Computationally Simulating Reproducible Estimates of Ionic Conductivity in Electrolyte Materials

Natalie A. W. Holzwarth in collaboration with D. Cory Lynch
Department of Physics, Wake Forest University, Winston-Salem, NC

OUTLINE

- ☐ Equations for ionic conductivity
- ☐ A list of important developments
- ☐ Examples
- ☐ Outlook

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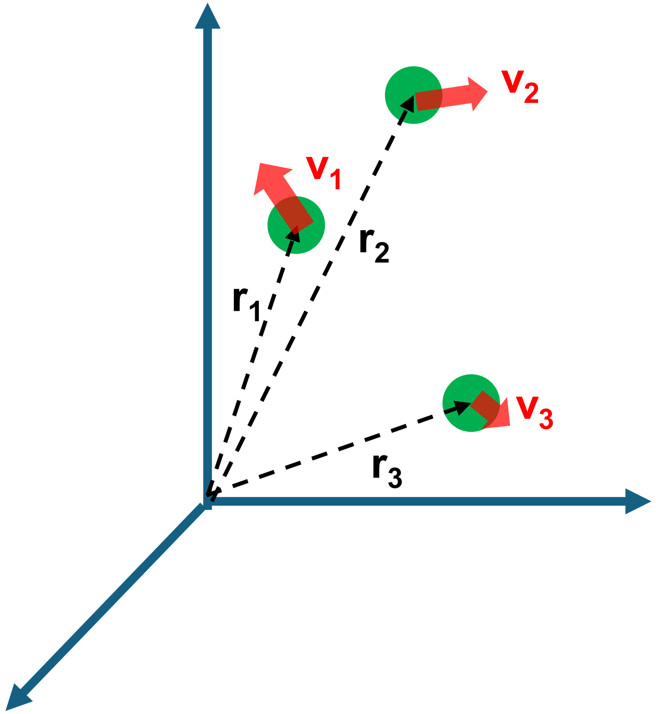
➔with special thanks to Sean Anderson (WFU) and Chuin Wei Tan (Harvard University)

Ionic conductivity from the mindset of atomistic modeling:



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

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

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

Green-Kubo formula for evaluating ionic conductivity

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

Boltzmann constant

Temperature

Ionic conductivity from the mindset of atomistic modeling (continued):

Green-Kubo formula for evaluating ionic conductivity

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

Performing time integral of current density to obtain polarization density:

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

Alternative form of Green-Kubo ionic conductivity:

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

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:

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

Some background to the Green-Kubo conductivity formulas

in its full formulation:

$$\sigma = \frac{\Omega}{6k_BT}\lim_{t_{\max}\to\infty}\frac{1}{t_{\max}}\left\langle \left|\mathbf{P}(t_{\max})-\mathbf{P}(0)\right|^2\right\rangle_{\text{configurations}}$$

and in its approximation:

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

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”

Some developments in classical molecular dynamics implementations

1964 – A. Rahman, Phys. Rev. 136, A405 (1964) – “Correlations in motion of atoms in liquid argon” – 864 particles interacting with a truncated Lennard-Jones pair potential at T=90K for ~ 4 ps. One of the first realistic molecular dynamics simulations of transport and other properties.

1985 – Roberto Car and Michele Parrinello, Phys. Rev. Lett. 55, 2471 (1985) “Unified approach for molecular dynamics and density functional theory” – evolved into the practice of “first principles” molecular dynamics simulations.

1990 – Steve Plimpton of Sandia National Laboratory and collaborators developed open source LAMMPS software package for large scale classical molecular dynamics simulations, mainly using empirical interaction potentials. Most recently LAMMPS has been adapted for use with several different projects which use “machine learned” interactions.

2007 – Jörg Behler and Michele Parrinello, Phys. Rev. Lett. 98, 146401 (2007) “Generalized neural-network representation of high-dimensional potential-energy surfaces”

Returning to discussion of the Green-Kubo formula and its success in modeling real ionic conductors --

Full Green-Kubo formula:

$$\sigma = \frac{\Omega}{6k_BT} \lim_{t_{\max}\to\infty} \frac{1}{t_{\max}} \left\langle \left| \mathbf{P}(t_{\max}) - \mathbf{P}(0) \right|^2 \right\rangle_{\text{configurations}}$$

Numerically difficult to evaluate

Tracer approximate Green-Kubo formula:

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

Numerically reasonable to evaluate

Some successful contributions -- One example

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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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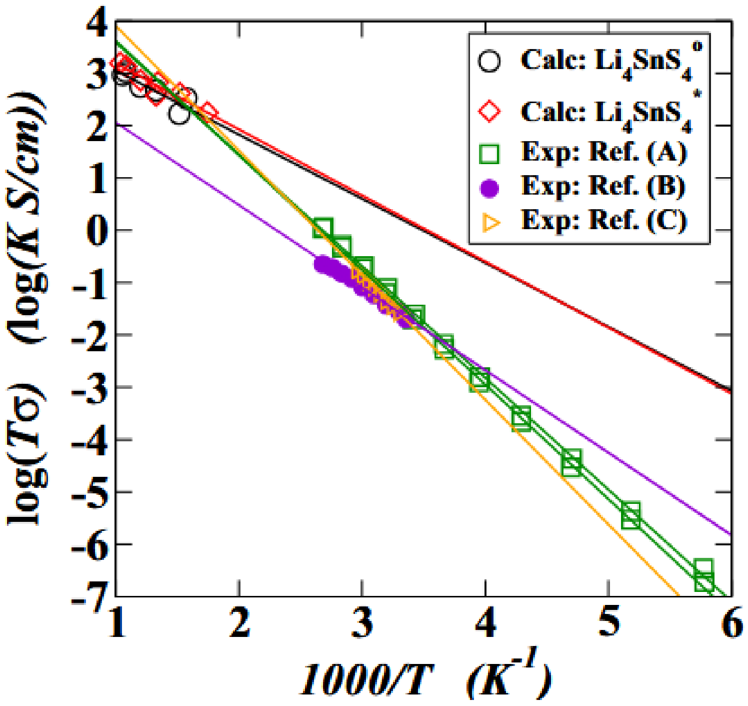
Computed approximate σ_{tr} to screen for promising conductors.

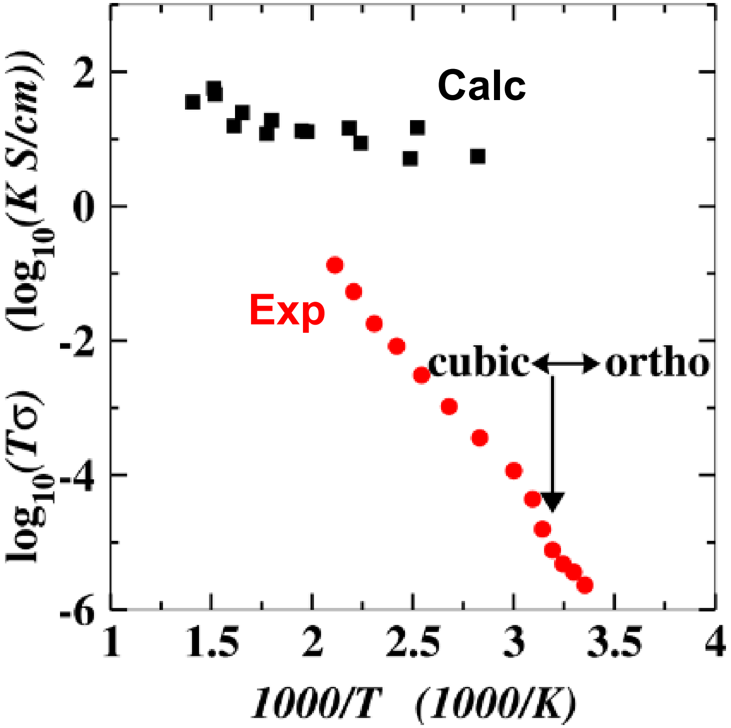
Some past results from our own group – typically finding σ_{tr} to overestimate the experimental conductivity

Li_4SnS_4



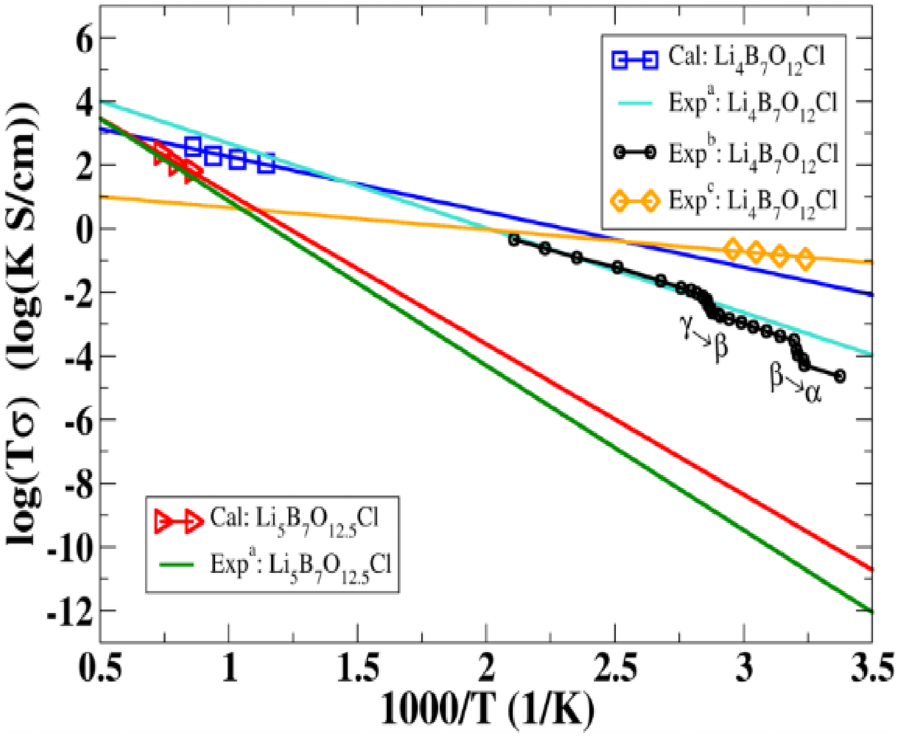
Ahmad Al-Qawasmeh, Jason Howard, and N. A. W. Holzwarth, JECS 164, A6386 (2017)

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 –

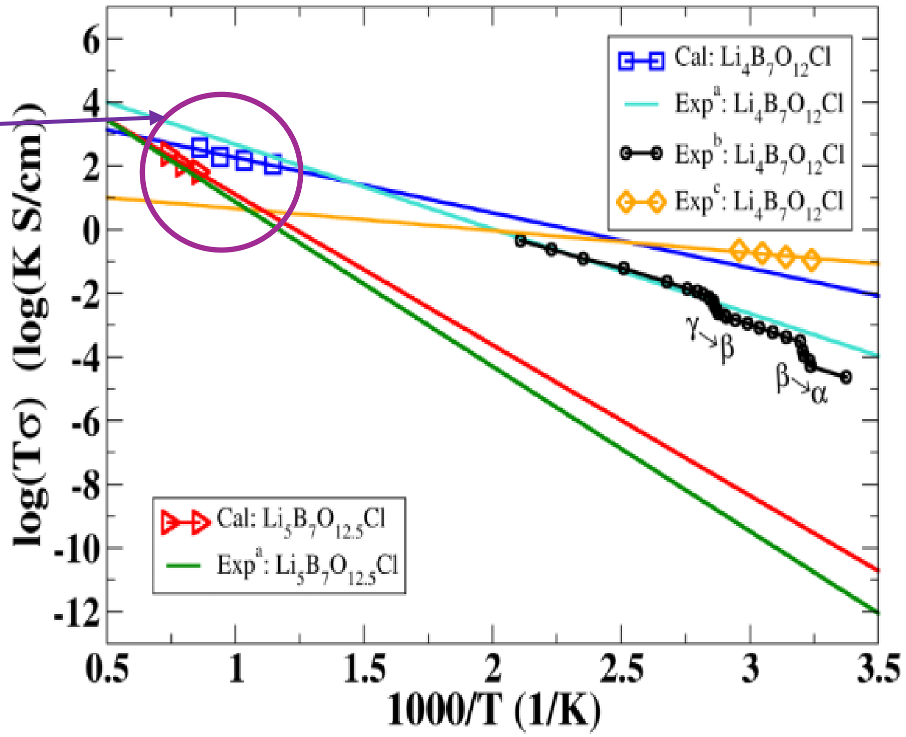
Thanks to the Born-Oppenheimer approximation, the positions of the atomic nuclei can be treated with classical mechanics, while for each atomic configuration, the electronic ground state energies and forces are determined from density functional theory using the projector augmented wave formalism (PAW) 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?

$Li_4B_7O_{12}Cl$

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

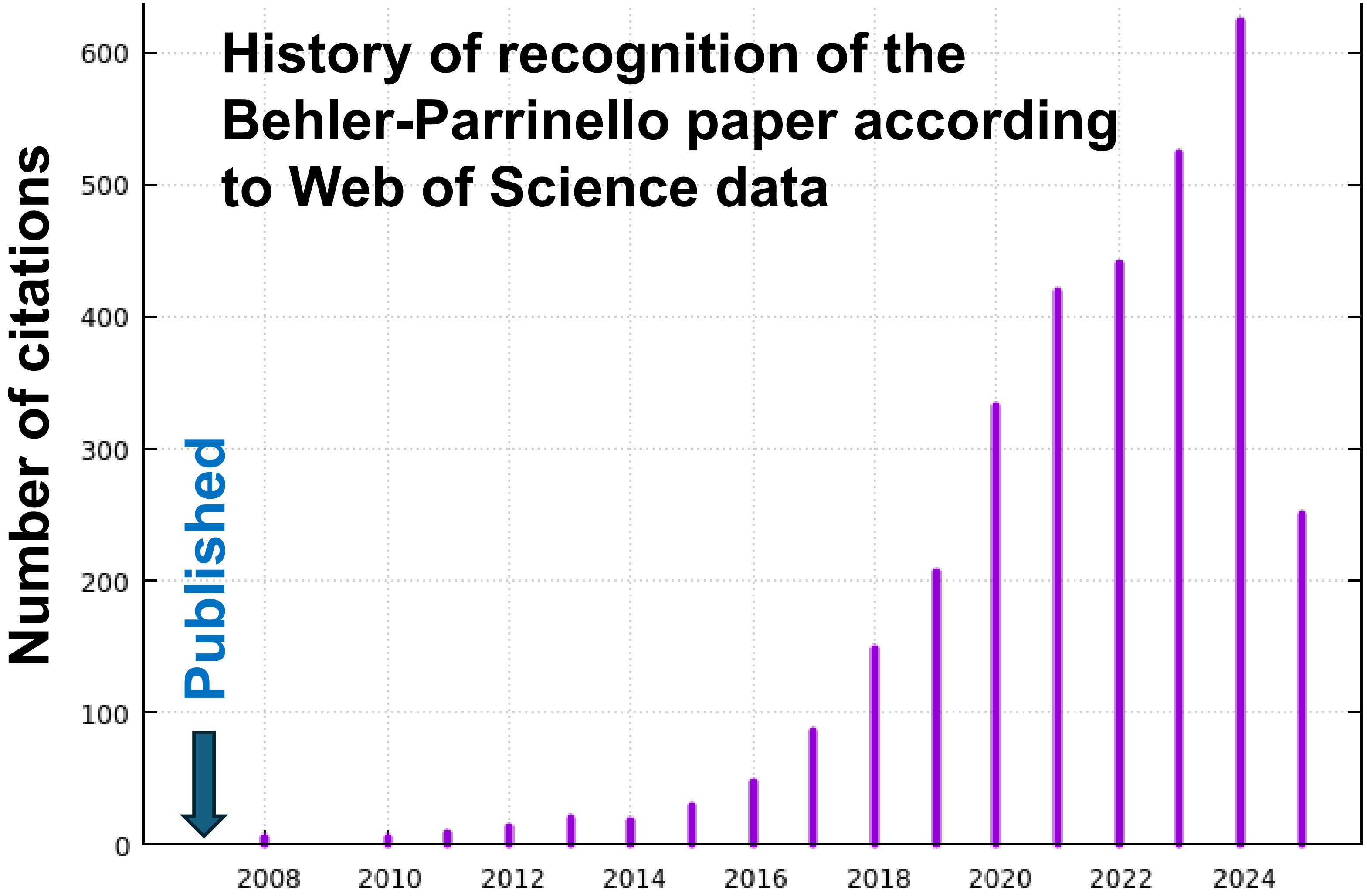


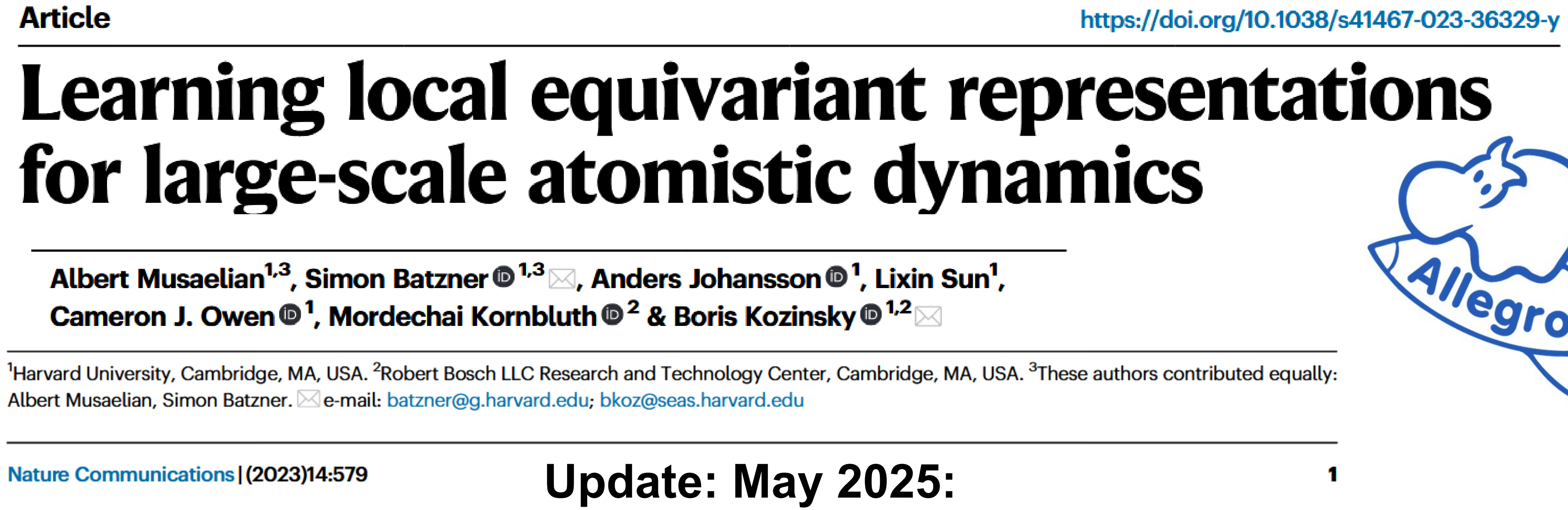
Yan Li, Z. D. Hood, and N. A. W. Holzwarth, PRM 6, 025401 (2022)

What could be a solution?

Possibly jump on the machine learning band wagon?

Evidence of the machine learning band wagon --





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

Learning local equivariant representations for large-scale atomistic dynamics

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]

[1]Harvard University, Cambridge, MA, USA. [2]Robert Bosch LLC Research and Technology Center, Cambridge, MA, USA. [3]These authors contributed equally: Albert Musaelian, Simon Batzner. ✉e-mail: batzner@g.harvard.edu; bkoz@seas.harvard.edu

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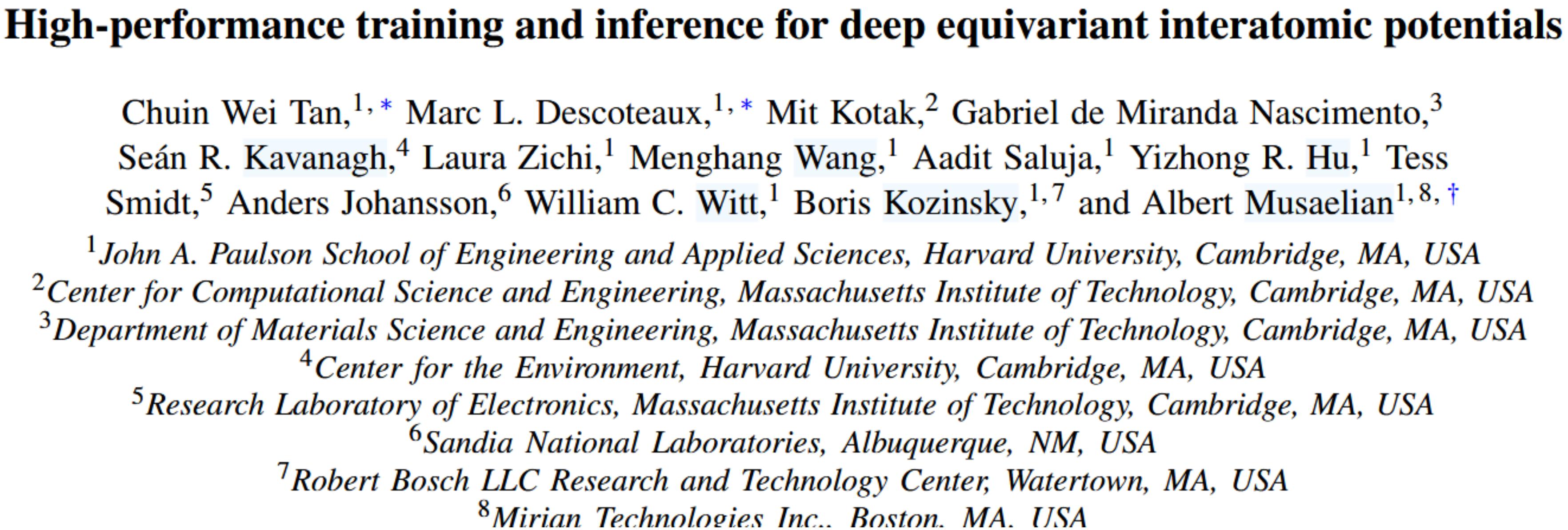
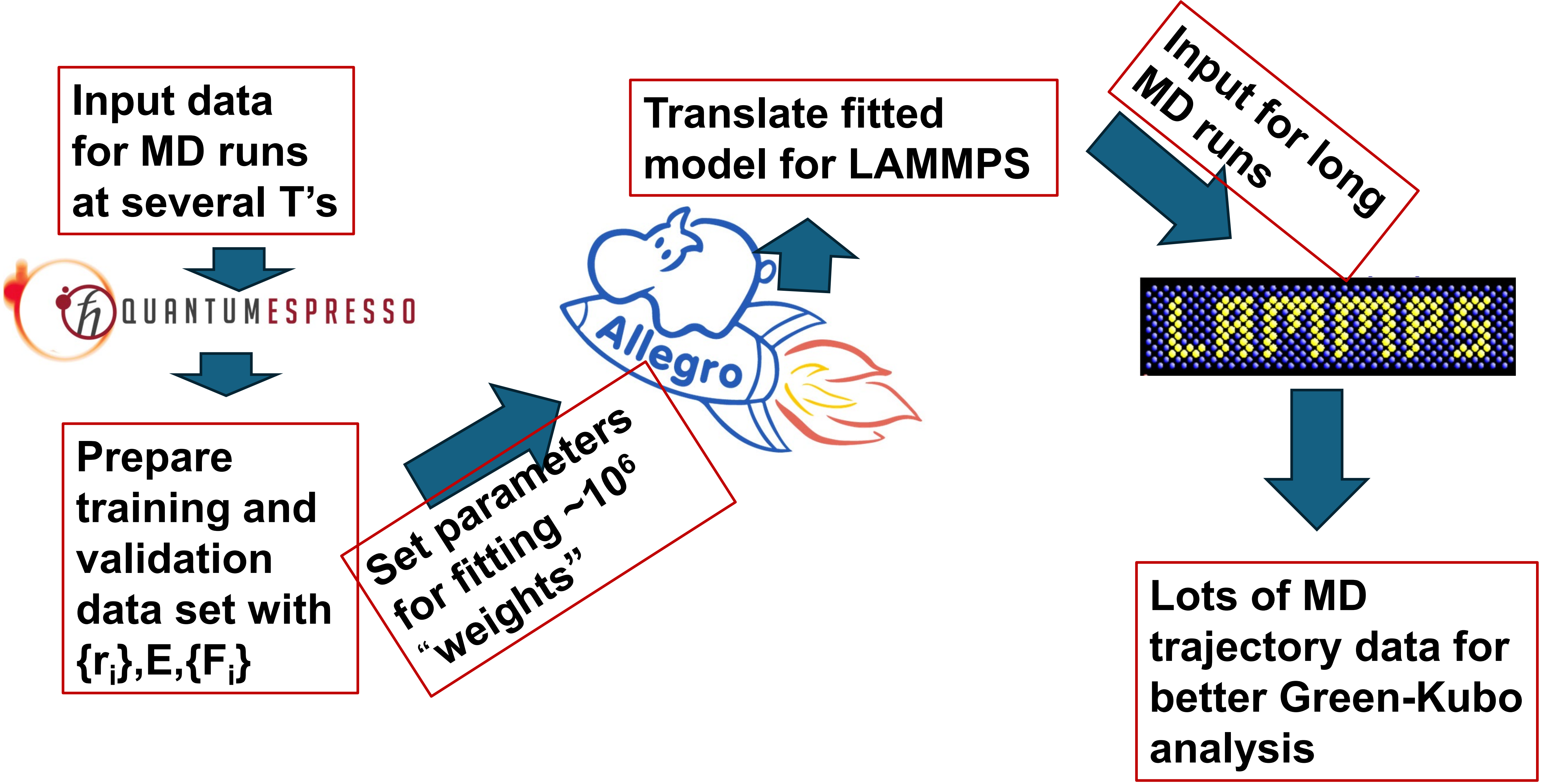
Update: May 2025:



High-performance training and inference for deep equivariant interatomic potentials

Chuin Wei Tan,[1,*] Marc L. Descoteaux,[1,*] Mit Kotak,[2] Gabriel de Miranda Nascimento,[3] Seán R. Kavanagh,[4] Laura Zichi,[1] Menghang Wang,[1] Aadit Saluja,[1] Yizhong R. Hu,[1] Tess Smidt,[5] Anders Johansson,[6] William C. Witt,[1] Boris Kozinsky,[1,7] and Albert Musaelian[1,8,†]

[1]*John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA, USA*
[2]*Center for Computational Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA*
[3]*Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA*
[4]*Center for the Environment, Harvard University, Cambridge, MA, USA*
[5]*Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, MA, USA*
[6]*Sandia National Laboratories, Albuquerque, NM, USA*
[7]*Robert Bosch LLC Research and Technology Center, Watertown, MA, USA*
[8]*Mirian Technologies Inc., Boston, MA, USA*



Input data for MD runs at several T's

Prepare training and validation data set with $\{r_i\}$,E,$\{F_i\}$

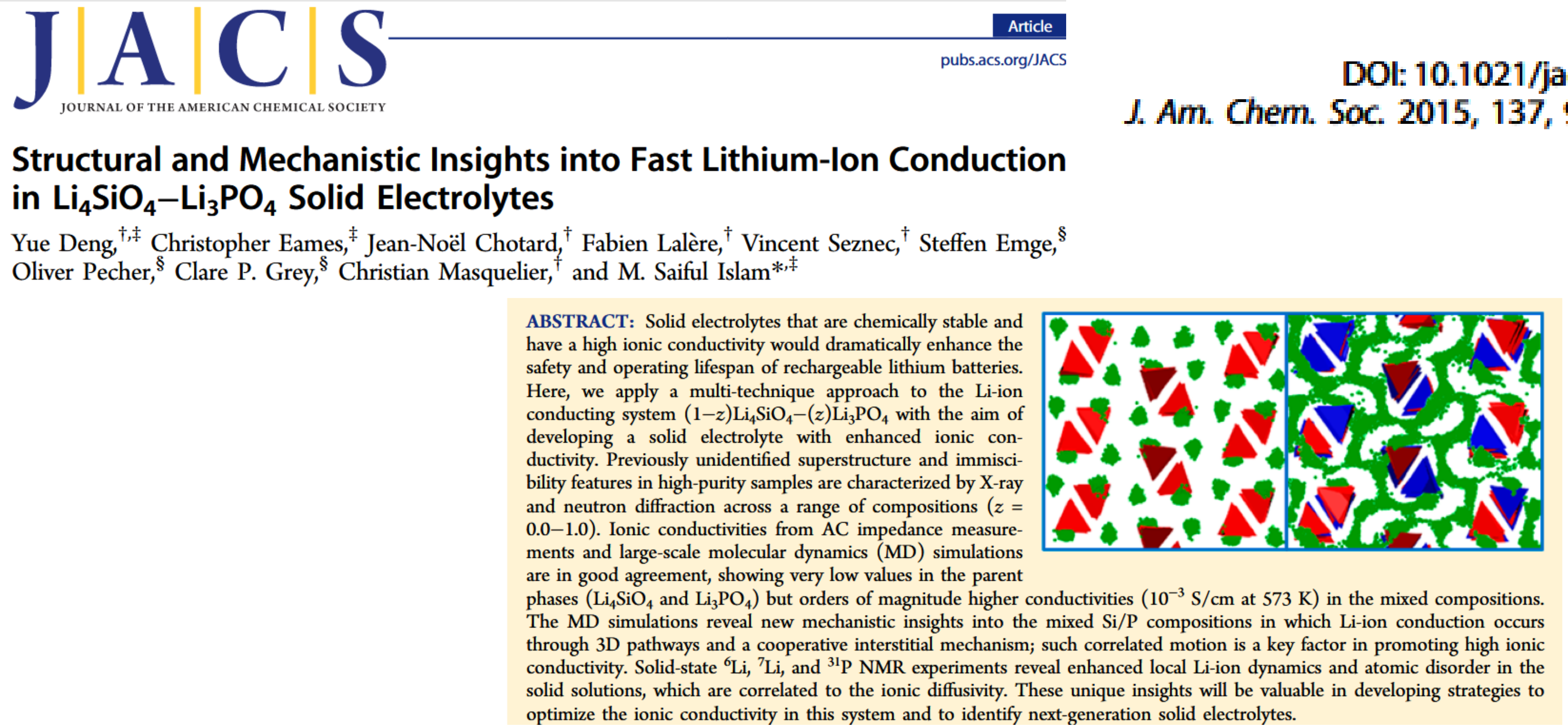
Set parameters for fitting ~10^6 "weights"

Translate fitted model for LAMMPS

Input for long MD runs

Lots of MD trajectory data for better Green-Kubo analysis

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 --



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Article

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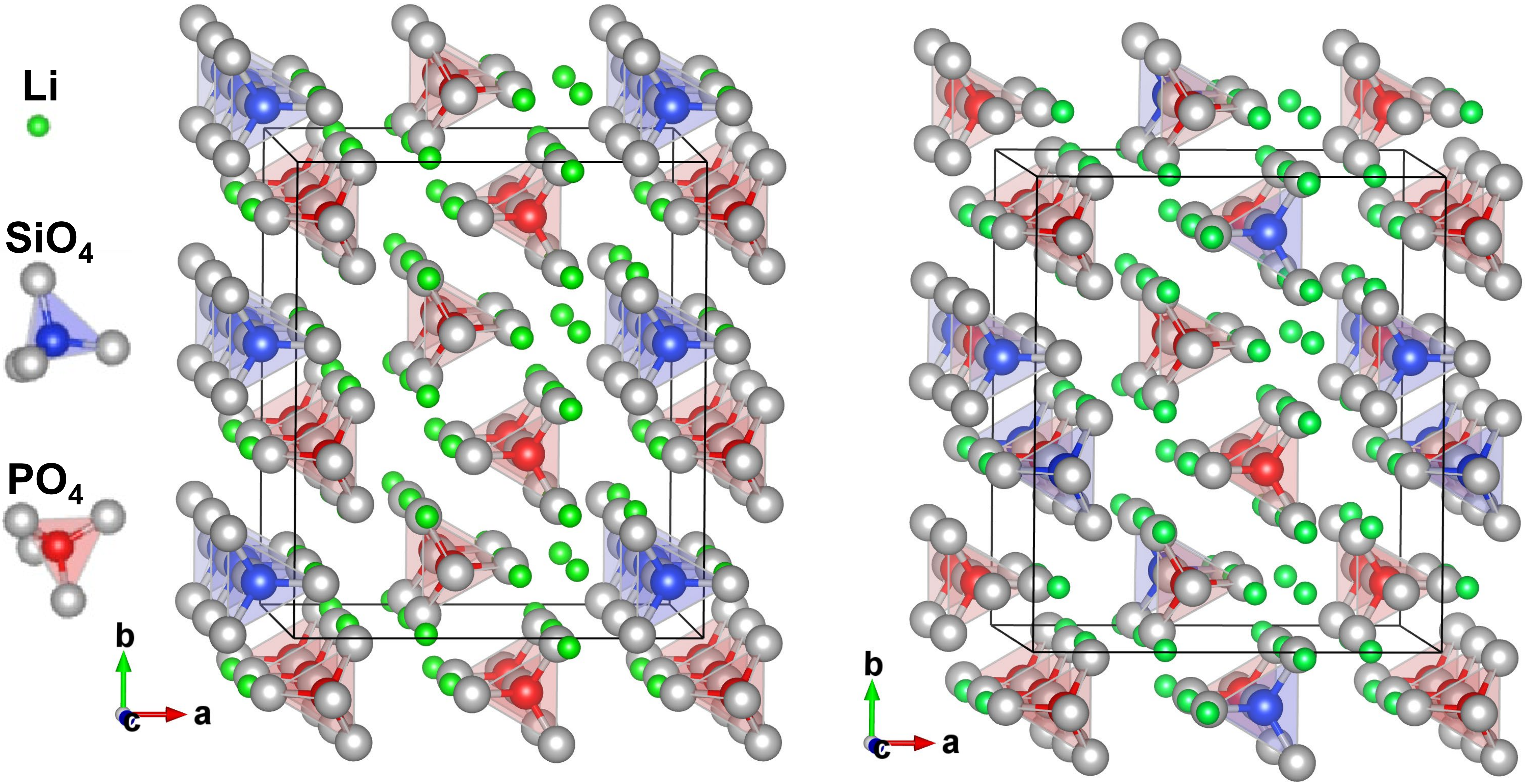
Structural and Mechanistic Insights into Fast Lithium-Ion Conduction in Li_4SiO_4–Li_3PO_4 Solid Electrolytes

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 ^6Li, ^7Li, 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.

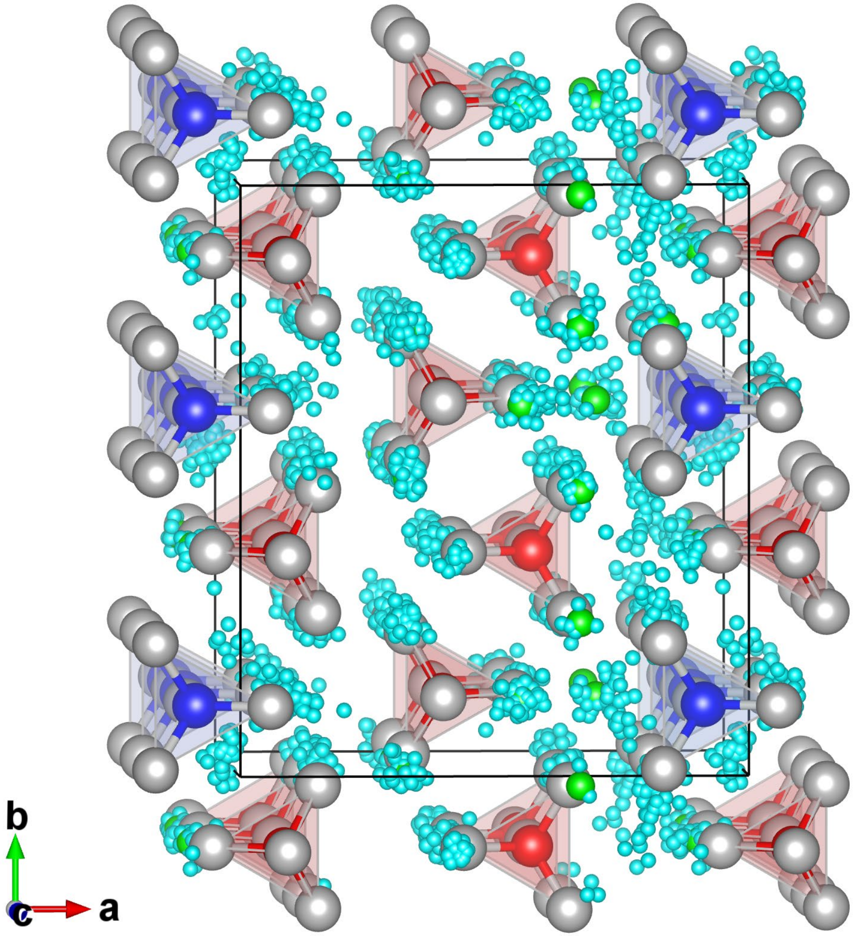
DOI: 10.1021/jacs.5b04444
J. Am. Chem. Soc. 2015, 137, 9136–9145

Structure 1 **Structure 2**

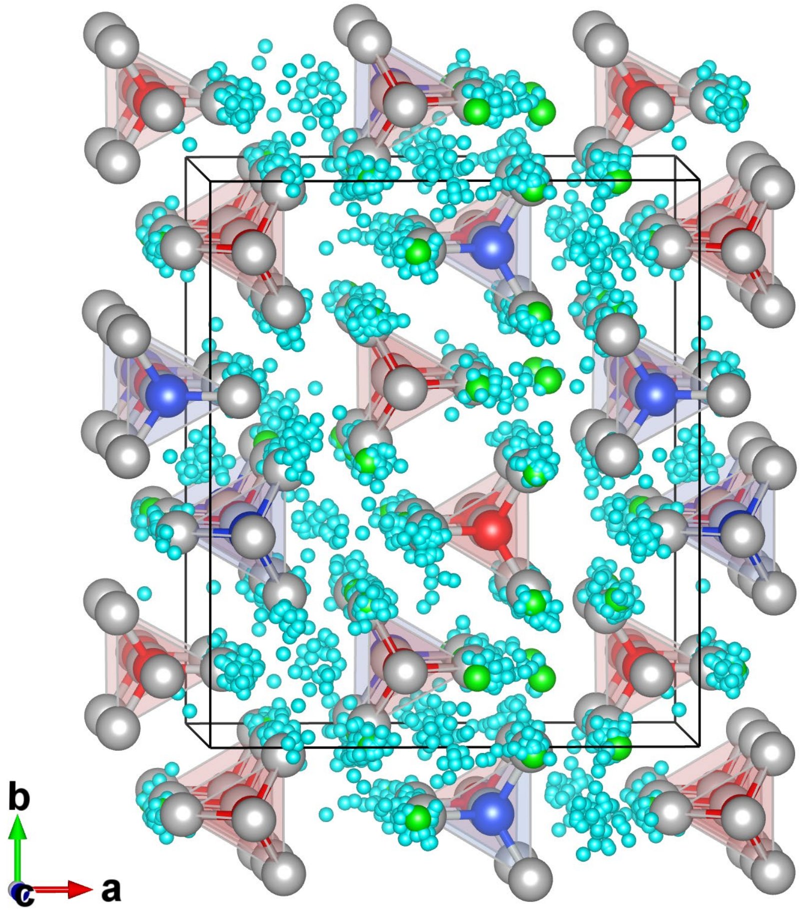


Visualization of Li ion migration during 44 time intervals of 0.3 ps

Structure 1

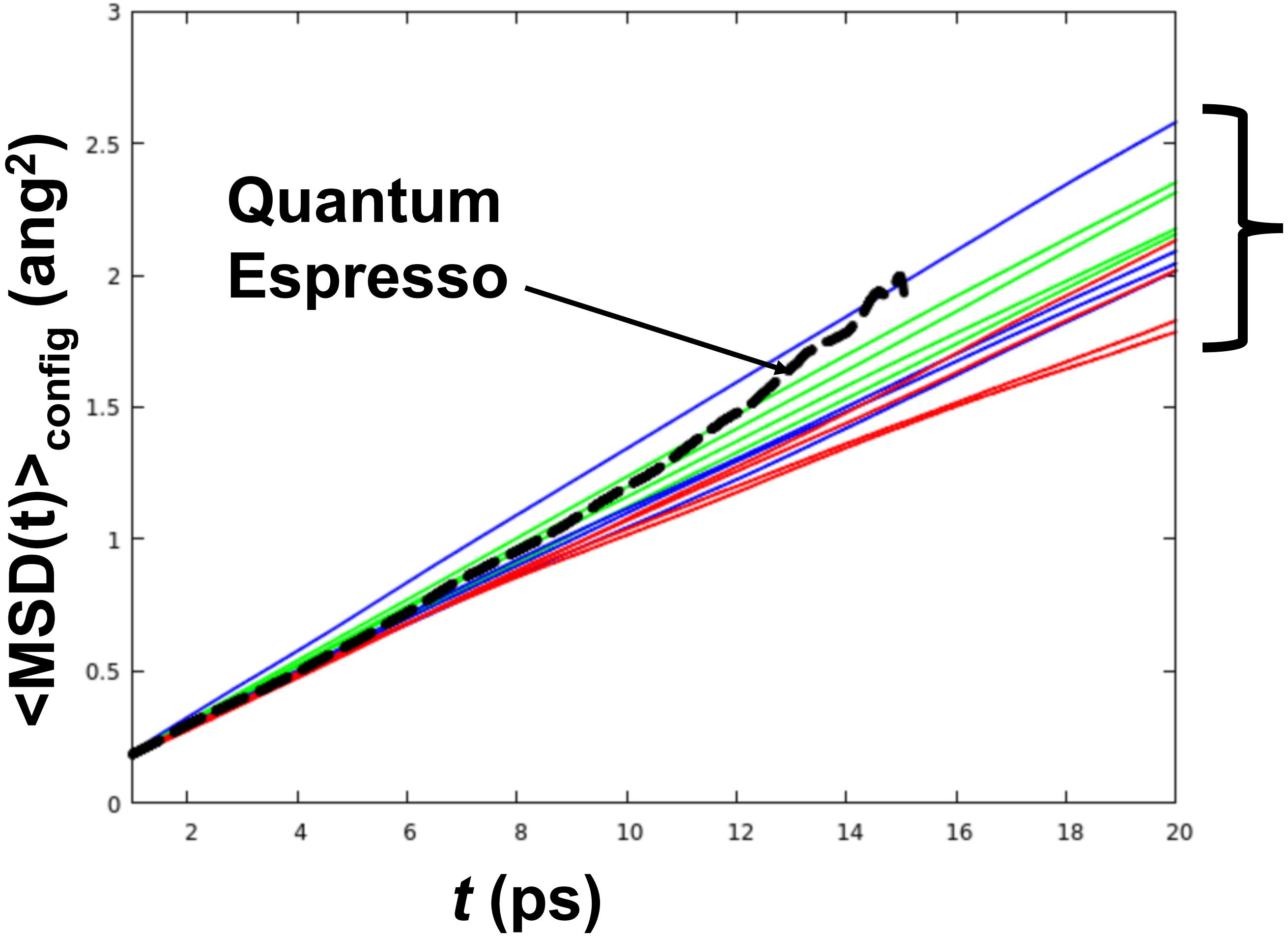


Structure 2



Preliminary results for calculating mean squared displacements of Li ions:

$$\mathrm{MSD}(t) \equiv \sum_{i \in D} \left| \Delta \mathbf{r}_i(t) - \Delta \mathbf{r}_i(0) \right|^2$$



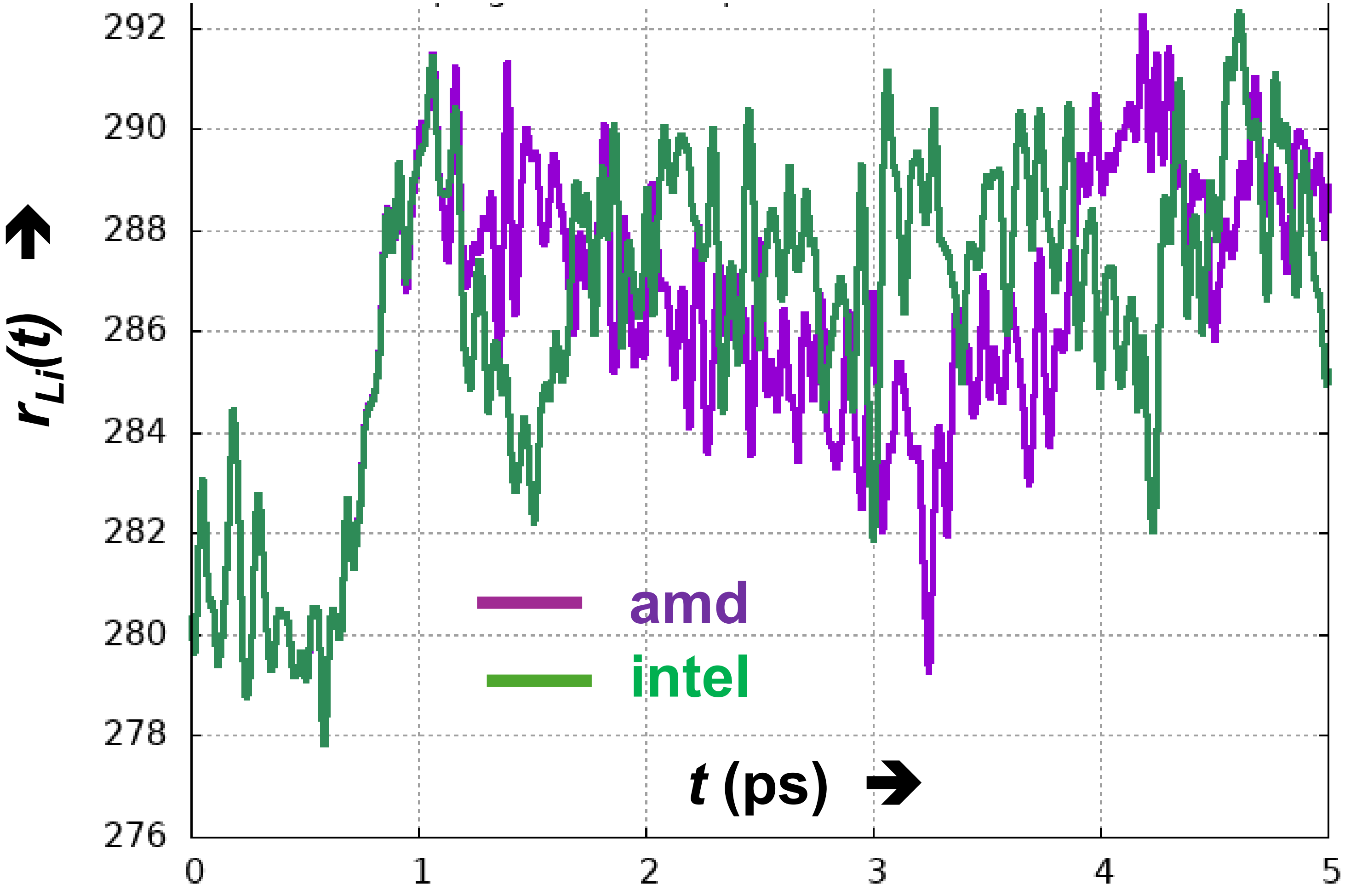
Allegro-LAMMPS with various configuration averages

Preliminary evaluations

- ☐ Allegro-Lammps MSD results seem reasonable and not very sensitive to choices of “hyperparameters”
- ☐ Green-Kubo analysis of long MD runs needs more work

Evidence of numerical issues –

Plot of a particular Li position as a function of time for two identical LAMMPS runs with different hardware



From “Understanding Molecular Simulation” by Frenkel and Smit:

“The Lyapunov instability might seem to deal a devastating blow to the very idea of Molecular Dynamics simulations. However, we have good reason to assume that the situation is, as the saying goes, desperate but not serious.” … “In short, our trust in Molecular Dynamics simulation as a tool to generate good approximations to real trajectories of a many-body system is based largely on belief… [T]here is clearly a skeleton in the closet. We believe this skeleton will not haunt us, and we quickly close the closet.”

For calculating ionic conductivity, it is important to calculate averages over trajectories and Frenkel and Smit (and many others) suggest that

1. **The approximate trajectories from MD simulations are reasonable**
2. **The “skeleton” helps insert more ‘diversity’ into the sampling**
3. **Need to improve configuration averaging methods.**

Outlook

- ☐ Using the allegro machine learning software package together with first principles molecular dynamics looks very promising for performing realistic simulations of materials in large supercells and/or for long times.

- ☐ This study helped us experience the Lyapunov instability which provides an interesting challenge for future work.

Thanks for your attention.