A Study of Advancements in Ionic Conductivity Methods and Machine Learned Interatomic Potentials to Calculate Ionic Conductivities with a Model Solid Electrolyte $(Li_4SiO_4)_x(Li_3PO_4)_{1-x}$

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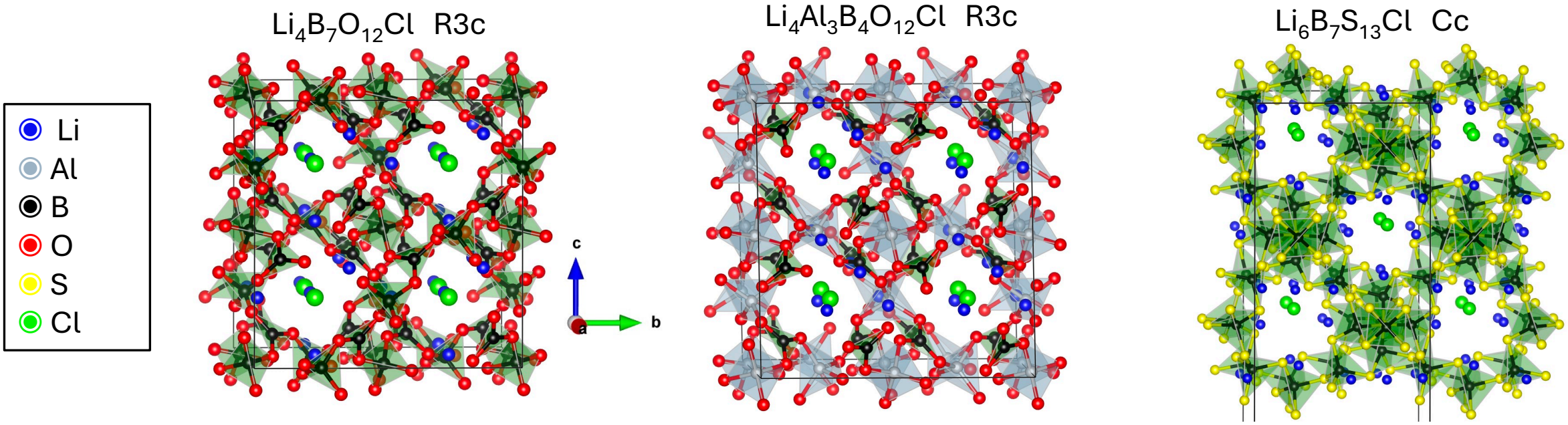
Previous Lithium (Thio)Boracite Investigation

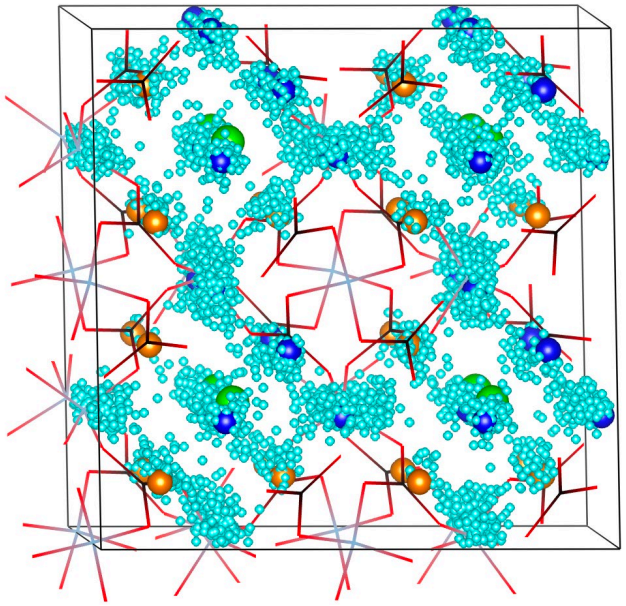


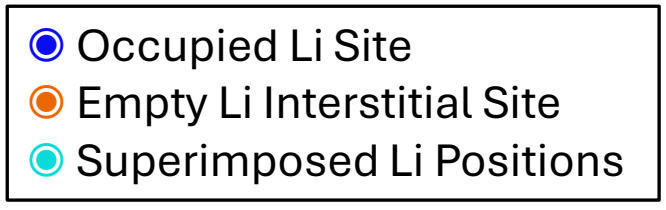
$Li_4B_7O_{12}Cl$ (left) and $Li_4Al_3B_4O_{12}Cl$ (center) rhombohedral R3c ground state structures and $Li_6B_7S_{13}Cl$ (right) monoclinic ground state structure

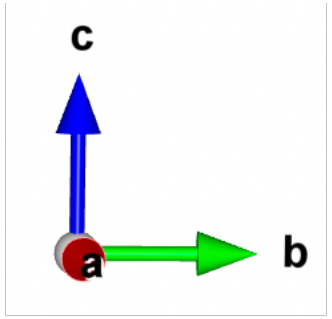
- Previous investigation into the family of 8 Lithium (Thio)Boracite materials as solid-state electrolytes consisting of 3 known and experimentally studied materials and 5 newly predicted materials
- Investigation gave insight into ground state structures and symmetries, phonon band structures and dynamic stability, and chemical stability through convex hull and voltage window analyses

Limitations of Current Methodologies

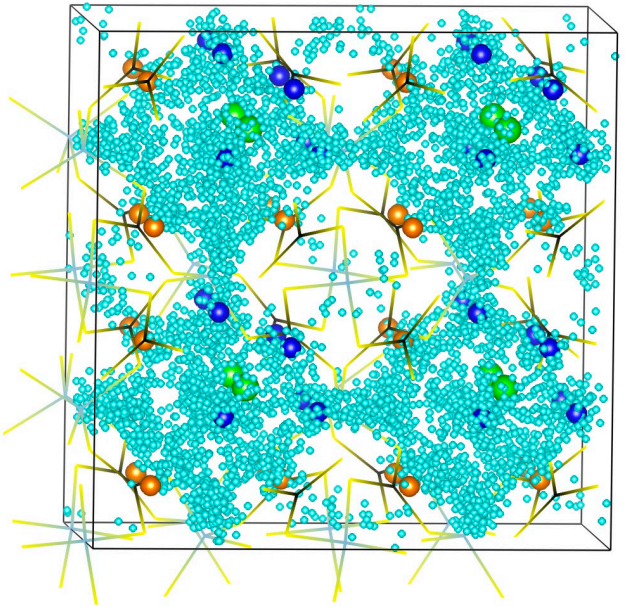
$Li_4Al_3B_4O_{12}Cl$ R3c







$Li_4Al_3B_4S_{12}Cl$ R3c

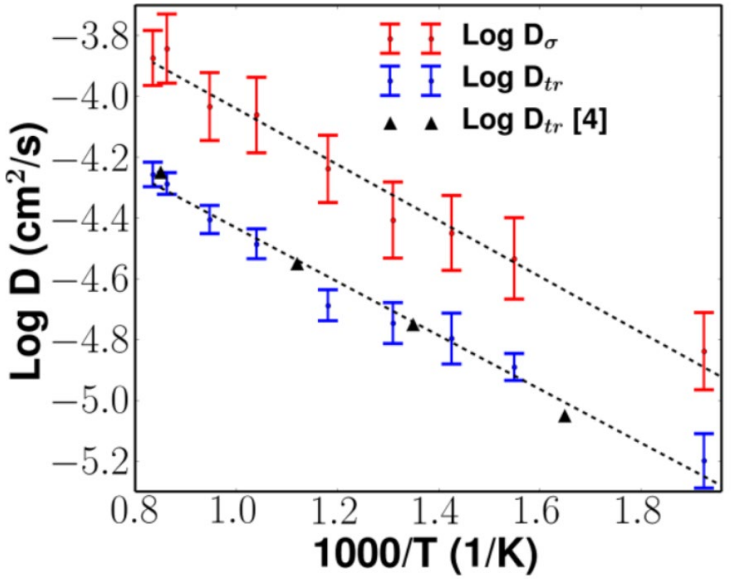


$Li_4Al_3B_4O_{12}Cl$ (left) and $Li_4Al_3B_4S_{12}Cl$ (right) Li-ion Superposition plots

- Lithium superposition plots qualitatively hint at good ionic diffusion
- Li positions superimposed over ~23 ps of simulation time
- Sampled every 50 timesteps at 1100K simulation temperature
- The desire to quantify ionic conductivity in these materials ran into computational roadblocks because of the large simulation cells for which AIMD methods can simulate only 0.12 ps per day

Conductivity Calculations

Comparison of Tracer vs Full Conductivity



$$\sigma_{Full} = \frac{\Omega}{6k_B T} \lim_{\tau \to \infty} \frac{1}{\tau} \langle |\boldsymbol{P}(\tau + t_i) \cdot \boldsymbol{P}(t_i)|^2 \rangle_{t_i}$$

$$\boldsymbol{P}(t) = \frac{1}{\Omega} \sum_i q_i \boldsymbol{r_i}(t)$$

Ω = volume

N_D = num. diffusing ions

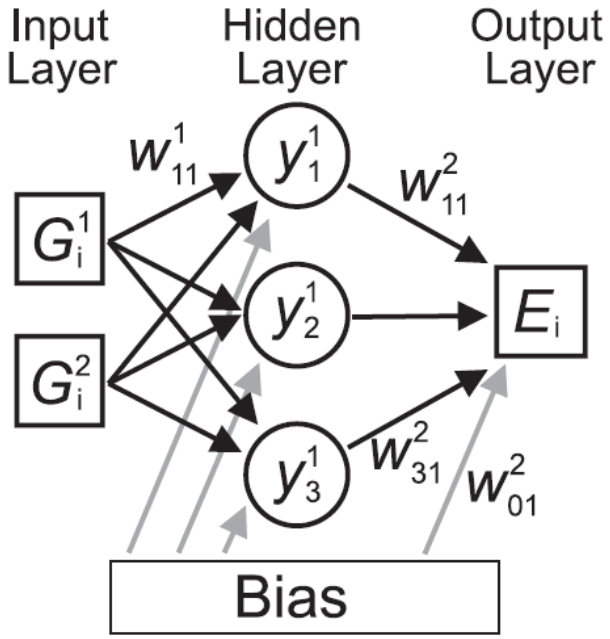
$$\sigma_{Tr} = \frac{q_D^2 N_D}{\Omega k_B T} \lim_{\tau \to \infty} \frac{1}{\tau} MSD(\tau)$$

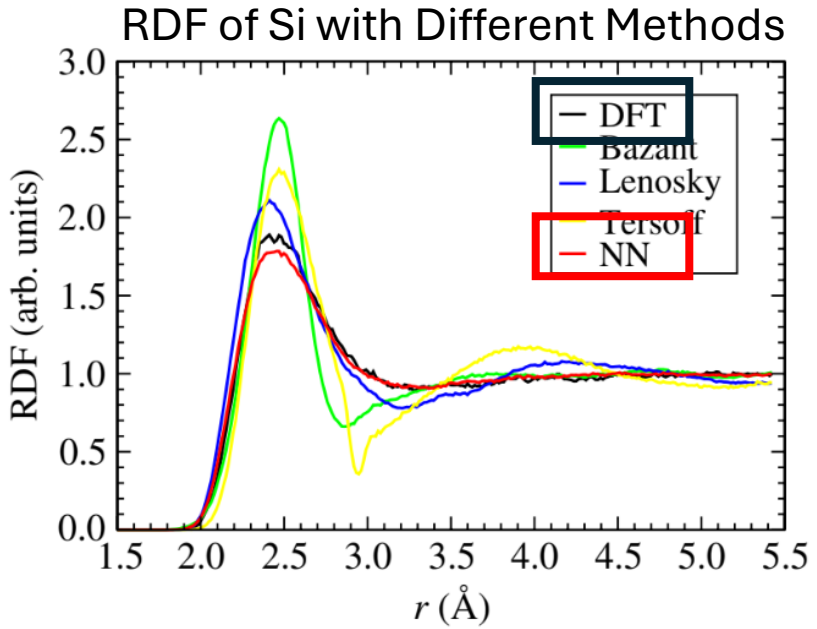
$$MSD(\tau) = \frac{1}{6N_D} \left\langle \sum_{j \in D} \left| \boldsymbol{r_j}(\tau + t_i) - \boldsymbol{r_j}(t_i) \right|^2 \right\rangle_{t_i}$$

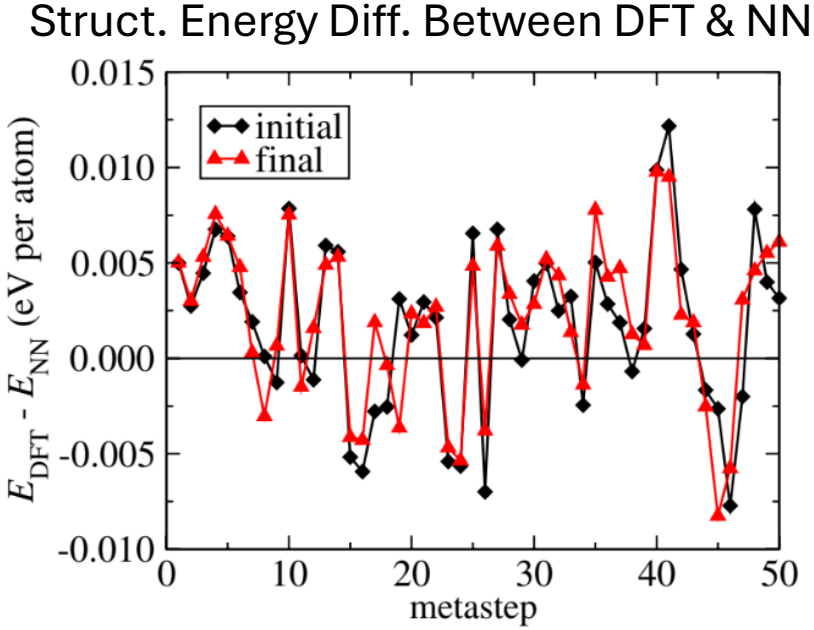
Marcolongo and Marzari 2017 (DOI: 10.1103/PhysRevMaterials.1.025402): Difference in full conductivity and Tracer approx. for $Li_{10}GeP_2S_{12}$ when ions are highly correlated (left) ; full and approx. conductivity equations (right)

- Historically, ionic conductivity results have been approximated by using the Tracer conductivity based on the MSD of the mobile ions
- It turns out for ionic conductors that are highly correlated, this is not a good approximation – we need to include correlated effects
- This can be done with the Green-Kubo formalism, but has historically been impossible due to the long simulation times needed for correlations

Machine Learned Interatomic Potentials



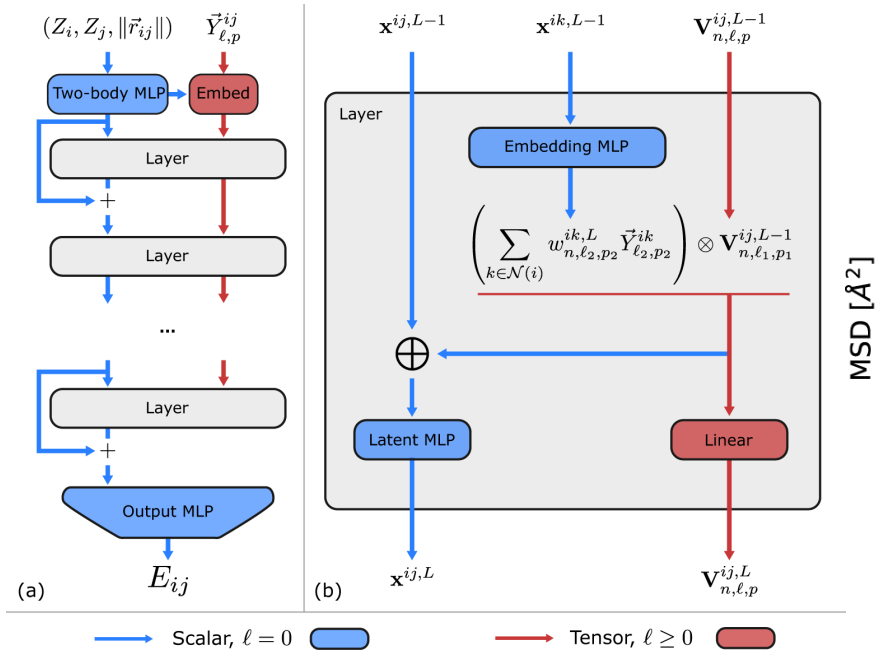


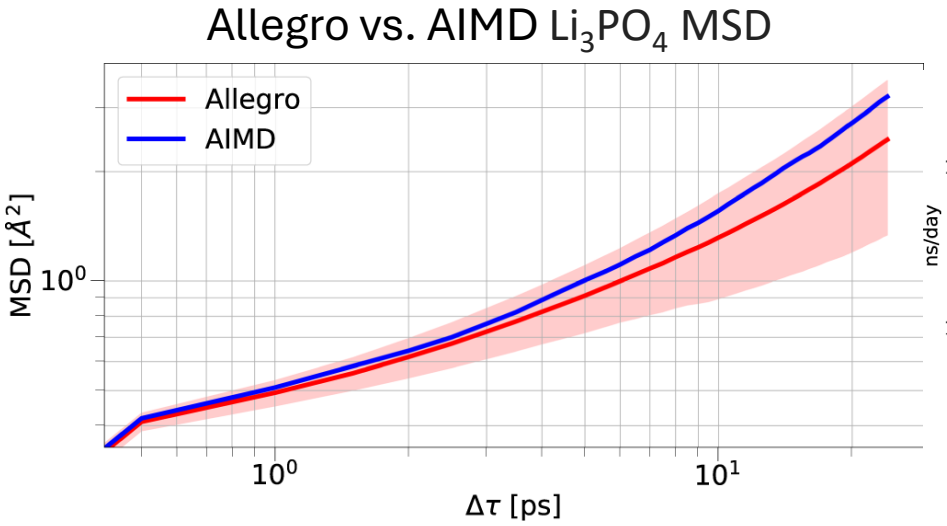


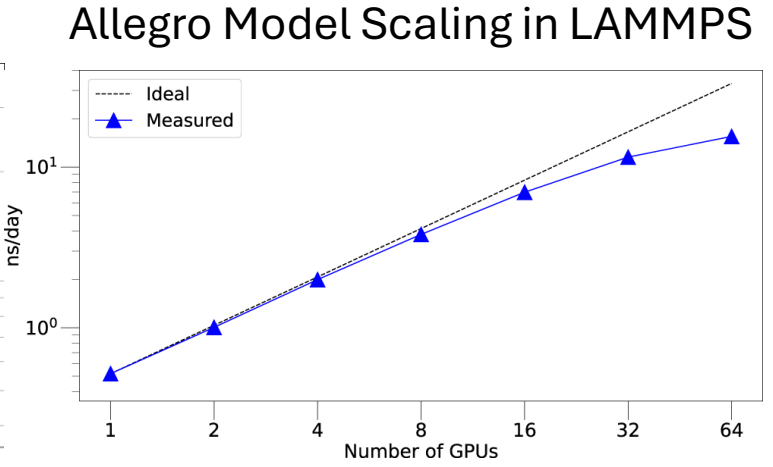
Behler and Parrinello 2007 (DOI: 10.1103/PhysRevLett.98.146401): NN based MLIP arch (left) trained on Si MD data; RDF function (center) and structural energies of initial and final structures at each MD metastep (right) compare well to MD

- Recent advancements in using machine learning tools to “learn” interatomic potential functions have been promising
- Basic idea is to “train” a machine learning model with AIMD data so that it can “learn” an accurate potential function that is fast
- Promises near AIMD accuracy with orders of magnitude speedup
- Common methods include various neural network approaches

Allegro Architecture from MIR Harvard Group





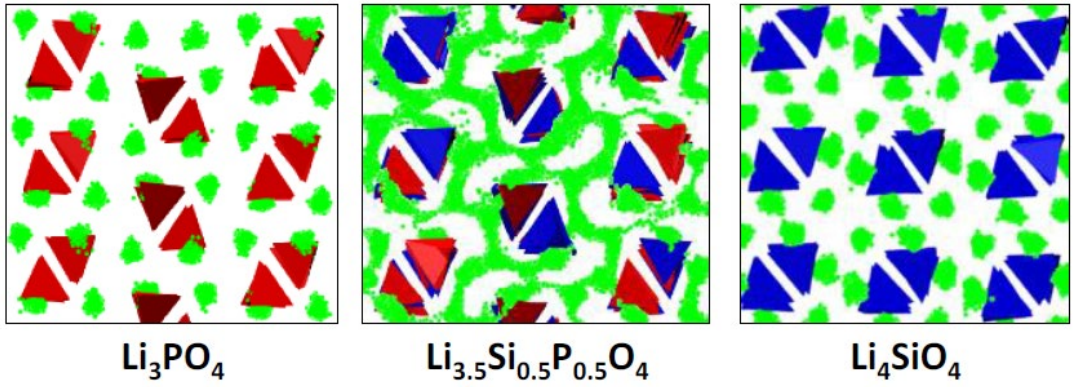


Musaelian, Batzner, Kozinsky, et. al. 2023 (DOI: 10.1038/s41467-023-36329-y): Allegro Graph Network architecture (left); MSD comparison between Allegro and AIMD for Li_3PO_4 (center); Allegro performance and scalability (right)

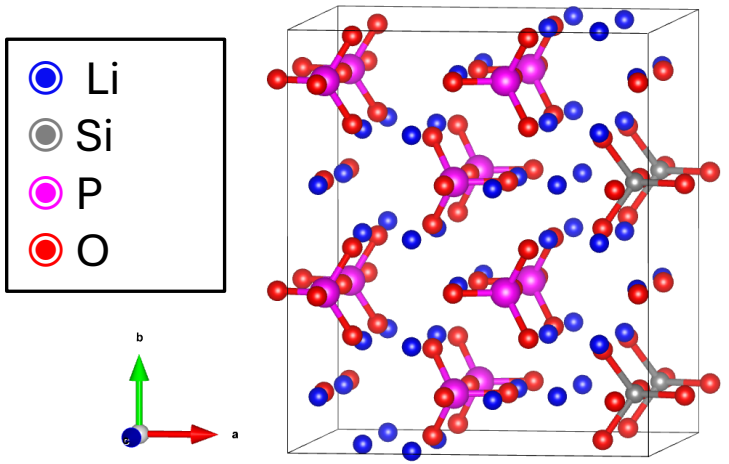
- The Allegro MLIP software is a Graph Network architecture with strictly local message passing between pair centered graph embeddings
- Utilizes equivariant tensor features composed of spherical harmonic irreducible representations of SO(3) – 3D rotations and translations
- Allegro is a highly scalable and fast architecture with good accuracy

Model Solid Electrolyte $(Li_4SiO_4)_x(Li_3PO_4)_{1-x}$

Li_3PO_4 , $Li_{3.5}Si_{0.5}P_{0.5}O_4$, and Li_3SiO_4



$(Li_4SiO_4)_{0.25}$ $(Li_3PO_4)_{0.75}$



Deng et. al. 2015 (DOI: 10.1021/jacs.5b04444): Lithium superposition plots showing good lithium-ion mobility with lithium silicate / lithium phosphate mixing (left); our model structure containing 75% Li_3PO_4 and 25% Li_4SiO_4 (right)

- Goal is to investigate the feasibility of using long simulation times generated from Allegro potentials in LAMMPs to calculate ionic conductivity with correlations
- We chose to look at an alloy of Lithium Silicate/Phosphate: $(Li_4SiO_4)_{0.25}$ $(Li_3PO_4)_{0.75}$
- 75% Li_3PO_4 and 25% Li_4SiO_4 ratio was chosen based Deng et. al.'s results
- The 132-atom cell here was relaxed in Quantum Espresso to find the ground state

Reproducibility of Long MD Simulations

We can define an ionic trajectory:

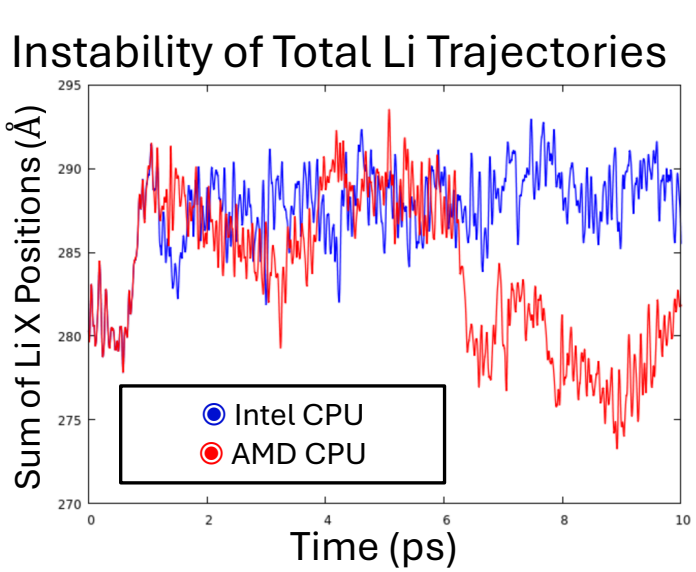
$$\vec{r}(t) = f(\vec{r}(0), \vec{p}(0); t)$$

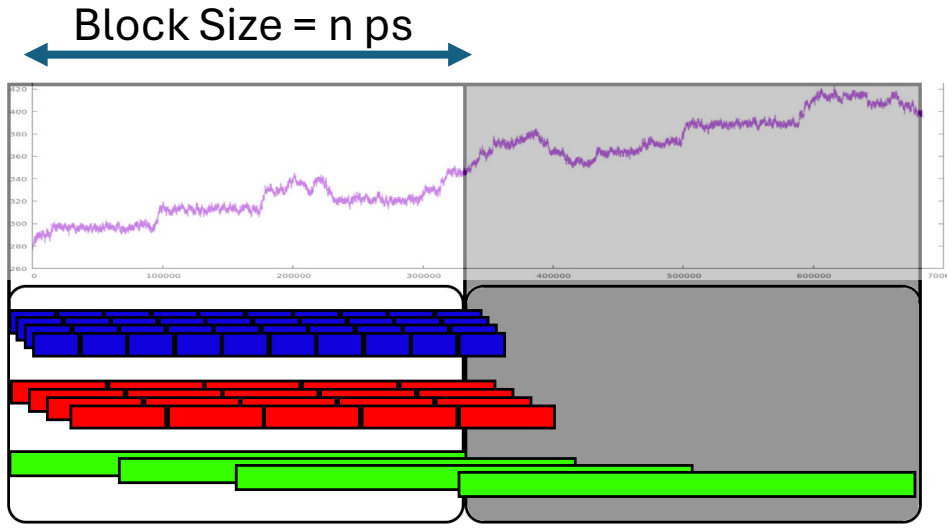
If we perturb the initial condition of the particle by changing the initial momentum by ε, we have a modified trajectory:

$$\vec{r}'(t) = f(\vec{r}(0), \vec{p}(0) + \varepsilon; t)$$

The difference $\Delta\vec{r}(t) = \vec{r}'(t) - \vec{r}(t)$ is linear in ε for small t but diverges exponentially at large t, i.e.:

$$\Delta\vec{r}(t) \sim \varepsilon e^{\lambda t} \text{ for } t \gg 0$$

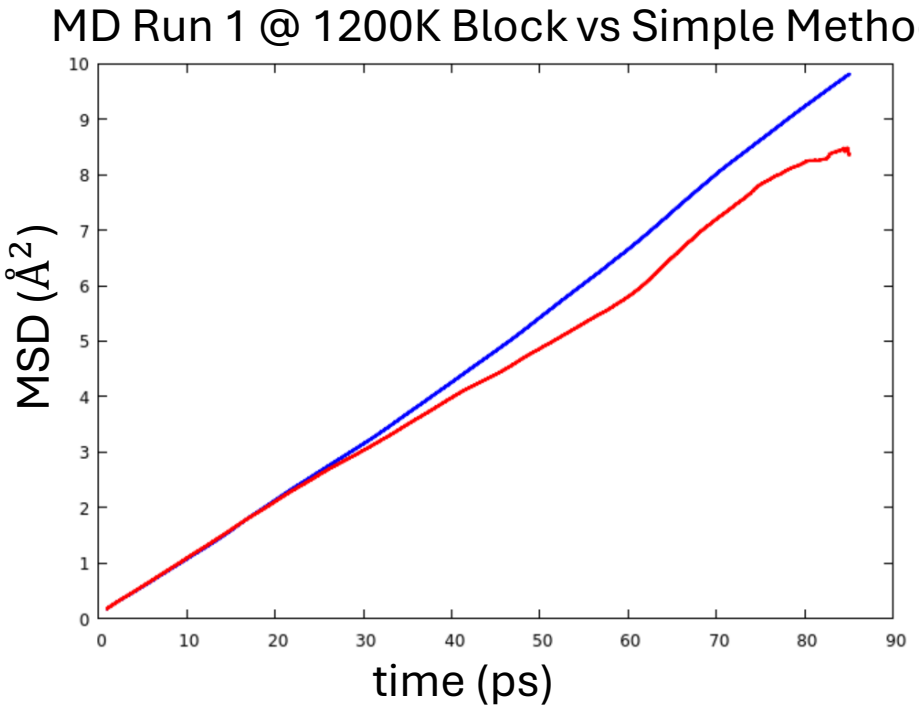


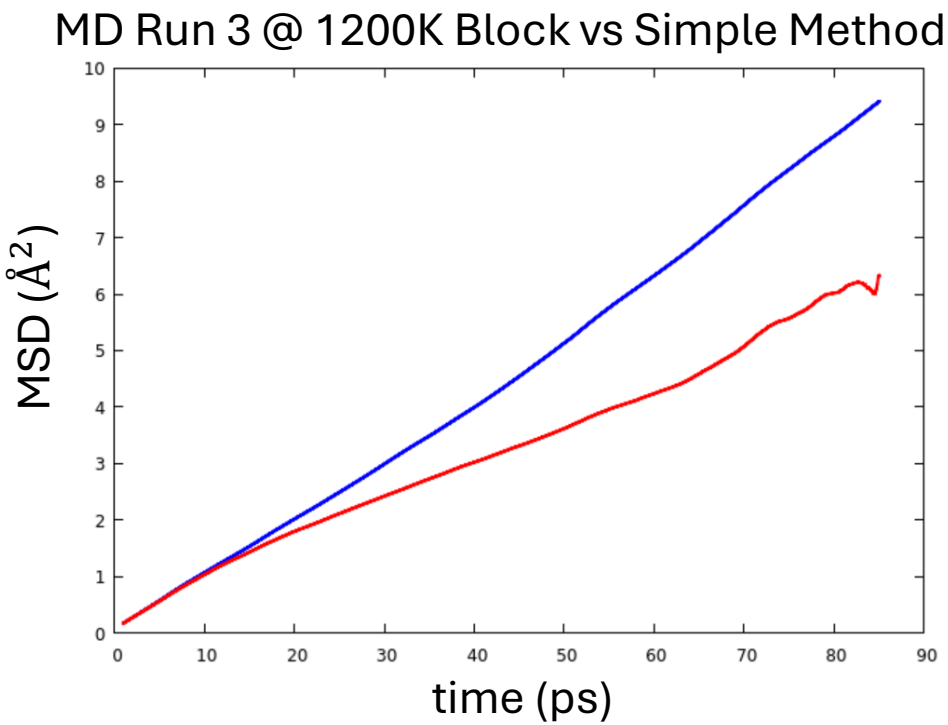


Details from Frenkel and Smit 2002 (ISBN-10: 0-12-267351-4) regarding Lyapunov instability (left); example showcasing trajectory divergence from fixed initial conditions (center); and block method depiction (right)

- With long MD runs, one must take into account Lyapunov instability – accumulation of integration errors resulting in unstable MD trajectories at long time scales
- One approach to mitigating this issue is by using block analysis on multiple parallel runs with different initial starting conditions
- This choice was informed by new research involving MLIPs to investigate Li_3PS_4 – Gigli, Tisi, Grasselli, and Ceriotti 2024 (DOI: 10.1021/acs.chemmater.3c02726)
- This allows for consistency in the calculations – each interval has the same number of samples with which to average over

Preliminary Results – Block Method Analysis





- Some results comparing block method to the so-called “simple” method for some example MD runs of our model $(Li_4SiO_4)_{0.25}$ $(Li_3PO_4)_{0.75}$ material at 1200K
- Simple method is simply averaging however many samples you have per interval size for a given MD simulation – it is not statistically consistent
- Showcases the block method produces better and more statistically reliable results which helps mitigate the Lyapunov instability

Preliminary Results – Allegro Testing and Error

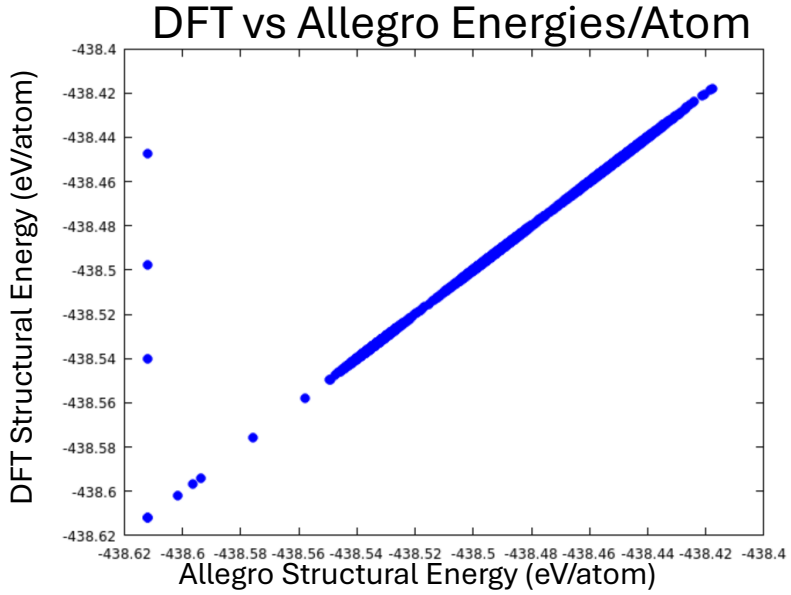
Hyperparameter Settings:

- r_max = 6.0 Å
- l_max = 3
- num_features = 128
- num_allegro_layers = 2
- polynomial_cutoff = 6
- num_basis = 8
- 2-body MLP dims = [128,256,512,1024]
- Latent MLP dims = [1024,1024,1024]
- Energy MLP dims = [128]
- n_train = 300
- n_validation = 30
- batch_size = 5
- metrics = validation_loss

Training Set Energy and Force Errors:

$$E_{MAE} = 0.041 \frac{eV}{struct} = 0.00031 \frac{eV}{atom}$$

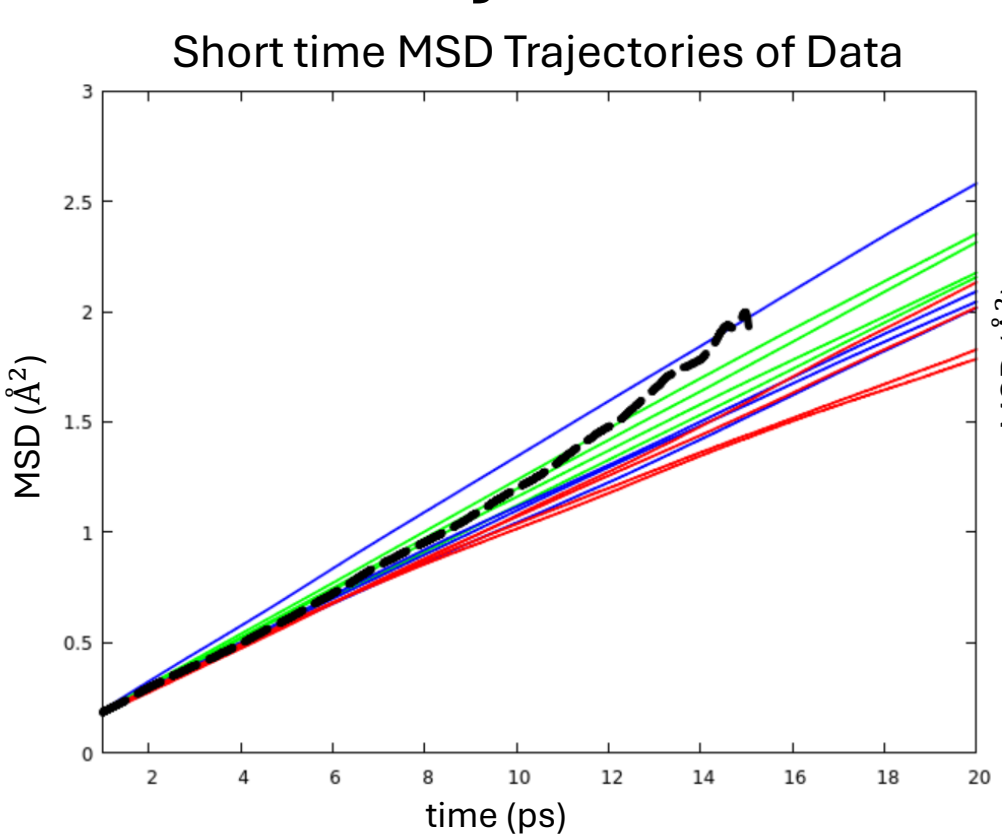
$$F_{MAE} = 0.0021\ eV/\text{Å}$$

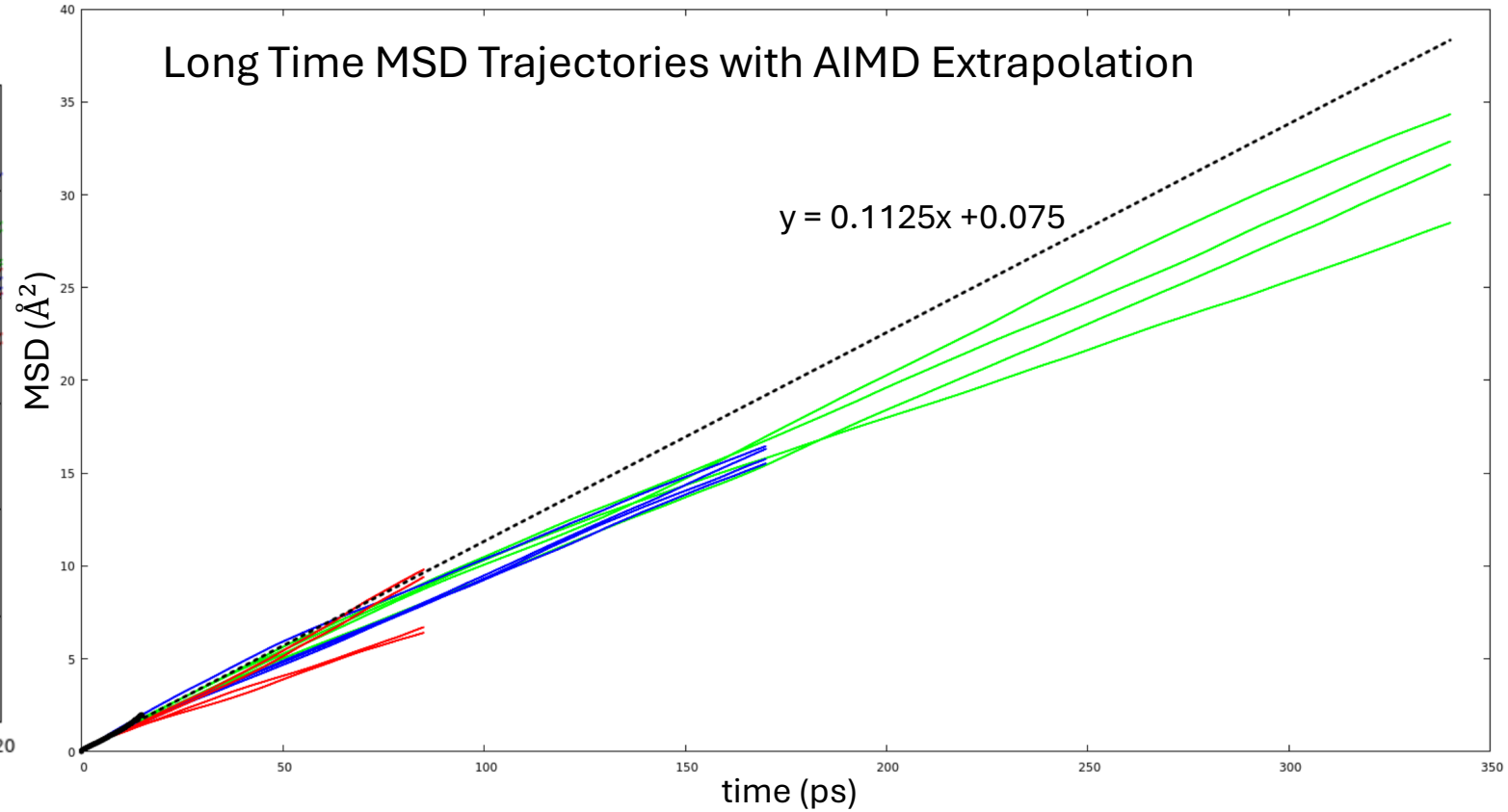


Hyperparameter settings for training (left); energy and force MAE reported for training set (center) and structural energies of Allegro model calculated with LAMMPs vs DFT in Quantum Espresso for 6180 structure dataset (right)

- Allegro was tested with dozens of hyperparameter configurations to determine which settings to use based on the tradeoff between accuracy and performance, as well as hardware limitations
- The hyperparameters that were found to most affect accuracy were the order of the tensor representations, the cutoff radius defining the neighbor list for a given pair, and the number of tensor features used to represent the local atomic pair environments
- Our Allegro model for $(Li_4SiO_4)_{0.25}$ $(Li_3PO_4)_{0.75}$ was trained using AIMD simulation data at 600K, 900K, and 1200K with the given hyperparameter choices, sampled from a total of 6180 structures
- Here we report the Energy and Force Mean Absolute Errors for our models as reported by Allegro
- Here we also plot the DFT vs LAMMPS (using Allegro model) calculated structural energies/atom

Preliminary Results – MSD Trajectories



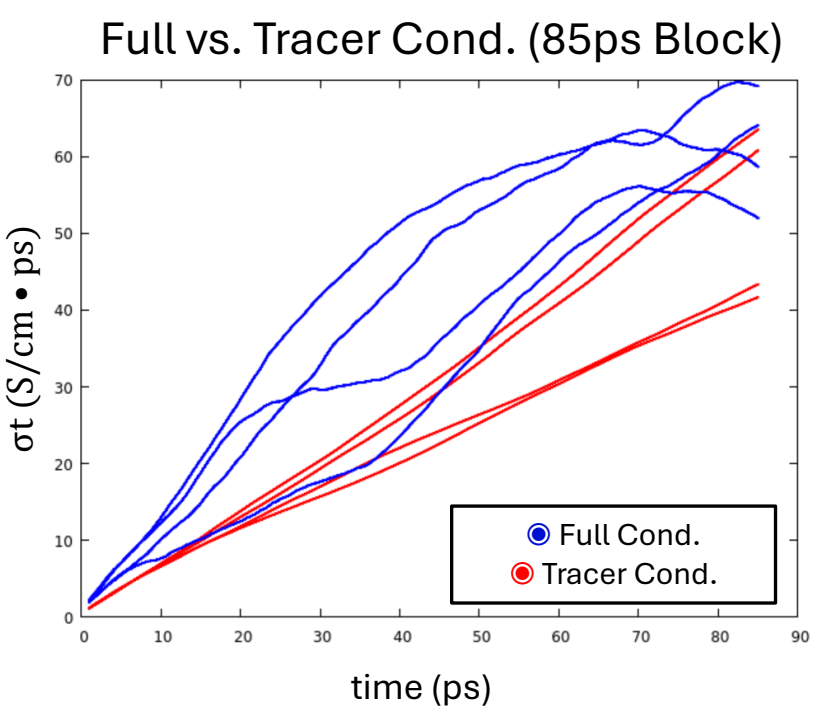


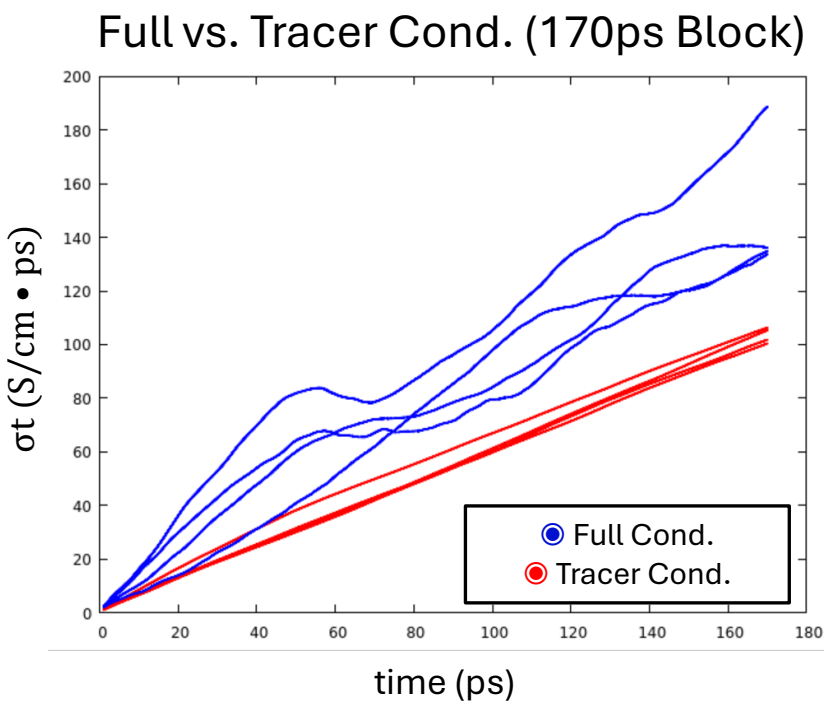
◉ 85ps LAMMPS block MSD ◉ 170ps LAMMPS block MSD ◉ 340ps LAMMPS block MSD ◉ ~14ps AIMD simple MSD (and extrapolation)

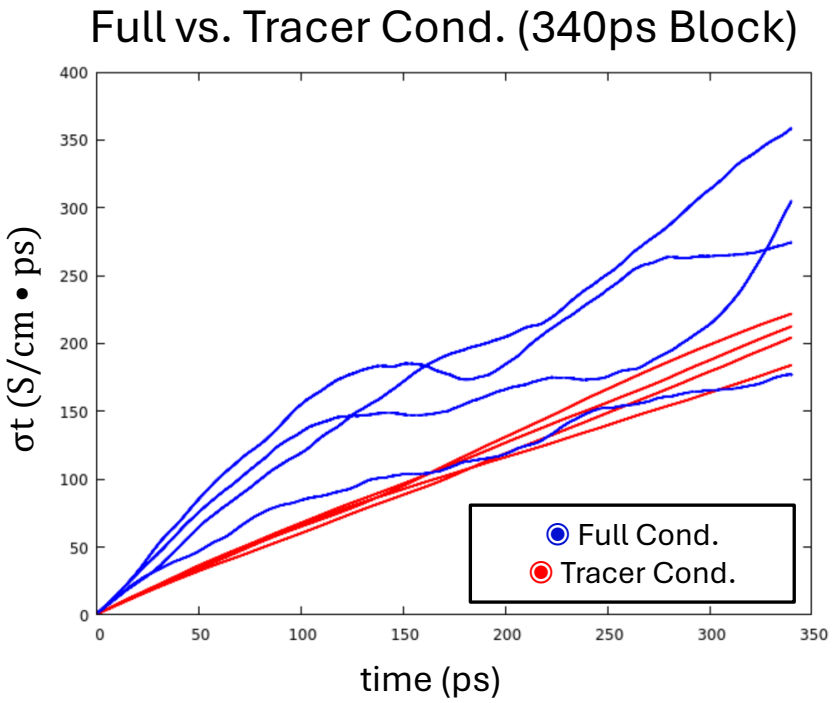
Li ion MSD of the Allegro models run in LAMMPS at 1200K for 3 different block sizes – 85ps, 170ps, and 340ps – each ran with 4 different starting velocity seeds. Left compares models to AIMD data at short time, right compares models to extrapolated AIMD data at long time

- Preliminary MSD results in LAMMPS with Allegro model are encouraging
- Ran MD at 1200K for 3 different block sizes (85, 170, 340 ps) with 4 different velocity seeds
- Great agreement with AIMD simple MSD in short time; good extrapolation to longer times

Preliminary Results – Full vs Tracer Conductivity



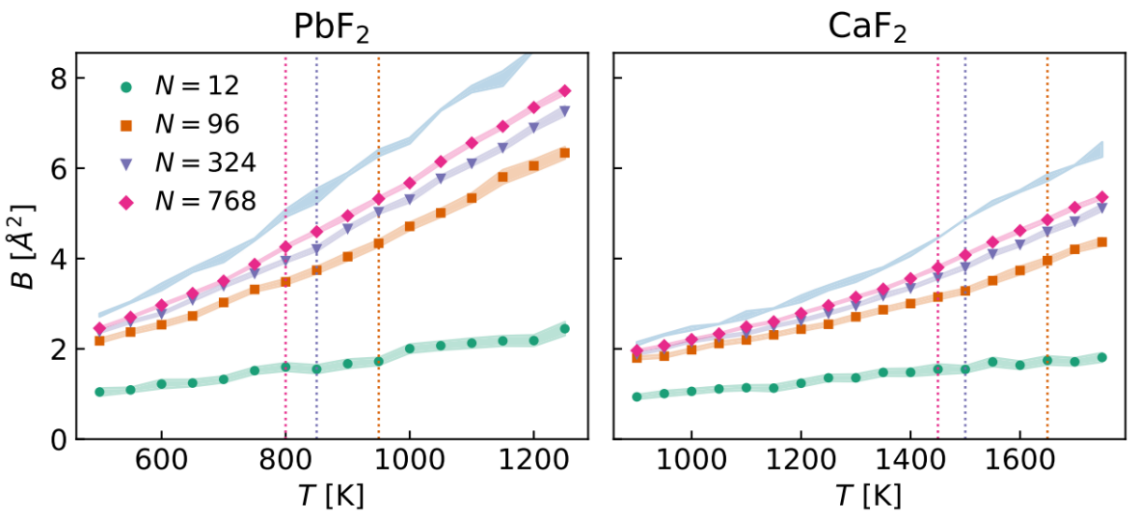


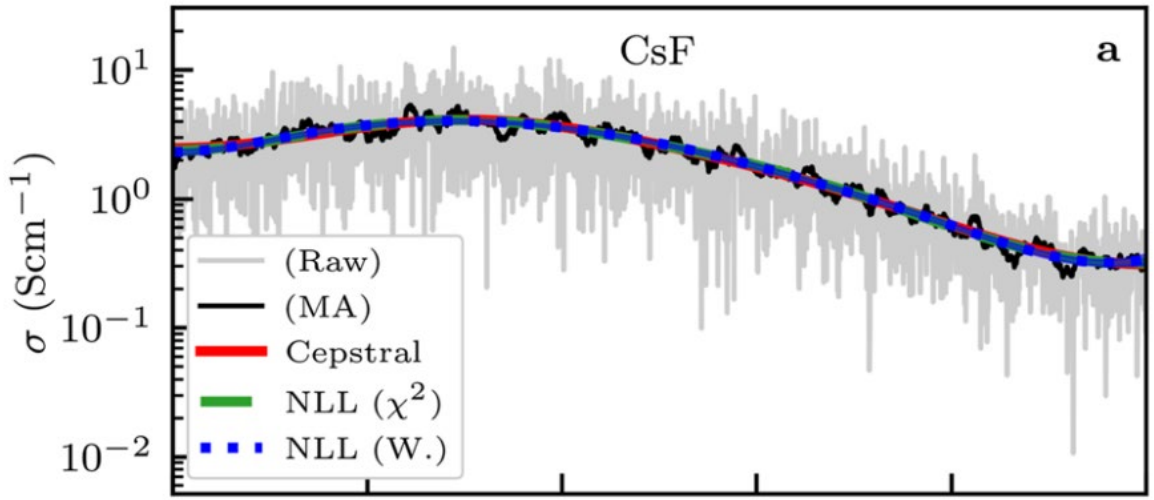


Full and Tracer conductivities for 4 MD runs at 1200K for the 85ps (left), 170ps (center) and 340 ps (right) block sizes

- Results showing the calculations of the full conductivity using the same 85ps, 170ps, and 340ps blocks seen earlier – each with four 1200K MD runs
- We see that although they are not yet converged and the plots are not quite linear, the full cond. is mostly larger than the Tracer approx. as expected

Future Investigations





Grasselli 2022 (DOI: 10.1063/5.0087382): Showcasing finite size effects on various systems by plotting their B-factors, which are related to the MSD (left); Pegolo, Drigo, Grasselli, Baroni 2025 (DOI: 10.1063/5.0249677): Figure depicting new statistical spectral method for analyzing transport coefficients from molecular dynamics (right)

- Finish this investigation into the feasibility of using the combined methods presented here to calculate ionic conductivity without need for approximation
- Look into the effects of cell size and determine if larger unit cells are needed in order to include the effects of ionic correlations accurately
- Look into the possibility of using more advanced statistical methods
- Hopefully apply these methods to study the (thio)boracite materials

Preliminary Conclusions

- Allegro software does a good job modelling the data from AIMD, yields low structural energy and atomic force errors compared to DFT
- Performance with Allegro model in LAMMPS is excellent, we see ns ranges of simulation time are feasible
- For our $(Li_4SiO_4)_{0.25}$ $(Li_3PO_4)_{0.75}$ structure of 132 atoms running on a single Nvidia A100 80GB GPU we can simulate 430ps/day
- Long MD runs with Allegro potentials are extrapolating well from AIMD data, but there is not yet convergence of full conductivity trajectories
- May need better approaches to take into account the Lyapunov instability, which may include newer statistical methods of analyzing the MD results, possible inclusion of larger simulation cells, and possibly running more simulations with different initial seeds for more trajectory averaging

Acknowledgements

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