Tutorial: Density of states

From GPUMD
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Introduction

- In this example, we calculate the phonon (vibrational) density of states (DOS) of graphene at 300 K and zero pressure. The method is based on the velocity auto-correlation (VAC) function. The DOS is calculated as the Fourier transform of the VAC [Dickey 1969].
- All the input and output files can be found here (https://github.com/brucefan1983/GPUMD/tree/master/examples/gpumd/density_of_states).

Preparing the Inputs

The xyz.in file

- The first few lines of the xyz.in file are:

```
8640 3 2.1 0 0 0
1 1 0 149.649 155.52 3.35
0 1.24708 0 0 12
0 0 0.72 0 12
0 0 2.16 0 12
0 1.24708 2.88 0 12
```

- Explanations for the first line:
  - The first number tells that the number of particles is 8640.
  - The second number 3 in this line is good for graphene described by the Tersoff potential, because no atom can have more than 3 neighbor atoms at room temperature. One can make this number larger, which only results in using more memory. If this number is not large enough, `GPUMD` will give an error message and exit.
  - The next number 2.1 means that the initial cutoff distance for the neighbor list construction is 2.1 angstrom. The point here is that we only need to consider the first nearest neighbors. Therefore, any number larger than the first nearest neighbor distance and smaller than the second nearest neighbor distance is OK here. Note that we will also not update the neighbor list. There is no such need in this problem.
  - The remaining three zeros in the first line mean:
    - the box is orthogonal;

    - the initial velocities are not contained in this file;
    - there are no grouping methods defined here.

- Explanations for the second line:
    - The numbers `1 1 0` mean that the x and y (in-plane) directions are periodic and the z direction is open (free).
    - The remaining three numbers are the box lengths in the three directions. The box length in a free direction is chosen based on some convention. This number will only affect the system volume.

- Starting from the third line, the numbers in the first column are all 0 here, which means that all the atoms are of type 0 (single atom-type system). The next three columns are the initial coordinates of the atoms. The last column gives the masses of the atoms. Here, we consider isotopically pure C-12 crystal. In some applications, one can consider mass disorder in a flexible way.

The `run.in` file

- The `run.in` input file is given below:

```
potential   potentials/tersoff/Graphene_Lindsay_2010_modified.txt 0
velocity    300

ensemble    npt_ber 300 300 0.01 0 0 0 0.0005
time_step   1
dump_thermo 100
run         200000

ensemble    nve
compute_dos 5 200 400.0
run         200000
```

- The first line of command tells that the potential to be used is specified in the file Graphene_Lindsay_2010_modified.txt (https://github.com/brucefan1983/GPUMD/blob/master/potentials/tersoff/Graphene_Lindsay_2010_modified.txt).

- The second line of the command tells that the velocities will be initialized with a temperature of 300 K.

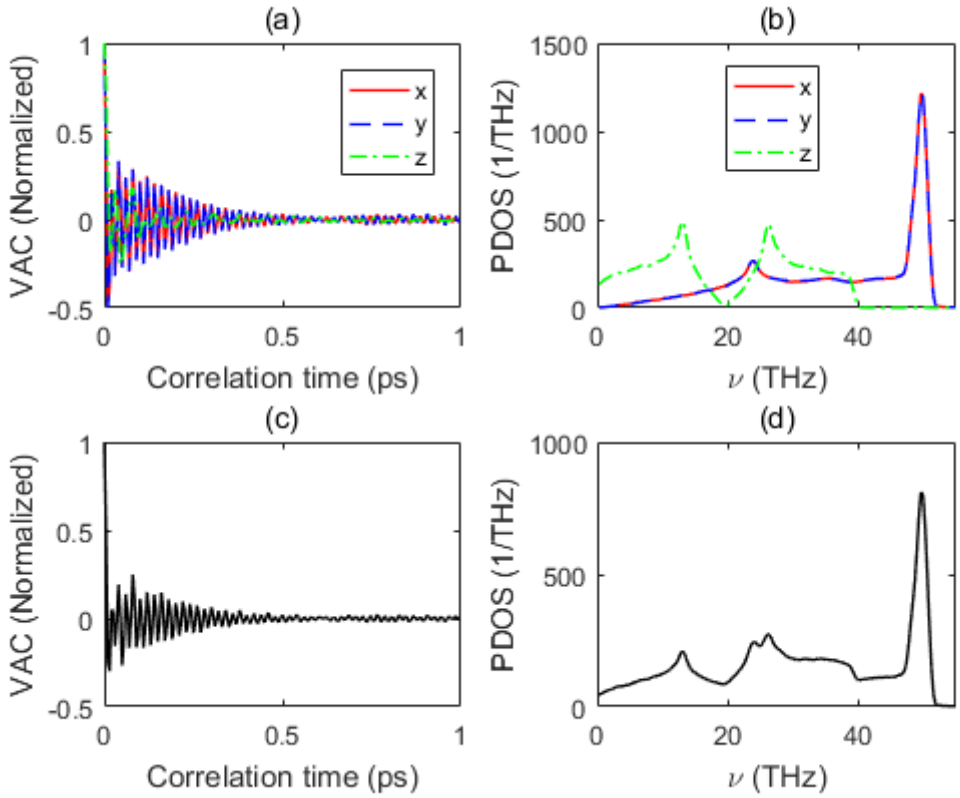
- There are two runs.
    - The first run serves as the equilibration stage, where the NPT ensemble (the Berendsen method) is used. The temperature is 300 K and the pressures are zero in all the directions. The coupling constants are 0.01 (dimensionless) and 0.0005 (in the natural unit system adopted by GPUMD) for the thermostat and the barostat, respectively. The time step for integration is 1 fs. There are 2×10^5 steps (200 ps) for this run and the thermodynamic quantities will be output every 1000 steps.
    - The second run serves as the production run, where the NVE ensemble is used. The line with `compute_dos` means that velocities will be recorded every 5 steps (5 fs) and 200 VAC data (the maximum correlation time is then about 1 ps) will be calculated. The last parameter in this line is the maximum angular frequency considered, $\omega_{\rm max} = 2\pi\nu_{\rm max} = 400$ THz, which is large enough for graphene. The production run lasts 200 ps.

Results and Discussion

Computation time

- This simulation takes about 1.5 min when a Tesla K40 is used.
- The speed of this simulation is about 4×10^7 atom x step / second.

VAC and DOS



(a) Normalized VAC for individual directions. (b) DOS for individual directions. (c) Total Normalized VAC. (d) Total DOS.

- For 3D isotropic systems, the results along different directions are equivalent and can be averaged, but for 2D materials like graphene, it is natural to consider the in-plane part (the x and y directions in the simulation) and the out-of-plane part (the z direction) separately. It can be seen that the two components behave very differently. We can see that the cutoff frequency for the out-of-plane component (about 40 THz) is smaller than that for the in-plane component (about 52 THz).

Quantum corrected heat capacity

- In classical MD simulations, the heat capacity per atom is almost $k_{\rm B}$ even at temperatures that are much lower than the Debye temperature. With the DOS available, one can obtaine the following quantum heat capacity per atom in direction α:

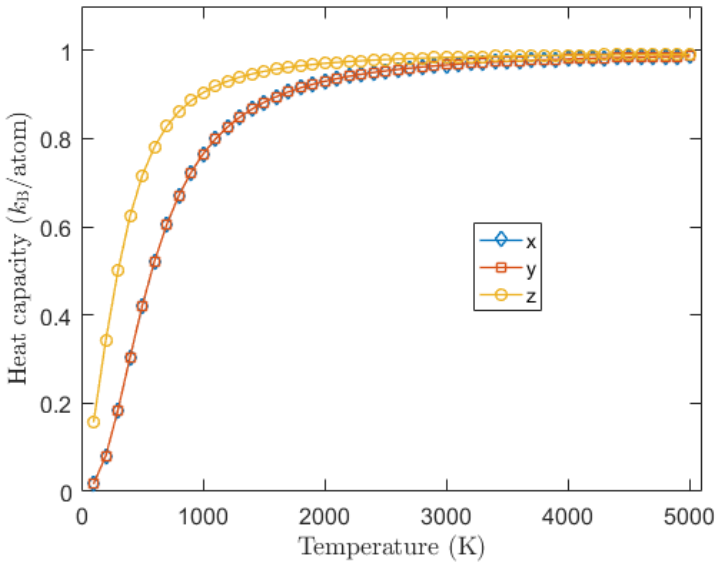
$$C_\alpha(T) = \int_0^\infty \frac{d\omega}{2\pi} \rho_\alpha(\omega) \frac{x^2 \exp(x)}{(\exp(x)-1)^2},$$

where

$$x = \frac{\hbar\omega}{k_{\rm B}T}$$

and $\rho_\alpha(\omega)$ is the density of states in direction α normalized to 1:

$$\int_0^\infty \frac{d\omega}{2\pi} \rho_\alpha(\omega) = 1.$$



Quantum heat capacity per atom as a function of temeprature.

- The above figure shows the calculated per-atom quantum heat capacity in different directions.
- Again, the in-plane (x and y directions) and out-of-plane (z direction) phonons behave differently.
- For every direction, the quantum heat capacity increases from 0 to $k_{\rm B}$ with increasing temperature.
- One can also calculate the Debye temperature as a function of temperature $\Theta(T)$, but we leave it to the reader.

References

- [Dickey 1969] J. M. Dickey and Arthur Paskin, *Computer Simulation of the Lattice Dynamics of Solids* (https://doi.org/10.1103/PhysRev.188.1407), Phys. Rev. **188**, 1407 (1969).