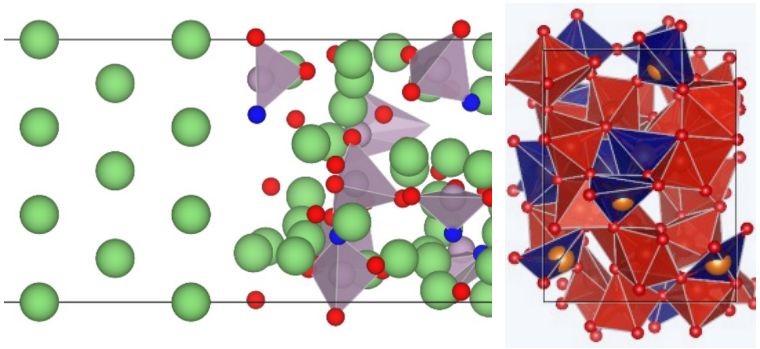

Machine learning guided exploration of amorphous electrodes and electrolytes

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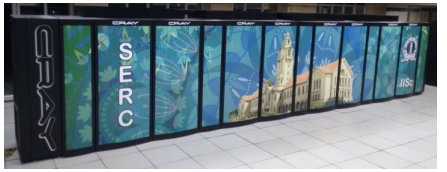
Aapali Psi-k, Pune
May 20, 2025

Acknowledgments

Group picture in Jan 2025

Param Siddhi (CDAC)



SERC (IISc)

Pritam (Poster)

Why amorphous materials?

Compositional and structural flexibility[1]

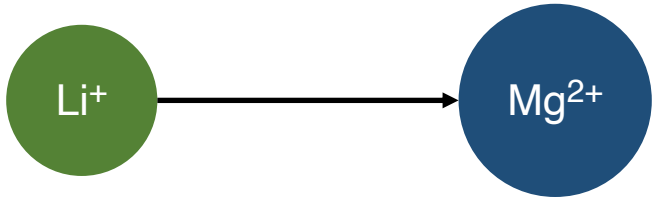
- Electrolytes: significant changes in (local) ionic content without phase transformations
- Electrodes: significant capacities without phase transformations

Electrolytes: can hinder nucleation of dendrites[2]

- Lack of structural 'inhomogeneities' that cause nucleation
- No grain boundaries

Electrodes: can improve ionic mobility in multivalent systems

- Such as Mg
- 'Flatter' potential energy landscapes

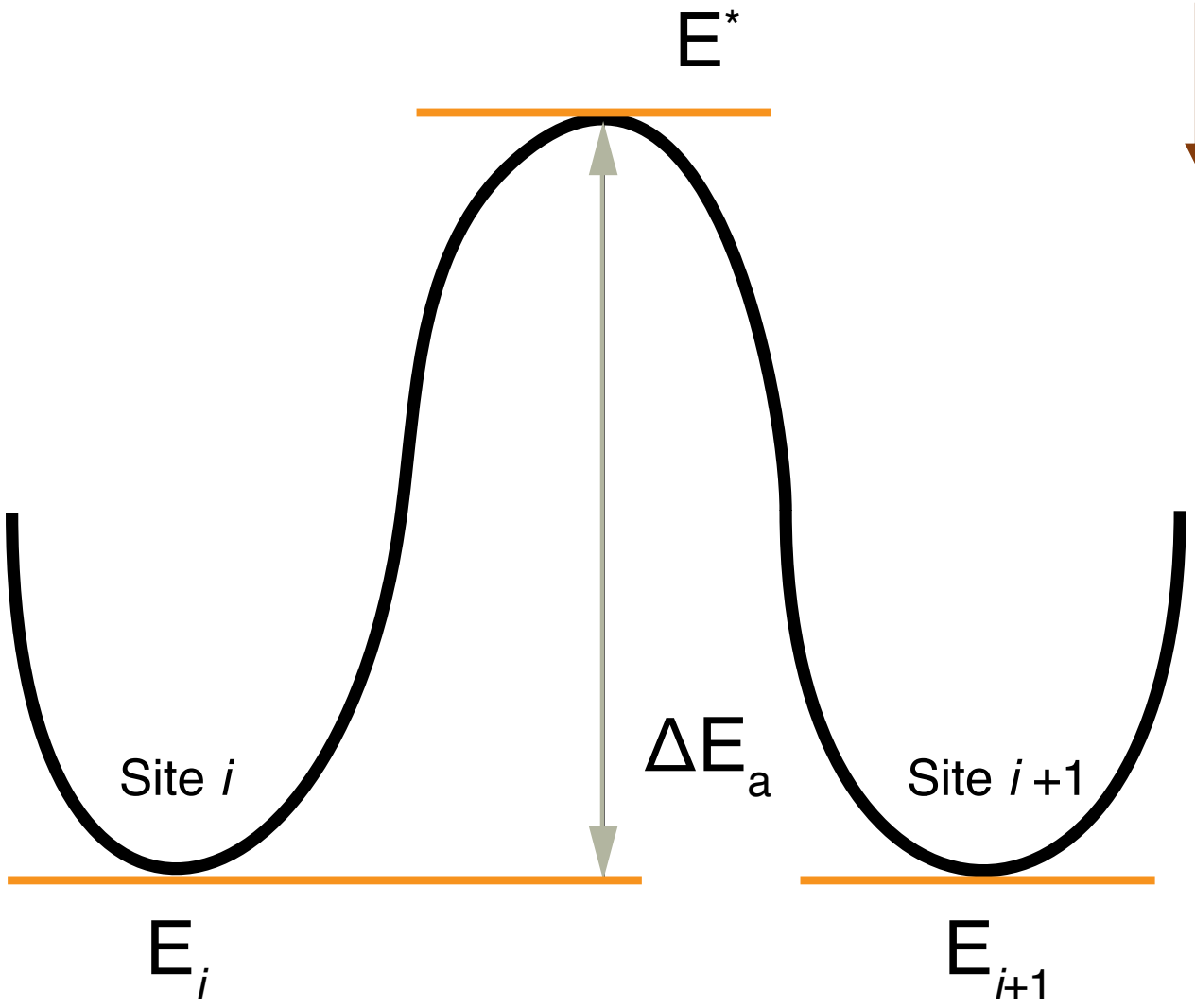


1. Hein et al., *J. Phys. Chem. C* 121, 3203 (2017)

2. Pora et al., *Adv. Energy Mater.* 7, 1701003 (2017)

How can amorphous materials improve ionic mobility?*

*Terms and conditions apply



Frustrated coordination
Non-close-packed lattice
Larger anions
Rotations

Amorphous systems→ Flat potential energy surfaces

Interstitials
Disordered sub-lattices
Lack of long-range order?

Objectives

Can we computationally model amorphous systems?

- Quantify ionic transport
- Other metrics?

How can we model?

- Use machine learned interatomic potentials (MLIPs)
- Train on density functional theory (DFT) generated data

What systems?

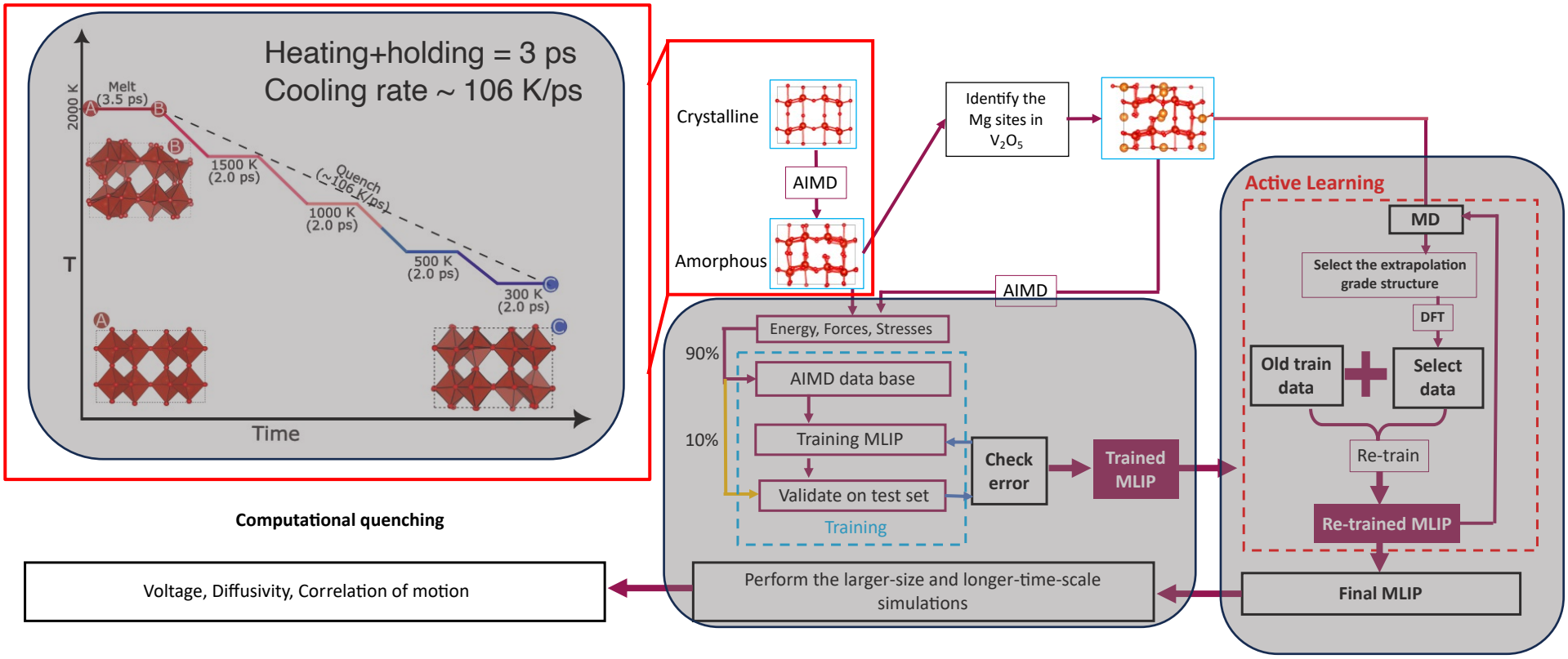
- Lithium phosphorous oxynitride (LiPON) as electrolyte in Li-ion
- V_2O_5 as positive electrode (cathode) in Mg

Quantities/metrics

- LiPON: structure, transport (bulk and interface)
- V_2O_5: structure, voltages, and transport (bulk)

Workflow

MD: Molecular dynamics
AIMD: Ab initio MD
MLIP: Machine learned interatomic potential



LiPON dataset: 13,454 configurations in computed dataset

- Li, Li_3P, Li_3N, Li_3PO_4, $LiPN_2$, Li_2O_2
  - Bulk, strained, melt+quenched, defective, slabs

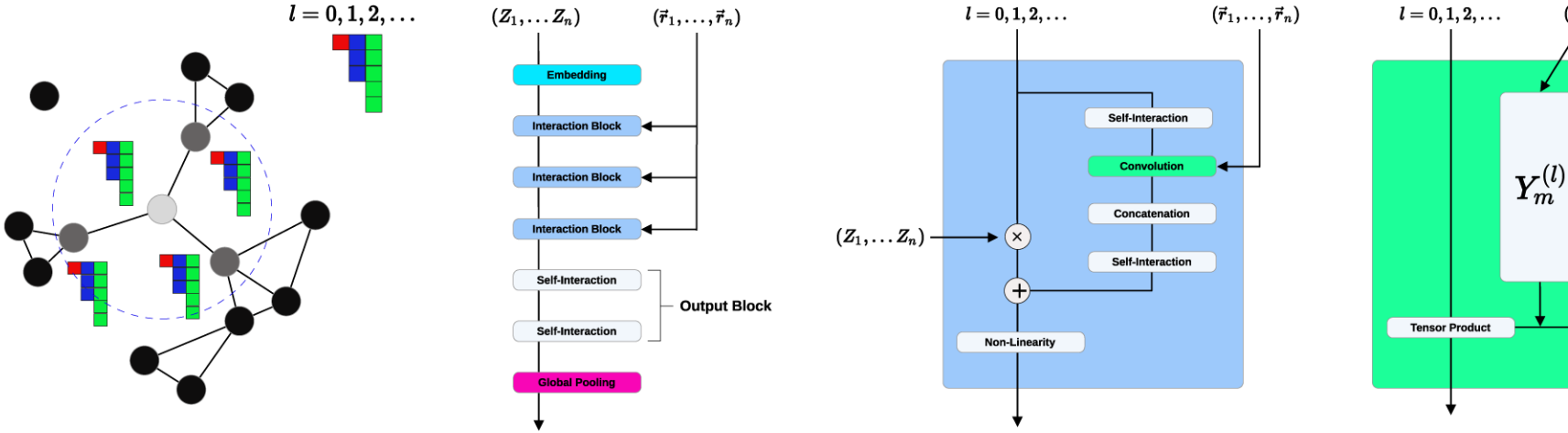
Neural equivariant interatomic potential (NequIP)

V_2O_5 dataset: 3,725 computed configurations

- Melt+quench (+active learning)
- V_2O_5 + MgV_2O_5

Moment tensor potential (MTP)

NequIP for LiPON



Based on deep, graph neural networks
- Nodes (atoms) and edges (bonds)
- Message passing
- Equivariance

Every atom has a feature vector of different orders
- Scalars, vectors, and tensors

Radial and angular basis functions

$$E_{pot} = \sum_{i \in N_{atoms}} E_{i,atomic}$$

$$\vec{F}_i = -\nabla_i E_{pot}$$

$$B(r_{ij}) = \frac{2}{r_c} \frac{\sin(\frac{b\pi}{r_c} r_{ij})}{r_{ij}} f_{env}(r_{ij}, r_c)$$

Batzner et al., Nat. Commun. 13, 2453 (2022)

MTP for V_2O_5

$$E^{\mathrm{mtp}}(\mathrm{cfg}) = \sum_{i=1}^{n} V(\mathbf{n}_i)$$

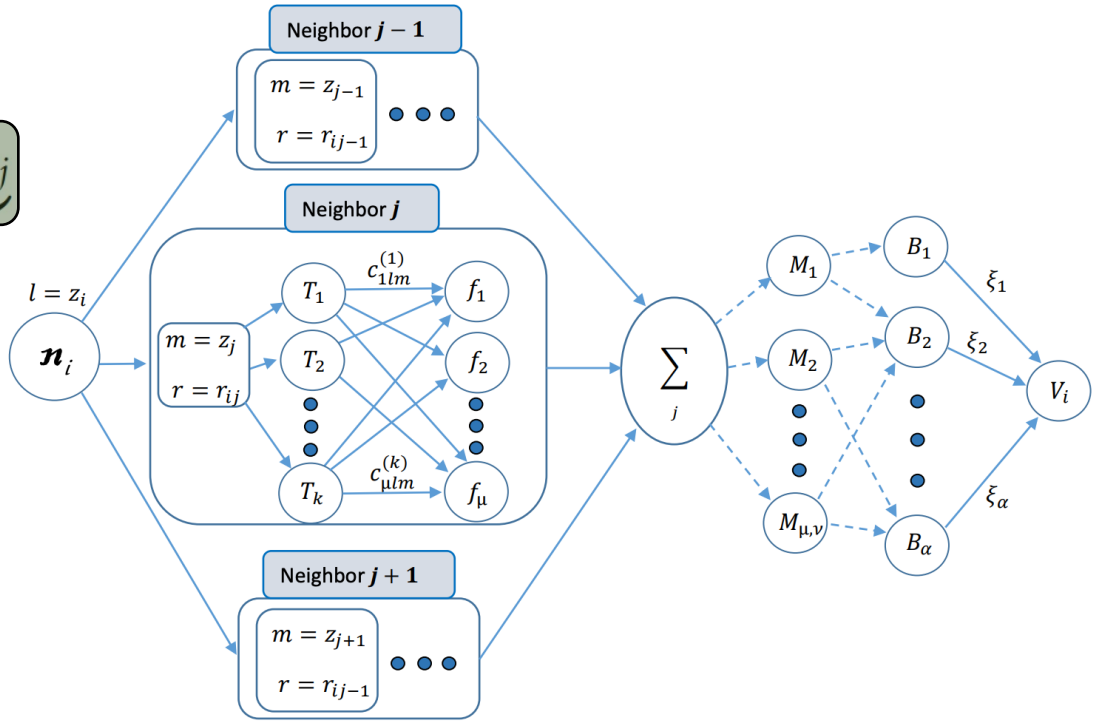
Total energy as a sum of atomic energies

$$V(\mathbf{n}_i) = \sum_{\alpha} \xi_\alpha B_\alpha(\mathbf{n}_i)$$

Atomic energies – sum of contracted moment tensors capturing many-body interactions

$$M_{\mu,\nu}(\mathbf{n}_i) = \sum_j f_\mu(|r_{ij}|, z_i, z_j)\underbrace{\mathbf{r}_{ij} \otimes \ldots \otimes \mathbf{r}_{ij}}_{\nu \text{ times}}$$

Radial component Angular component



V: function invariant to permutations, rotations, and reflections

- Smooth with respect to exchange of atoms from neighborhood

Choyal et al., *J. Chem. Theory Comput.* 20, 4844-4856 (2024)

Novikov et al. *Mach. Learn.: Sci. Technol.* 2, 025002 (2021)
https://www.skoltech.ru/app/data/uploads/2019/09/THESIS_FINAL.pdf

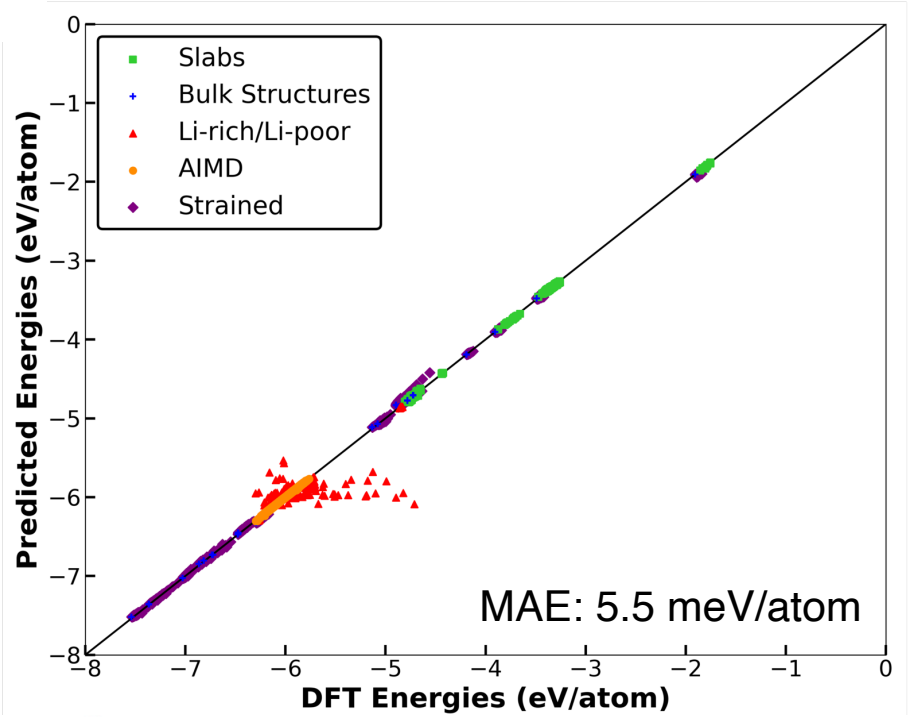
Results

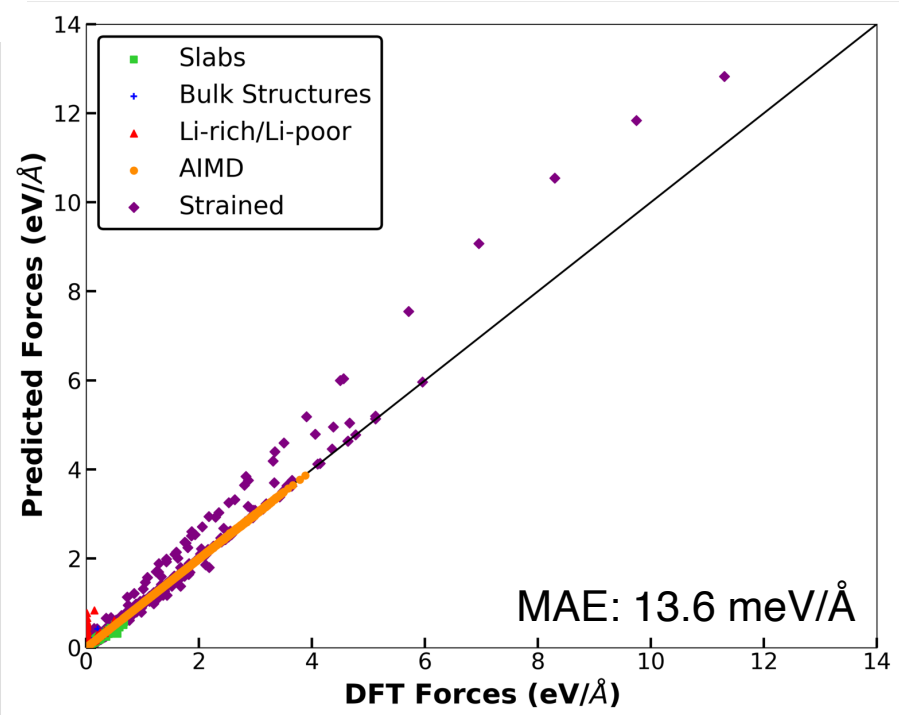
- Are MLIPs accurate?
- Structures are amorphous?

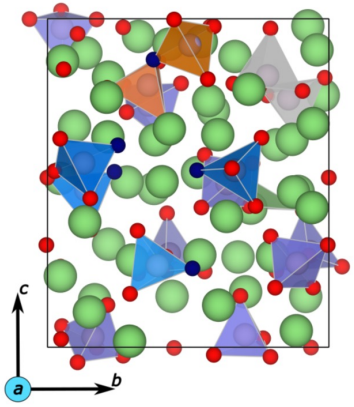
- LiPON: Bulk and interfacial transport?

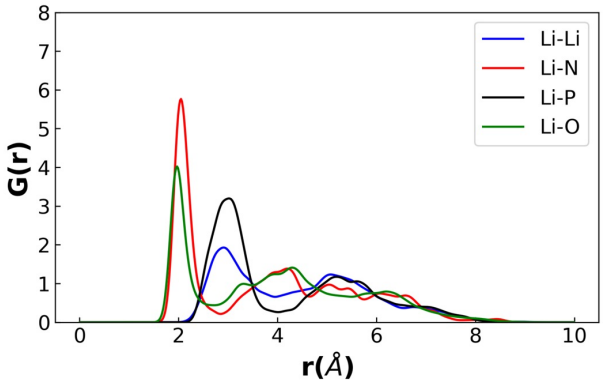
- V_2O_5: What is the loss on voltages?
- V_2O_5: Amorphous → better Mg diffusivity?

LiPON: Accuracy and amorphous structure









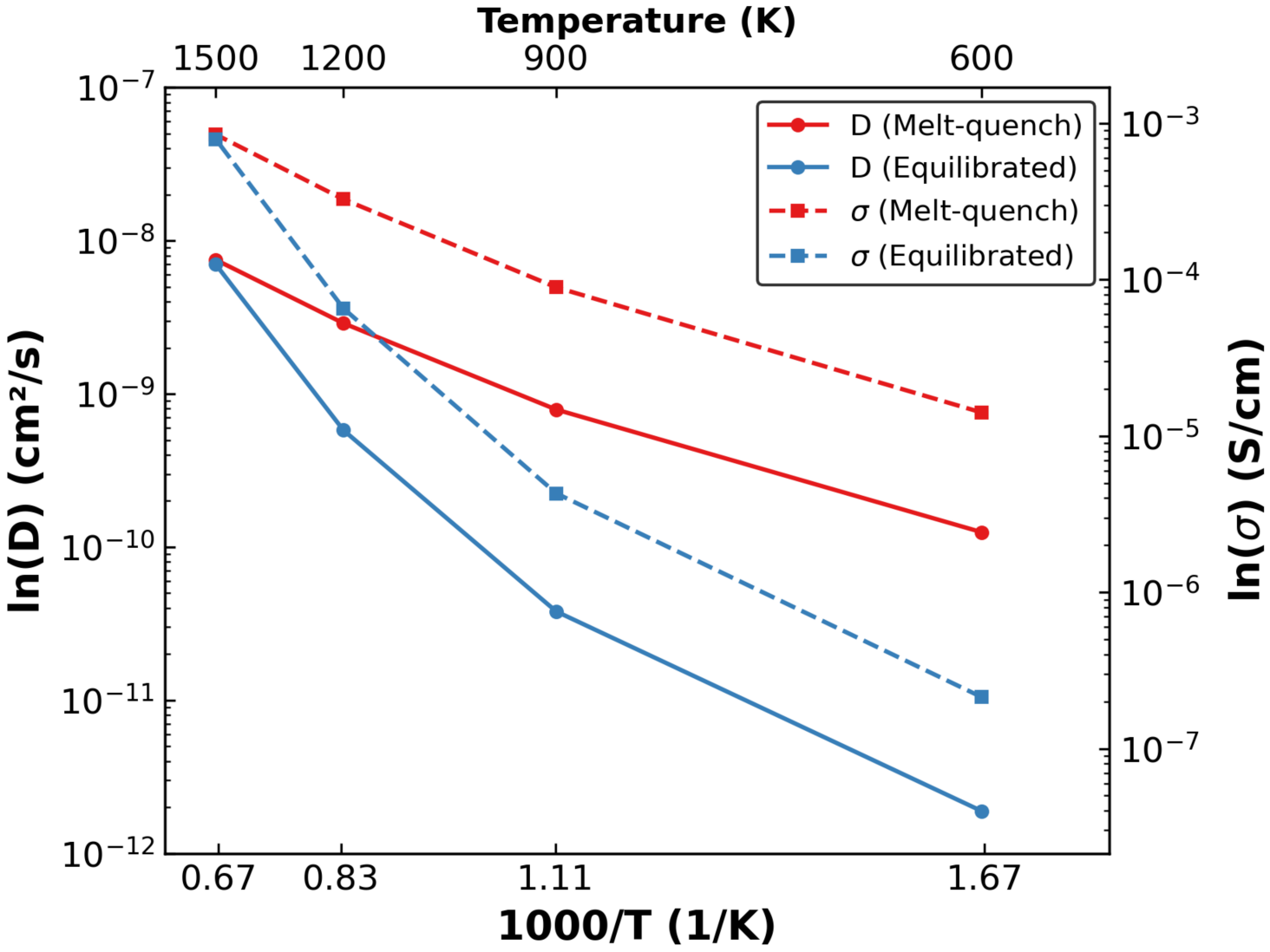
$Li_{2.94}PO_{3.5}N_{0.31}$

- Purple, grey (without N)
- Blue, orange (with N)

Quenched to 250 K

- Broad peaks beyond 4 Å

LiPON: bulk diffusivities higher in structures with higher disorder



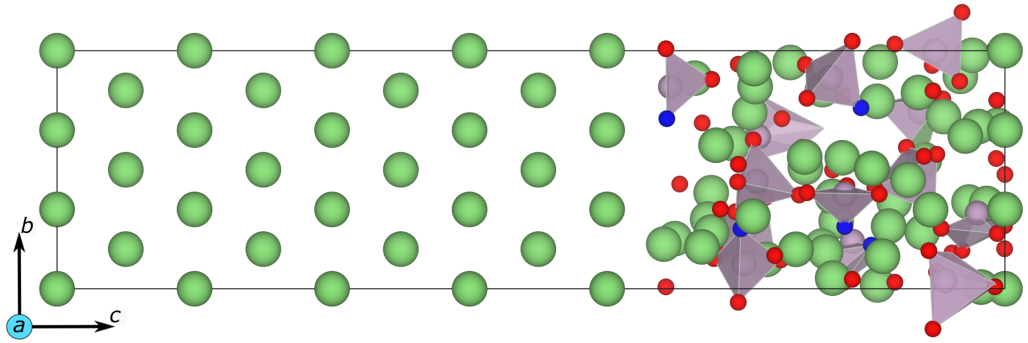
Statistics over a minimum of 100 ps, 124 atoms

- $Li_{2.94}PO_{3.5}N_{0.31}$

Higher orientational disorder → flatter landscape

Calculated σ (~1×10^{-6} S/cm) at 300 K matches experiment (~3×10^{-6} S/cm)

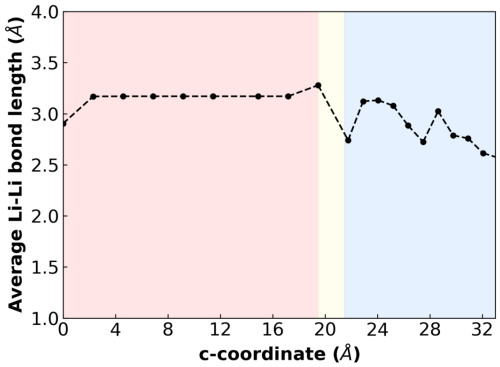
Li(110)||LiPON interface

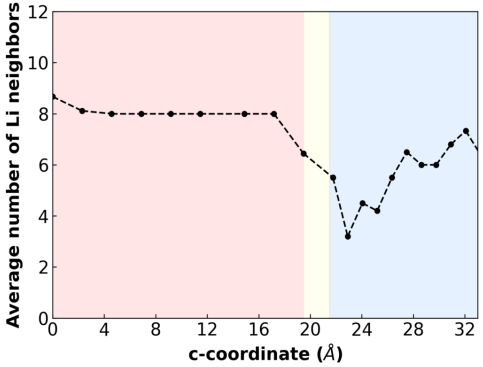


'Smaller' model: ~200 atoms

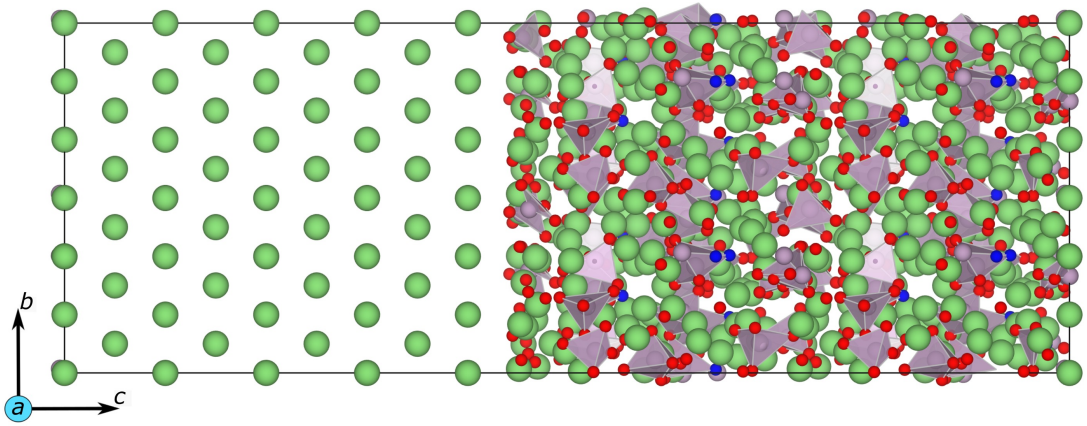
- 75ps of sampling

Also Li(111)||LiPON interface



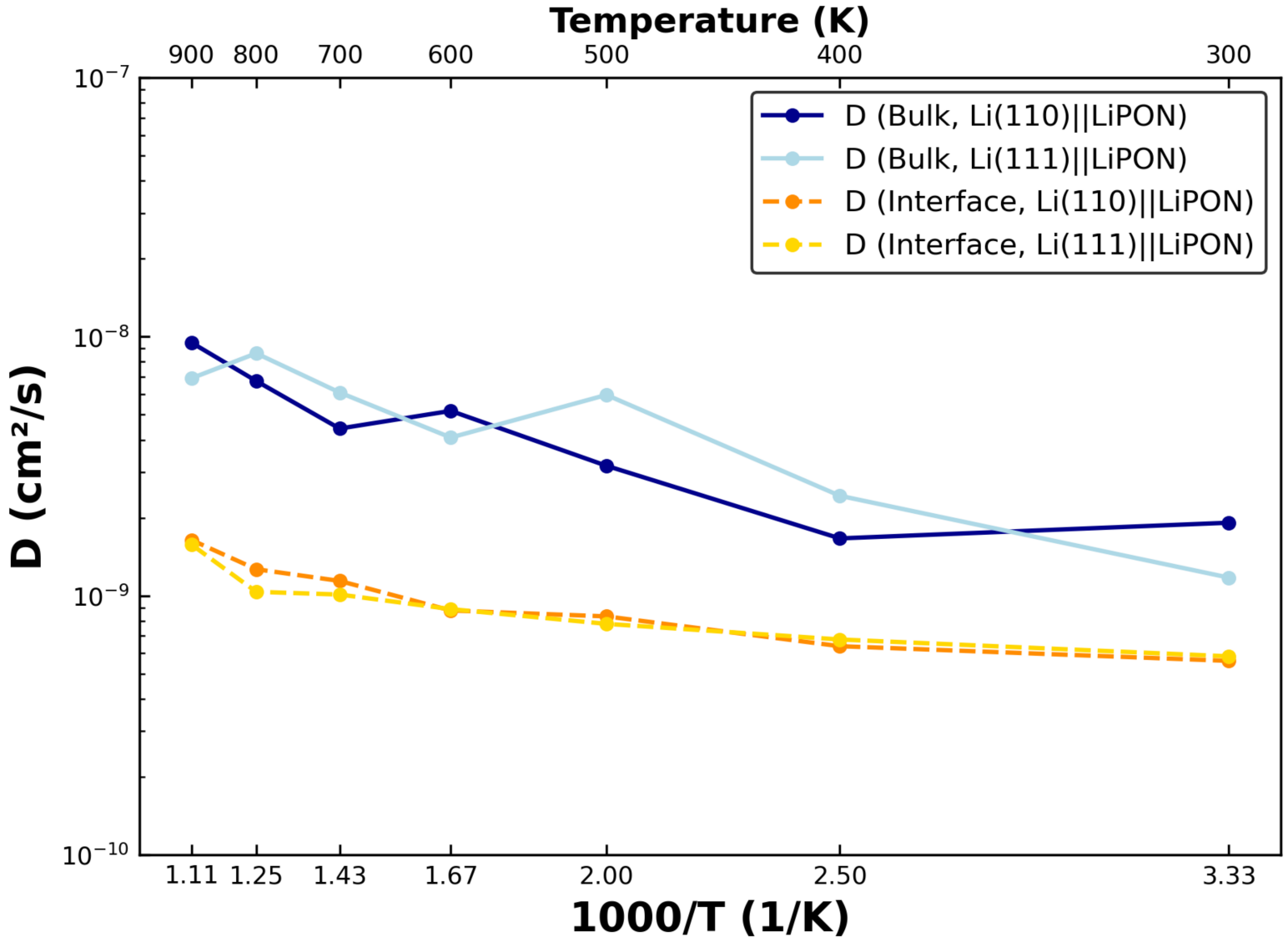


Distribution of Li-neighborhood in the interface model

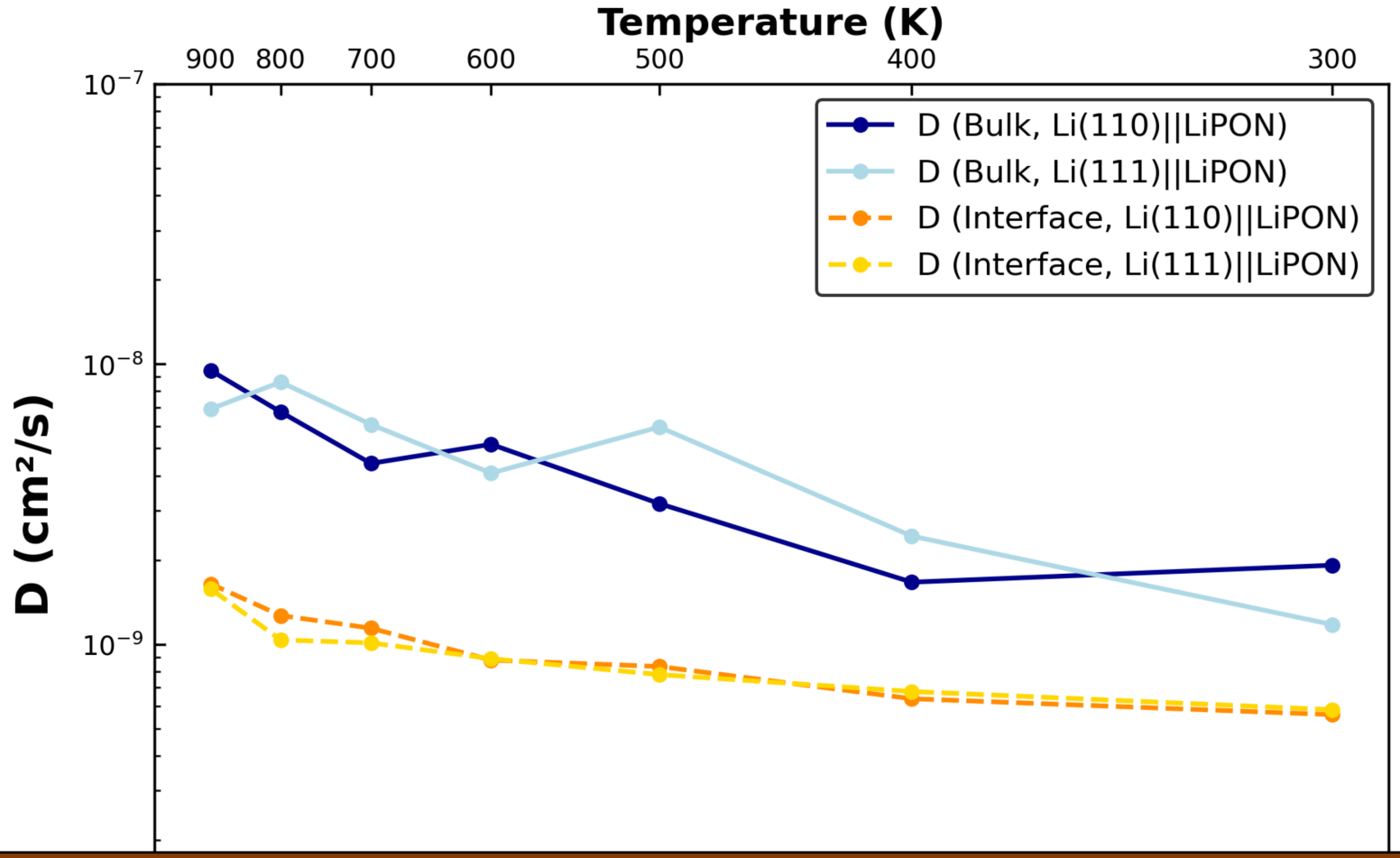


'Larger' model: ~1300 atoms

LiPON: Diffusivity across the interface (marginally)slower than bulk



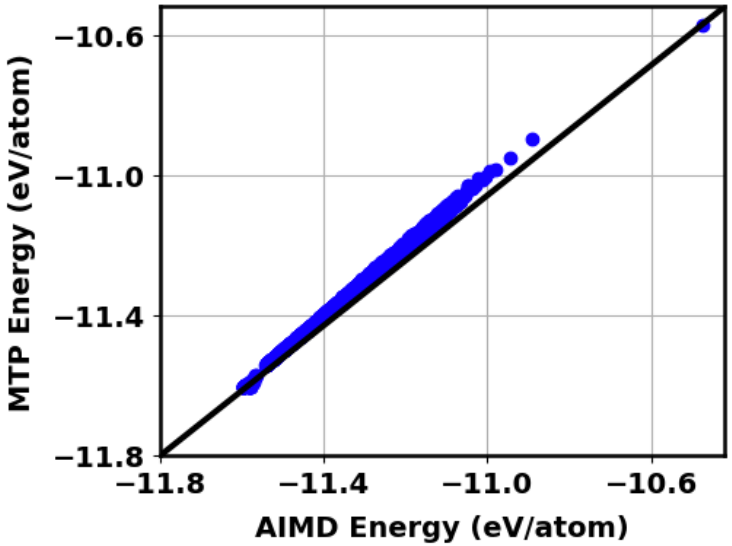
LiPON: Diffusivity across the interface (marginally)slower than bulk



Similarity in Li transport between bulk and interface → mitigate Li-dendrite propagation

V_2O_5: MTPs are accurate

Train

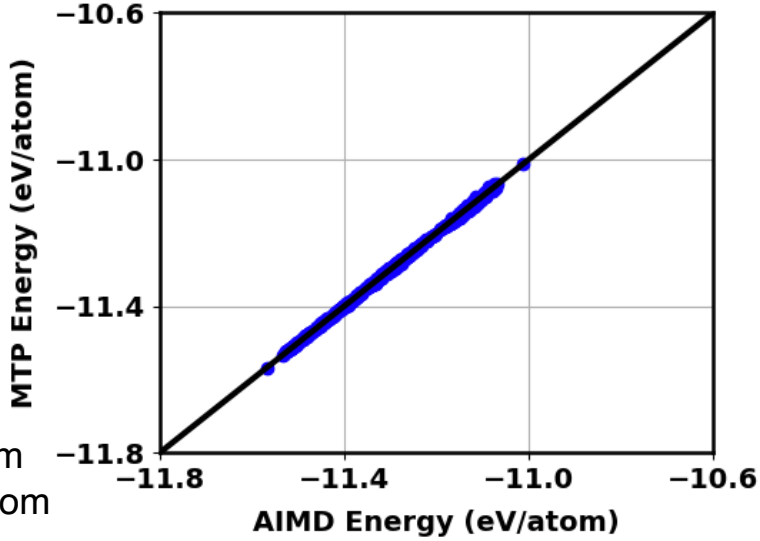


Errors

MAE: 2.97 meV/atom
RMSE: 4.68 meV/atom

MAE: 2.33 meV/atom
RMSE: 3.16 meV/atom

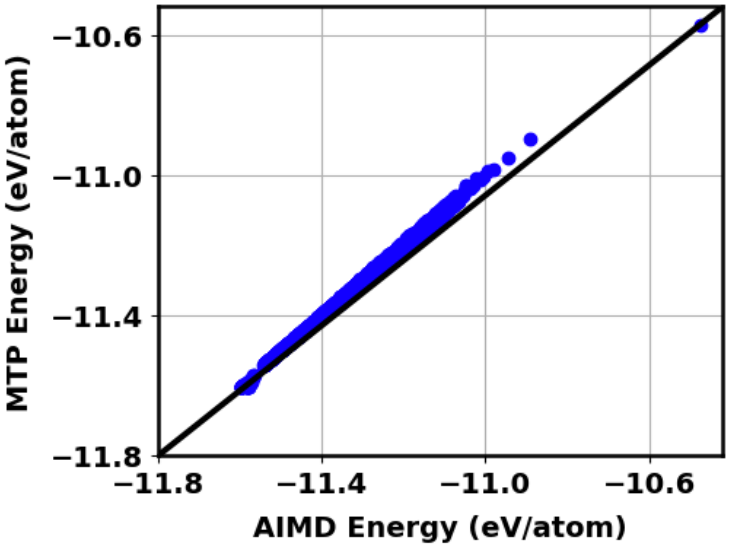
Test



MAE: Mean absolute error; RMSE: Root mean square error

V_2O_5: MTPs are accurate

Train



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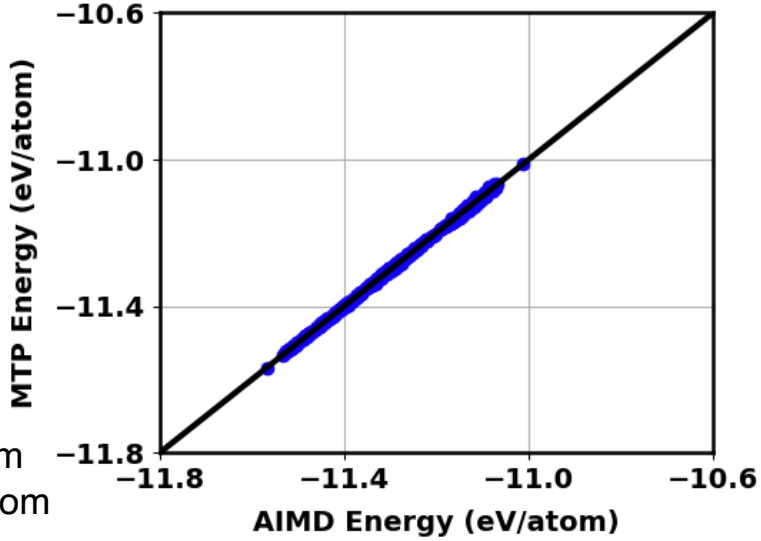
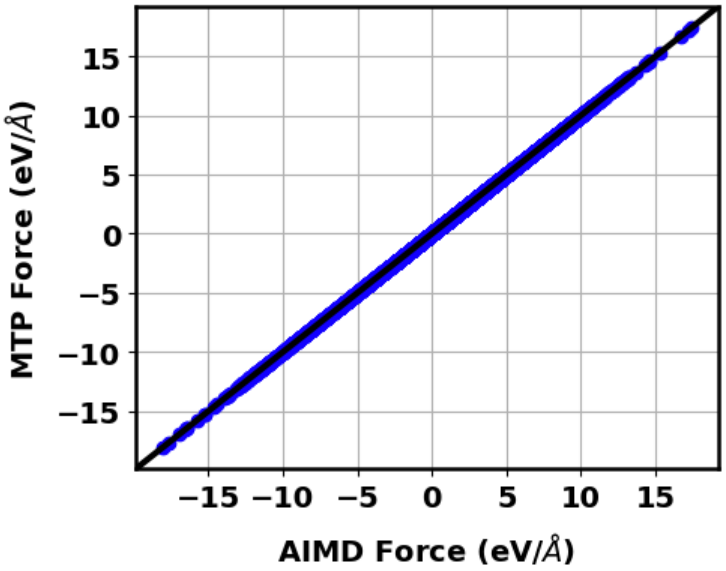
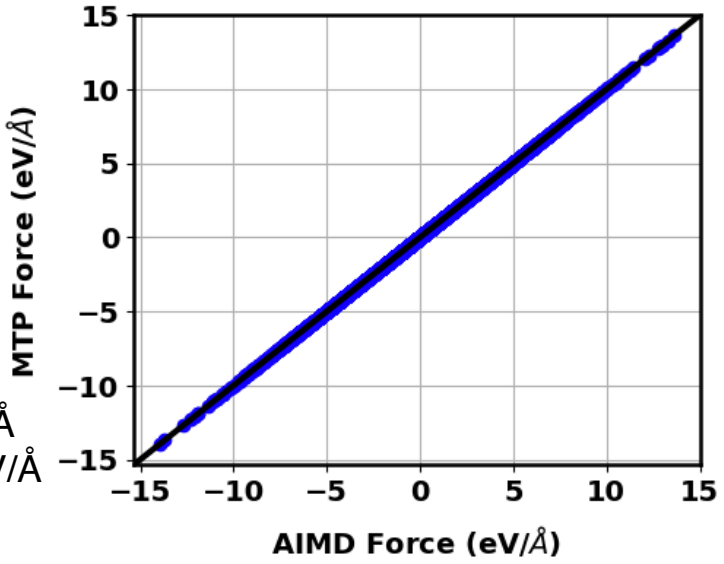


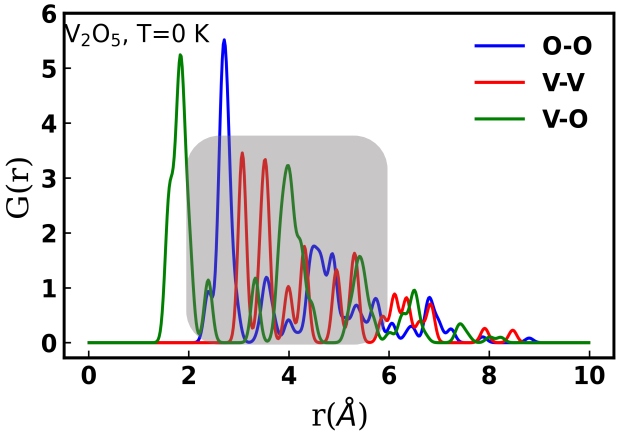


MAE: 0.11 eV/Å
RMSE: 0.24 eV/Å

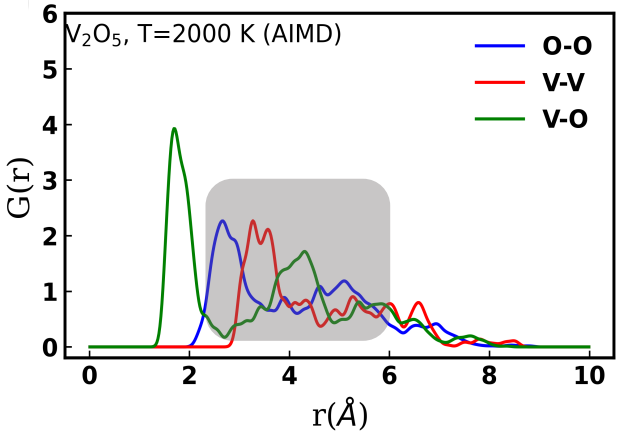
MAE: 0.12 eV/Å
RMSE: 0.24 eV/Å



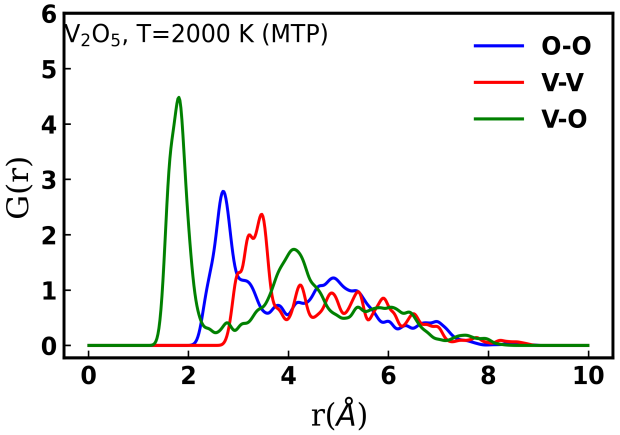
Melt+quench generates (reasonable) amorphous structures



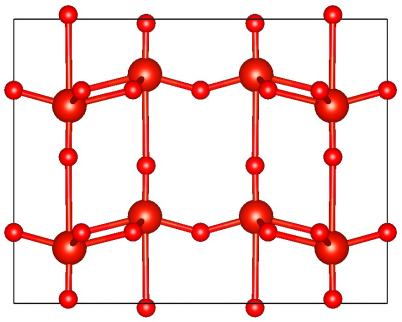
Crystalline V_2O_5

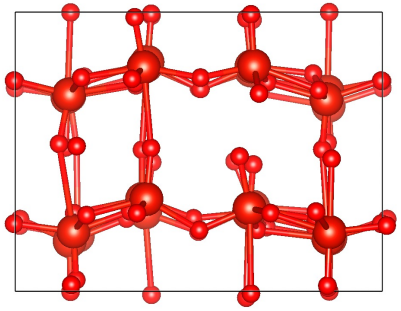


Amorphous V_2O_5 (@2000K)

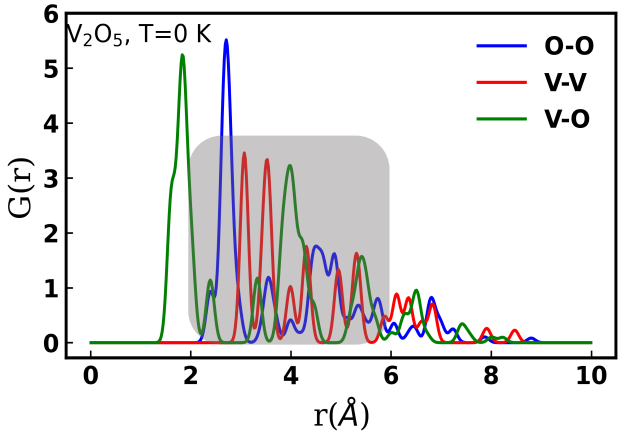


MTP

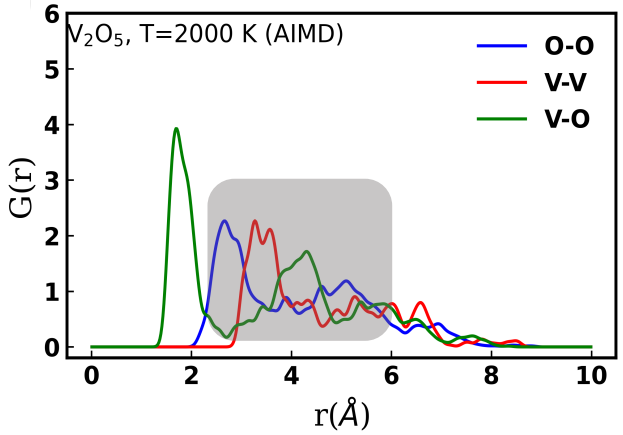




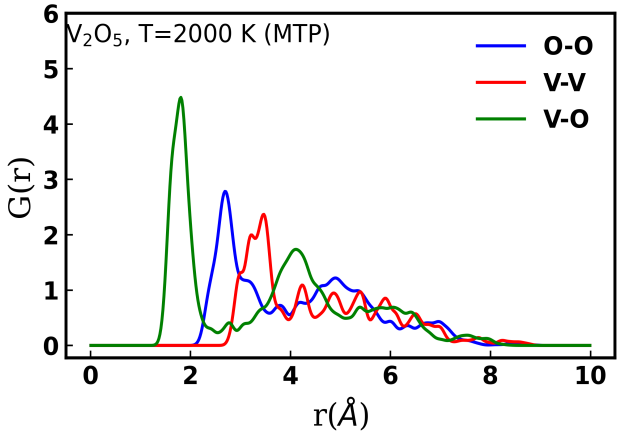
Melt+quench generates (reasonable) amorphous structures



Crystalline V_2O_5

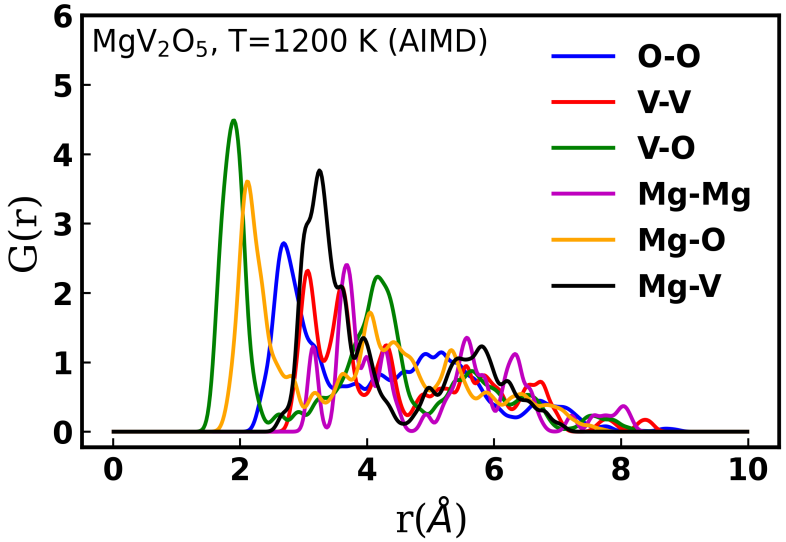


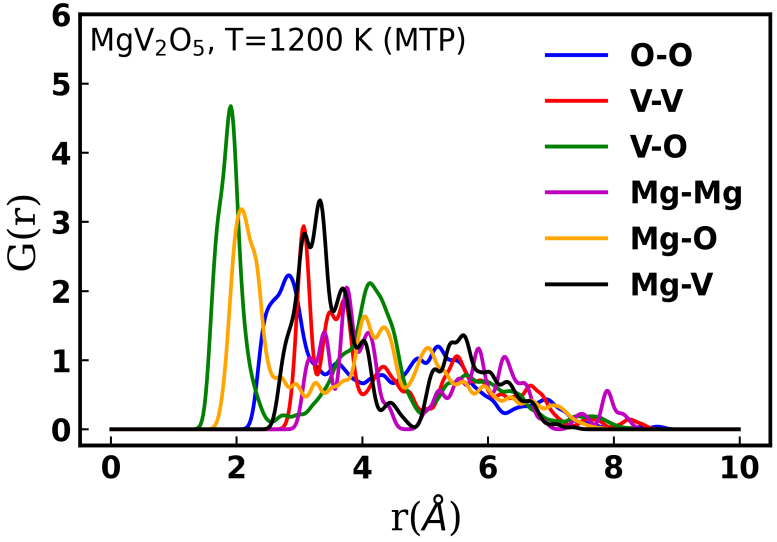
Amorphous V_2O_5 (@2000K)



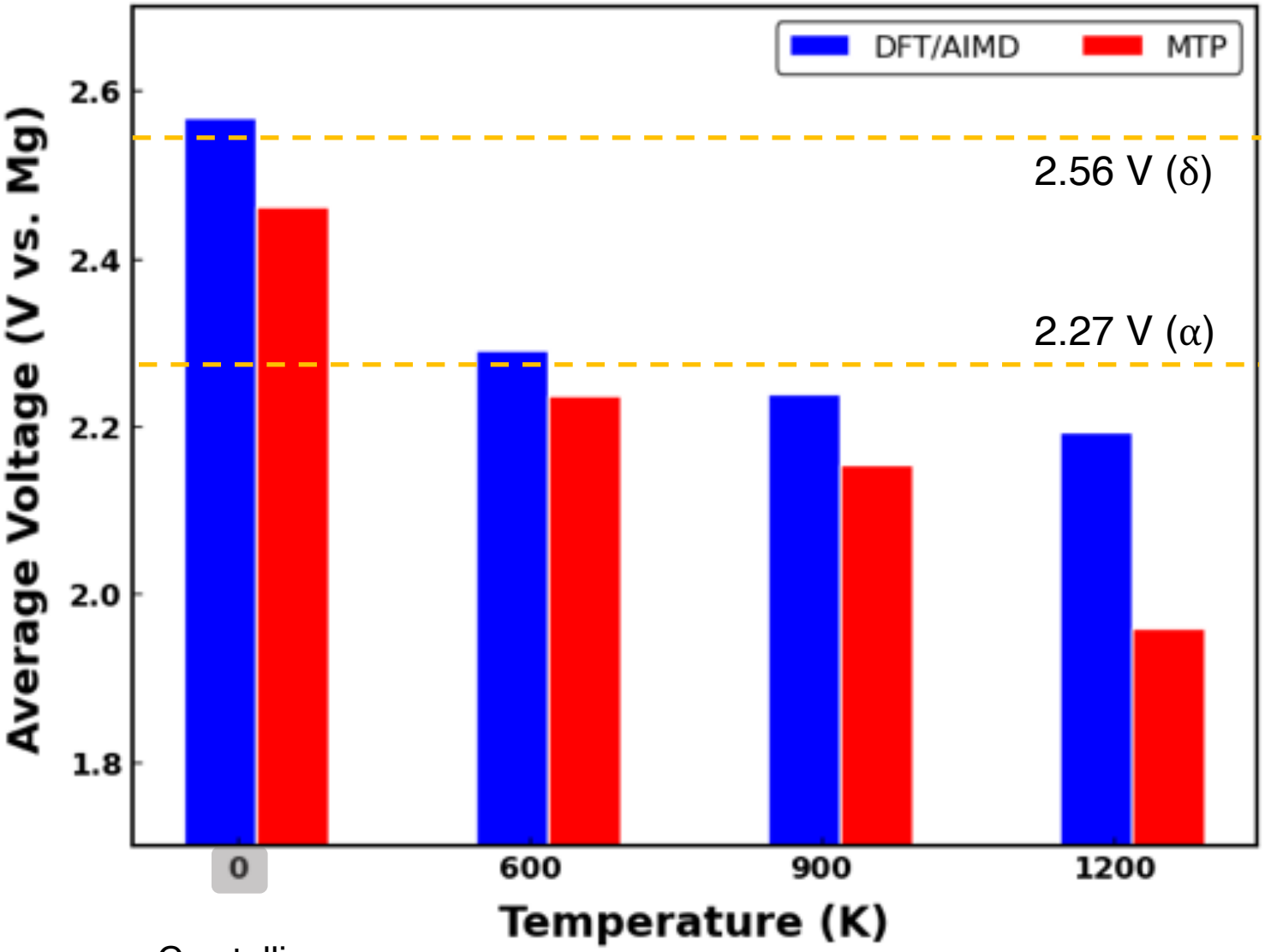
MTP

MgV_2O_5 (@1200 K)





V_2O_5: Going amorphous doesn't affect voltages (much)



Crystalline

Temperatures→ Structures

MD: MTP-MD

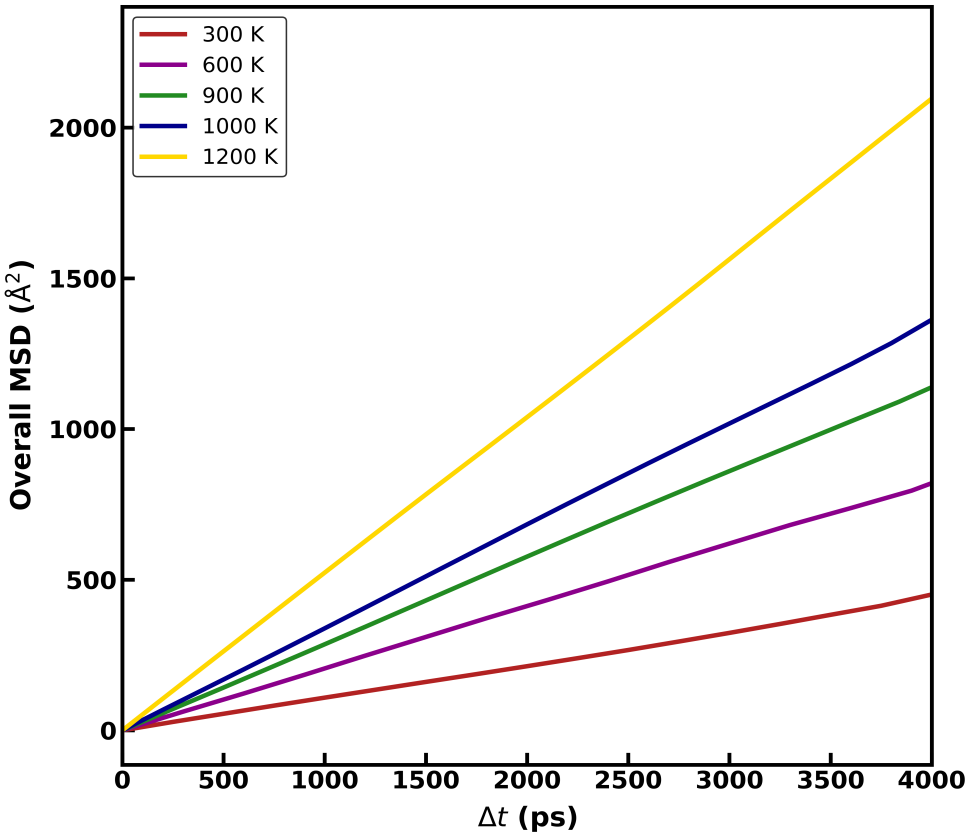
Take structure and do non-relax density functional theory for voltage

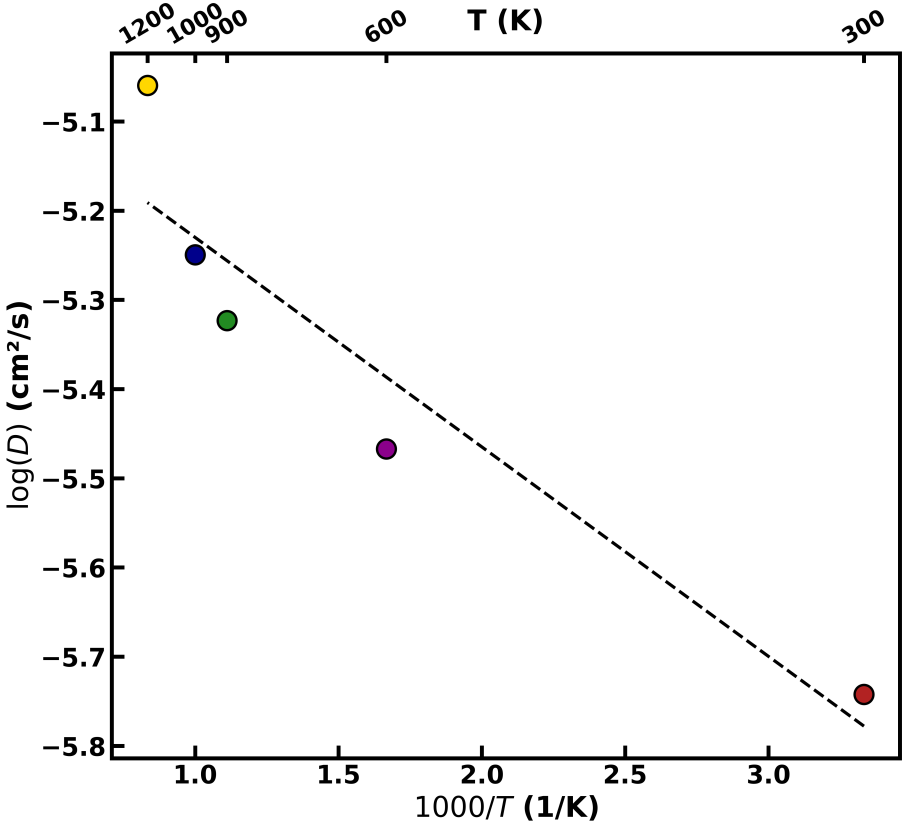
MTP: can yield ~0.1 V difference

Possible drop of ~0.2-0.3 V with amorphous, 10-14% drop

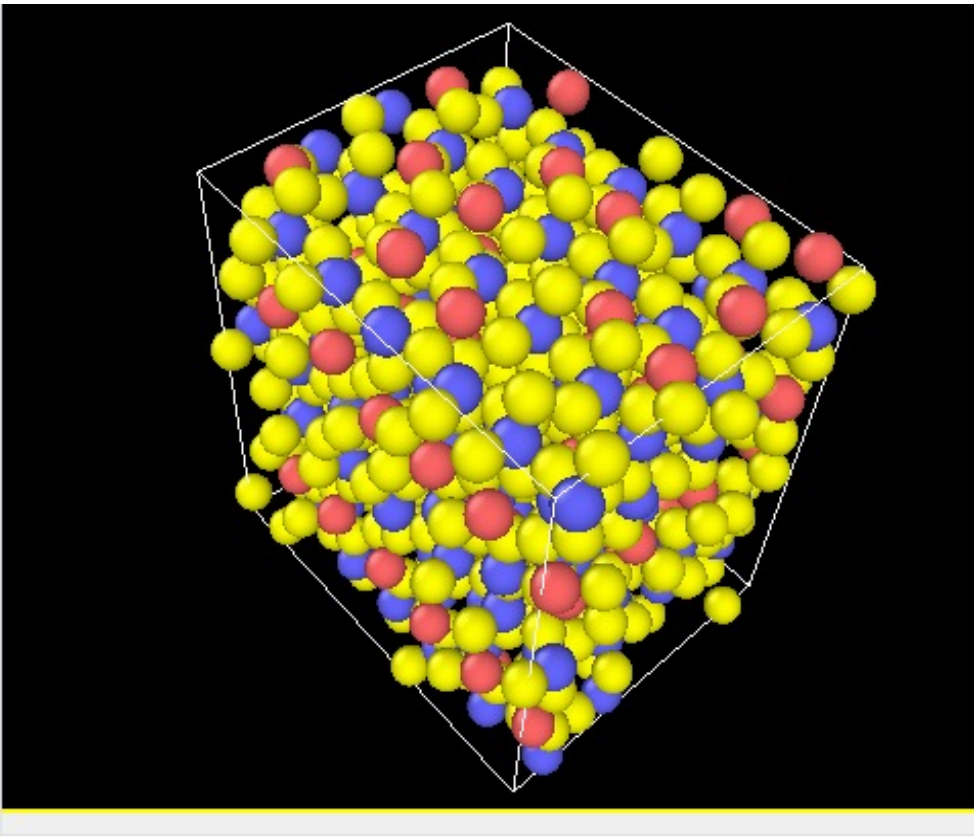
Sai Gautam et al., *Chem. Mater.* 27, 3733-3742 (2015)

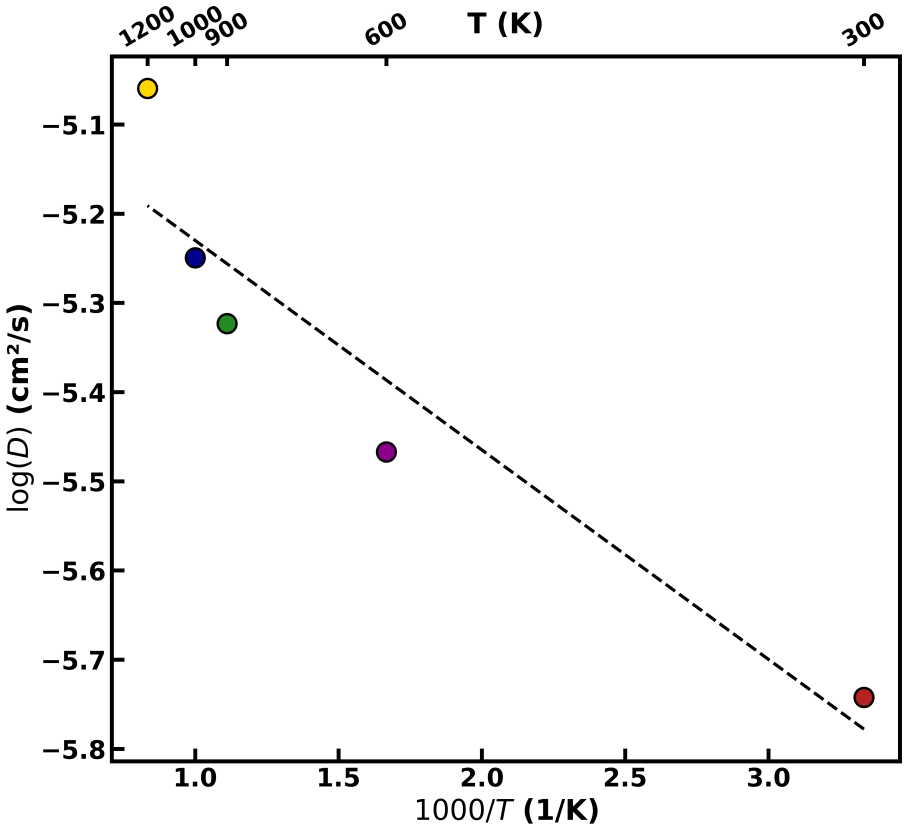
Amorphous V_2O_5 exhibits higher Mg mobility





Amorphous V_2O_5 exhibits higher Mg mobility





MTP; 1ns; 1000 K

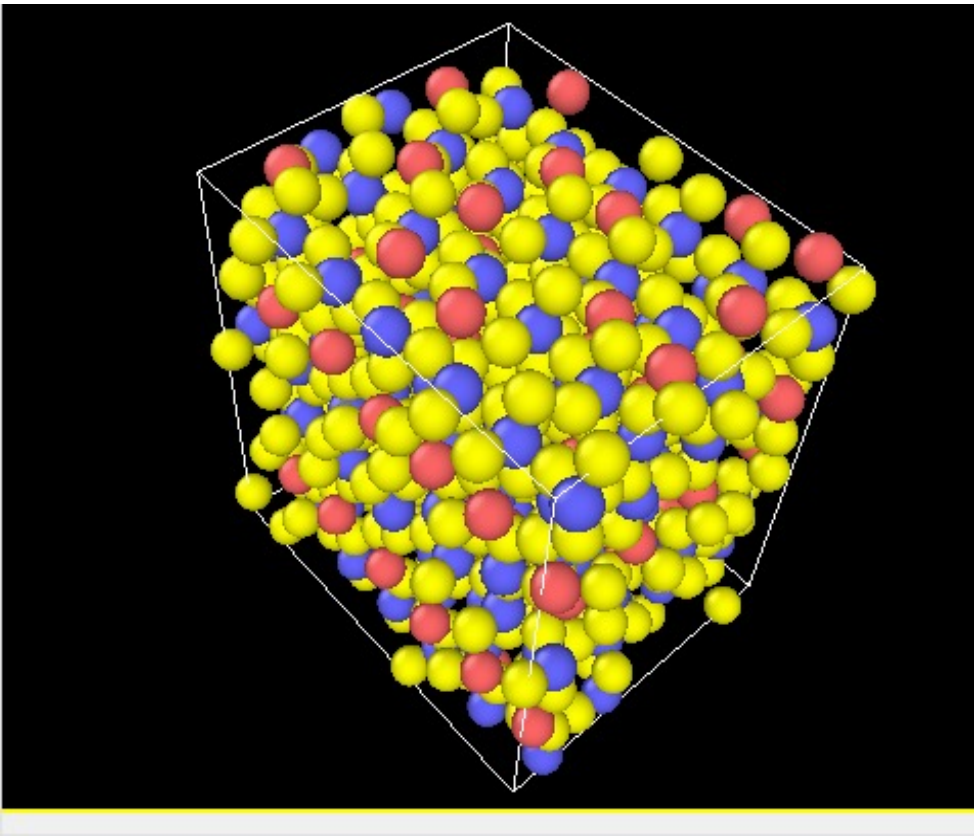
Amorphous Diffusivity: ~10^{-6} cm^2/s; Barrier*: ~46 meV

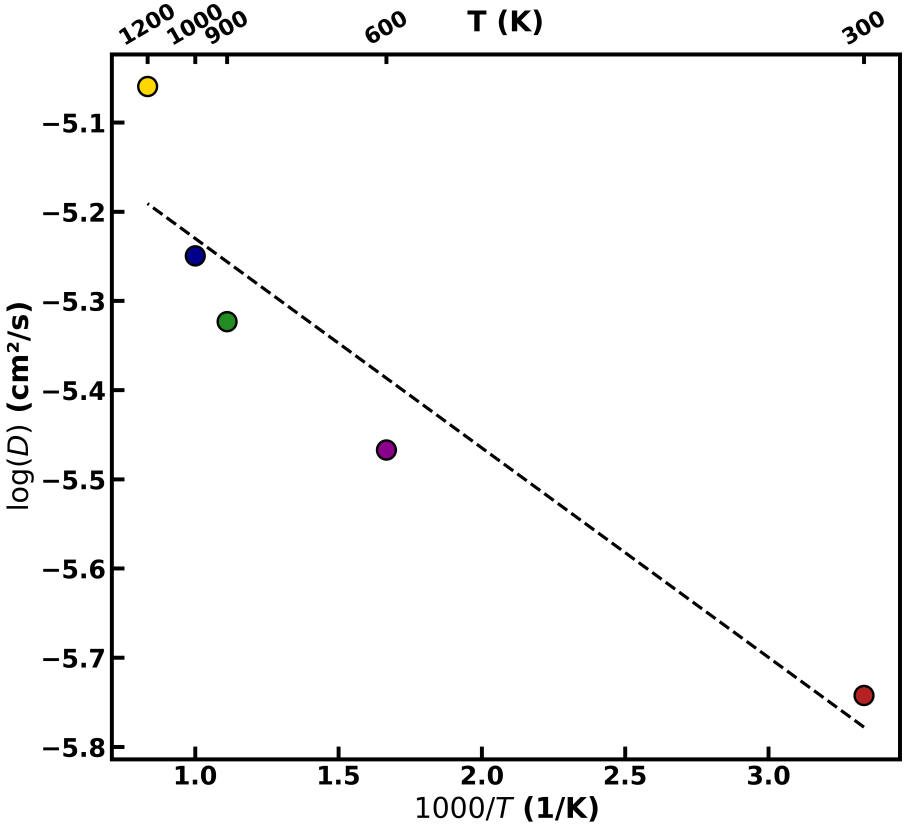
Crystalline [*Chem. Mater.* 27, 3733-3742 (2015)]
Diffusivity (δ): ~10^{-13}-10^{-16} cm^2/s; Barrier: 600-750 meV
Diffusivity (α): ~10^{-20}-10^{-22} cm^2/s; Barrier: 975-1120 meV

7 orders of magnitude boost due to amorphization

5 orders of magnitude higher than $Mg_xTi_2S_4$

Amorphous V_2O_5 exhibits higher Mg mobility





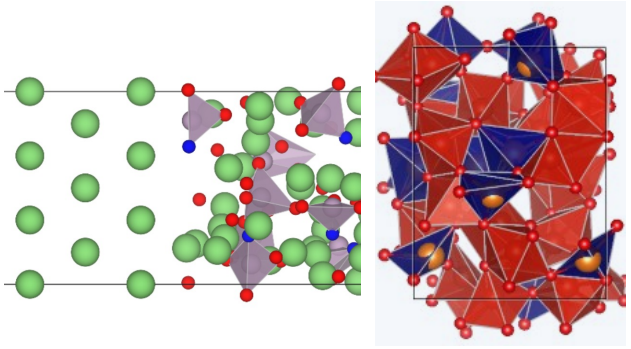
MTP; 1ns; 1000 K

Amorphous Diffusivity: ~10^{-6} cm^2/s; Barrier*: ~46 meV

7 orders of magnitude boost due to

Can obtain significant diffusivity boost in amorphous (Mg) electrodes with low voltage loss

Conclusions



- Amorphous materials can have use cases in batteries
  - As dendrite-suppressing solid electrolytes in Li
  - As cathodes in Mg
- Use NequIP to model Li|LiPON interface
  - Low diffusivity difference between bulk and interface
- Amorphous V_2O_5 seems reasonable
  - 7 orders-of-magnitude boost in diffusivity

"Investigating Ionic Diffusivity in Amorphous LiPON using Machine-Learned Interatomic Potentials", A. Seth, R. P. Kulkarni, G. Sai Gautam, *ACS Mater. Au*, 5, 458-468 (2025; 'Rising Stars 2024' collection).

"Machine learning guided exploration of amorphous V_2O_5 as cathode for Mg-batteries ", V. Choyal, D. Dey, and G. Sai Gautam, *arXiv*, 2505.10967 (2025).