A Comparative Study of Molecular Dynamics Approaches for Simulating Ionic Conductivity in Solid Lithium Electrolytes

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1. Introduction

Accurate prediction of ionic conductivity is essential for the design of high-performance solid electrolytes in energy storage applications. In this work, we aim to benchmark various molecular dynamics (MD) approaches to calculate ionic conductivity in 21 solid-state lithium electrolytes for which experimental ionic conductivity has been previously reported in the literature. The simulations will use forces derived from density functional theory (DFT), universal machine learning interatomic potentials (uMLIPs), or uMLIPs fine-tuned on DFT data. uMLIPs are state-of-the-art for enabling large-scale MD simulations, but it remains unclear how accurately MD simulations driven by uMLIPs reproduce emergent transport properties such as ionic conductivity. This motivates a systematic benchmarking against ab initio molecular dynamics. We will examine the impact of different parameters on conductivity calculations, comparing direct room-temperature simulations with Arrhenius extrapolation, as well as the effect of defects. While the present results in the abstract focus on simulations using a MACE [1] uMLIP, the full framework, to be explored in future work, is designed for consistent comparisons across all methods. Our results will highlight the trade-offs between computational efficiency and accuracy across these methods, offering insights for future simulations of lithium solid-state electrolytes. Beyond this specific application, they shall offer a way to quantify the performance of uMLIPs and their fine tuning strategies on long-time-scale diffusion simulations involving many atoms.

1.1 *Related work*

High-throughput and machine-learning-based approaches are now central to the discovery of solid ionic conductors. Early screening frameworks relied on workflows based on physics and molecular dynamics to estimate lithium diffusion across large materials databases [2]. Machine learning was subsequently introduced as a data-driven pre-screening tool to prioritize promising Li-ion conductors and reduce the cost of first-principles simulations [3], and later combined with cloud high-performance computing to enable screening of tens of millions of candidates with experimental validation of selected solid electrolytes [4]. More recently, machine-learned interatomic potentials have been used to model ion diffusion directly through MD in representative electrolytes [5], while other studies have leveraged uMLIPs or ML models to infer transport trends [6] or predict migration barriers [7], without running MD. Generative modeling has also been used to accelerate MD simulations in Lithium solid electrolytes [8].

1.2 *Contributions*

Although the above-mentioned works share conceptual overlap with the present study, our approach introduces **three key contributions**:

1. **A consistent dataset:** We consider a relatively large set of materials for which ionic conductivities have been experimentally measured, enabling a direct and systematic comparison between simulations and experiment.

2. **A unified procedure** We propose a unified procedure for ionic conductivity estimation that standardizes parameter choices and uncertainty quantification, providing a statistically meaningful basis for data-driven comparison across methods.

3. **A comparison of multiple simulation approaches:** Within this dataset, we assess the performance of several simulation methods—ab initio molecular dynamics as well as both general and fine-tuned uMLIPs—and how they compare to experiment using an identical simulation protocol.

2. Methods

2.1 *Ionic Conductivity from Molecular Dynamics Simulations*

Room temperature ionic conductivity σ is a key property that characterizes ion transport in solid state materials. One approach to extract σ is to use MD simulations, which track the time evolution of atoms in a material based on Newton's equations of motion. These simulations allow the study of ionic diffusion at finite temperatures by modeling atomic interactions through different levels of theory, DFT, empirical potentials, or uMLIPs. After performing an MD simulation, the self diffusion coefficient D for mobile ions (in this case, lithium ions) is obtained using the Einstein relation

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

where $d = 3$ is the system's dimensionality and $\mathrm{MSD}(t)$ is the per ion mean square displacement at time t. In practice, D is calculated from the slope of the $\mathrm{MSD}(t)$ plot over a finite time window. Once D is determined, the ionic conductivity σ is obtained via the Nernst-Einstein relation

$$\sigma(T) = \frac{Nq^2 D(T)}{V k_B T}, \tag{2}$$

where N is the total number of lithium ions, q is the charge of the diffusing ion, V is the cell volume, k_B is the Boltzmann constant and T is the temperature. Because room-temperature ionic conductivity requires long MD timescales, which are computationally prohibitive, especially for ab initio MD (AIMD), simulations are instead performed at higher temperatures. The diffusion coefficients extracted at these temperatures are used to fit the Arrhenius equation:

$$D(T) = D_0 \exp\left(-\frac{E_a}{k_B T}\right), \tag{3}$$

where E_a is the activation energy. This relation is then extrapolated to estimate the conductivity at room temperature. Despite the widespread use of the Arrhenius fitting, strict Arrhenius behavior is not universal and deviations have been observed [9].

2.2 *Materials and parameters choice*

A set of 21 materials covering a wide range of ionic conductivities were selected from the OBELiX database [10], a collection of synthesized solid electrolytes and their experimentally measured room-temperature conductivities compiled from the literature. Further details are provided in Appendix A.

We considered three classes of force calculators: fully *ab initio* calculations, uMLIPs, and uMLIPs finetuned on DFT data. In the present work, we focus on a single uMLIP, namely the MACE model [1], using the `medium-mpa-0` checkpoint. We are currently working on extending this benchmark to other uMLIPs.

In our procedure, MD simulations were performed on supercells with minimum dimensions of 10Å × 10Å×10Å [1]. From these simulations, for each material, we obtained the diffusion coefficient D at 5 different temperatures that we then used to fit (3) and obtain the extrapolated room temperature diffusion coefficient $D(T = 300\mathrm{K})$. Simulations were carried out at temperatures ranging from 800 to 1200 K in 100 K increments in the NVT ensemble using a Nosé–Hoover thermostat and a time step of 2 fs. Each MD trajectory was 100 ps long, with the first 5 ps discarded prior to diffusion analysis. MD simulations using MACE models were carried out with the Atomic Simulation Environment (ASE) [11]. AIMD and finetuning results are not presented in this abstract, as they are part of ongoing work. The parameters planned for these simulations are detailed in Appendix B.

Uncertainty estimation for diffusion coefficients was carried out using the `Kinisi-2.0.1` package [12, 13]. In this framework, ionic diffusion is statistically analyzed by modeling atomic displacements over time and propagating their uncertainties to obtain confidence intervals on the diffusion coefficient. The parameters used in the documentation examples were used throughout and no ablation study was conducted to assess sensitivity to these settings.

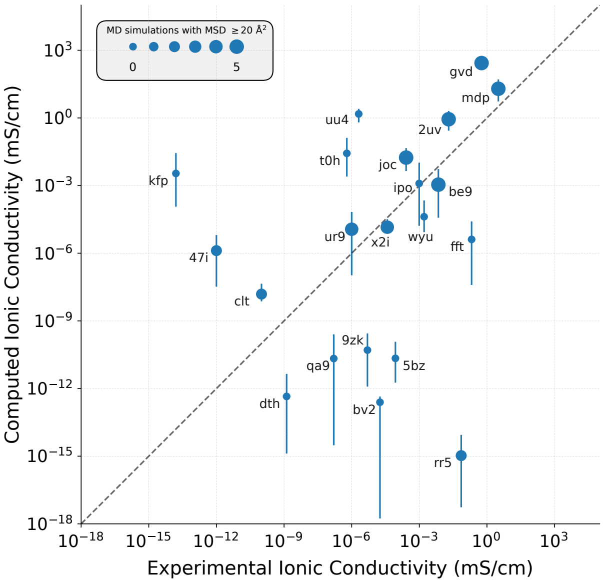

Fig. 1: Parity plot comparing computed ionic conductivity using the MACE foundation model with experimental values reported in [10]. The size of the circles reflect the number of simulations that reached at least MSD = 20 Å^2.

For each material, as a measure of reliability, we also report how many of the five simulations (one for each temperature) had at least some ionic movement (MSD = 20 Å^2).

3. Preliminary results

In this section, we present preliminary results for the analysis discussed above. Figure 1 shows a parity plot of the predicted ionic conductivity using the MACE foundation model versus the experimental values reported in [10]. The materials are labeled with their corresponding names in OBELiX. The chemical formulas are given in Appendix A. We are currently working on similar plots for the other calculators.

The figure also shows how many of the 5 MD simulations had MSD above threshold for each material. We observe that the five materials passing all checks have predicted conductivities close to the experimental values. Some materials, namely fft (β-Li_3N) and rr5 ($LiTi_2(PO_4)_3$), which are known to exhibit high diffusion experimentally, show little diffusion in our simulations. We anticipate that a diffusion mechanism mediated by a small concentration of defects—either not significant enough to be reported in experiments or not directly measurable—is necessary for diffusion in these cases. Future work will extend this analysis.

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[1] Exceptions were made for AIMD simulations. See Appendix B.

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References

[1] Ilyes Batatia, Philipp Benner, Yuan Chiang, Alin M. Elena, Dávid P. Kovács, Janosh Riebesell, Xavier R. Advincula, Mark Asta, William J. Baldwin, Noam Bernstein, Arghya Bhowmik, Samuel M. Blau, Vlad Cărare, James P. Darby, Sandip De, Flaviano Della Pia, Volker L. Deringer, Rokas Elijošius, Zakariya El-Machachi, Edvin Fako, Andrea C. Ferrari, Annalena Genreith-Schriever, Janine George, Rhys E. A. Goodall, Clare P. Grey, Shuang Han, Will Handley, Hendrik H. Heenen, Kersti Hermansson, Christian Holm, Jad Jaafar, Stephan Hofmann, Konstantin S. Jakob, Hyunwook Jung, Venkat Kapil, Aaron D. Kaplan, Nima Karimitari, Namu Kroupa, Jolla Kullgren, Matthew C. Kuner, Domantas Kuryla, Guoda Liepuoniute, Johannes T. Margraf, Ioan-Bogdan Magdău, Angelos Michaelides, J. Harry Moore, Aakash A. Naik, Samuel P. Niblett, Sam Walton Norwood, Niamh O'Neill, Christoph Ortner, Kristin A. Persson, Karsten Reuter, Andrew S. Rosen, Lars L. Schaaf, Christoph Schran, Eric Sivonxay, Tamás K. Stenczel, Viktor Svahn, Christopher Sutton, Cas van der Oord, Eszter Varga-Umbrich, Tejs Vegge, Martin Vondrák, Yangshuai Wang, William C. Witt, Fabian Zills, and Gábor Csányi. A foundation model for atomistic materials chemistry. 2023.

[2] Leonid Kahle, Aris Marcolongo, and Nicola Marzari. High-throughput computational screening for solid-state li-ion conductors. *Energy & Environmental Science*, 13(3):928–948, 2020.

[3] Austin D Sendek, Ekin D Cubuk, Evan R Antoniuk, Gowoon Cheon, Yi Cui, and Evan J Reed. Machine learning-assisted discovery of solid li-ion conducting materials. *Chemistry of Materials*, 31(2):342–352, 2018.

[4] Chi Chen, Dan Thien Nguyen, Shannon J Lee, Nathan A Baker, Ajay S Karakoti, Linda Lauw, Craig Owen, Karl T Mueller, Brian A Bilodeau, Vijayakumar Murugesan, et al. Accelerating computational materials discovery with machine learning and cloud high-performance computing: from large-scale screening to experimental validation. *Journal of the American Chemical Society*, 146(29):20009–20018, 2024.

[5] Natascia L Fragapane and Volker L Deringer. Li-ps electrolyte materials as a benchmark for machine-learned interatomic potentials. *arXiv preprint arXiv:2511.16569*, 2025.

[6] Artem Maevskiy, Alexandra Carvalho, Emil Sataev, Volha Turchyna, Keian Noori, Aleksandr Rodin, AH Neto, and Andrey Ustyuzhanin. Predicting ionic conductivity in solids from the machine-learned potential energy landscape. *arXiv preprint arXiv:2411.06804*, 2024.

[7] Artem D Dembitskiy, Innokentiy S Humonen, Roman A Eremin, Dmitry A Aksyonov, Stanislav S Fedotov, and Semen A Budennyy. Benchmarking machine learning models for predicting lithium ion migration. *npj Computational Materials*, 11(1):131, 2025.

[8] Juno Nam, Sulin Liu, Gavin Winter, KyuJung Jun, Soojung Yang, and Rafael Gómez-Bombarelli. Flow matching for accelerated simulation of atomic transport in crystalline materials. *Nature Machine Intelligence*, pages 1–11, 2025.

[9] Ji Qi, Swastika Banerjee, Yunxing Zuo, Chi Chen, Zhuoying Zhu, ML Holekevi Chandrappa, Xiangguo Li, and Shyue Ping Ong. Bridging the gap between simulated and experimental ionic conductivities in lithium superionic conductors. *Materials Today Physics*, 21:100463, 2021.

[10] Félix Therrien, Jamal Abou Haibeh, Divya Sharma, Rhiannon Hendley, Leah Wairimu Mungai, Sun Sun, Alain Tchagang, Jiang Su, Samuel Huberman, Yoshua Bengio, et al. Obelix: A curated dataset of crystal structures and experimentally measured ionic conductivities for lithium solid-state electrolytes. *arXiv preprint arXiv:2502.14234*, 2025.

[11] Ask Hjorth Larsen, Jens Jørgen Mortensen, Jakob Blomqvist, Ivano E Castelli, Rune Christensen, Marcin Dułak, Jesper Friis, Michael N Groves, Bjørk Hammer, Cory Hargus, et al. The atomic simulation environment—a python library for working with atoms. *Journal of Physics: Condensed Matter*, 29(27):273002, 2017.

[12] Andrew R McCluskey, Samuel W Coles, and Benjamin J Morgan. Accurate estimation of diffusion coefficients and their uncertainties from computer simulation. *Journal of Chemical Theory and Computation*, 21(1):79–87, 2024.

[13] Andrew R McCluskey, Alexander G Squires, Josh Dunn, Samuel W Coles, and Benjamin J Morgan. kinisi: Bayesian analysis of mass transport from molecular dynamics simulations. *Journal of Open Source Software*, 9(94):5984, 2024.

[14] Georg Kresse and Jürgen Furthmüller. Computational mater. *Sci*, 6(1):15, 1996.

[15] Georg Kresse and Jürgen Furthmüller. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical review B*, 54(16):11169, 1996.

[16] Georg Kresse and Jürgen Hafner. Ab initio molecular dynamics for liquid metals. *Physical review B*, 47(1):558, 1993.

[17] Georg Kresse and Daniel Joubert. From ultrasoft pseudopotentials to the projector augmented-wave method. *Physical review b*, 59(3):1758, 1999.

Appendix A. Materials Selection

As mentioned before, the materials were selected from the OBELiX database [10]. As a first filter, only materials with fully occupied sites were considered to avoid complexities related to partial occupancies. For this subset, the range of ionic conductivities was divided on a logarithmic scale into 20 equal bins, from $\sigma = 10^{-7}$ mS/cm^2 to the highest measured value in the dataset, 25 mS/cm^2. Two bins were empty, and one material was randomly selected from each of the remaining 18 bins. To include poorly conducting materials, the lower conductivity range, $\sigma = 10^{-15}$–10^{-7} mS/cm^2, was further divided into four equal bins, from which one material per bin was selected, resulting in a total of 22 materials. MD simulations using the MACE uMLIP failed for $LiClC_3H_7NO$, and therefore this material was excluded from further analysis. This procedure resulted in a total of 21 materials. Table A1 gives the chemical formulas of the selected materials.

Table A1: Selected materials and their chemical formulas.

OBELiX ID	Reduced chemical formula
qa9	Li_3BN_2
t0h	Li_2ZrO_3
ur9	$LiZr_2(PO_4)_3$
uu4	$LiVO_3$
9zk	Li_5GaO_4
bv2	$LiYO_2$
x2i	$LiBiO_2$
5bz	Li_3BN_2
joc	Li_3PS_4
ipo	$Li_7La_3Hf_2O_{12}$
wyu	$Li_7La_3Zr_2O_{12}$
be9	$LiGaBr_4$
2uv	Li_4SnSe_4
rr5	$LiTi_2(PO_4)_3$
goi	$LiClC_3H_7NO$
fft	β-Li_3N
gvd	α-Li_3N
mdp	$Li_7P_3S_{11}$
dth	Li_4GeO_4
clt	$Li_6CuB_4O_{10}$
47i	$Li_4P_2O_7$
kfp	$Li_2BaP_2O_7$

Appendix B. AIMD and Finetuning Parameters

AIMD simulations were performed using the Vienna *Ab initio* Simulation Package (VASP) [14, 15, 16, 17], employing a minimal Γ-centered $1 \times 1 \times 1$ k-point grid to reduce computational cost and an energy cutoff of 520 eV. Regarding the supercell size, exceptions to minimum dimensions of 10Å×10Å×10Å were made for AIMD simulations of materials Li_5GaO_4, $LiTi_2(PO_4)_3$, and $LiZr_2(PO_4)_3$, for which only primitive cells were used to keep the number of atoms computationally feasible, and for $Li_6CuB_4O_{10}$, where one lattice dimension was not expanded beyond 10 Å. In all cases, the remaining dimensions were at least 8 Å.

Fine-tuning of the MACE model was performed using configurations sampled from MD trajectories generated with the foundation model. For each material, 50 structures were uniformly selected from each of five MD runs, yielding a total of 250 configurations. Single-point DFT calculations were then performed on these configurations to obtain energies and forces, which were used to fine-tune the uMLIP. All fine-tuning hyperparameters followed the MACE tutorial recommendations and examples, and no additional hyperparameter optimization was performed.