Enabling the Investigation of the Conductivity of Select Lithium (Thio)Boracite Materials Using the Allegro Machine Learned Interatomic Potential Package

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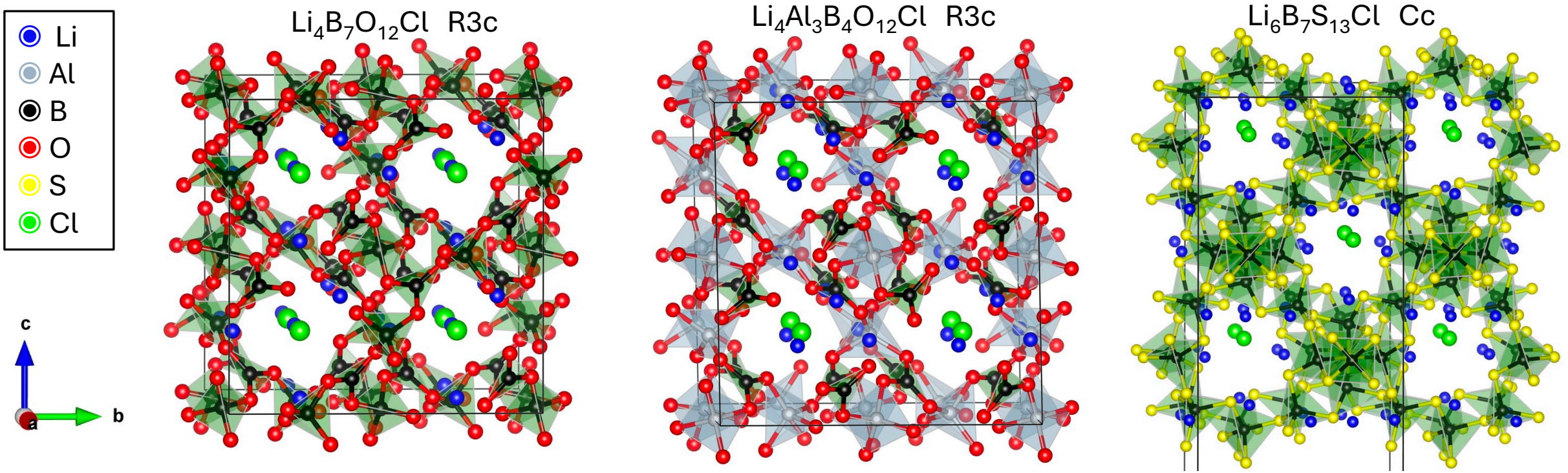
Previous Lithium (Thio)Boracite Investigation

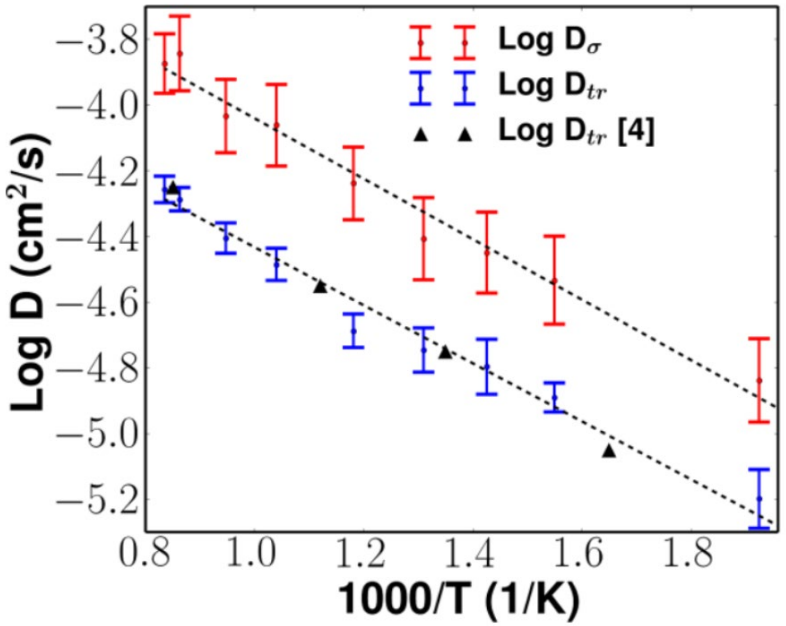


$Li_4B_7O_{12}Cl$ (left) and $Li_4Al_3B_4O_{12}Cl$ (center) rhombohedral R3c ground state structures and $Li_6B_7S_{13}Cl$ (right) monoclinic Cc ground state structure
Lynch, Li, Canepa, Holzwarth 2024. (https://doi.org/10.1103/PhysRevMaterials.8.065401)

- Previous investigation of ground state structures, phonon bands, stability:
  - 8 Lithium (Thio)Boracite materials as solid-state electrolytes, including:
    - 3 known and experimentally studied materials
    - 5 newly predicted materials
- Desired to continue investigation and estimate ionic conductivities

Conductivity Calculations

Comparison of Tracer vs Full Diffusivity



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

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

Ω = volume

N_D = num. diffusing ions

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

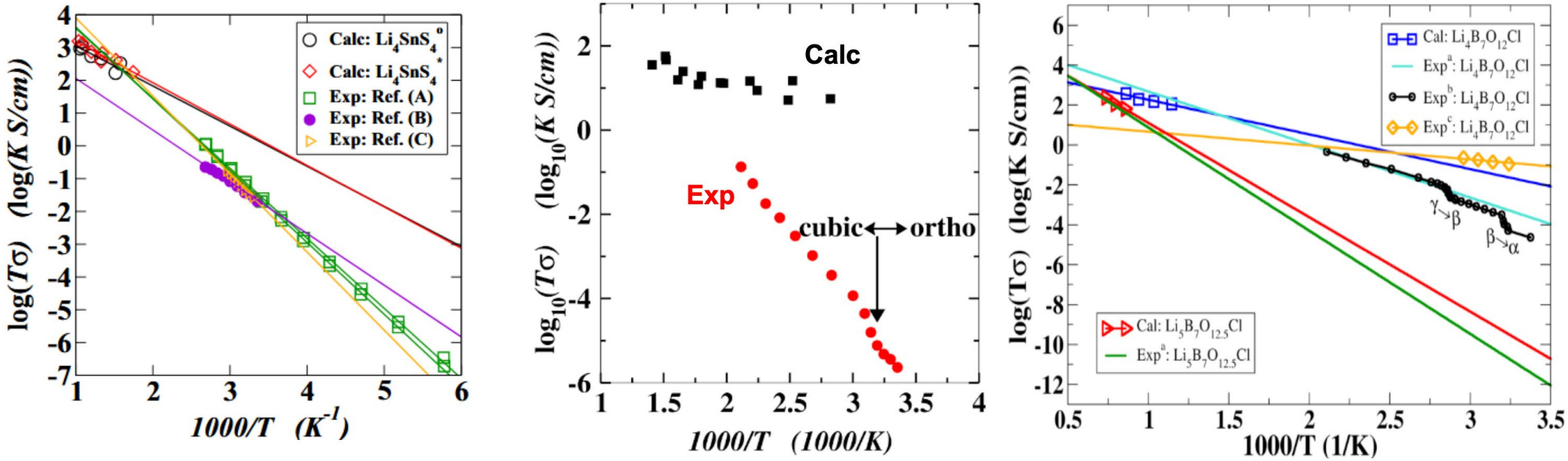
$$MSD(\tau) = \frac{1}{6N_D} \left\langle \sum_{j\in D} \left| \boldsymbol{r_j}(\tau + t_i) - \boldsymbol{r_j}(t_i) \right|^2 \right\rangle_{t_i}$$

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

- Historically, ionic conductivity is approximated with Tracer conductivity
- For ionic conductors that are highly correlated, this is not sufficient
- Exact Green-Kubo formalism needed, but not feasible
- Long simulation times (~ns) needed for correlations to occur

Low Temperature Extrapolation Limitations

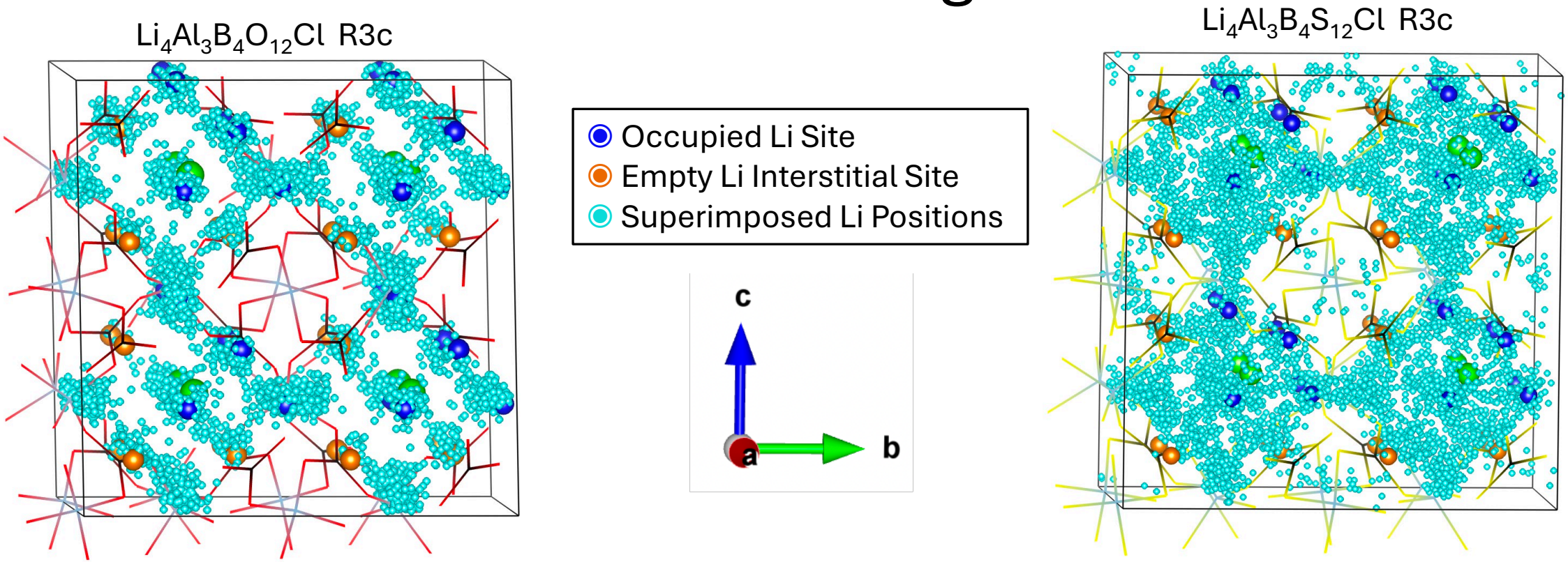
Li_4SnS_4 **Li_2OHCl** **$Li_4B_7O_{12}Cl$**



Plots showcasing poor extrapolation to low temp from previous works. Left: Ahmad Al-Qawasmeh, Jason Howard, and N. A. W. Holzwarth, JECS 164, A6386 (2017)
Center: Jason Howard, Z. D. Hood, and N. A. W. Holzwarth, PRM 1, 075406 (2017) Right: Yan Li, Z. D. Hood, and N. A. W. Holzwarth, PRM 6, 025401 (2022)

- FPMD runs are typically done at high temperatures for sufficient ionic diffusion
- Low temperatures can't be run long enough for sufficient diffusion to occur
- Previous works show this doesn't extrapolate well to lower temperatures

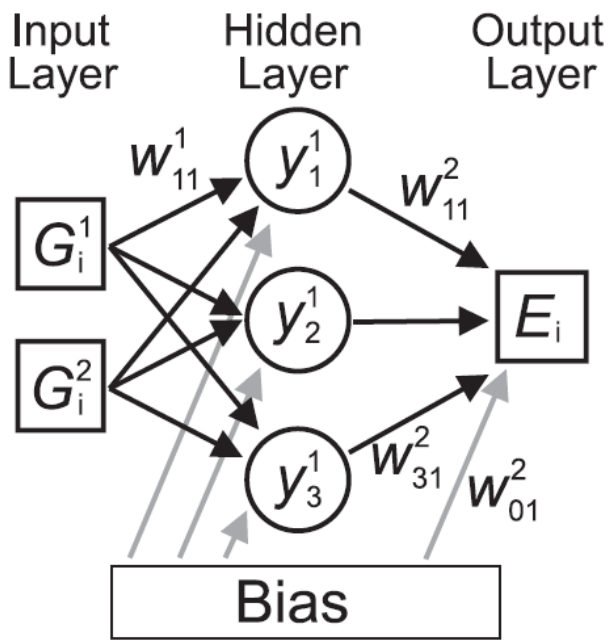
Limitations of Current Methodologies

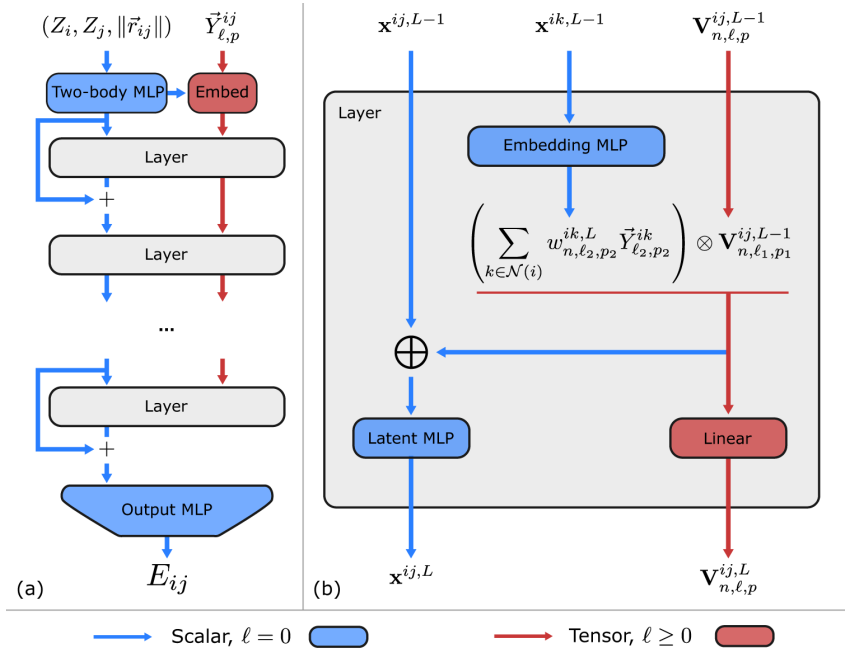


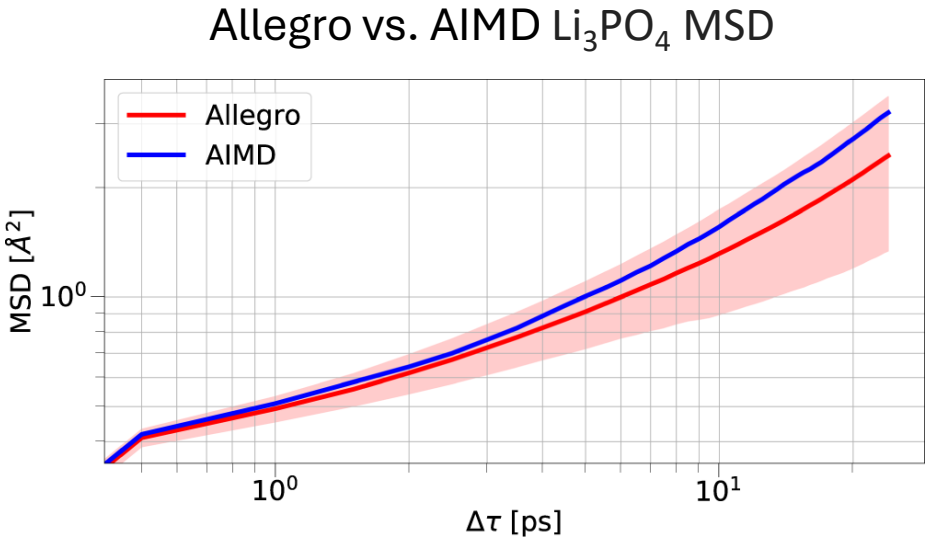
$Li_4Al_3B_4O_{12}Cl$ (left) and $Li_4Al_3B_4S_{12}Cl$ (right) Li-ion Superposition plots

- Li superposition plots qualitatively suggest good ionic diffusion
- ~23 ps of simulation time sampled every 50 timesteps at 1100K
- Desire to quantify ionic conductivity met computational roadblocks --- FPMD methods can only simulate ~0.1 ps per day

Machine Learning – Allegro Software Package





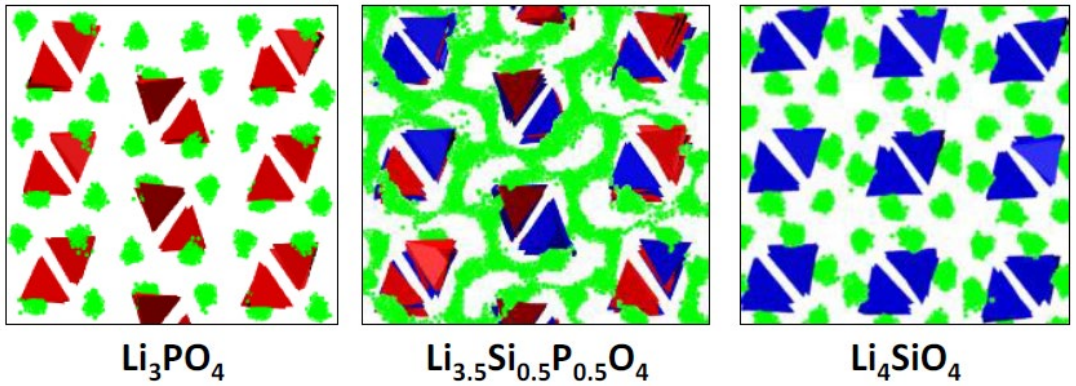


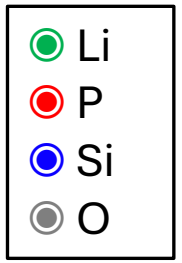
Behler and Parrinello 2007 (DOI: 10.1103/PhysRevLett.98.146401): NN based MLIP arch (left);
Musaelian, Batzner, Kozinsky, et. al. 2023 (DOI: 10.1038/s41467-023-36329-y): Allegro Graph Network architecture (center); MSD comparison between Allegro and AIMD for Li_3PO_4 (right)

- Neural Networks can "learn" interatomic potential functions (Behler 2007)
- Allegro Architecture – Graph Neural Network with strictly local interactions
- Shown to have excellent scaling and accuracy compared to DFT

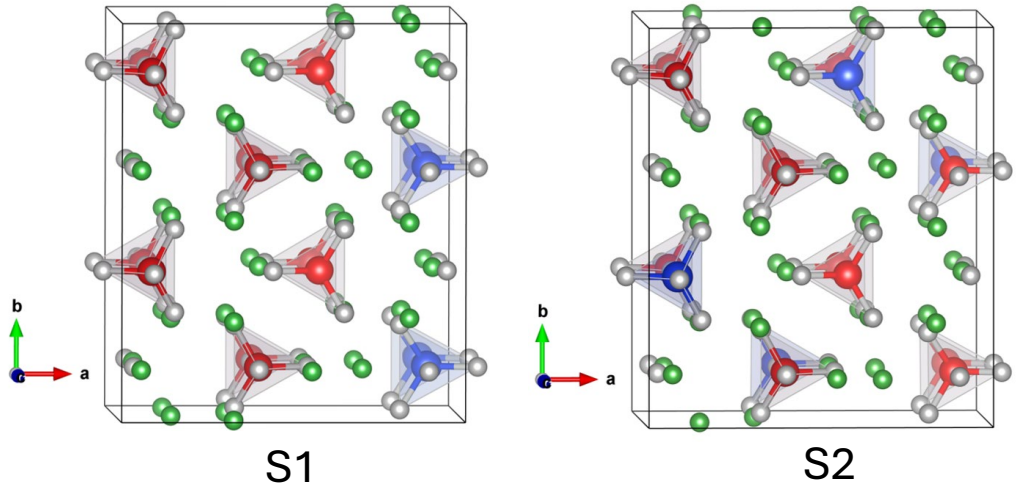
Model Solid Electrolyte $(Li_4SiO_4)_x(Li_3PO_4)_{1-x}$

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





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

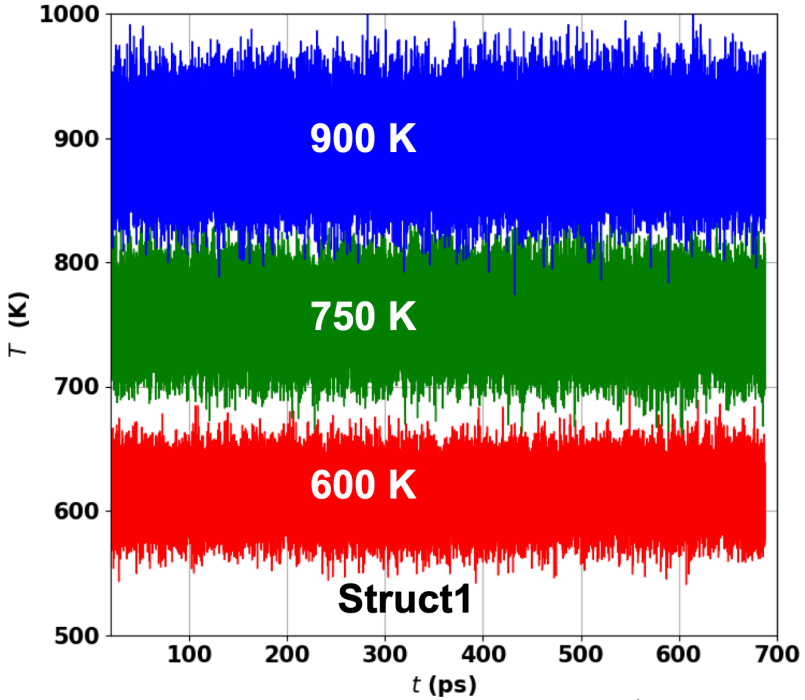


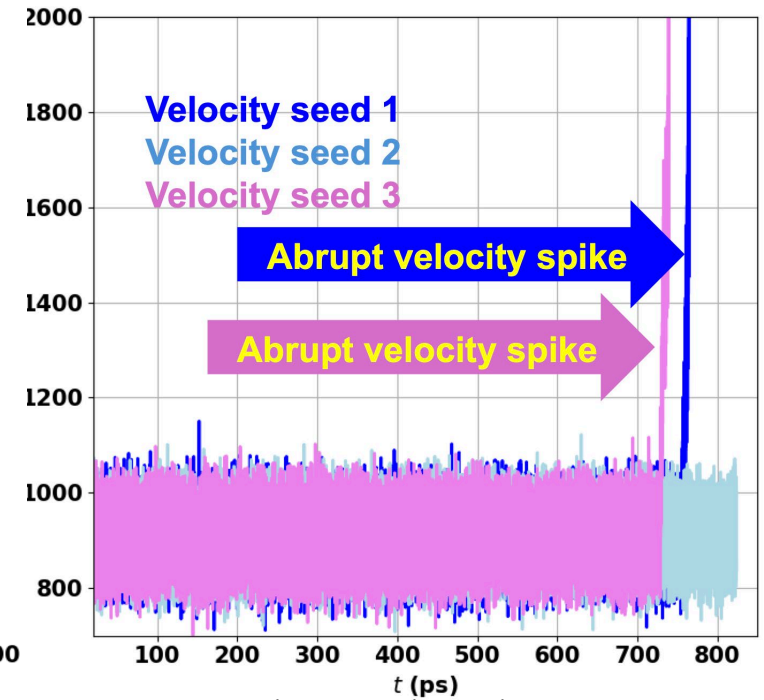
S1 S2

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 structures S1 and S2 containing 75% Li_3PO_4 and 25% Li_4SiO_4 (right)

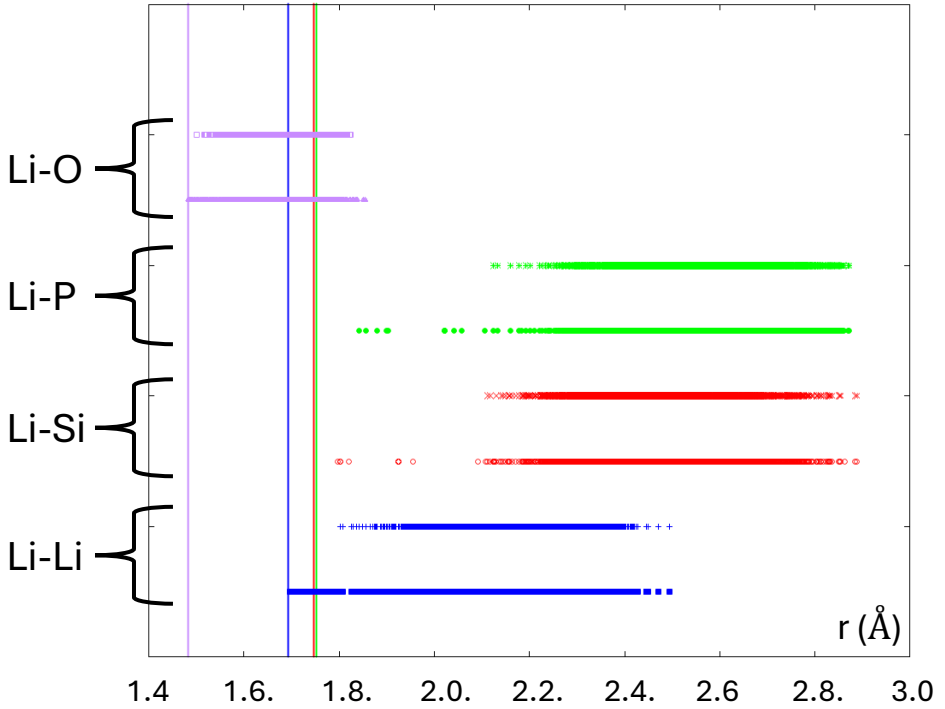
- Goal: use Allegro potentials to calculate full ionic conductivity at low temperature
- We chose an alloy of Lithium Silicate/Phosphate: $(Li_4SiO_4)_{0.25}$ $(Li_3PO_4)_{0.75}$
- 75% Li_3PO_4 and 25% Li_4SiO_4 -- ratio was chosen based Deng et. al.'s results
- 2 configurations of substituted Si sites chosen, loosely based on Deng et. al. cell
- Both 132-atom cells were relaxed in Quantum Espresso to find their ground states

Training Dataset Generation





Temperature plots showcasing stable (left) and unstable (right) MD simulations



Li-X min pair distances per frame plotted over training data, with (bottom) and without (top) “close” frames added

- Short (~10 ps) FPMD simulations at 100K, 400K, 600K, and 900K for structs S1 and S2 ran in QE
- FPMD across multiple temps and structures generate diverse training data
- Even with models trained on diverse FPMD data, unpredictable catastrophic MD instability can occur
- Well known problem with works attempting to address the issue → Hao Wang et. al 2019 (https://doi.org/10.48550/arXiv.1904.00360)
- Occurs when model fails to correctly represent untrained configs → unphysically large forces/energies
- Seems to be poor representation of close pair distance configurations
- We attempt to systematically construct ”close” Li-X configs to include in training set to mitigate the issue

Allegro Training Error Assessment

$$WS^D = \lambda_E E^D_{MAE} + \lambda_F F^D_{MAE} + \lambda_S S^D_{MAE}$$

Allegro Training Metrics					
Model (A#)	Training Set	WS (unitless)	E_{MAE} (eV)	F_{MAE} (eV/Å)	S_{MAE} (eV/Å^3)
Small 1 (A1)	S1+S2	2.85×10^{-1}	8.35×10^{-1}	1.81×10^{-2}	5.03×10^{-4}
Small 2 (A2)	S1+S2	1.83×10^{-2}	4.39×10^{-2}	1.08×10^{-2}	1.83×10^{-4}
Small 3 (A3)	S1+S2	1.62×10^{-2}	3.79×10^{-2}	1.04×10^{-2}	1.86×10^{-4}
Small 4 (A4)	S1+S2	1.16×10^{-1}	3.32×10^{-1}	1.45×10^{-2}	3.65×10^{-4}
Small 5 (A5)	S1+S2	1.45×10^{-2}	3.28×10^{-2}	1.04×10^{-2}	1.81×10^{-4}
Small 6 (A6)	S1+S2	3.20×10^{-1}	9.40×10^{-1}	1.91×10^{-2}	6.54×10^{-4}
Medium 1 (A7)	S1+S2	9.84×10^{-3}	2.46×10^{-2}	4.79×10^{-3}	1.21×10^{-4}
Medium 2 (A8)	S1+S2	9.58×10^{-3}	2.37×10^{-2}	4.96×10^{-3}	1.15×10^{-4}
Small S1 (A9)	S1	2.58×10^{-2}	6.59×10^{-2}	1.12×10^{-2}	2.19×10^{-4}
Small S2 (A10)	S2	2.17×10^{-2}	5.39×10^{-2}	1.10×10^{-2}	1.91×10^{-4}

$$E^D_{MAE} = \frac{1}{N_S} \sum_{i=1}^{N_S} |\hat{E}_i - E_i|$$

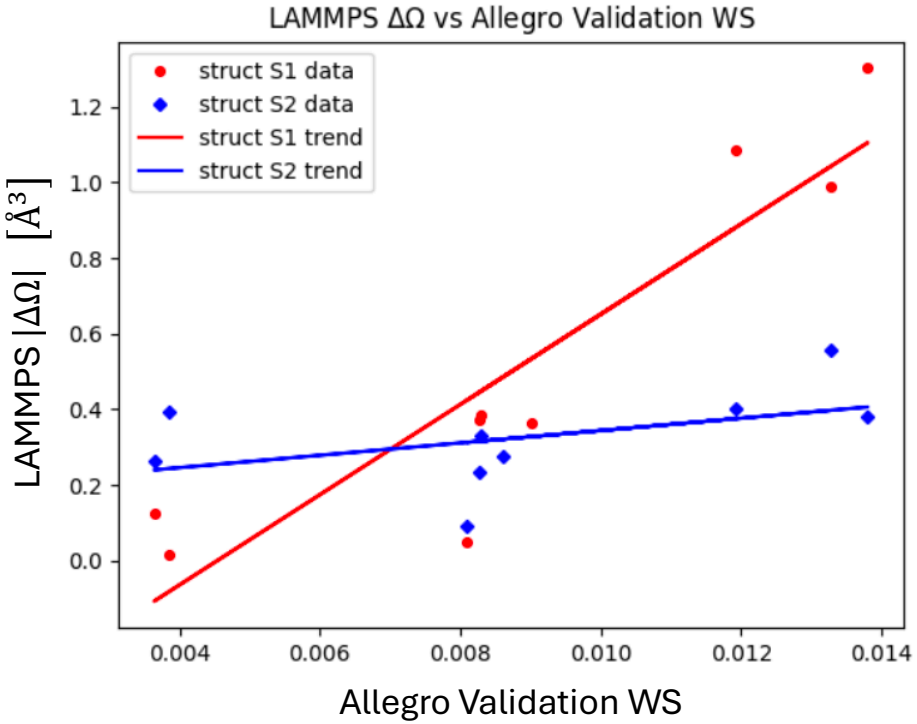
$$F^D_{MAE} = \frac{1}{3N_S N_A} \sum_{i=1}^{N_S} \sum_{j=1}^{N_A} \sum_{k=1}^{3} |\hat{F}_{i,j,k} - F_{i,j,k}|$$

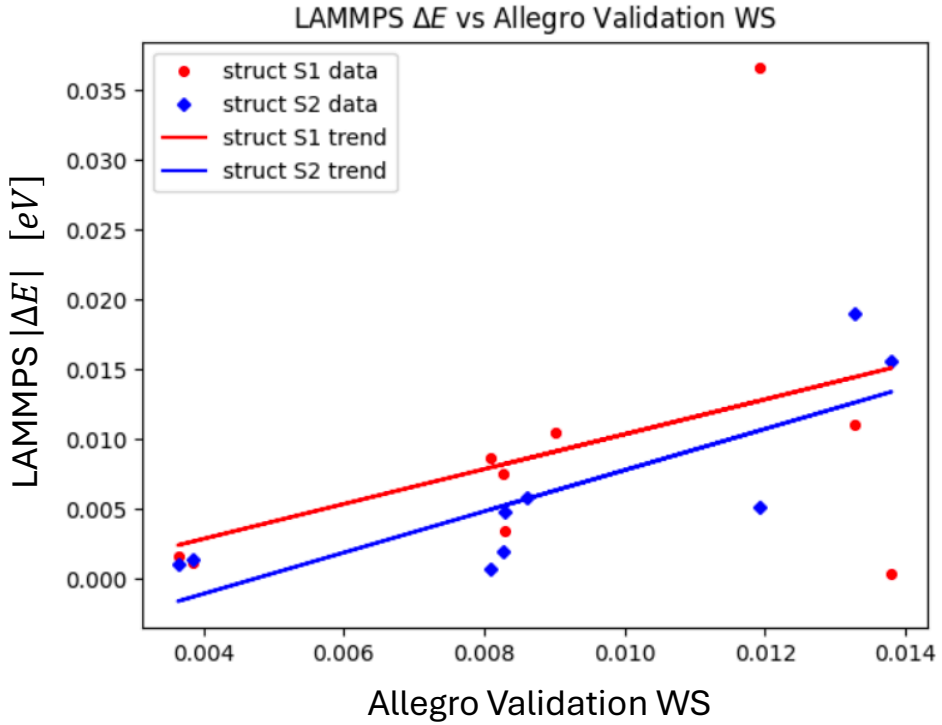
$$S^D_{MAE} = \frac{1}{9N_S} \sum_{i=1}^{N_S} \sum_{k=1}^{3} |\hat{S}_{i,k} - S_{i,k}|$$

- "Small" and "medium" model configurations:

  Small: $\ell = 1$, ~10k learned params Medium: $\ell = 2$, ~100k learned params
- Models trained with both S1+S2 and S1/S2 independently
- Trained with configs sampled from FPMD @ 100K – 900K + "close" pair distance configs
- Dataset error metrics along with 900K MD stability test used for initial assessment
- 2 models failed the stability test (in red) – qualitative improvement from previous testing without additional "close" training configs

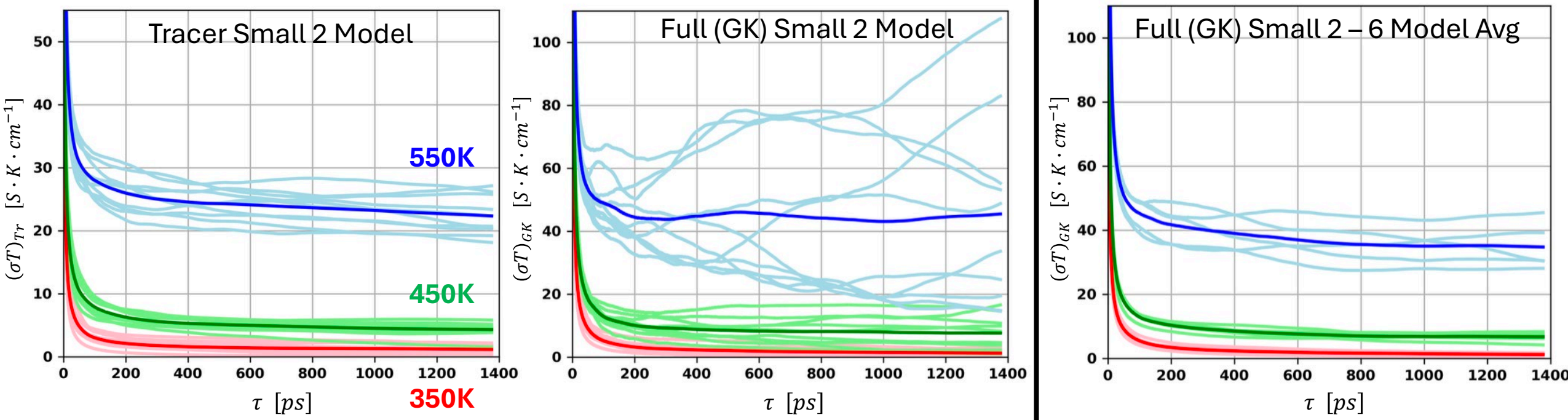
LAMMPS Minimize Calculations





- Want to ensure ground state is well represented by the model
- Attempt to correlate to validation error through LAMMPS minimize calculations
- Run minimize in LAMMPS to relax input ground state structure
- If model can ”correctly” predict the ground state, it will not relax
- Larger volume/energy change corresponds to poorer prediction capability
- Validation set error seems to correlate to the model’s ability to correctly predict the GS

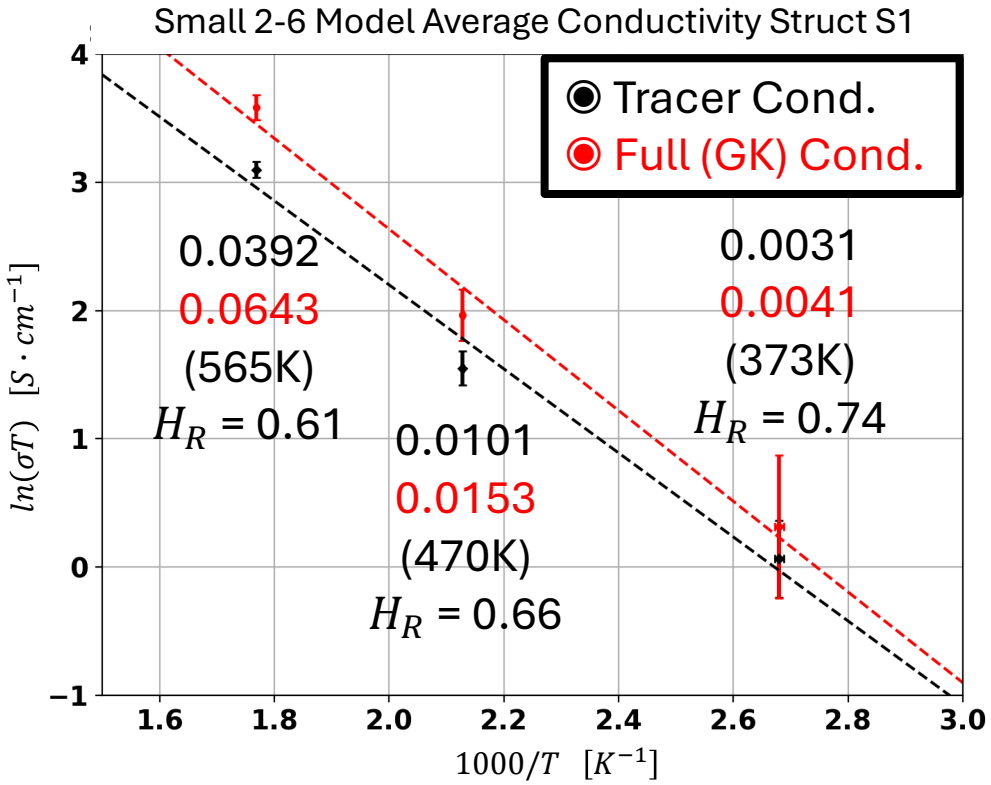
Select Struct S1 LAMMPS MD Results

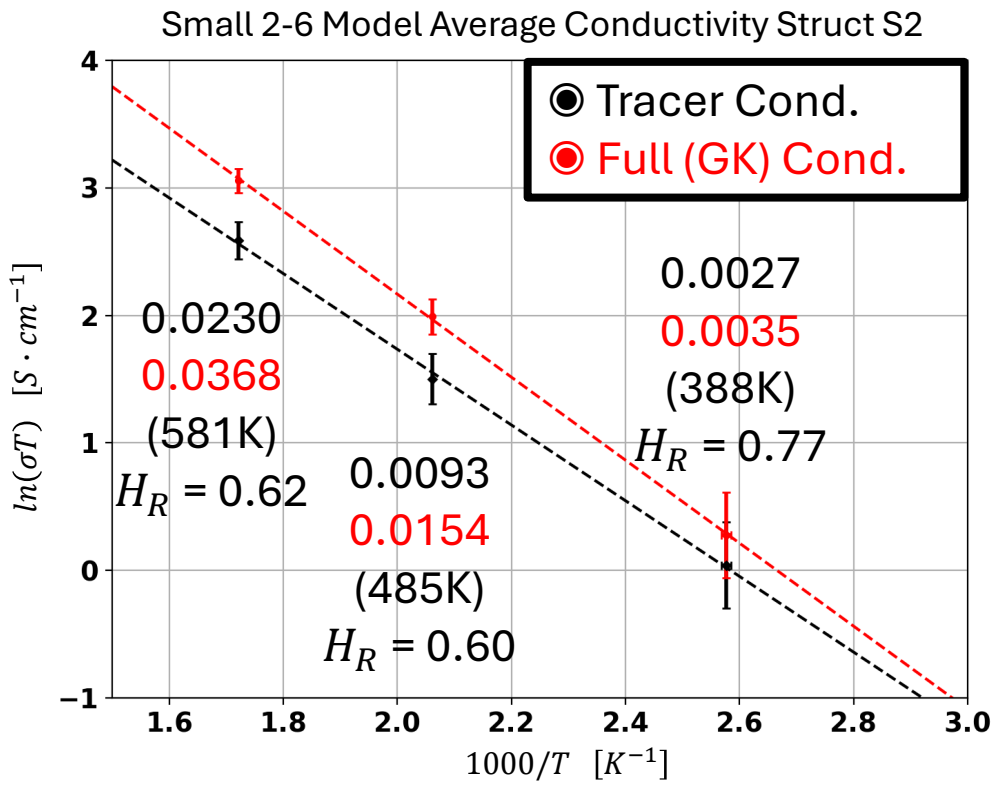


Small 2 model Tracer (left) and full (center) results averaged over 10 simulations; small2-small6 model average (right)

- MD run in LAMMPS with 5 stable small models trained on S1 + S2 data
- Low temps (350K, 450K, 550K) and long simulation time (2.8ns) achieved
- 10 simulations with different starting velocity configurations were performed for each temperature and each structure – 60 simulations per model, 300 total
- Even with long runs, Lyapunov variability still present – requires block averaging over simulation intervals and further averaging over many starting velocity configs

Conductivity Results





$$H_R = \frac{\sigma_{Tr}}{\sigma_{GK}}$$

Fit	E_a
Tr, S1	0.2823
GK, S1	0.3047
Tr, S2	0.2558
GK, S2	0.2805

- Arrhenius plots of the tracer and full conductivity for S1 (left) and S2 (center)
- Datapoints obtained by fitting the conductivity plots and taking the long-time limit
- Results suggest that structure S1 has higher conductivity than S2
- Full conductivity > Tracer conductivity → highly correlated ionic motion, $H_R < 1$
- Conductivity results seem reasonable, but not directly comparable to experiment

Conclusions and Future Works

- FPMD based conductivity estimates have limitations
- Poor extrapolation to low temps and poor approximation for highly correlated materials due to inherently short simulation times
- Using the Allegro NN, we can overcome these limitations and calculate the full conductivity at low temps from long LAMMPS simulations
- Long simulation time is still insufficient to overcome Lyapunov issue – we need further averaging over many different initial velocity configurations
- Using datasets generated from FPMD at many different temperatures across different structural configurations is not sufficient – MD instability can occur from close pair distances not correctly predicted
- Adding constructed “close pair” frames to the dataset seems to help reduce instability
- Next steps: Apply what we’ve learned to the boracite materials to enable conductivity calculations, activation energy prediction, etc.

Acknowledgements and Questions

- Dr. N. A. W. Holzwarth (Wake Forest University): Coauthor and PhD Advisor
- Materials Intelligence Research (Harvard University): Allegro software
- Chun Wei Tan (Harvard University): Allegro software developer and support
- Dr. Federico Grasselli (University of Modena and Reggio Emilia, Italy): correspondence
- Dr. Fan Yang (Wake Forest University): correspondence
- NSF Grant DMR-2242959
- Wake Forest University High Performance Computing Facility DOI: 10.57682/G13Z-2362
- Dr. Sean Anderson (Wake Forest University): DEAC Software Support