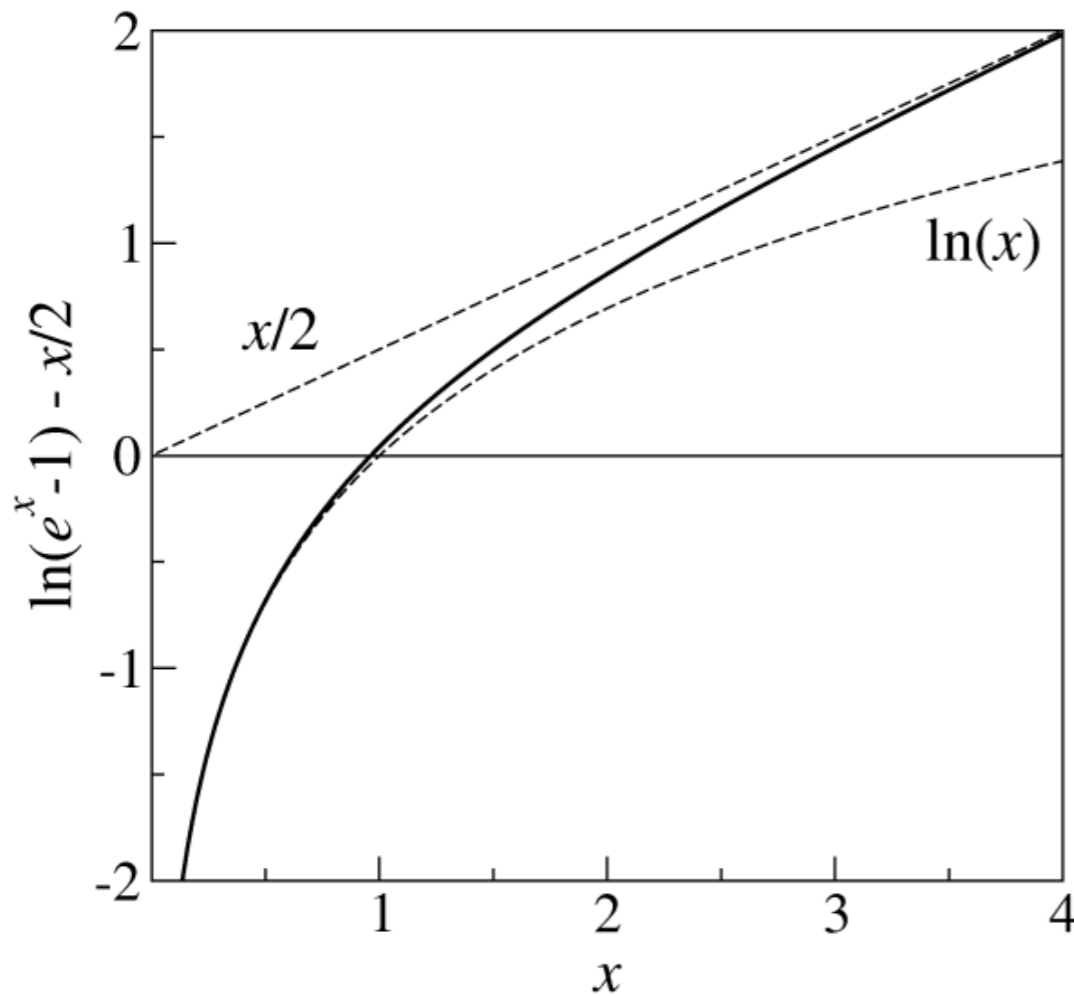
$$S = -\frac{\partial F}{\partial T} = k_B \int_0^{\omega_{\max}} \left[\frac{x}{e^x - 1} - \ln(1 - e^{-x}) \right] g(\omega) d\omega.$$

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

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

vibent : Vibration contributions to entropy

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



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

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.

velcf : Molecular dynamics

Verlet algorithm:

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

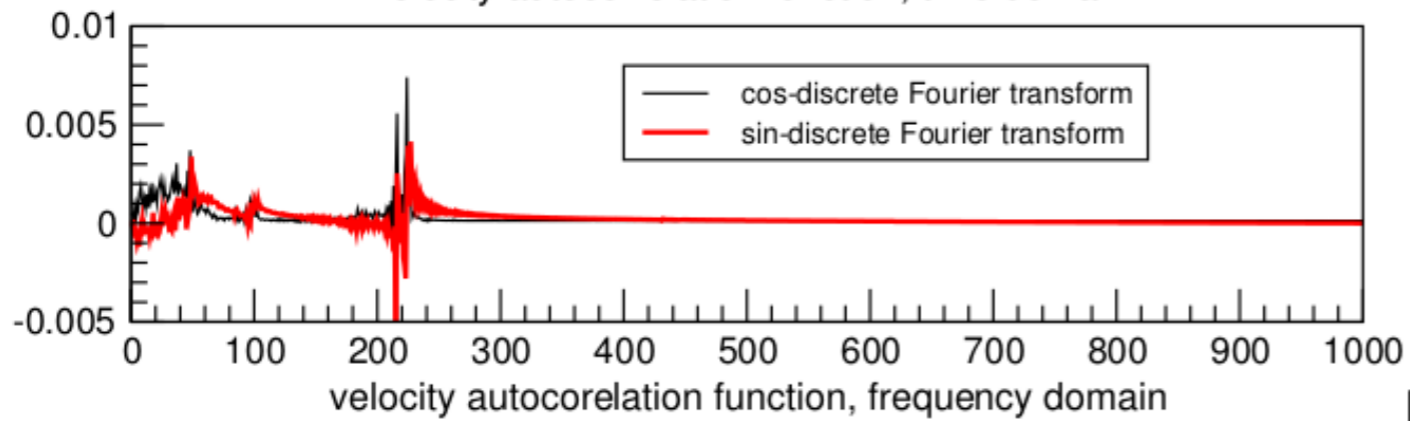
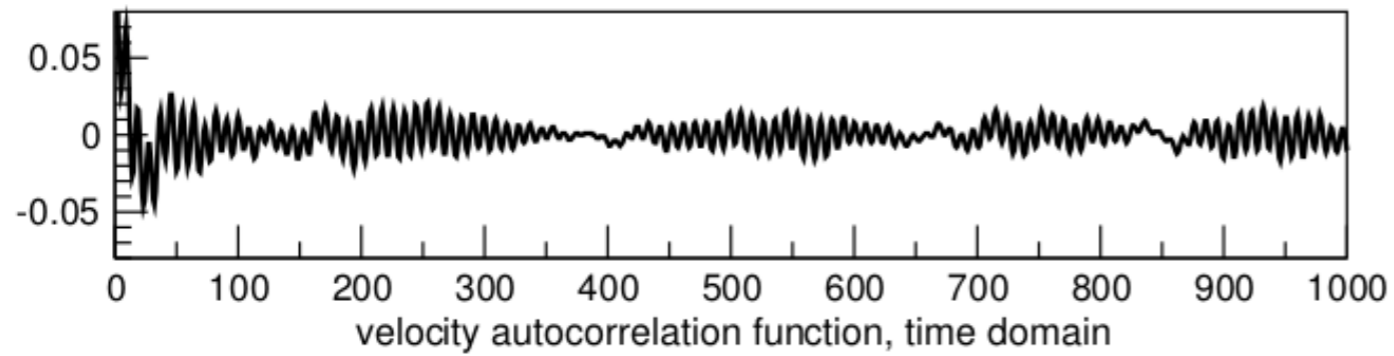
Velocity autocorrelation function:

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

Vibrational density of states:

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

velcf : Molecular dynamics



A test case:
Ni₄ molecular magnet

