Progress and Assessment of Computational Challenges in Simulating Ionic Conductivities of Electrolyte Materials Using Machine-Learned Potentials Trained from First Principles Molecular Dynamics and Statistical Analysis*

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➔with special thanks to Sean Anderson (WFU) and Chuin Wei Tan (Harvard University)

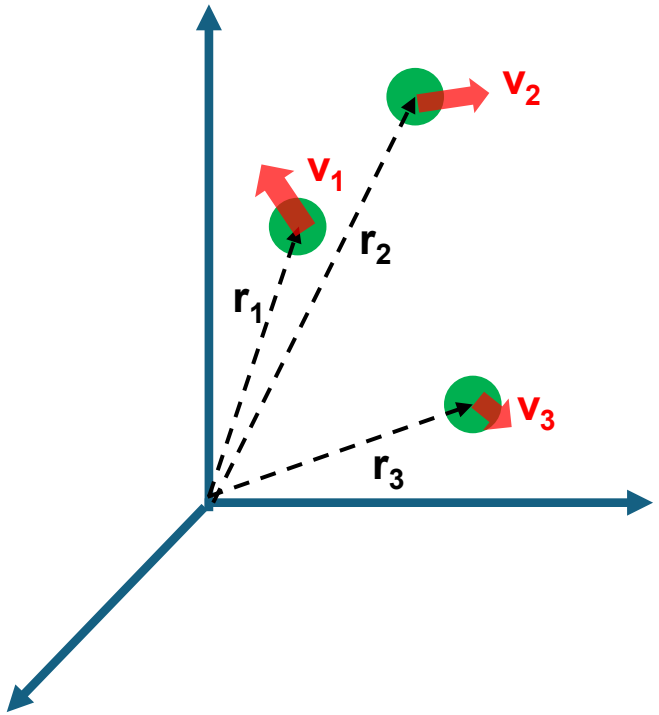
Special Acknowledgements

- Chuin Wei Tan – MIR Group, Harvard University for help using the updated Allegro software package
- LAMMPS software developers from Sandia National Lab
- QUANTUMESPRESSO software developers
- Dr. Sean Anderson – from Wake Forest University for installing and maintaining software on the DEAC system
- Professor Fan Yang – Computer Science Dept, Wake Forest University for advice about Machine Learning methodologies
- Professor Federico Grasselli – University of Modena and Reggio Emilia (Unimore) in Italy for advice about the Green-Kubo formalism

Outline

- ❑ Motivation for this study
- ❑ Green-Kubo equations and various developments
- ❑ Brief description of Allegro machine learning process
- ❑ Some results
- ❑ Some surprises
- ❑ Outlook

Ionic conductivity from the mindset of atomistic modeling:



For particles, i each having charge q_i, in a volume Ω,

the current as a function of time t density is $\mathbf{J}(t) = \frac{1}{\Omega}\sum_{i=1}^{N} q_i \mathbf{v}_i(t)$

where velocity is $\mathbf{v}_i(t) \equiv \frac{d\mathbf{r}_i(t)}{dt}$

Green-Kubo formula for evaluating ionic conductivity

$$\sigma = \frac{\Omega}{3k_B T}\int_0^{\infty} dt \left\langle \mathbf{J}(t)\cdot\mathbf{J}(0)\right\rangle_{\text{configurations}}$$

Boltzmann constant

Temperature

Some background for the development of the Green-Kubo formula

$$\sigma = \frac{\Omega}{3k_B T}\int_0^\infty dt \left\langle \mathbf{J}(t)\cdot\mathbf{J}(0)\right\rangle_{\text{configurations}}$$

1931 – Lars Onsager – Phys Rev 37, 405 (1931) & 38, 2265 (1931) – "Reciprocal relations in irreversible processes" – Showed how macroscopic, linearized hydrodynamic equation are affected by atomic level dynamics of the system at equilibrium; also called the fluctuation-dissipation theorem.

1954 – M. S. Green – J. Chem. Phys. 22, 398 (1954)

1957 – R. Kubo – J. Phys. Soc. Jpn. 12, 570 (1957) – "Statistical-mechanical theory of irreversible process"

Mathematically equivalent formulation in terms of polarization density:

Performing time integral: $\mathbf{P}(t)-\mathbf{P}(0)=\int_0^t dt'\,\mathbf{J}(t')=\frac{1}{\Omega}\sum_{i=1}^{N} q_i\left(\mathbf{r}_i(t)-\mathbf{r}_i(0)\right)$

Alternative Green-Kubo form: $\sigma = \frac{\Omega}{6k_B T}\lim_{t_{\max}\to\infty}\frac{1}{t_{\max}}\left\langle\left|\mathbf{P}(t_{\max})-\mathbf{P}(0)\right|^2\right\rangle_{\text{configurations}}$

Ionic conductivity from the mindset of atomistic modeling (further simplification):

In the previous formulation all ions are included in the evaluation however, in most cases, it is reasonable to focus on the diffusing particles, $i \in D$ with $q_i \equiv q_D$,

defining for each $i \in D$ $\Delta \mathbf{r}_i(t) \equiv \mathbf{r}_i(t) - \mathbf{r}_F(t)$,

where $\mathbf{r}_F(t)$ represents the center of charge of the "framework" or non-diffusing part of the electrolyte at each time t. Making the assumption that the diffusing particles move independently of each other, it is convenient to define a "mean squared displacement": $\mathrm{MSD}(t) \equiv \sum_{i \in D} \left| \Delta \mathbf{r}_i(t) - \Delta \mathbf{r}_i(0) \right|^2$.

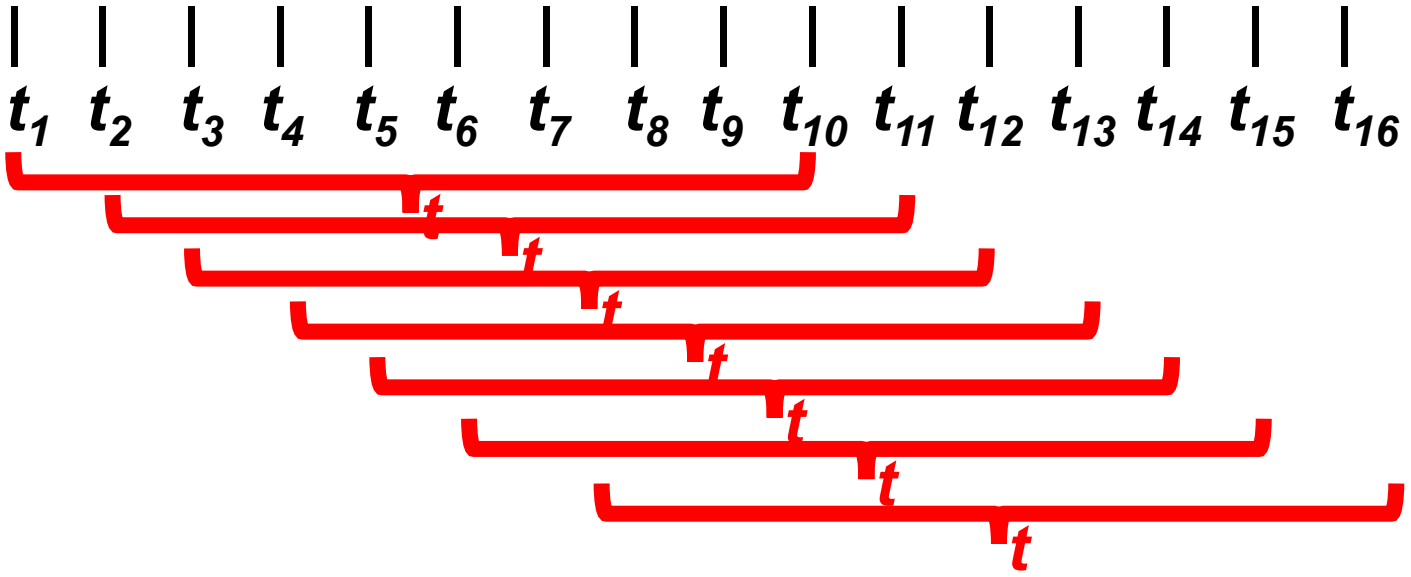
This leads to an approximate form of Green-Kubo ionic conductivity:

$$\sigma_{\mathrm{MSD}} \equiv \sigma_{tr} = \frac{q_D^2}{6\Omega k_B T} \lim_{t_{\max} \to \infty} \frac{1}{t_{\max}} \left\langle \mathrm{MSD}(t_{\max}) \right\rangle_{\text{configurations}}$$

Some details for the full and tracer Green-Kubo formulas

$$\sigma = \frac{\Omega}{6k_B T} \lim_{t_{\max}\to\infty} \frac{1}{t_{\max}} \left\langle \left| \mathbf{P}(t_{\max}) - \mathbf{P}(0) \right|^2 \right\rangle_{\text{configurations}} \qquad \sigma_{tr} = \frac{q_D^2}{6\Omega k_B T} \lim_{t_{\max}\to\infty} \frac{1}{t_{\max}} \left\langle \text{MSD}(t_{\max}) \right\rangle_{\text{configurations}}$$

Performing configuration average $\left\langle \mathcal{F}(t) \right\rangle_{\text{configurations}}$ for each time $t \to t_{\max}$



MD evaluation times

➔Multiple instances (~ 3x10^5) of time interval *t* averaged to perform <>configurations

Basic evaluation tool – numerical evaluation of classical molecular dynamics equations of particle motions --

For a given particle interaction potential describing the system: $\Phi\left(\left\{\mathbf{r}_j(t)\right\}\right)$

For each particle i of mass m_i, experiencing a force $\mathbf{F}_i(t)$, numerically evaluate

Newton's equations to find the trajectory $\mathbf{r}_i(t)$: $\dfrac{d^2\mathbf{r}_i(t)}{dt^2} = \dfrac{\mathbf{F}_i(t)}{m_i} = \dfrac{-\nabla_i \Phi\left(\left\{\mathbf{r}_j(t)\right\}\right)}{m_i}$

Typical numerical integration scheme for time sequence $t = 0, \delta t, 2\delta t, 3\delta t, 4\delta t, 5\delta t.....$

$$\mathbf{r}_i(t) = 2\mathbf{r}_i(t-\delta t) - \mathbf{r}_i(t-2\delta t) + \frac{\mathbf{F}_i(t-\delta t)}{m_i}\left(\delta t\right)^2 + O\left(\delta t\right)^4$$

Velocity-Verlet algorithm

Some “first-principles” molecular dynamics (FPMD) implementations using the Born-Oppenheimer approximation and density functional theory --

$$\Phi^{DFT}\left(\left\{\mathbf{r}_j(t)\right\}\right) \equiv E^{DFT}_{total\ electron}\left(\left\{\mathbf{r}_j(t)\right\}\right)$$

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Cite this: *Energy Environ. Sci.*, 2020, **13**, 928

High-throughput computational screening for solid-state Li-ion conductors†

Leonid Kahle, * Aris Marcolongo ‡ and Nicola Marzari

We present a computational screening of experimental structural repositories for fast Li-ion conductors, with the goal of finding new candidate materials for application as solid-state electrolytes in next-generation batteries. We start from ~1400 unique Li-containing materials, of which ~900 are insulators at the level of density-functional theory. For those, we calculate the diffusion coefficient in a highly automated fashion, using extensive molecular dynamics simulations on a potential energy surface (the recently published pinball model) fitted on first-principles forces. The ~130 most promising candidates are studied with full first-principles molecular dynamics, including an estimate of the activation barrier for the most diffusive structures. The results of the first-principles simulations of the candidate solid-state electrolytes found are discussed in detail.

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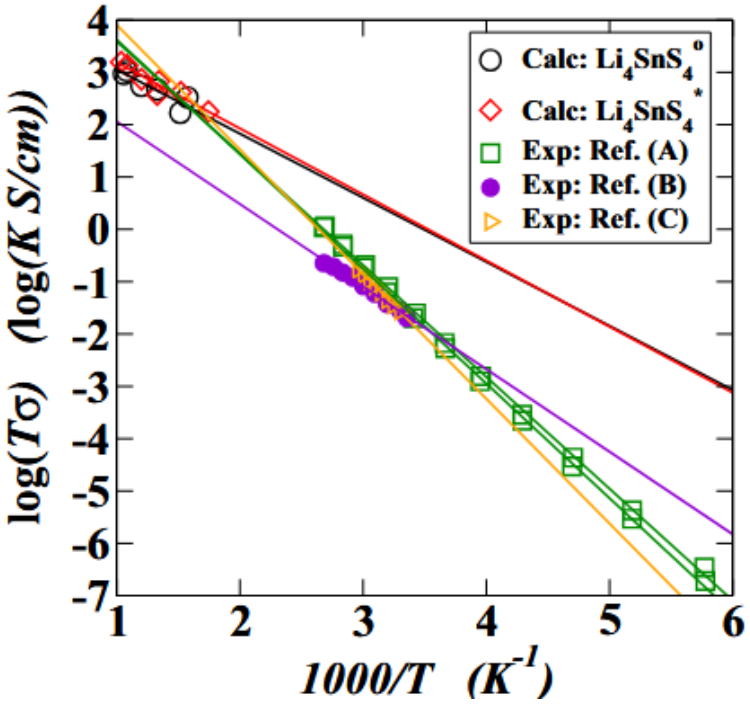
rsc.li/ees

Computed σ_{tr} to screen for materials with high ionic conductivity.

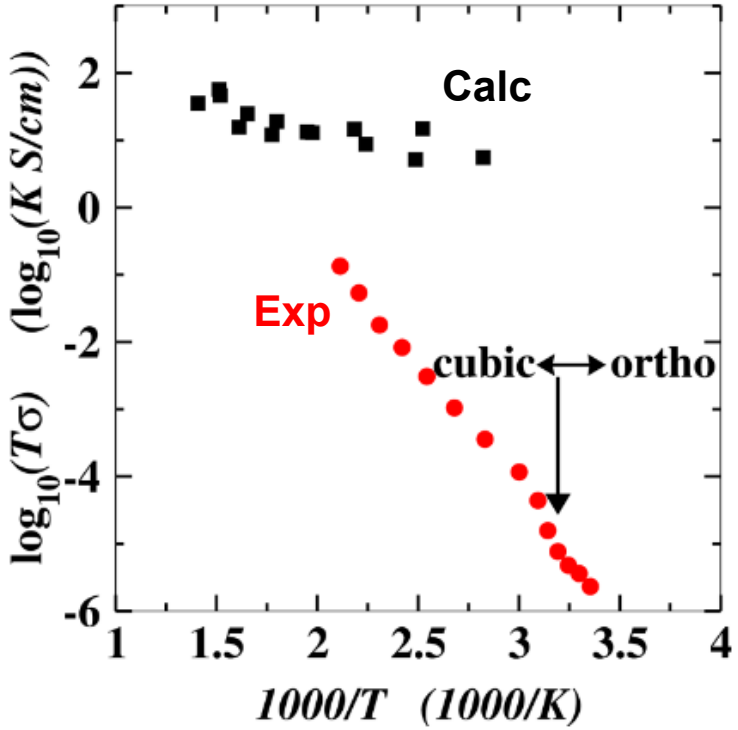
Some past results from our own group – typically finding σ_{tr} to overestimate the experimental conductivity

Li_4SnS_4



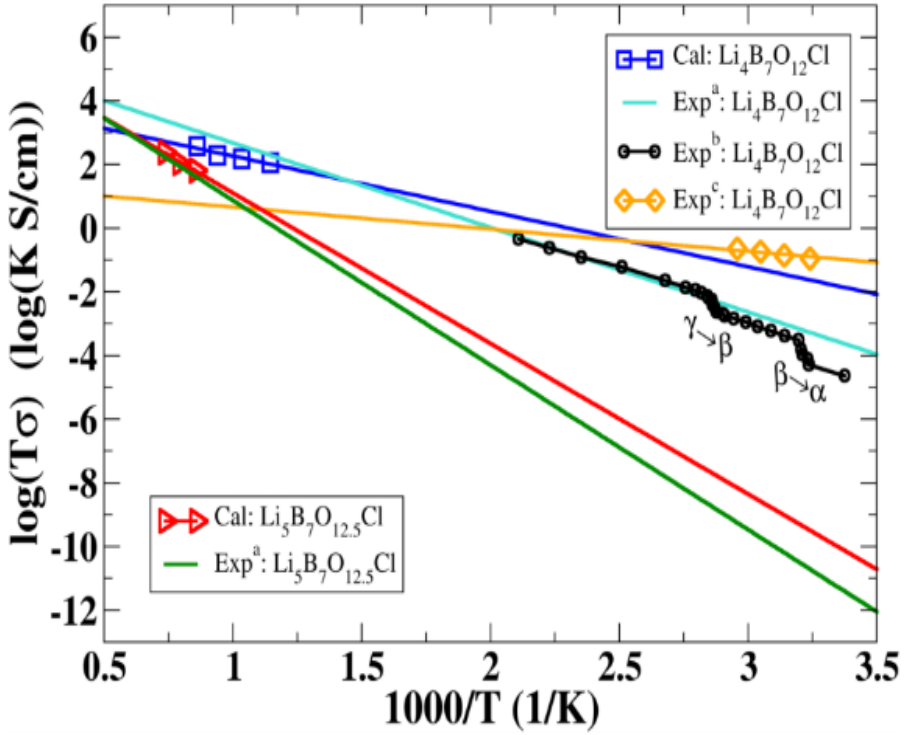
Ahmad Al-Qawasmeh, Jason Howard, and N. A. W. Holzwarth, JECS 164, A6386 (2017)

Li_2OHCl



Jason Howard, Z. D. Hood, and N. A. W. Holzwarth, PRM 1, 075406 (2017)

$Li_4B_7O_{12}Cl$



Yan Li, Z. D. Hood, and N. A. W. Holzwarth, PRM 6, 025401 (2022)

Some details of computational methods –

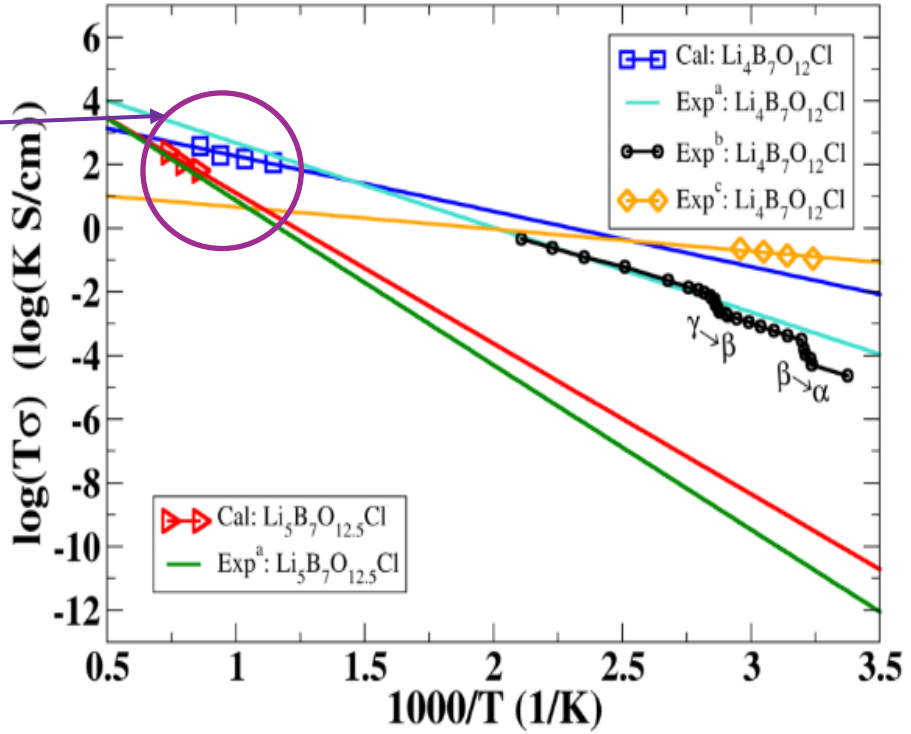
Thanks to the Born-Oppenheimer approximation, the positions of the atomic nuclei can be treated with classical mechanics, while for each atomic configuration, the electronic ground state energies and forces are determined from density functional theory using the projector augmented wave formalism (PAW) of Blöchl (1994) DOI: 10.1103/PhysRevB.50.17953 **and the PBESOL exchange-correlation functional of Perdew (2008)** DOI: 10.1103/PhysRevLett.100.136406 **Density functional calculations were performed with the open source Quantum Espresso package.**

Typical first principles molecular dynamics runs represent simulation times of ~ 100 ps or less.

What could be the problem?

Simulations performed at High T to increase the number of events; extrapolation to experimental temperatures may be inaccurate.

$Li_4B_7O_{12}Cl$



Yan Li, Z. D. Hood, and N. A. W. Holzwarth, PRM 6, 025401 (2022)

Inspiration --

Faraday Discussions

Cite this: *Faraday Discuss.*, 2025, **255**, 411

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Tracking Li atoms in real-time with ultra-fast NMR simulations†

Angela F. Harper, *[a] Tabea Huss, [a] Simone S. Köcher [ab] and Christoph Scheurer[a]

Used a machine-learning methodology to simulate solid state NMR detection of ionic conductivity in Li_3PS_4 near ROOM TEMPERATURE for micro-seconds!!!!

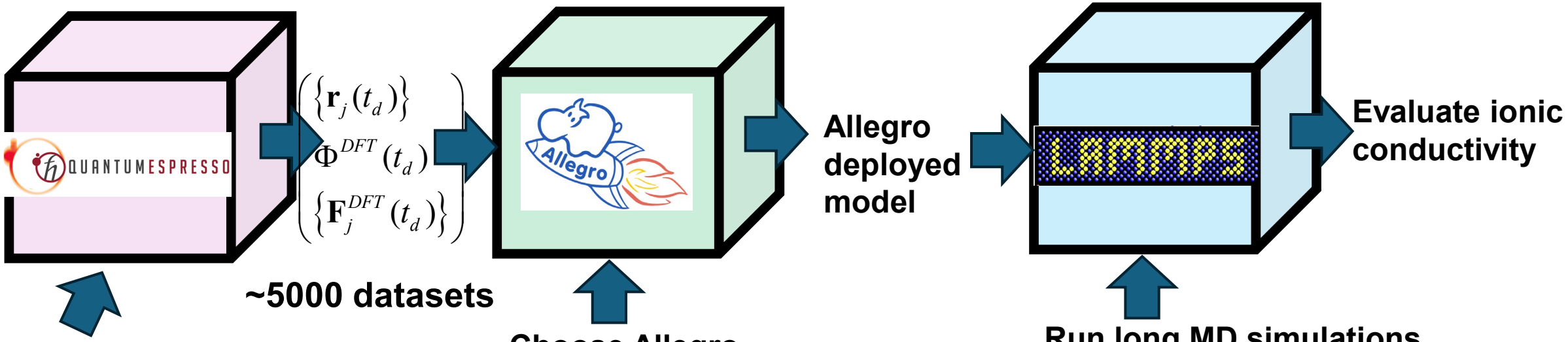
➔Motivated the present work using machine-learning at lower temperatures to study the full and approximate Green-Kubo equations for various solid electrolytes.

Process for using machine learning to expand capabilities of “first principles” conductivity simulations

Prepare data for training

Perform training and validation

Run several long MD simulations



~5000 datasets

Allegro deployed model

Evaluate ionic conductivity

For each material, perform several FPMD simulations at various temperatures

Choose Allegro “hyperparameters”

Run long MD simulations for large simulation cells at various temperatures

Some details of the Allegro software package

nature communications

Article

https://doi.org/10.1038/s41467-023-36329-y

Learning local equivariant representations for large-scale atomistic dynamics

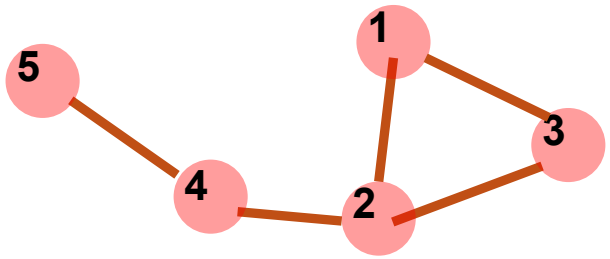
Received: 16 June 2022

Accepted: 23 January 2023

Albert Musaelian[1,3], Simon Batzner[1,3] ✉, Anders Johansson[1], Lixin Sun[1], Cameron J. Owen[1], Mordechai Kornbluth[2] & Boris Kozinsky[1,2] ✉

+ major update in Apr. 2025 with Chuin Wei Tan and others

Allegro achieves efficiency without loss of accuracy by focusing on calculating pair energies and forces within a cut off radius R_c



$$\Phi^{\text{Allegro}}\left(\{\mathbf{r}_j\}\right) = \sum_{i=1}^{N}\left(s_{Z_i}E_i + \mu_{Z_i}\right) \qquad i = \text{site index},\ Z_i = \text{atom type}$$

$$\text{where}\quad E_i = \sum_{j \text{ for } r_{ij} \le R_c} s_{Z_i Z_j} E_{ij} \qquad s_{Z_i}, s_{Z_i Z_j} = \text{scale factors} \qquad \mu_{Z_i} = \text{shift}$$

More details of the Allegro software package

The Allegro model is determined by optimizing a loss function $\mathcal{L}$ based on the difference between model minus first principles potential energies and forces for each training data point d:

$\mathcal{L} = \lambda_E \sum_d \left(\Phi_d^{Allegro} - \Phi_d^{DFT} \right)^2 + \lambda_F \sum_{id} \left(\left| \nabla_i \Phi_d^{Allegro} - \nabla_i \Phi_d^{DFT} \right|^2 \right)$ where λ_E, λ_F are chosen scale factors.

The loss function is optimized using stochastic optimization of the "learned" weights $\{\mathrm{W}^\alpha\}$

$$\Phi^{\mathrm{Allegro}}\left(\{\mathbf{r}_j\}\right) = \Phi^{\mathrm{Allegro}}\left(\{\mathrm{W}^\alpha\}, \{\mathbf{r}_j\}\right) = \sum_{i=1}^{N} \left(s_{Z_i} E_i + \mu_{Z_i} \right) \qquad E_i = \sum_{j \text{ for } r_{ij} \le R_c} s_{Z_i Z_j} E_{ij}$$

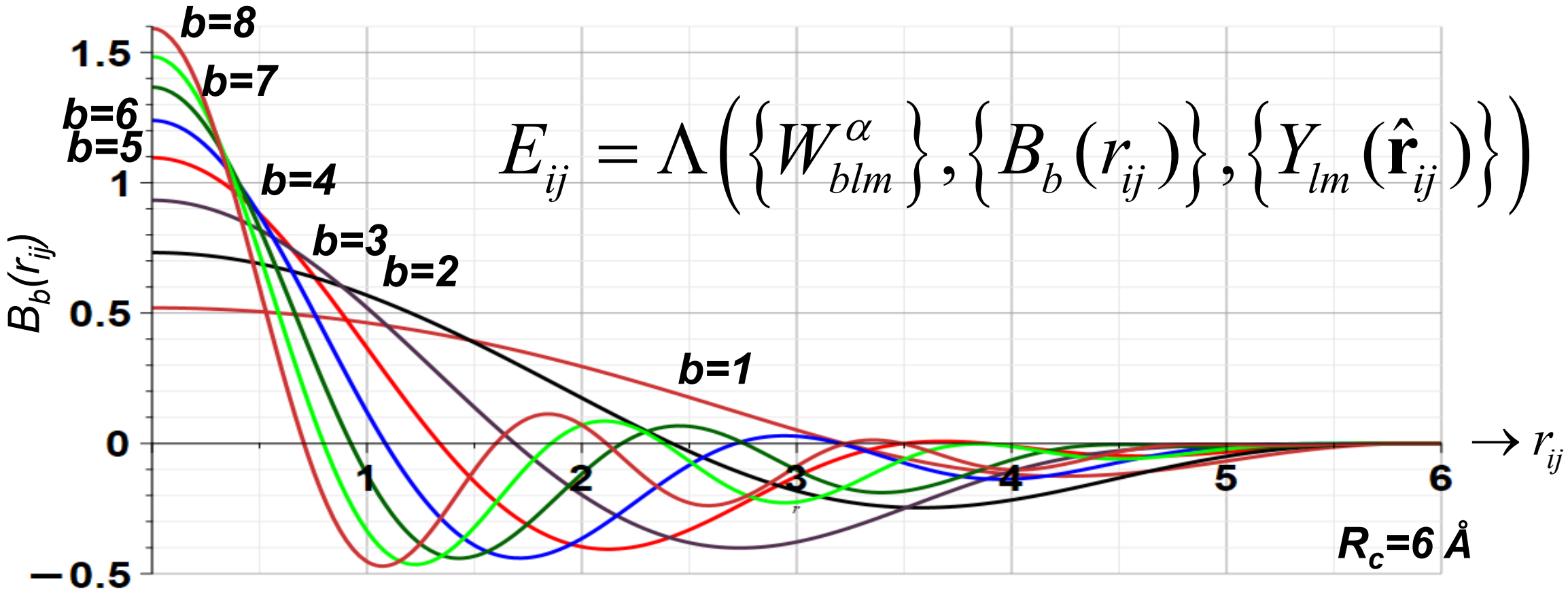
The "learned" weights $\{\mathrm{W}^\alpha\}$ appear in the E_{ij} terms as linear coefficients which multiply linear combinations of radial basis functions and spherical hamonic functions:

$$E_{ij} = \Lambda\left(\left\{ W_{blm}^\alpha \right\}, \left\{ B_b(r_{ij}) \right\}, \left\{ Y_{lm}(\hat{\mathbf{r}}_{ij}) \right\} \right)$$

(Here the $\Lambda\left(\left\{ W_{blm}^\alpha \right\}, \left\{ B_b(r_{ij}) \right\}, \left\{ Y_{lm}(\hat{\mathbf{r}}_{ij}) \right\} \right)$ is a complicated nonlinear function of the weights $\left\{ W_{blm}^\alpha \right\}$, radial basis functions $\left\{ B_b(r_{ij}) \right\}$, and spherical harmonic functions $\left\{ Y_{lm}(\hat{\mathbf{r}}_{ij}) \right\}$.

Typically, the number of "learned weights" $\{\mathrm{W}^\alpha\}$ is $10^4 - 10^6$.

Form of radial basis functions $B_b(r_{ij})$ used in Allegro



$$E_{ij} = \Lambda\left(\left\{W^{\alpha}_{blm}\right\},\left\{B_b(r_{ij})\right\},\left\{Y_{lm}(\hat{\mathbf{r}}_{ij})\right\}\right)$$

Model system – solid electrolyte composed of lithium phosphate and silicate alloys – specifically $(Li_3PO_4)_{0.75}(Li_4SiO_4)_{0.25}$ as inspired by --

JACS
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Article

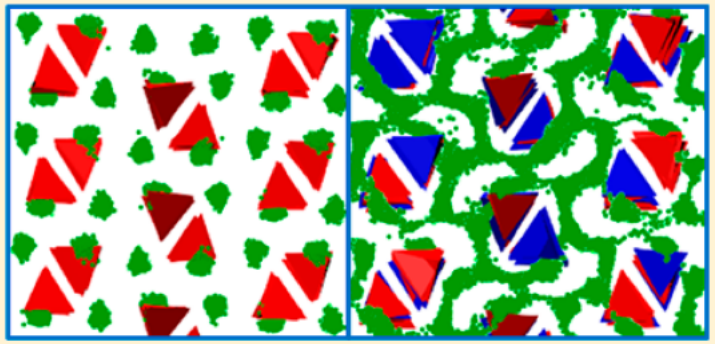
pubs.acs.org/JACS

DOI: 10.1021/jacs.5b04444
J. Am. Chem. Soc. 2015, 137, 9136–9145

Structural and Mechanistic Insights into Fast Lithium-Ion Conduction in Li_4SiO_4–Li_3PO_4 Solid Electrolytes

Yue Deng,[†,‡] Christopher Eames,[‡] Jean-Noël Chotard,[†] Fabien Lalère,[†] Vincent Seznec,[†] Steffen Emge,[§] Oliver Pecher,[§] Clare P. Grey,[§] Christian Masquelier,[†] and M. Saiful Islam*[,‡]

ABSTRACT: Solid electrolytes that are chemically stable and have a high ionic conductivity would dramatically enhance the safety and operating lifespan of rechargeable lithium batteries. Here, we apply a multi-technique approach to the Li-ion conducting system $(1-z)Li_4SiO_4-(z)Li_3PO_4$ with the aim of developing a solid electrolyte with enhanced ionic conductivity. Previously unidentified superstructure and immiscibility features in high-purity samples are characterized by X-ray and neutron diffraction across a range of compositions (z = 0.0–1.0). Ionic conductivities from AC impedance measurements and large-scale molecular dynamics (MD) simulations are in good agreement, showing very low values in the parent phases (Li_4SiO_4 and Li_3PO_4) but orders of magnitude higher conductivities (10^{-3} S/cm at 573 K) in the mixed compositions. The MD simulations reveal new mechanistic insights into the mixed Si/P compositions in which Li-ion conduction occurs through 3D pathways and a cooperative interstitial mechanism; such correlated motion is a key factor in promoting high ionic conductivity. Solid-state ^{6}Li, ^{7}Li, and ^{31}P NMR experiments reveal enhanced local Li-ion dynamics and atomic disorder in the solid solutions, which are correlated to the ionic diffusivity. These unique insights will be valuable in developing strategies to optimize the ionic conductivity in this system and to identify next-generation solid electrolytes.



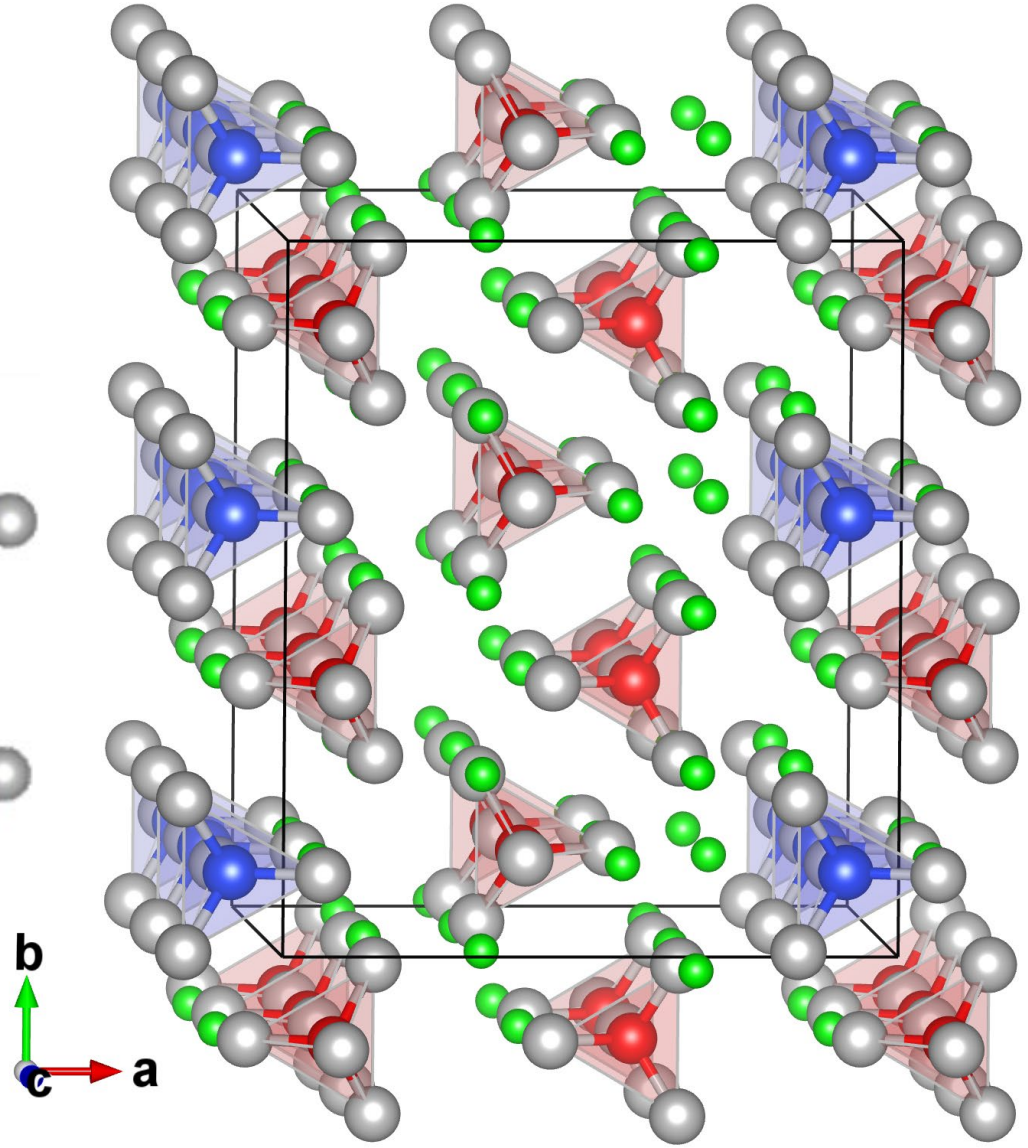
Structure 1

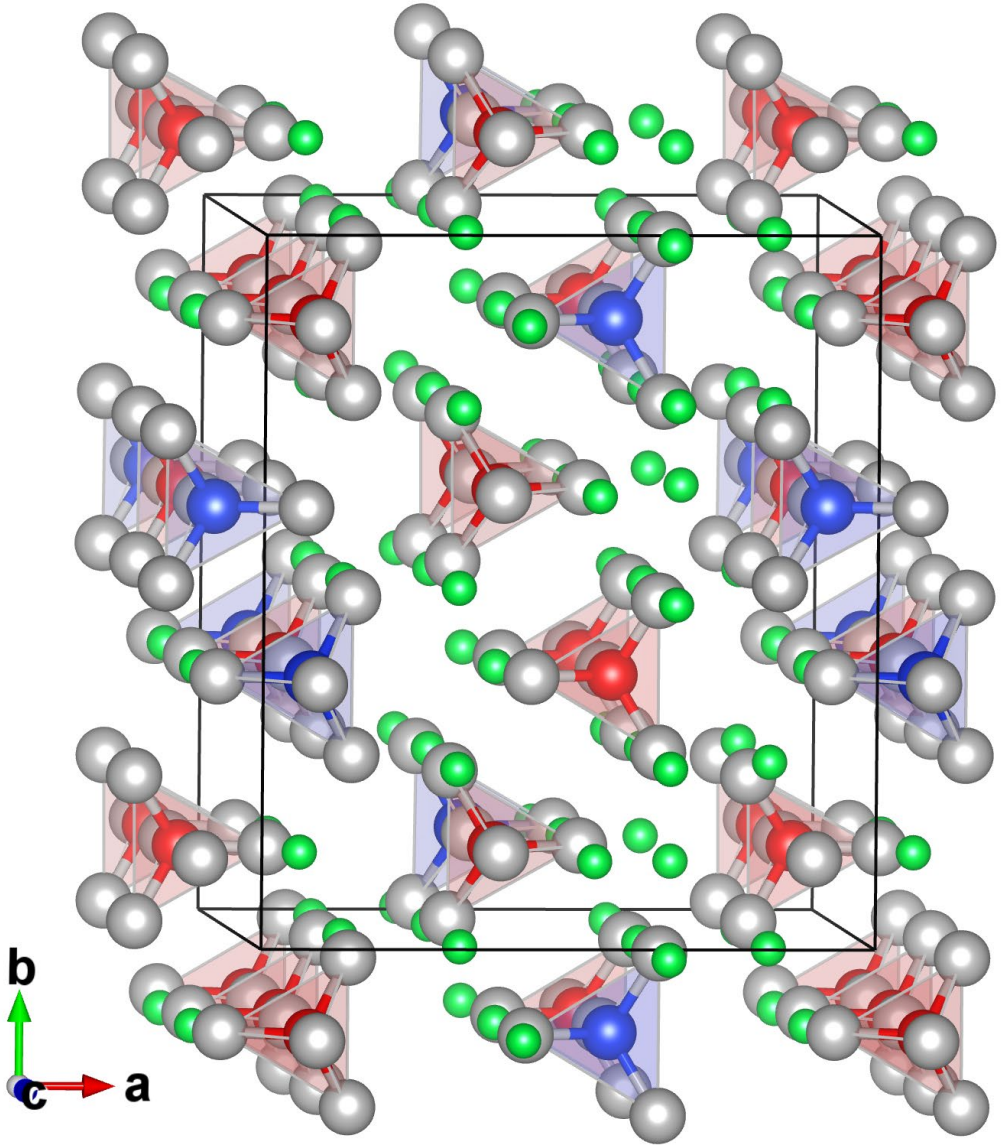
Structure 2

Li

SiO_4

PO_4

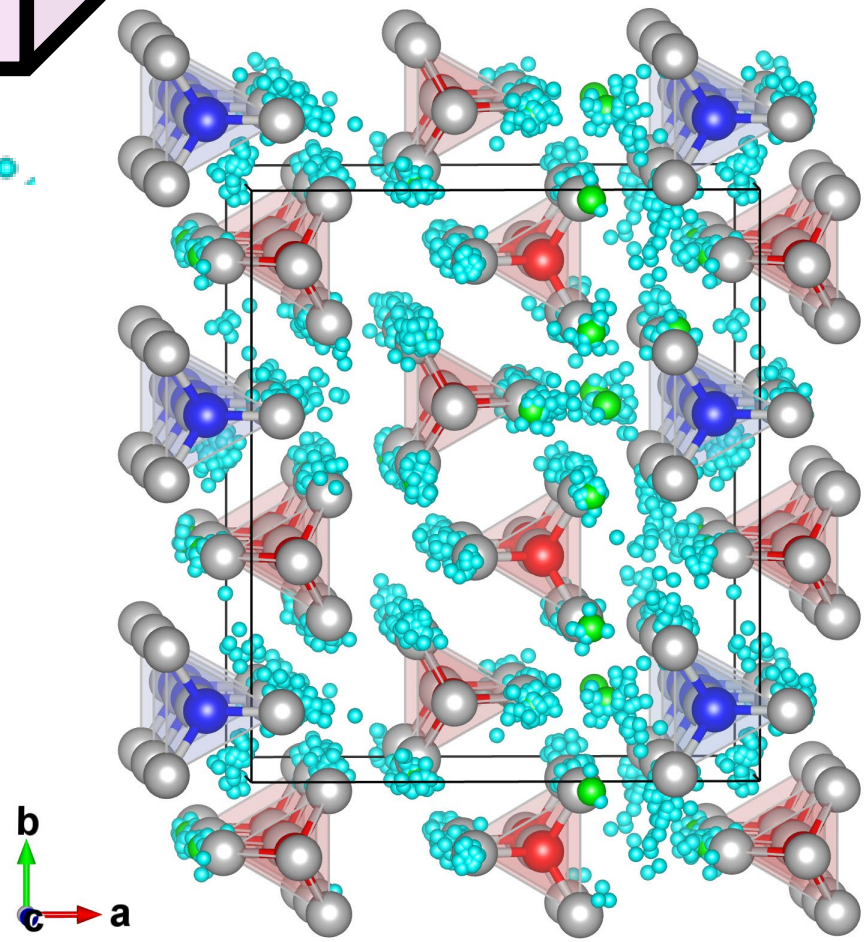




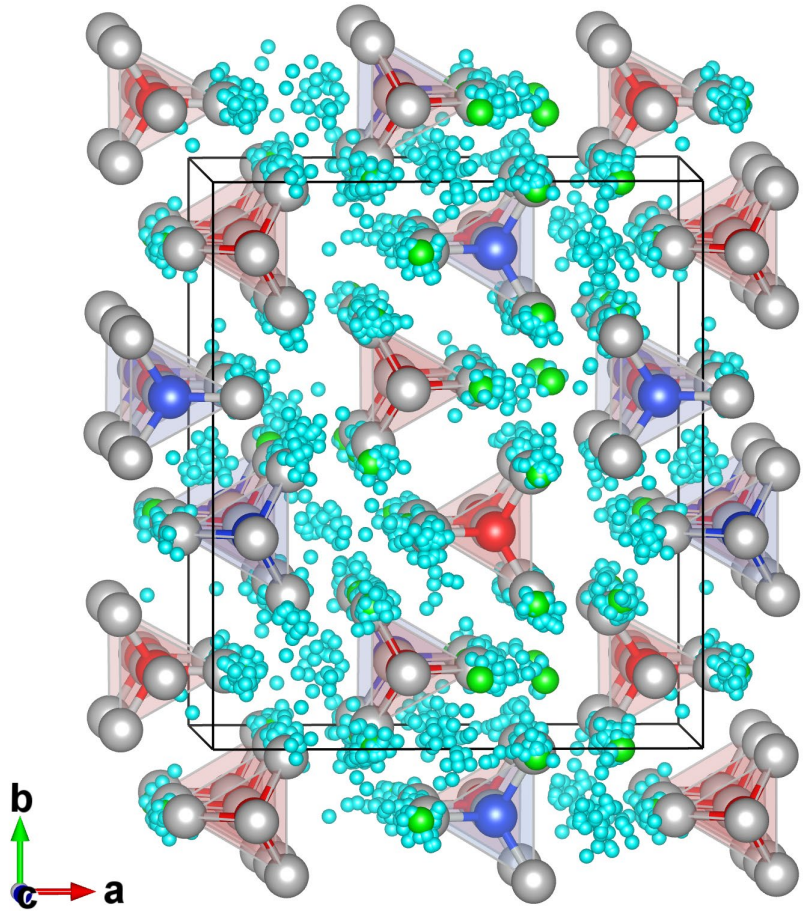
Visualization of Li ion migration during 44 time intervals of 0.3 ps

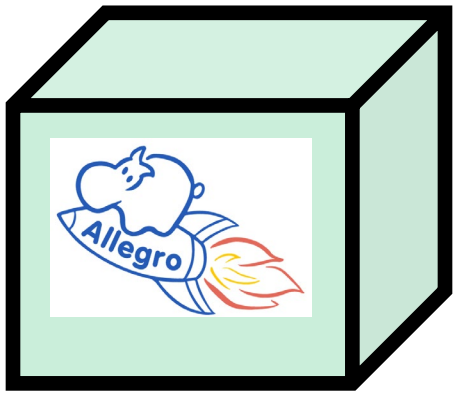
Migrating Li

Structure 1



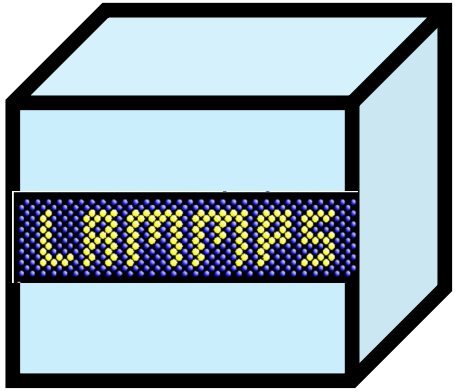
Structure 2



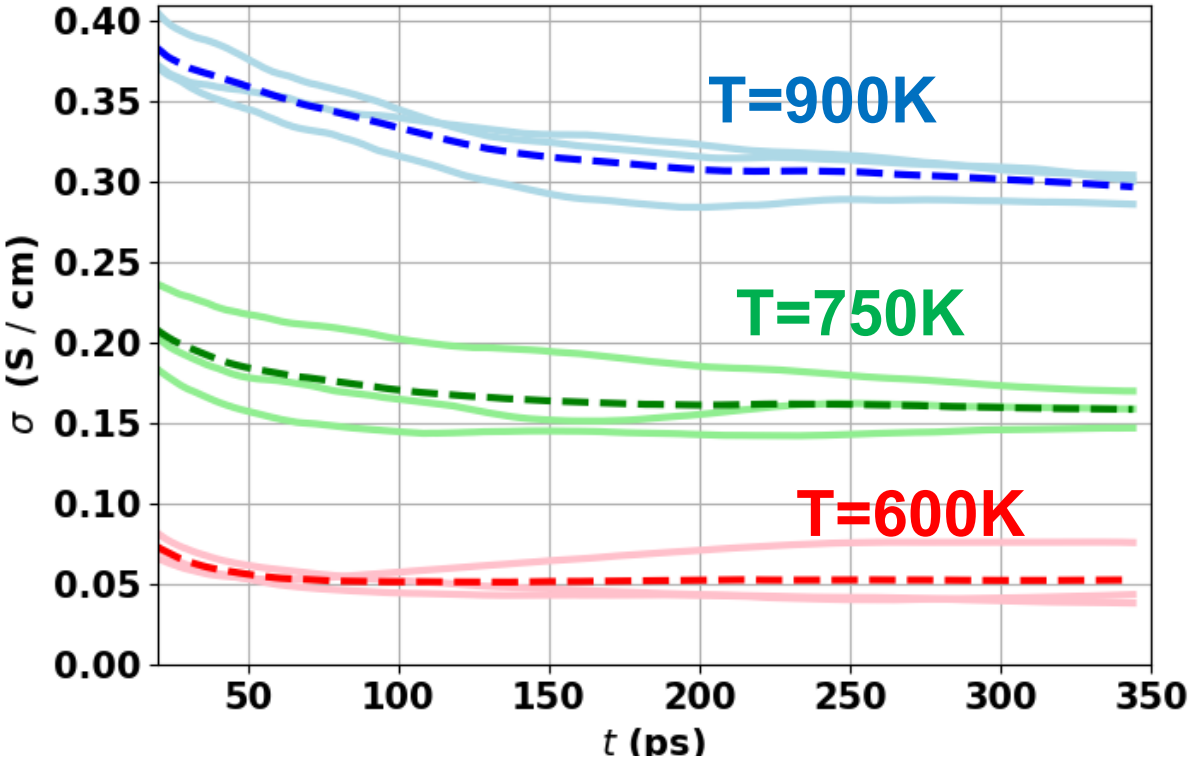


Results for two structures and various choices of Allegro “hyperparameters”

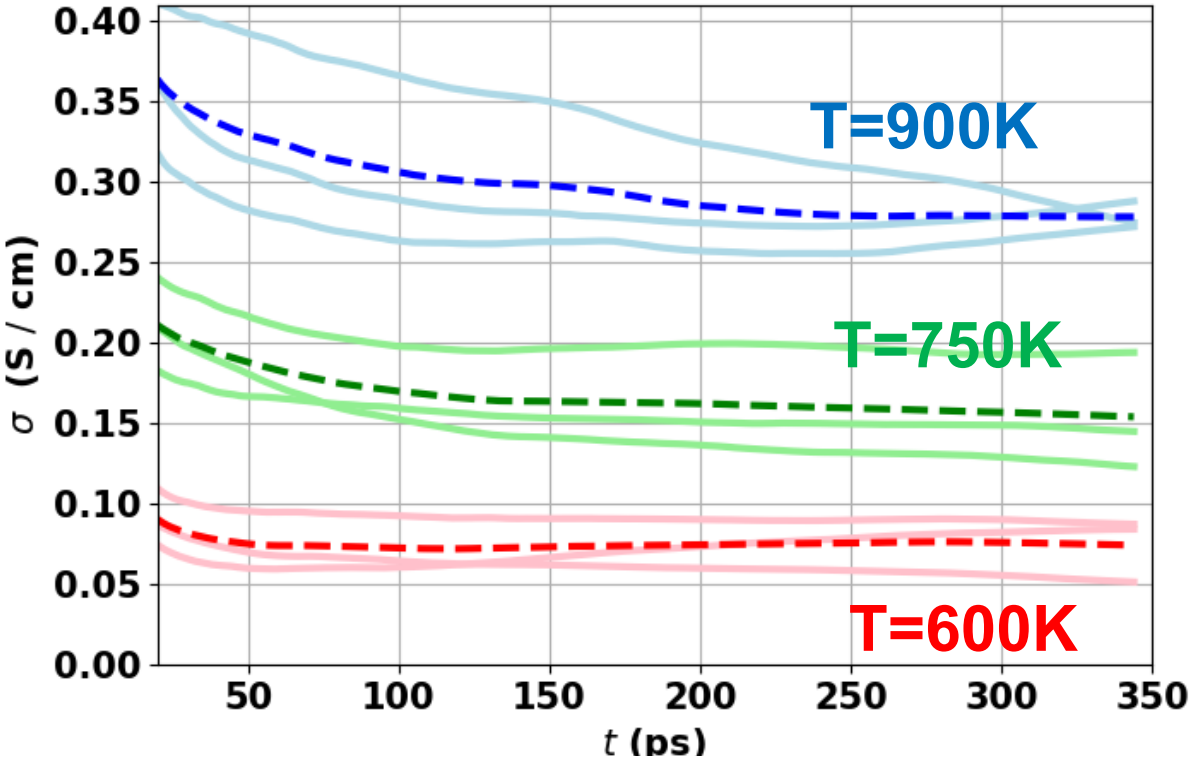
Name	Structure	# Weights	Status
Small	Struct1	~24,500	Completed
Small	Struct2	~24,500	LAMMPS failed
Medium	Struct1	~91,100	Completed
Medium	Struct2	~91,100	Completed



σ_{tr} results, comparing small and medium Allegro hyperparameters using 3 velocity seeds (lines) and their average (dashes)

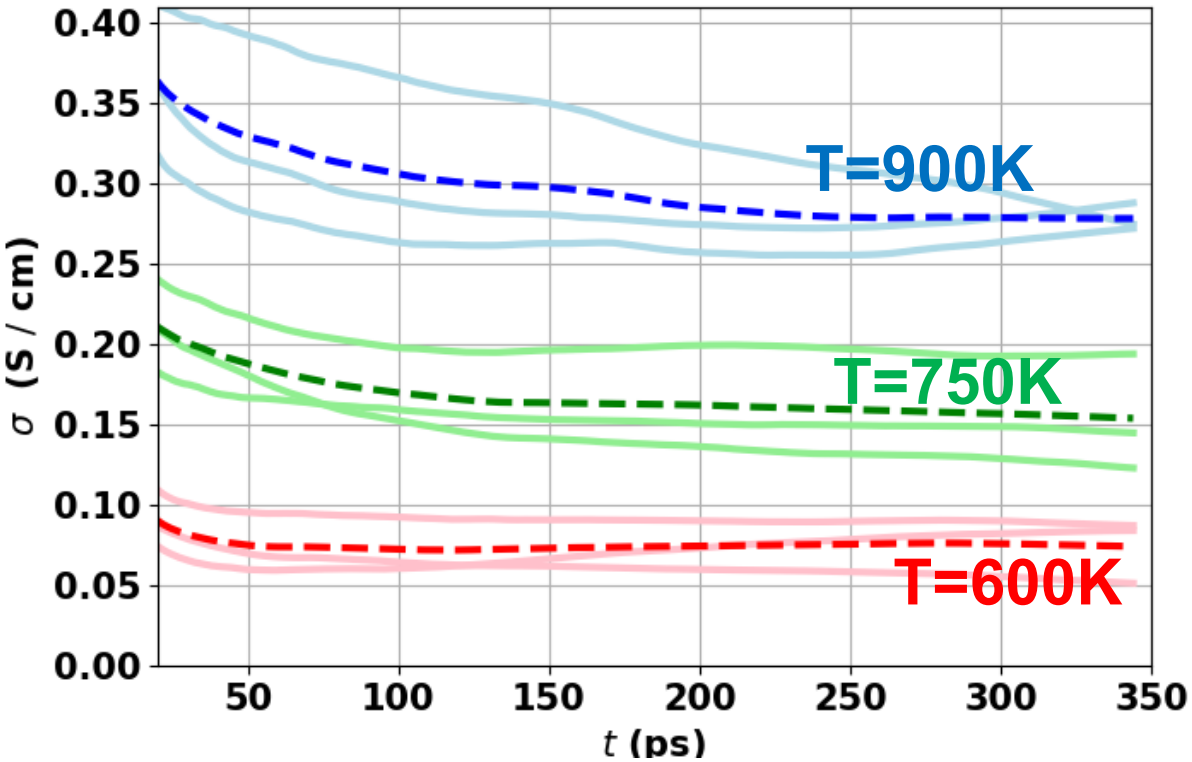


Struct1 -- Small

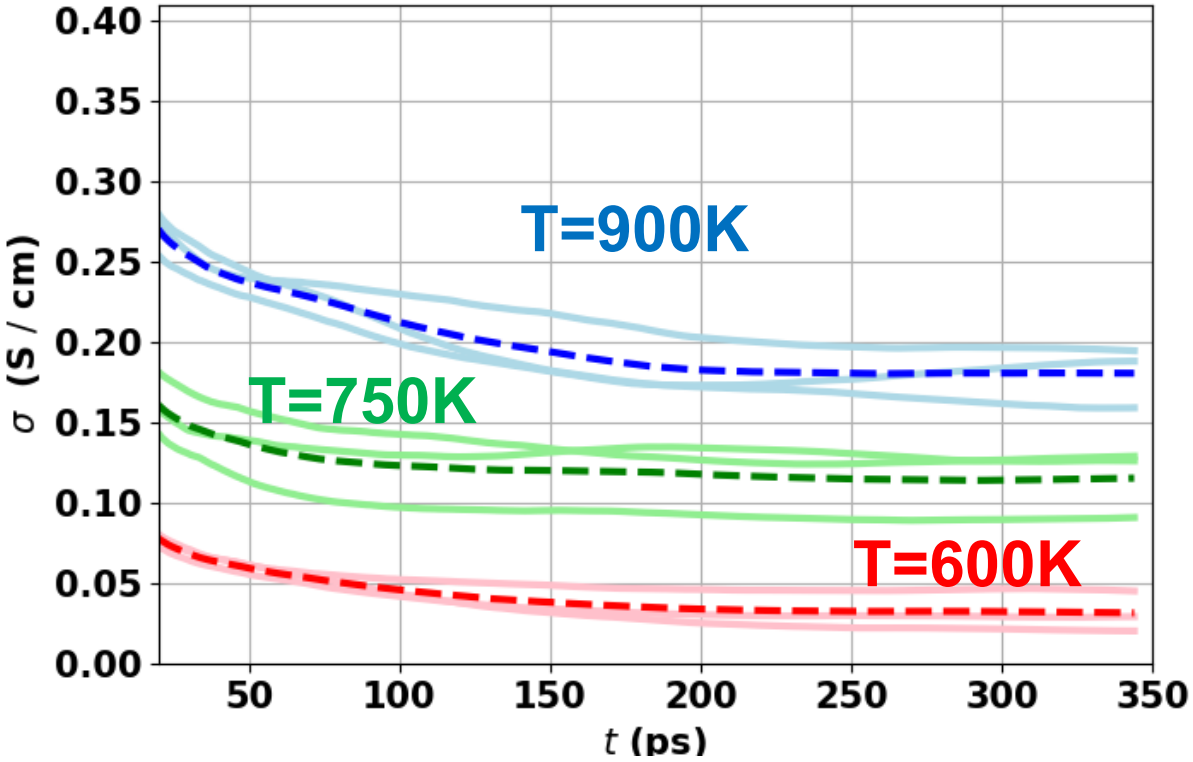


Struct1 -- Medium

σ_{tr} results, comparing Struct1 & Struct2 with medium Allegro hyperparameters using 3 velocity seeds (lines) and their average (dashes)



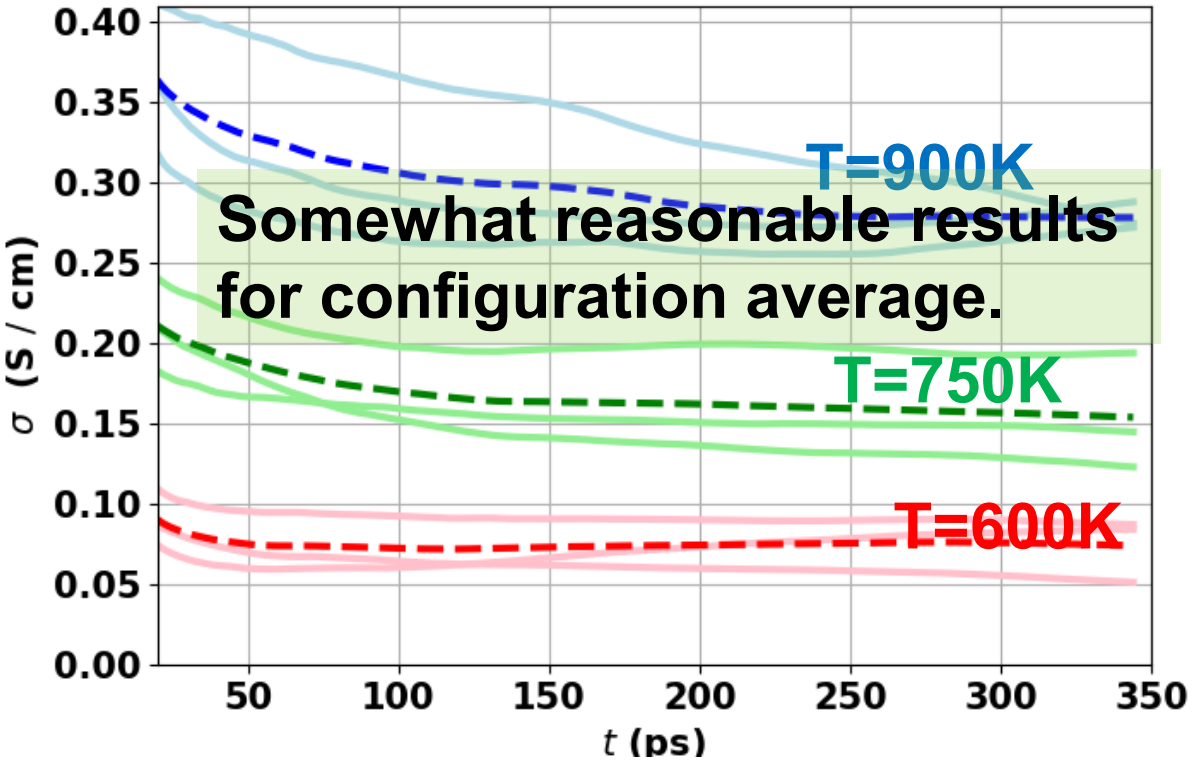
Struct1 -- Medium



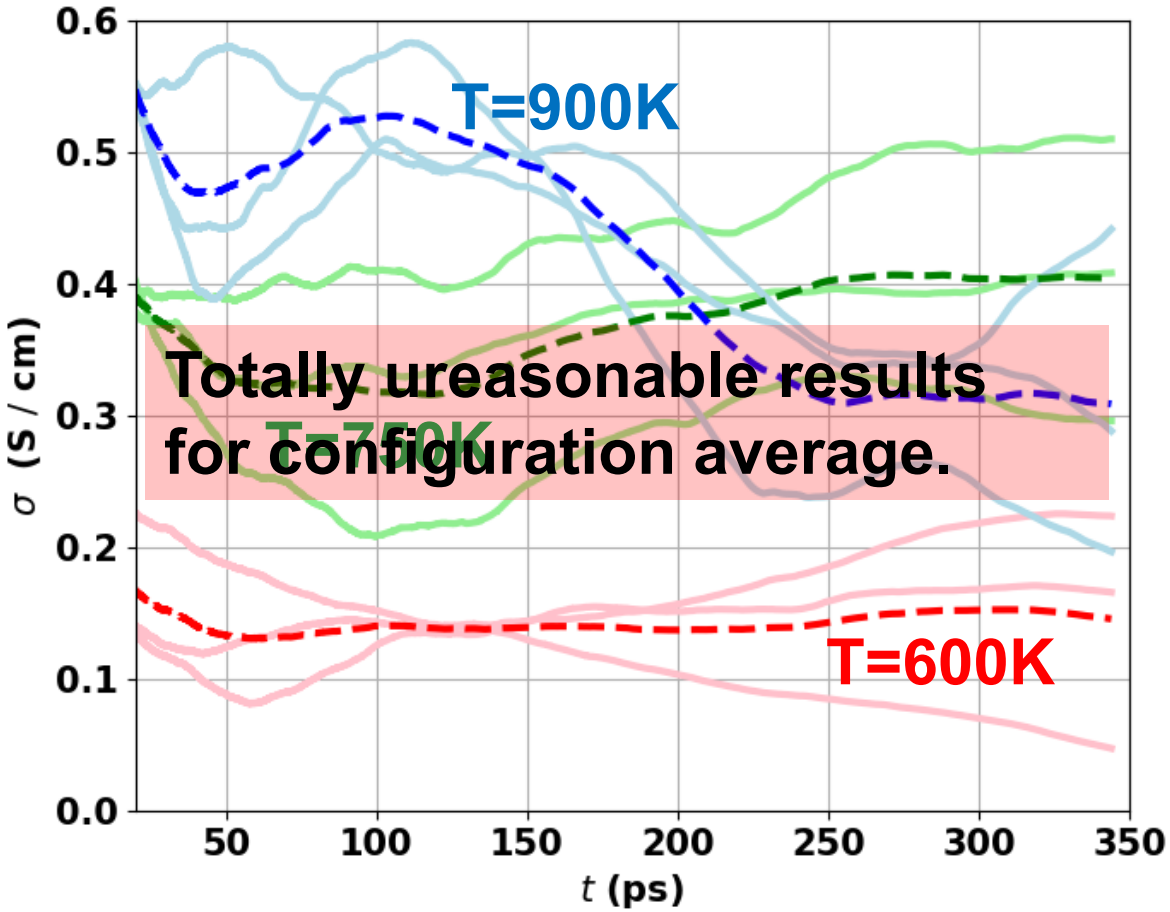
Struct2 -- Medium

Note that these results at 600K are in rough agreement with those of Deng and coworkers.

Struct1 with medium Allegro hyperparameters using 3 velocity seeds (lines) and their average (dashes), comparing σ_{tr} and σ

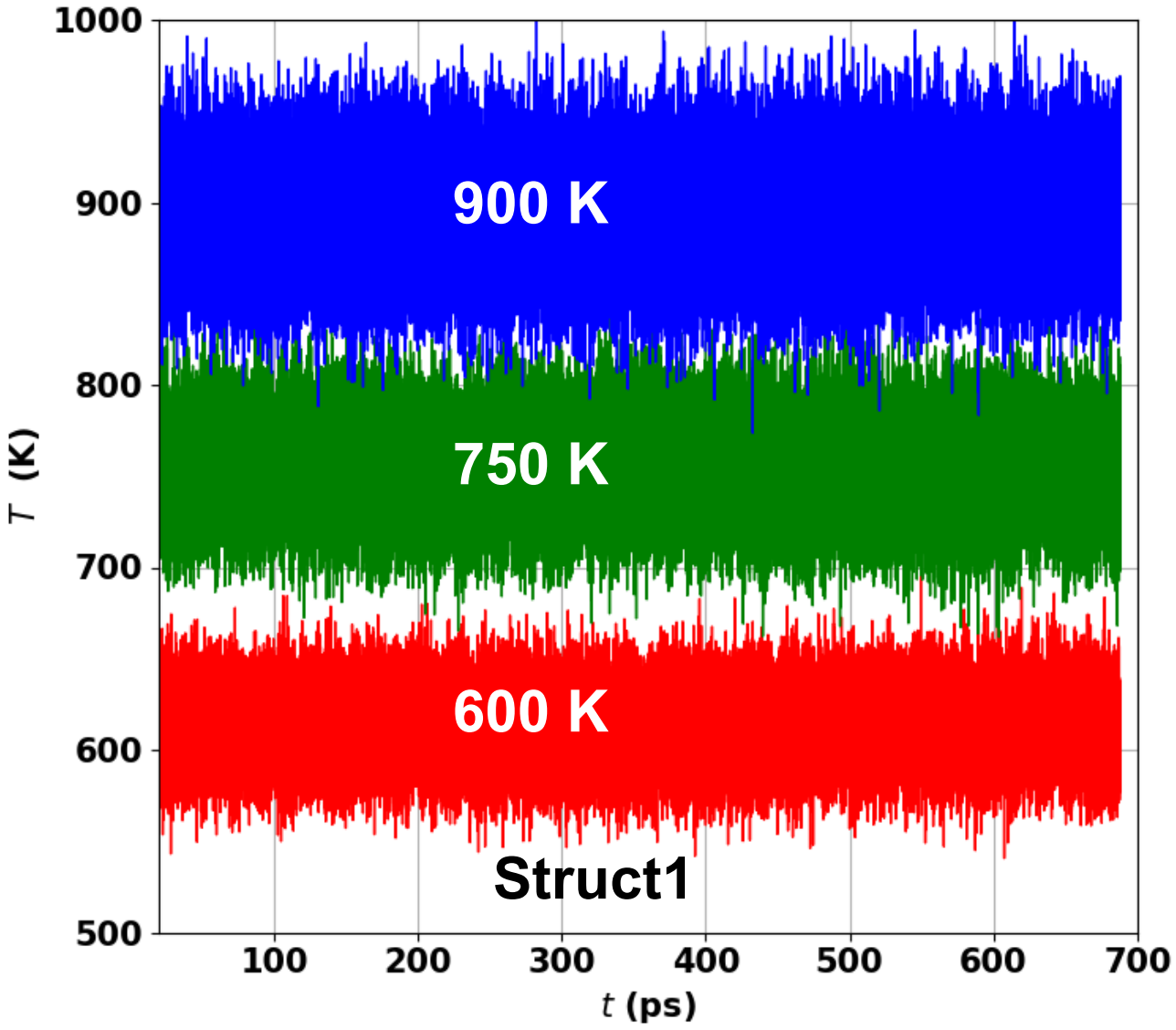


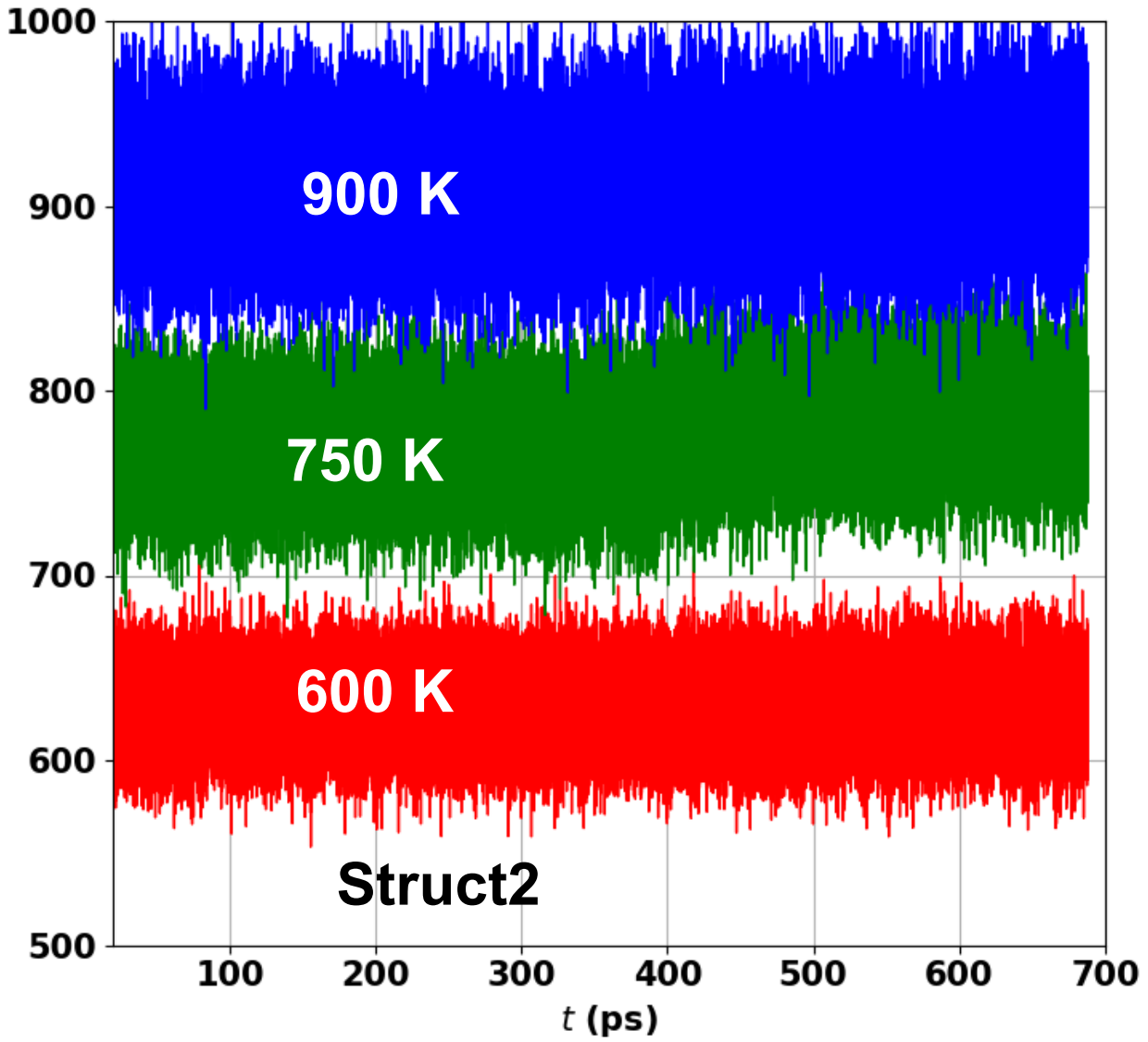
σ_{tr}



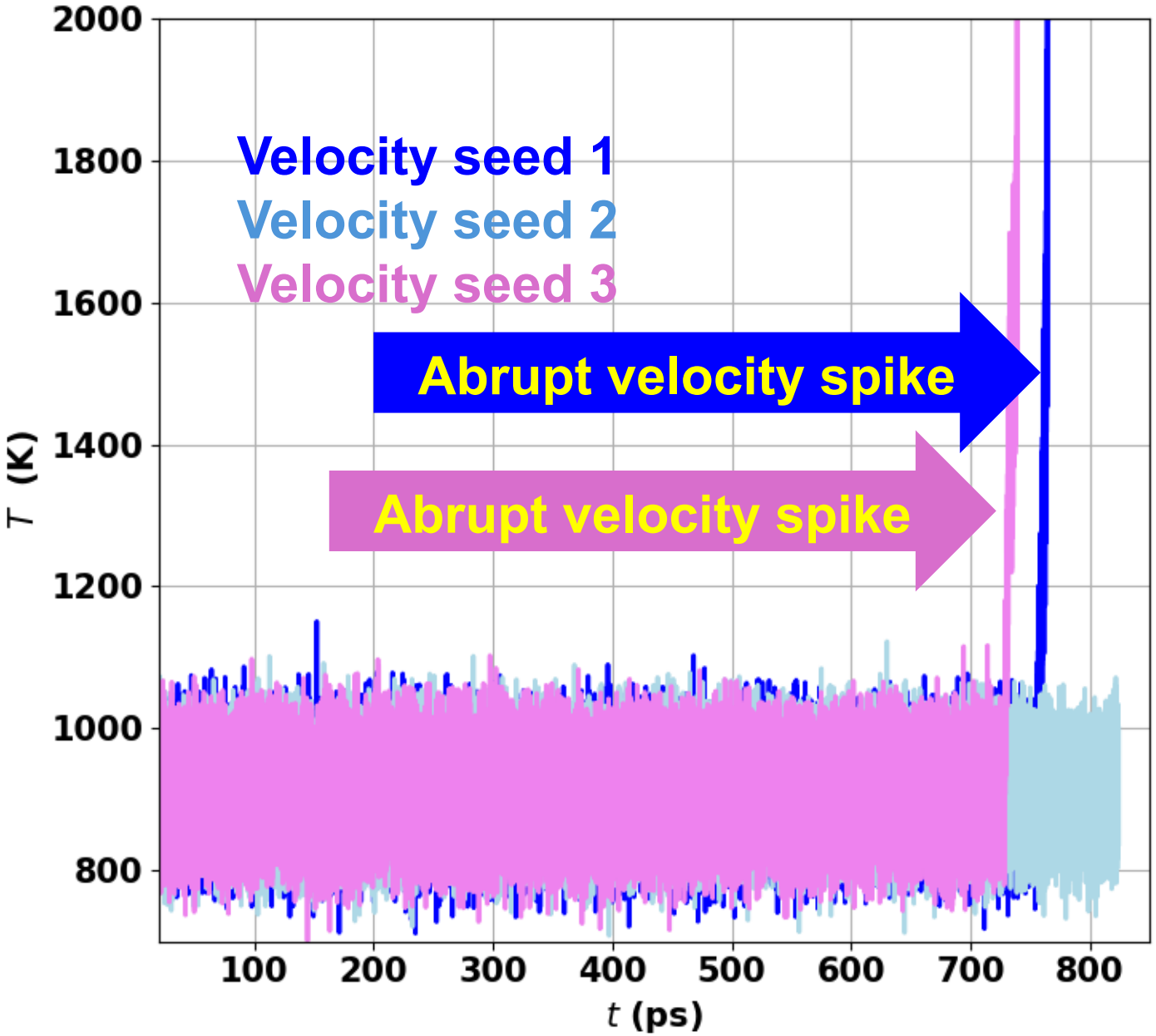
σ

LAMMPS temperatures (averaged over 3 seeds) for Medium set





Surprise failure of Allegro "small" deploy set for Struct2 during long LAMMPS MD simulation, **although** Allegro training and validation process indicated good convergence and small training and validation errors.



Outlook

Successes

- Used Allegro software to study 2 structures in the $(Li_3PO_4)_{3/4}(Si_4PO_4)_{1/4}$ system of electrolytes, speeding up the efficiency of calculating σ_{tr} by 10 times, thanks also to LAMMPS MD software.
- The Allegro-LAMMPS combination allows for long atomistic simulations to be performed at lower average temperatures.
- Allegro representations of training and validation data seems to be relatively insensitive to reasonable hyperparameter choices.

Needs further work

- Need to avoid the surprise failures.
- While there are clear improvements in calculating the tracer conductivity, there is yet no improvement in calculating the full conductivity which is a long standing issue with MD simulations.

Why we might want to calculate the full ionic conductivity –

1. **To help discover correlated mechanisms for ionic conductivity and reliably compute the Haven ratio.**
2. **To meet the challenges of the numerical instability of long MD simulations.**