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 SourceFiles and 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).

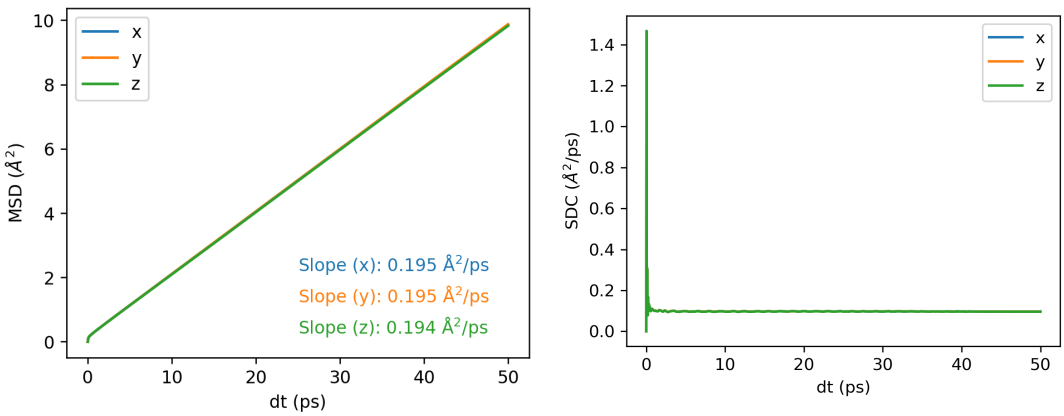
The data in this file are organized as follows:

- **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

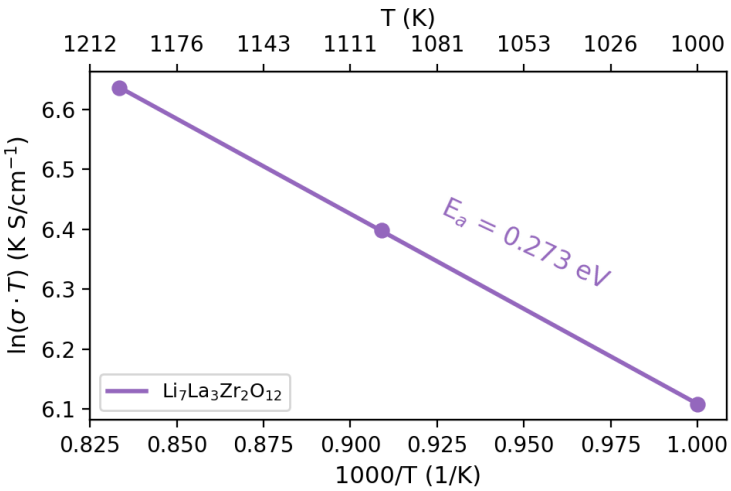
Taking the natural logarithm:

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

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.