Ionic Conductivity Calculations

This tutorial demonstrates how to calculate the ionic conductivity of lithium ions (Li^+) use the `GPUMD` package. We will use the garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO), a well-known solid electrolyte, as our model system. You will learn how to:

- Compute the mean squared displacement (MSD) of Li^+ ions.
- Derive the diffusion coefficient from MSD data.
- Convert the diffusion coefficient to ionic conductivity using the Nernst-Einstein relation.
- Estimate the activation energy of Li^+ diffusion.

Setup and Resources

To follow this tutorial, you will need the following:

- **Input Structure**: `model.xyz` file for the cubic LLZO (c-LLZO).
- **Potential File**: a well-trained NEP (`nep.txt`) for the c-LLZO system.

In this tutorial, I provide the `NEP25-ZBL` model trained in our previous work [1], which is a NEP trained with only 25 configurations and successfully describes various properties of LLZO, including phase transitions, atomic local environments, and ionic diffusion properties. For more details, refer to arXiv:2504.15925.

Step 1: Simulation Setup

Here is an example input file for performing the simulation at 1000K:

```
potential ../nep.txt
velocity    1000

ensemble    npt_mttk temp 1000 1000 aniso 0 0
run        50000

ensemble    npt_mttk temp 1000 1000 aniso 0 0
compute_msd 10 5000 group 0 0
dump_thermo 100
dump_exyz 1000000
run        1000000
```

Explanation of Input Parameters

- `potential ../nep.txt`: Specifies the NEP file for LLZO.
- `velocity 1000`: Initializes atomic velocities at 1000 K.
- `ensemble npt_mttk temp 1000 1000 aniso 0 0`: Uses the NPT ensemble with the Martyna-Tuckerman-Tobias-Klein thermostat and barostat at 1000 K.
- `run 50000`: Performs a 50 ps equilibrium run.
- `compute_msd 10 5000 group 0 0`: Calculates the MSD of Li^+ ions (group 0). The position data will be recorded every 10 steps, and the maximum number of correlation steps is 5000. See here for details of `compute_msd` command.
- `dump_thermo 100`: Outputs thermodynamic properties to thermo.out every 100 fs.
- `dump_exyz 1000000`: Saves the final configuration as an extxyz file.

- `run 1000000`: Performs a 1 ns production run.

Step 2: Calculating and Visualizing MSD

The MSD quantifies the average distance traveled by Li^+ ions over time, a key quantity for calculating ionic diffusivity. The MSD is calculated using the relation:

$$\mathrm{MSD}(t) = \frac{1}{N}\sum_{i=1}^{N}\left\langle \left|\mathbf{r}_i(t) - \mathbf{r}_i(0)\right|^2 \right\rangle$$

- $\mathbf{r}_i(t)$ is the position of ion (i) at time (t).
- $\mathbf{r}_i(0)$ is the initial position of ion (i).
- N is the number of Li^+ ions.
- $\langle\ \rangle$ denotes the time average.
- $\frac{1}{N}\sum_{i=1}^{N}$ denotes the averages over all Li^+ ions.

After running the simulation, `GPUMD` generates an `msd.out` file containing the MSD data for Li^+ ions. See here for details of `msd.out` file.

Visualizing MSD

The `msd.out` file contains the MSD and self diffusion coefficient (SDC).

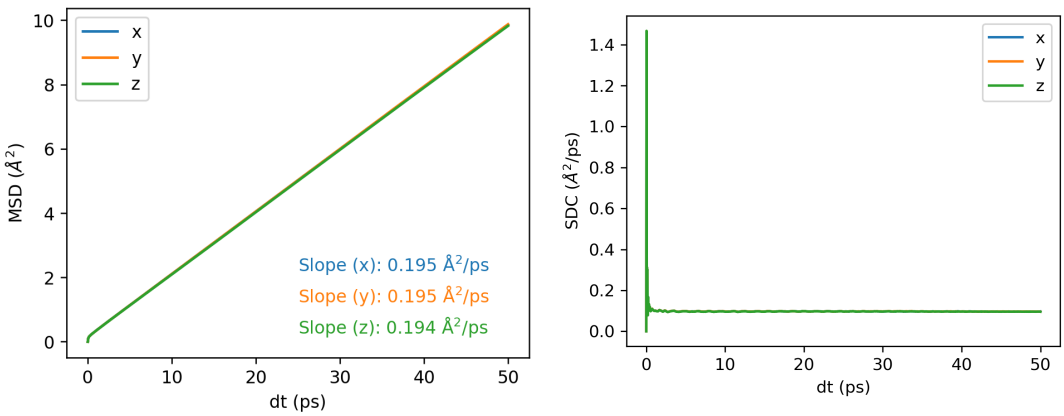
The data in this file are organized as follows:

- **column 1:** correlation time (in units of ps)
- **column 2:** MSD (in units of Å2) in the x direction
- **column 3:** MSD (in units of Å2) in the y direction
- **column 4:** MSD (in units of Å2) in the z direction
- **column 5:** SDC (in units of Å2/ps) in the x direction
- **column 6:** SDC (in units of Å2/ps) in the y direction
- **column 7:** SDC (in units of Å2/ps) in the z direction

You can use any software to visualize the data, here I recommend the plt_msd.py and plt_sdc.py script, which is integrated into the GPUMDkit package and can be called with the following command:

```
gpumdkit.sh -plt msd/sdc
```

then you will see:



Step 3: Calculate Diffusion Coefficient

The **diffusion coefficient (D)** measures the rate of Li^+ ion diffusion in LLZO, a critical step toward calculating ionic conductivity. It is derived from the MSD using the Einstein relation:

$$D = \frac{1}{2N} \lim_{t \to \infty} \frac{d}{dt} \mathrm{MSD}(t)$$

where:

- N is the number of dimensions (e.g., (N = 3) for 3D diffusion in LLZO.
- $\frac{d}{dt}\mathrm{MSD}(t)$ is the slope of the MSD versus time in the diffusive regime, where MSD grows linearly.

The `msd.out` file provides the time (in ps) and MSD components (in $Å^2$). We can fit a straight line in the linear region to obtain the slope (k) (in Å²/ps) and convert the slope to the diffusion coefficient in unit of cm^2/s using:

$$D = \frac{k}{2N} \times 10^{-4}$$

Step 4: Compute Ionic Conductivity

Next, you can calculate the ionic conductivity (σ) from the diffusion coefficient (D) using the ***Nernst-Einstein*** relation:

$$\sigma = \frac{nq^2D}{k_BT}$$

Where:

- n is the number density of ions
- q is the elementary charge
- D is the diffusion coefficient
- k_B is the Boltzmann constant
- T is the temperature

For LLZO, you need the number density (n), which depends on the number of Li^+ ions and the cell volume.

- Count the number of Li^+ ions (N_{ion}) in your `model.xyz` file. Herein, we use a $4 \times 4 \times 4$ supercell of LLZO with 3584 Li^+ ions.
- Obtain the average volume (V) (in $Å^3$) from the `thermo.out` file. Convert to cm^3 ($Å^3 = 10^{-24}\mathrm{cm}^3$).
- $n = \frac{N_{\text{ion}}}{V}$ (in cm^{-3}).

Calculate D and σ by GPUMDkit

In fact, the `function 401` in GPUMDkit can be used to calculate σ easily. You only need to specify the element and charge, then you will get the following results:

```
Number of ions: 3584
Average Volume: 143800.291 Å^3
Average Temperature: 999.928 K
------------------------------
Diffusivity (D):
  D_x: 9.717e-06 cm^2/s
  D_y: 9.724e-06 cm^2/s
```

```
  D_z: 9.665e-06 cm^2/s
  D_total: 9.702e-06 cm^2/s
------------------------------
Ionic Conductivity:
  Sigma_x: 4.503e+02 mS/cm
  Sigma_y: 4.506e+02 mS/cm
  Sigma_z: 4.479e+02 mS/cm
  Sigma_total: 4.496e+02 mS/cm
------------------------------
```

The script reads the `model.xyz` and `thermo.out` files, calculating the `number of ions`, `average volume`, and `average temperature`. If these two files do not exist, you will be asked to enter these parameters manually. Finally, it will output the D and σ like the above one.

Step 5: Determining the Activation Energy

The activation energy (E_a) represents the energy barrier for Li^+ ion diffusion. It is determined by analyzing the temperature dependence of ionic conductivity using the Arrhenius equation:

$$\sigma T = A \exp\left(-\frac{E_a}{k_B T}\right)$$

where:

- σ: Ionic conductivity
- T: Temperature
- A: Pre-exponential factor
- E_a: Activation energy
- k_B: Boltzmann constant

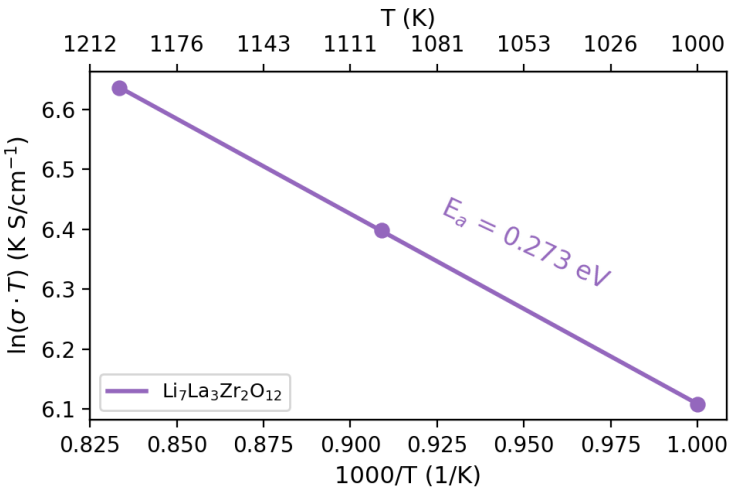
Taking the natural logarithm:

$$\ln(\sigma T) = \ln A - \frac{E_a}{k_B T}$$

Plotting $\ln(\sigma T)$ versus $\frac{1}{T}$ yields a straight line, where the slope is $-\frac{E_a}{k_B}$. Alternatively, using $\frac{1000}{T}$ (in K^{-1}) is common, giving a slope of $-\frac{E_a}{k_B \cdot 1000}$. The activation energy is then:

$$E_a = -\text{slope} \cdot k_B \cdot 1000$$

I provide a `plt_arrhenius.py` script for reference only, and you will get the following figure:



The calculated activation energy of c-LLZO is in good agreement with the literature [2].

References

[1] Zihan Yan, Zheyong Fan and Yizhou Zhu, Improving robustness and training efficiency of machine-learned potentials by incorporating short-range empirical potentials, arXiv:2504.15925.

[2] Zihan Yan and Yizhou Zhu, Impact of Lithium Nonstoichiometry on Ionic Diffusion in Tetragonal Garnet-Type $Li_7La_3Zr_2O_{12}$, *Chem. Mater.* 2024, 36, 23, 11551–11557.