

MedeA: MD Phonon: Calculate vibrational properties from MD

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1 Introduction

By applying quantum statistics to the normal vibrational modes of a system thermodynamic properties such as entropy or Helmholtz free energy can be calculated accurately and efficiently. In the *MedeA MD Phonon* module this is done using velocity auto-correlation functions obtained from molecular dynamics simulations.

Key Benefits

- Study systems with low symmetry. For example amorphous systems or crystalline structures with defects.
- Automated plot creation facilitates analysis of results.
- View the plots for velocity auto-correlation functions of each element in each subset
- Study the vibration density of states, its partial contributions of all elements, and all subsets in automatically generated plots on the JobServer and within *MedeA*'s analysis tool.
- Evaluate thermodynamic properties such as internal energy, entropy, Helmholtz free energy, and heat capacity.

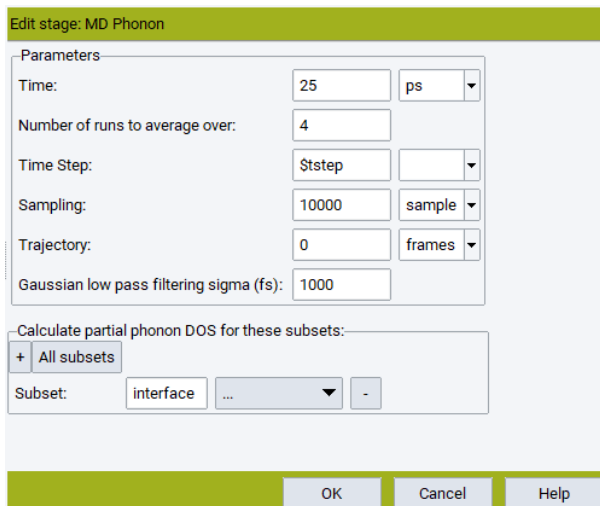
Hint: The *MedeA MD Phonon* module works with *MedeA LAMMPS* classical molecular dynamics simulations. Ab initio MD trajectories are not supported.

2 Setting up a MedeA MD Phonon Simulation

The *MedeA MD Phonon* module can be accessed in a *MedeA LAMMPS* Flowchart by inserting the **MD Phonon** stage into any **LAMMPS** stage. The vibrational density of state is calculated from the velocity auto-correlation function.

Note: Ensure that the structure has been equilibrated prior to the *MD Phonon* stage. Use appropriately configured NPT and NVT stages for this.

The following illustrates the *MedeA MD Phonon* stage:



The parameters are:

- Time:** Duration of a simulation run to calculate the velocity auto-correlation function. The appropriate value for this parameter is, in most cases, between 10 - 100 ps.
 Lower values will reduce the resolution of the calculated vibrational density of states to a too low value. Higher values will not further improve the results. The density of states frequency resolution is defined by the reciprocal of the simulation time. A 1 ps simulation yields a resolution of 1 THz. Increasing this time to 10 ps yields a resolution of 0.1 THz.
- Number of runs to average over:** The specified number of runs with a time length as defined by the variable *time* is performed. These runs are performed in parallel and the calculated velocity auto-correlation functions of each run are then averaged. Increasing this number will provide smoother results. Note, that the total simulation time is defined by $time \times number\ of\ runs$.
- Time step:** Time step size employed in solving the equations of motion in an NVE ensemble.
- Sampling:** Number of samples employed in performing averaging.
- Trajectory:** Number of trajectory frames saved during the molecular dynamics calculation.
- Gaussian low pass filtering sigma (fs):** Define the width of the Gaussian used for the low pass filter in fs. For best results match this value with the decorrelation times of the velocity auto-correlation functions.
- Subset:** One or more subsets of atoms for which partial vibrational density of states and thermodynamic properties are calculated.

3 Assessing the Results

The `Job.out` file provides a brief summary on the calculation setup of the *MD Phonon* stage as well as the calculated thermodynamic properties at the simulated temperature:

Property	Value	+/- Uncertainty	Units	After Steps	% Run
Evib:	45132.2		kJ/mol		
Evib_QC:	17621.5		kJ/mol		
Avib:	34837.2		kJ/mol		
Avib_QC:	9608.6		kJ/mol		
ZPE:	38554.9		kJ/mol		
SvibT:	10295.1		kJ/mol		
Svib:	34499.7		J/K/mol		

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Svib_QC:    26852.0          J/K/mol
Cv:         50859.3          J/K/mol
    
```

The thermodynamic properties printed above are given for the whole structure Al1848N1848 containing in total 3696 atoms.

Thermodynamic properties have been calculated at a temperature of 298.4 K by integrating over the phonon density of states obtained from the molecular dynamics simulation.

Definitions:

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Evib(T)      : vibrational internal energy
Evib_QC(T)   : quantum contributions to vibrational internal energy
Avib(T)      : vibrational Helmholtz free energy
Avib_QC(T)   : quantum contributions to vibrational Helmholtz free energy
ZPE          : zero point energy
SvibT        : vibrational entropy times temperature
Svib(T)      : vibrational entropy
Svib_QC(T)   : quantum contributions to vibrational entropy
Cv(T)        : vibrational heat capacity at constant volume
    
```

If not specified differently the thermodynamic functions contain both the classical and quantum contributions.

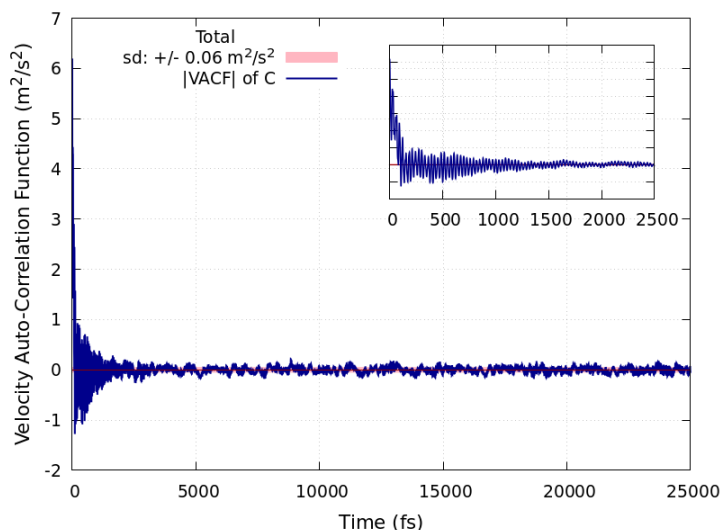
In addition, the calculated thermodynamic properties are provided per formula unit, per subset (as fraction of formula units), and per element.

The following thermodynamic functions are provided for the empirical formula AlN.

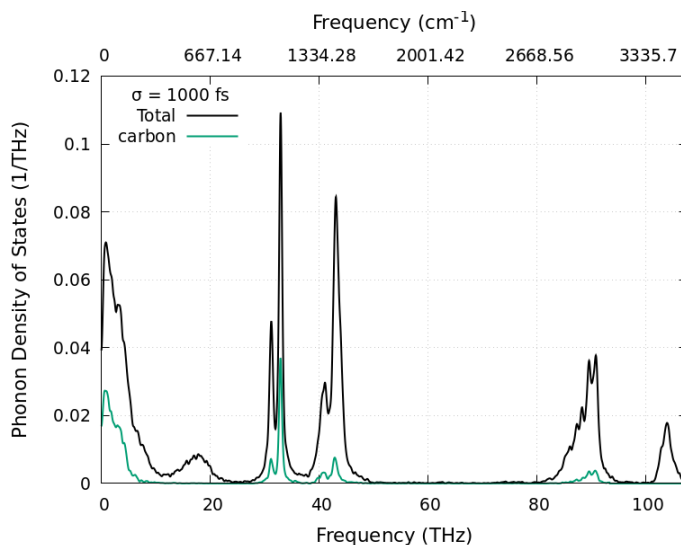
	Evib	Evib_QC	Avib	Avib_QC	ZPE	SvibT	Svib	Svib_QC	Cv
	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	J/K/mol	J/K/mol	J/K/mol
Total:	24.4222	9.5354	18.8513	5.1994	20.8631	5.5709	18.6687	14.5303	27.5213
Al:	10.8269	3.3835	7.1789	1.8176	8.5279	3.6480	12.2246	5.2476	16.4391
N:	13.5930	6.1496	11.6685	3.3806	12.3319	1.9244	6.4489	9.2793	11.0867

Besides information contained in the Job.out file graphical output is provided by the files:

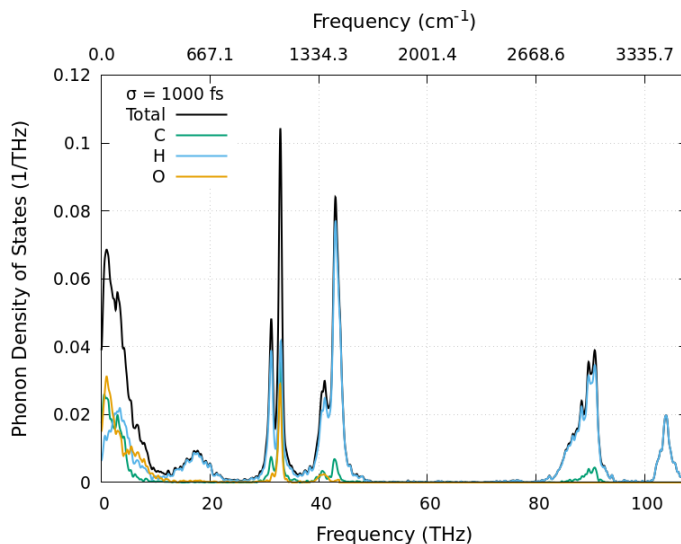
- **VACF<subset>_<element>.avg.png** shows the velocity auto-correlation function of a given subset and element/isotope:



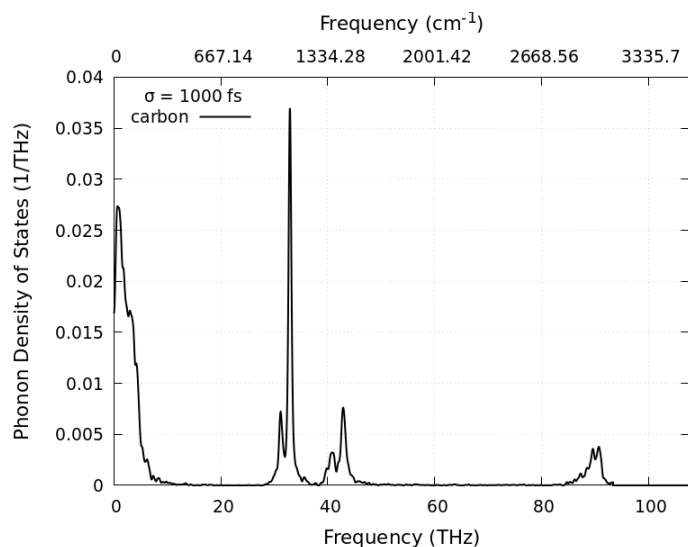
- **phonon_DOS.png** contains the total vibrational density of states and, if subsets were considered, the partial vibrational density of states of each subset:



- **Phonon_DOS_Total.png** contains the total vibrational density of states as well as the partial contributions of each element/isotope:

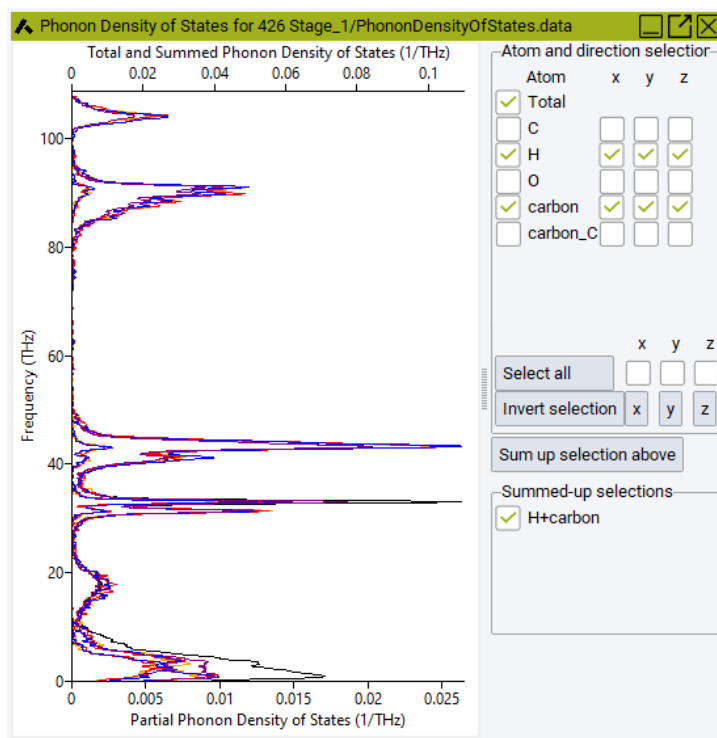


- **Phonon_DOS_subset<number>.png** contains for each subset the partial vibrational density of states as well as the partial contributions of each element/isotope:

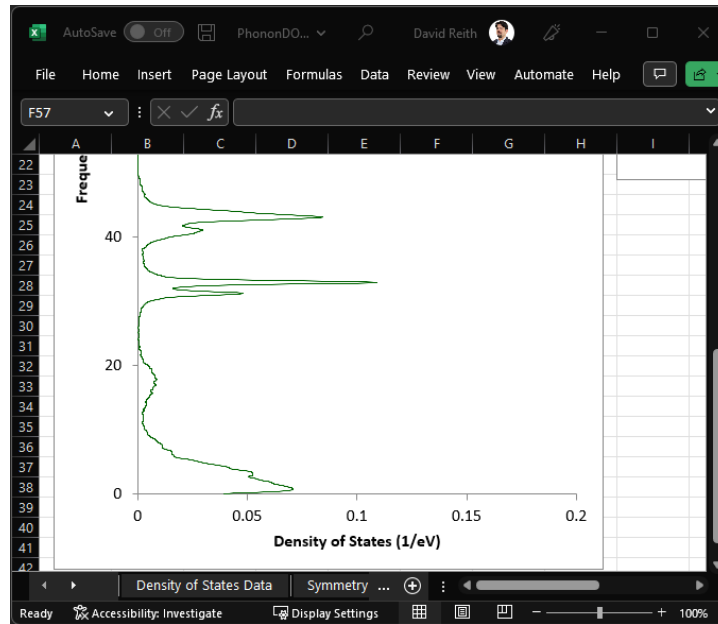


3.1 Viewing Vibrational Density of States in MedeA

By clicking on **Analysis** >> **Phonon Density of States** and selecting the results from the relevant completed job the vibrational density of states can be viewed interactively in *MedeA*. For more information on this refer to the section on viewing the phonon DOS in the *MedeA Phonon* documentation.



On Windows, the vibrational Density of states can also be exported to an Excel spreadsheet with **Analysis** >> **Export Phonon Dispersions and DOS**. The section on exporting DOS in the *MedeA Phonon* documentation provides more information on this functionality.



4 Theoretical Background

The vibrational density of state, $DOS(\omega)$, is defined as the distribution of normal modes of a system [1]. Hence, the vibrational intensity at a given frequency ω is calculated by the sum of all N atomic contributions [2] in the x, y, and z direction, as indicated by the sum over $3k$, at temperature T with

$$DOS(\omega) = \frac{1}{3N(2\pi)^3 k_B T} \sum_{j=1}^N \sum_{k=1}^3 m_j s_j^k(\omega),$$

where m_j defines the mass of atom j and k_B the Boltzmann constant. The spectral density, $s_j^k(\omega)$, can be described by the Fourier transform of the integrated velocity auto-correlation function, $\langle v_j^k(t + \tau) \cdot v_j^k(t) \rangle$. This allows for a rewrite of the equation above to

$$DOS(\omega) = \frac{1}{3N(2\pi)^3 k_B T} \sum_{j=1}^N \sum_{k=1}^3 m_j \int_{-\infty}^{\infty} \langle v_j^k(t + \tau) \cdot v_j^k(t) \rangle e^{-i\omega\tau} d\tau,$$

putting the density of state into direct relation with the velocity auto-correlation function. The velocity auto-correlation function is calculated on-the-fly by LAMMPS during a NVE MD simulation.

Once $DOS(\omega)$ has been established the thermodynamic properties, such as internal energy, entropy, Helmholtz free energy, and heat capacity, can be calculated by appropriate integrals.

Helmholtz free energy:

$$A_{vib} = k_B T \int_{\omega=0}^{\infty} DOS(\omega) \ln \left(2 \sinh \left(\frac{\beta \hbar \omega}{2} \right) \right) d\omega$$

Potential energy:

$$E_{vib} = \frac{1}{2} \int_{\omega=0}^{\infty} DOS(\omega) \hbar \omega \left(\frac{\exp(\beta \hbar \omega) + 1}{\exp(\beta \hbar \omega) - 1} \right) d\omega$$

Entropy:

$$S_{vib} = \frac{E_{vib} - A_{vib}}{T}$$

Specific heat:

$$C_V = k_B \int_{\omega=0}^{\infty} DOS(\omega) (\beta \hbar \omega)^2 \frac{\exp(\beta \hbar \omega)}{(\exp(\beta \hbar \omega) - 1)^2} d\omega$$

In the above equations \hbar stands for the Planck constant and $\beta = 1/(k_B T)$. These equations contain both the classical and quantum mechanical contributions. The classical potential energy can be calculated simply with $E_{vib}^{cl} = 3k_B T$ and the classical Helmholtz free energy with $A_{vib}^{cl} = k_B T \int DOS(\omega) \ln(\beta \hbar \omega) d\omega$.

[1] Peter H. Berens, Donald H. J. Mackay, Gary M. White, and Kent R. Wilson, J. Chem. Phys. **79**, 2375 (1983)

[2] Shiang-Tai Lin, Mario Blanco, and William A. Goddard III, J. Chem. Phys. **119**, 11792 (2003)