

Nature of the Amorphous–Amorphous Interfaces in Solid-State Batteries Revealed Using Machine-Learned Interatomic Potentials

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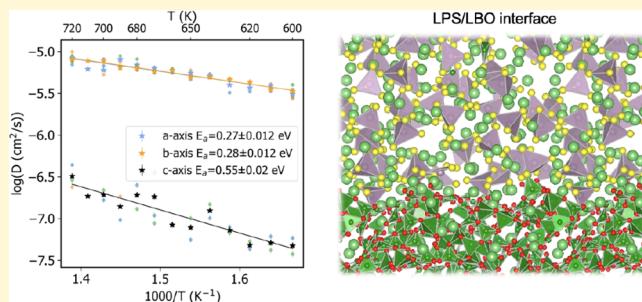
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ABSTRACT: Non-crystalline solid materials have attracted growing attention in energy storage for their desirable properties such as ionic conductivity, stability, and processability. However, compared to bulk crystalline materials, fundamental understanding of these highly complex metastable systems is hindered by the scale limitations of density functional theory (DFT) calculations and resolution limitations of experimental methods. To fill the knowledge gap and guide the rational design of amorphous battery materials and interfaces, we present a molecular dynamics (MD) framework based on machine-learned interatomic potentials trained on the fly to study the amorphous solid electrolyte Li_3PS_4 and its protective coating, amorphous $\text{Li}_3\text{B}_{11}\text{O}_{18}$. The use of machine-learned potentials allows us to simulate the materials at time and length scales that are not accessible to DFT while maintaining a near-DFT level of accuracy. This approach allows us to calculate amorphization energies, amorphous–amorphous interface energies, and the impact of the interface on lithium ion conductivity. This study demonstrates the promising role of actively learned interatomic potentials in extending the application of ab initio modeling to more complex and realistic systems such as amorphous materials and interfaces.



INTRODUCTION

Li-ion batteries have revolutionized the portable electronics industry.¹ All-solid-state Li-ion batteries employing nonflammable solid electrolytes are attracting growing attention due to their enhanced safety and higher energy density.^{2–4} Although several classes of inorganic solid electrolytes with high ionic conductivity have been identified, the performance of all-solid-state batteries is often compromised by interfacial side reactions.^{5–9} At present, a major challenge faced by all-solid-state batteries is developing materials that enable high mobility of lithium ions in the bulk as well as across interfaces.^{10,11}

Computation has become an important approach for advancing material research for batteries.^{12,13} Density functional theory (DFT) has been particularly successful in evaluating thermodynamic stability, providing bounds for electrochemical stability windows, predicting ionic diffusion mechanisms, and guiding interface engineering.^{14–16} In recent years, high-throughput computational screening over wide chemical spaces has emerged as a valuable tool to improve upon experimental trial and error.¹⁶ Simulations of specific material structures have provided insights on atomic and electronic scales, thus aiding the interpretation of experimental observations.^{17,18} Due to the computational cost of DFT calculations, currently, most atomic-level studies of materials focus on crystalline materials.¹⁹

State-of-the-art solid electrolytes are composed of crystals, glass ceramics, and glasses.^{3,20} Inducing disorder into the structure has emerged as a potential route to enhance the rate

of ionic conduction.^{21,22} Compared to crystalline structures, the amorphous counterparts could provide percolation pathways and avoid problems with lattice mismatch, contributing to improved rate capability and long-term cyclability. As opposed to energetically favorable migration paths, in particular directions characterized in various crystalline lithium borate materials,²³ the diffusion rate of charge carriers in the amorphous phase is independent of its orientation, which facilitates processing to achieve the theoretical rate capability. The benefits of non-crystalline materials are reflected in the fact that many state-of-the-art coatings used in batteries, including LiNbO_3 , LiTaO_3 , Li_4GeO_4 , Li_3PO_4 , Al_2O_3 , $\text{Li}_{3.5}\text{Si}_{0.5}\text{P}_{0.5}\text{O}_4$, and lithium borate obtained by various preparation methods, exhibit low crystallinity in experimental characterizations.^{24–30} Despite the increasing interest in using amorphous materials as solid electrolytes and electrode coatings,^{31–33} relatively little is known about the interfacial properties and atomistic mechanisms of ionic diffusion in these materials, leaving a gap in our knowledge of how to improve cycling performance in batteries with amorphous materials.

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This is in part due to the challenge of using experimental methods to accurately characterize atomic structures of amorphous materials.³⁴

First-principles modeling of amorphous structures is challenging because unlike crystals, amorphous structures lack translational symmetry. It is thus necessary to use large simulation cells, which can be prohibitively expensive to model, especially if long time scales are required. Ab initio molecular dynamics (AIMD) has been used in several studies on solid electrolyte materials with high lithium ion conductivity,^{35–37} but there have only been a few reported studies that simulated amorphous coatings, and these were mainly done with empirically parametrized models such as classical force-field-based molecular dynamics simulations and Monte Carlo annealing.^{37–39} It is a non-trivial task to develop interatomic potentials for new glass chemistries, and it becomes even more challenging for highly complex systems such as amorphous–amorphous interfaces. To circumvent the limitation of inaccurate empirical interatomic potentials, other approaches have been employed to construct atomistic models for disordered and heterogeneous systems including reverse Monte Carlo modeling (RMC)⁴⁰ and hybrid reverse Monte Carlo (HRMC),⁴¹ which combines RMC with molecular dynamics(MD). Although these methods can be effective, they require experimental diffraction data, which is not always readily available.

Machine learning has proven to be versatile for circumventing the limitations of first-principles calculations, facilitating the prediction of material properties that are otherwise hard to access.^{42–45} In our previous work, we developed a screening scheme for solid-state ionic conductors based on active learning of moment tensor potential (MTP) models and achieved better agreement with experimentally determined activation energies than what could be achieved by DFT alone.^{46–48} In this scheme, structures that are significantly different from those used to train the potential are identified on the fly during MD and added to the training set, preserving the accuracy of the machine-learned potential and minimizing the cost of generating training data. Such an active learning scheme is also promising for amorphous materials as it provides accuracies close to that of DFT but allows simulations on much longer time and length scales. In this work, combining the capability of first-principles methods to accurately treat arbitrary configurations with the high speed of machine-learned interatomic potential models, we present an active learning scheme to achieve accurate atomistic modeling of amorphous materials. We demonstrate this scheme by applying it to the commonly employed amorphous solid electrolyte Li_3PS_4 and the novel amorphous protective coating $\text{Li}_3\text{B}_{11}\text{O}_{18}$.³⁰

While most simulations on battery materials so far have studied bulk structures, understanding the atomic dynamics across interfaces is critical to improving the cycling performance of all-solid-state batteries.⁴⁹ Due to the unique chemical environment at the interface, ionic dynamics in its vicinity may differ from that in the constituent phases on either side. It is non-trivial to estimate the conduction rate or the diffusion mechanism across the interface even when both bulk materials are well characterized. Recently, several DFT studies have examined the geometry and electronic properties of systems such as $\text{Li}/\text{Li}_2\text{O}$, $\text{Li}/\text{Li}_3\text{PS}_4$, $\text{Li}/\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, and Li/LiPON on the anode side^{50–52} and $\text{LiCoO}_2/\text{Li}_3\text{PS}_4$ and $\text{LiFePO}_4/\text{Li}_3\text{PS}_4$ on the cathode side.^{53,54} Among these studies, a few

reported diffusion activation energies across crystalline interfaces by performing climbing-image nudged elastic band (CI-NEB)^{55,56} calculations with a manually determined diffusion paths.^{52,54} Such an approach could be very challenging for amorphous materials due to their high structural complexity, wide variety of local atomic environments, and cooperative atomic motions involved in diffusion. To address this challenge, we extend our active learning-driven MD study to investigate the atomic structure and ionic diffusion at the amorphous–amorphous interface between $\text{Li}_3\text{B}_{11}\text{O}_{18}$ and Li_3PS_4 . This approach enables us to predict the interfacial energy between two amorphous ionic compounds, which is rarely found in the literature. We further quantify the effect of the interface on the overall ionic conductivity of the coated solid electrolyte. The result provides atomic-scale insights into the experimentally observed enhanced rate performance by the borate coating.³⁰

■ METHODS

Molecular Dynamics. Ab initio MD simulations were performed using the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation exchange–correlation functional⁵⁷ and projector augmented wave⁵⁸ potentials (PAW_PBE Li, PAW_PBE P, PAW_PBE S, PAW_PBE B, and PAW_PBE O) using the Vienna Ab initio Simulation Package (VASP).^{59,60} We used a plane wave energy cutoff of 400 eV and a minimal Γ -centered $1 \times 1 \times 1$ k -point mesh, which has been shown to provide a satisfactory balance between computational accuracy and cost in large systems.^{61,62} Non-spin-polarized calculations were performed. A time step of 2 fs was adopted for MD. The temperature control for NVT-AIMD simulations and NPT-AIMD simulations was achieved by using a Nosé–Hoover thermostat with a Nosé–mass corresponding to a period of 40 time steps (SMASS = 0)^{63,64} and Langevin thermostat^{65,66} respectively.

Our learning on-the-fly (LOTF)-MD scheme automatically switches between MTP-MD in LAMMPS⁶⁷ and DFT retraining in VASP. During the dynamic evolution of the structure in MTP-MD, MTP retraining was conditionally activated by the occurrence of an “extrapolating” configuration as determined by the D-optimality criterion,⁶⁸ corresponding to the extrapolation grade⁶⁹ parameter coded in MLIP. The MTP-MD was terminated once the extrapolation grade exceeded the selection threshold, which we set to 10, consistent with a recent publication.⁴⁶ Structures that had extrapolation grades above 1.5 were selected from the MD trajectory to be added to the DFT training set. The MTP was retrained on the updated training set, and MTP-MD run was restarted with the new potential. The active learning process was managed by the Machine Learning of Interatomic Potentials (MLIP) software package.⁶⁹ The MTP cutoff radius and the maximum level of basis functions, lev_{max}, were chosen to be 5.0 Å and 12, respectively. MTP-MD simulations in the isothermal-isobaric (NPT) ensemble used the Nosé–Hoover thermostat and barostat.^{63,64} The Nosé–Hoover thermostat was also used to maintain the temperature in the canonical (NVT) ensemble. We applied a time step of 2 fs in LAMMPS, consistent with that used in AIMD. Details of the active learning criteria, DFT validation error of energies and forces on various crystalline structures, and experimental benchmark results on diffusion barrier energy prediction can be found in our previous publication.⁴⁶

Workflow. The initial structures of bulk glasses were constructed by randomly distributing Li atoms and PS_4 tetrahedral units (96 atoms in total) in $12 \text{ \AA} \times 12 \text{ \AA} \times 14.87 \text{ \AA}$ simulation boxes for Li_3PS_4 and Li, B, and O atoms (128 atoms in total) in $12 \text{ \AA} \times 12 \text{ \AA} \times 10.64 \text{ \AA}$ simulation boxes for $\text{Li}_3\text{B}_{11}\text{O}_{18}$ to match the densities of their crystalline counterparts.^{70,71} Interface structures were initialized by stacking randomly initialized bulk components. The vertical displacements of the top component were adjusted within the range of 1.2–1.5 Å to ensure a Li–Li distance of at least 2.5 Å. We obtained an

ensemble of four independently initialized structures for each composition of bulk materials and the solid–solid interfaces.

Amorphous structures were optimized using the melt-quench method, as shown in Figure 1. To generate the initial training dataset

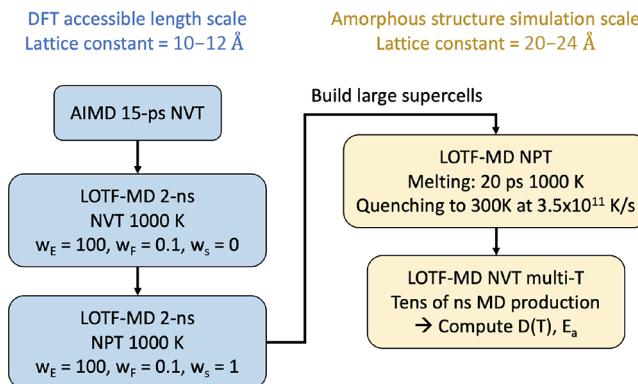


Figure 1. Potential training and MD production of bulk Li_3PS_4 , bulk $\text{Li}_3\text{B}_{11}\text{O}_{18}$, and $\text{Li}_3\text{PS}_4/\text{Li}_3\text{B}_{11}\text{O}_{18}$ interface. Initial AIMD and learning on-the-fly MD in supercells of $10\text{--}12\text{ \AA}$ followed by melt-quench in large simulation cells (>20 angstroms between periodic images) to obtain equilibrated amorphous structure models and calculate ionic diffusion coefficients.

for moment tensor potentials,⁷² an AIMD simulation was carried out for 15 ps at 1000 K in the NVT ensemble. In each AIMD run, the first 2 ps were used for equilibration and then a 13 ps dynamic trajectory was produced for training. The initial training data for the interatomic potential was generated by taking snapshots of the AIMD simulation at intervals of 10 fs. This potential was then used in learning on-the-fly MD (LOTF-MD) at 1000 K until the MD simulation ran for at least 2 ns without activating DFT retraining. Then, LOTF-MD simulations in the NPT ensemble were performed at 1000 K for a duration of at least 2 ns to relax the lattice strain. MTP-MD runs in the subsequent iterations were initialized by the last non-extrapolating snapshot from the previous MD run. In this way, the quality of amorphous structures and the potential models were simultaneously improved during LOTF-MD iterations. During MTP learning on-the-fly, the training weights of energy, force, and stresses were 100:0.1:0 and 100:0.1:1 for NVT-MD and NPT-MD, respectively. The ensemble of independently generated training sets, with compositions of Li_3PS_4 , $\text{Li}_3\text{B}_{11}\text{O}_{18}$, and $\text{Li}_3\text{PS}_4/\text{Li}_3\text{B}_{11}\text{O}_{18}$, was consolidated into one training set containing a diverse sampling of local atomic configurations. A single interatomic potential was trained on this combined set of training data. To validate the prediction accuracy of the trained potential and compare the energies of structures generated by LOTF-MD with those from AIMD, we performed AIMD static calculations on 200

snapshots evenly selected from a 2 ns LOTF-MD trajectory with 10 ps time interval for each composition.

To calculate the diffusion properties of the bulk amorphous materials, we constructed $2 \times 2 \times 2$ supercells of the final structure from the previous LOTF-MD runs. For the interface, we constructed a $2 \times 2 \times 1$ supercell. The supercells contain 1024, 768, and 896 atoms for compositions of Li_3PS_4 , $\text{Li}_3\text{B}_{11}\text{O}_{18}$, and $\text{Li}_3\text{PS}_4/\text{Li}_3\text{B}_{11}\text{O}_{18}$ interface, respectively. The potential trained on the combined training data was used to melt the system at 1000 K in the NPT ensemble for 20 ps, which ensures loss of the memory of the initial configuration. The system was subsequently cooled linearly to 300 K in 2 ns with a cooling rate at $3.5 \times 10^{11} \text{ K/s}$. We then equilibrated the glassy system at 300 K at 1 atm pressure in the NPT ensemble for 1 ns to relax any stress.

We applied the following equation to compute the tracer diffusivity:

$$D_{\text{tr}} = \lim_{t \rightarrow \infty} \frac{1}{6} \frac{\langle \Delta^2 r(t) \rangle}{t} \quad (1)$$

where $\langle \Delta^2 r(t) \rangle$ is the mean square displacement (MSD) of the Li atom after time t , and the constant 6 is used for three-dimensional diffusion. To calculate the tracer diffusivity as a function of temperature, we performed LOTF-MD in the NVT ensemble with the lattice dimension fixed at that of the room-temperature equilibrated structures. The initial temperature (T) for LOTF-MD simulations of each simulation snapshot was 720 K, and the MD simulation temperature was decremented by 10 K until the diffusivity of Li was so low that no site-to-site hopping was detected within 100 ns. The temperature-dependent diffusivities were used to fit the Arrhenius relationship

$$D(T) = D(\infty) e^{-E_a/k_B T} \quad (2)$$

We denote the estimated tracer diffusivity at temperature T as $D(T)$. The activation energy, E_a , can be calculated from a linear fit of $\log(D(T))$ to $\frac{1}{k_B T}$, where k_B is the Boltzmann's constant. As demonstrated by He *et al.*,⁷³ the variance of the independent variable D should be considered when fitting the Arrhenius equation for a statistically meaningful estimation of E_a . Following their method, we estimated the variance of the diffusivity of lithium ions and propagated to the variance of the activation energy E_a . These variances were then used in a weighted least-squares regression to estimate E_a . The equation for variance calculation and weighted least-squares regression are provided in Section S1 of the Supporting Information. The room-temperature conductivity $\sigma_{300\text{K}}$ was calculated using the Nernst–Einstein relation under the assumption that the Haven ratio is equal to 1.^{74,75}

$$\sigma_{300\text{K}} = \frac{ne^2 z^2}{k_B T} D_{300\text{K}} \quad (3)$$

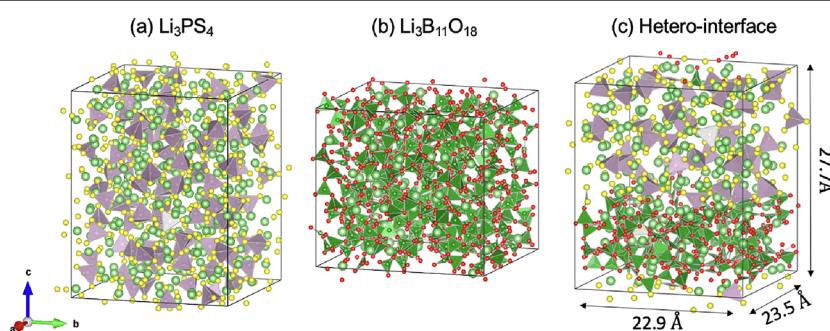


Figure 2. Snapshots from LOTF-MD trajectories in the final production steps at 300 K for the amorphous structures of (a) LPS, (b) LBO, and (c) the interface between LPS and LBO. Green, yellow, and red spheres represent Li, S, and O, respectively. Purple tetrahedra, green tetrahedra, and triangles represent PS4, BO4, and BO3 ionic units, respectively. The dimensions of the unit cell used for the interface are shown on the schematic.

where n is the volume density of the diffusing species, e is the unit electron charge, z is the charge of the ionic conductor (here, 1 for Li^+), and $D_{300\text{K}}$ is the extrapolated room-temperature tracer diffusivity.

Calculation of Interfacial Energy. The interfacial energy, $\gamma_{\text{interface}}$, is computed with respect to the two constituent bulk phases:

$$\gamma_{\text{interface}} = \frac{1}{2A}(E_{\text{interface}} - N_{\text{LBO}}E_{\text{bulk,LBO}} - N_{\text{LPS}}E_{\text{bulk,LPS}}) \quad (4)$$

where $E_{\text{interface}}$ denotes the total energy of the simulated interface model, $E_{\text{bulk,LBO}}$ and $E_{\text{bulk,LPS}}$ are the energy per formula unit of amorphous Li_3PS_4 and $\text{Li}_3\text{B}_{11}\text{O}_{18}$, respectively, N_{LBO} and N_{LPS} are the number of formula units of $\text{Li}_3\text{B}_{11}\text{O}_{18}$ and Li_3PS_4 in the interface system, and A is the area of each interface in the simulation cell.

■ RESULTS AND DISCUSSION

Structure of Simulated Glasses. We evaluate the atomic ordering in the amorphous structures generated by the melt-quench method (Figure 2) by calculating the pair radial distribution functions (RDFs) of Li–Li, B–O, and P–S pairs with reference to their crystalline counterparts (Figure 3). The

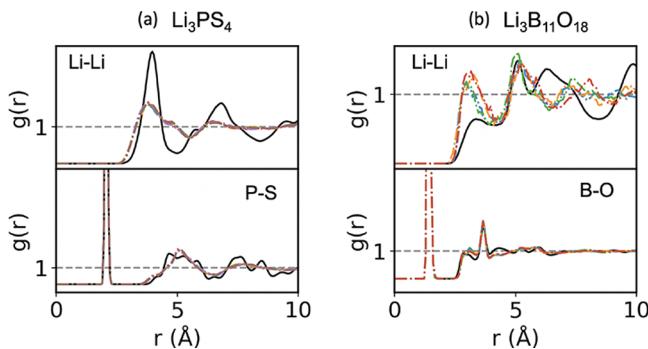


Figure 3. Pair radial distribution functions (RDFs) at 300 K of (a) amorphous Li_3PS_4 for atom pairs Li–Li and P–S and (b) amorphous $\text{Li}_3\text{B}_{11}\text{O}_{18}$ for atom pairs Li–Li and B–O with reference to their crystalline counterparts. Colored dashed lines represent the RDFs from the LOTF-MD trajectories of multiple independently simulated amorphous structures. Black solid lines represent the RDFs of crystalline Li_3PS_4 and crystalline $\text{Li}_3\text{B}_{11}\text{O}_{18}$.

Li–Li RDF in both bulk materials exhibits no sharp peaks, suggesting a highly disordered Li distribution in the glasses at room temperature. In contrast, the clear peaks in the P–S and B–O pair distribution functions indicate that the PS_4 tetrahedra, BO_4 tetrahedra, and BO_3 triangular anion units remain largely intact in the amorphous structures during Li diffusion (Figure 3). Our computed RDF of amorphous Li_3PS_4 agrees with previous experimental characterization where the first peak around 2.0 Å is due to the P–S covalent bond in

PS_4^{3-} , which are the predominant anion units in the structure.⁷⁶ The RDF of non-lithium species in the amorphous structures differs from crystals in the longer range features. Integrating the curves for P–S and B–O pairs (Figure 3) up to the first minimum (~2.5 Å), the average coordination number of P by S atoms and B by O atoms are 4 and 3.2, respectively. A similar analysis was conducted on the geometry of interfaces, and approximately the same coordination number of P–S and B–O were obtained. This suggests that the short-range ordering of anion units in the interface resembles that in the bulk phase.

The thermal history of glasses is critical to the structural properties of amorphous systems.^{77,78} However, given the timescale accessible to AIMD, which are generally less than a nanosecond, the simulated cooling rate in an AIMD simulation is typically on the order of 10^{13} – 10^{15} K/s, which is much higher than that performed experimentally (1–100 K/s).^{79–81} Several computational studies have investigated the effect of thermal history on the structures and properties of silicate, borate, phosphate, borosilicate, and aluminosilicate glasses.^{82–85} It was found that cooling rates in the range of 5×10^{12} – 1×10^{11} K/s yield reasonable structural properties.^{78,86,87} Enabled by the high efficiency of LOTF-MD, we carry out cooling over 2 ns time duration at a rate of 3.5×10^{11} K/s, which would be prohibitively expensive with AIMD in large unit cells.

To better understand the effects of cooling rate on the amorphous structure, we compare the radial distribution functions produced by cooling at 3.5×10^{11} K/s with those produced by fast quenching at 3.5×10^{14} K/s (Figure 4). The fast quenching rate resulted in considerably more spread in the pair distribution functions than the quenching rate that was three orders of magnitude slower, suggesting that the pair distribution functions had not yet converged. This provides evidence that high quenching rates might result in unrealistic structures in the amorphous system, which highlights the important role of active learning potential models in studies of amorphous materials. Although additional structural refinement might be achieved with even slower quenching, convergence of the cation spatial distribution among multiple MD initializations indicates that the simulated quenching provides a reasonable approximation to the actual amorphous structure. It has previously been reported that intermolecular S–S units can emerge from fast quenching.⁸⁸ An RDF analysis of S–S pairs (SI Figure S1) in our samples shows a similar peak for intermolecular S–S bond formation at the fast cooling rate, but the peak is not apparent at the slow cooling rate.

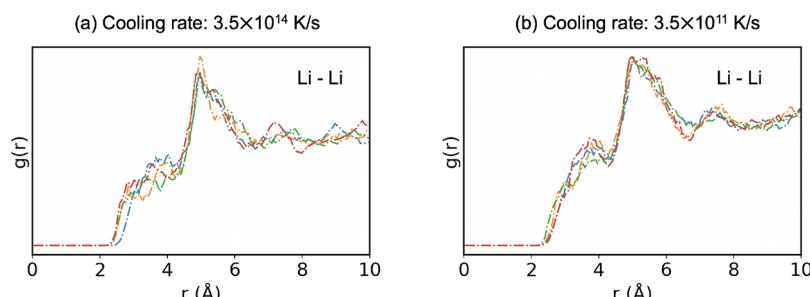


Figure 4. Li–Li pair radial distribution functions (RDFs) of glass $\text{Li}_3\text{B}_{11}\text{O}_{18}$ at 300 K in configurations produced by cooling at rates of (a) 3.5×10^{14} K/s and (b) 3.5×10^{11} K/s.

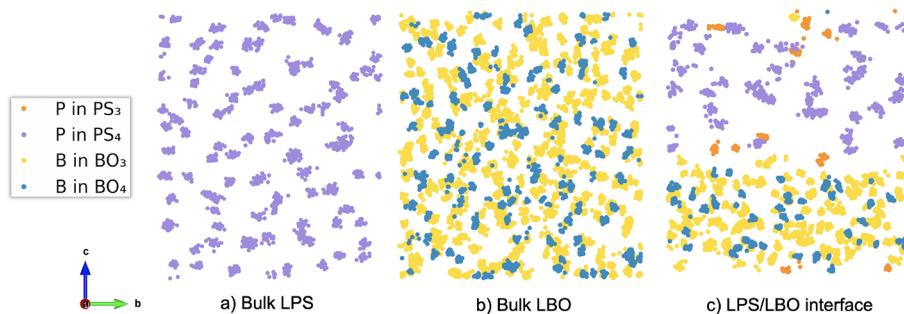


Figure 5. Trajectories of B and P atoms during 20 ns LOTF-MD at 700 K in the unit cell projected on the $b-c$ plane for (a) bulk LPS, (b) bulk LBO, and (c) a LPS/LBO interface. Coordination environments of B and P atoms are colored according to the legend.

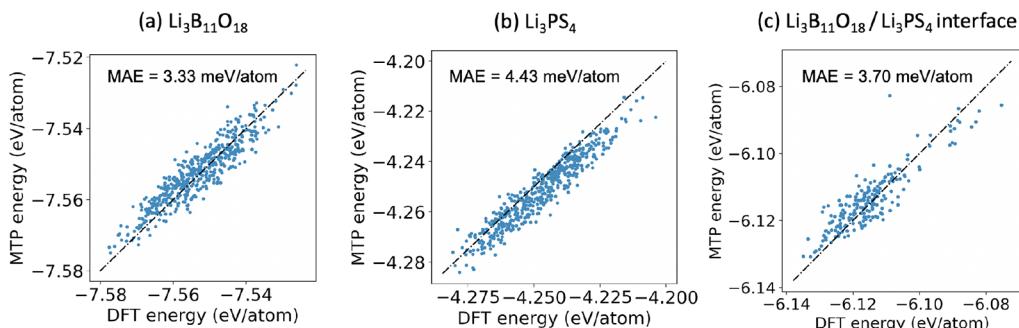


Figure 6. Comparison of DFT- and MTP-predicted energies for snapshots selected from 2 ns LOTF-MD trajectories for (a) bulk $Li_3B_{11}O_{18}$, (b) bulk Li_3PS_4 , and (c) the $Li_3B_{11}O_{18}/Li_3PS_4$ interface. The corresponding mean absolute errors (MAE) are labeled on the plots.

For the interface structures, most of the time, a clear boundary between the two materials can be recognized, while occasionally, B–O units diffuse into the solid electrolyte. There are two types of polyhedra (BO_3 and BO_4) in the lithium borate glassy network. To investigate the arrangement of the polyatomic anions at the interface, we analyze the coordination numbers of boron with oxygen and phosphorus with sulfur over the course of 20 ns of LOTF-MD production. As shown in the trajectory plot (Figure 5), the distribution of polyatomic anions in the bulk materials is similar to that near the interface. The molar fraction of BO_4 tetrahedra with reference to the total number of B–O units (0.26) is slightly higher than the molar fraction in the unit cells containing an interface (0.22).

To validate the generated structures (Figure 2 and Supporting Information Figure S2), we compared the calculated densities to those previously reported in the literature. The density of Li_3PS_4 relaxed by LOTF-MD in the NPT ensemble at room temperature is 1.79 ± 0.014 g/cm³ averaged over four independent simulation cells. Experimental measurements of the density vary between 1.45 and 1.89 depending on the molding conditions.⁸⁹ The AIMD-calculated densities of LPS glasses, calculated using melt-quench procedures, have been reported as 1.79 and 1.56 g/cm³.^{37,90} In the paper reporting the lower density,³⁷ it was suggested that the difference might be attributed to the fact that the computational cell was constrained to be cubic in the calculation that yielded the higher density.³⁷ To clarify this discrepancy, we performed AIMD in the NPT ensemble following the procedures in ref 37 where a density of 1.56 g/cm³ was reported, and we obtained a density of 1.802 g/cm³ after 30 ps AIMD. The density evolution over the course of AIMD simulation is shown in SI Figure S3. This indicates that LOTF-MD reproduces the AIMD optimized density well. The

LOTF-MD-calculated density averaged over an ensemble of four $Li_3B_{11}O_{18}$ is 2.09 ± 0.01 g/cm³, which achieves good agreement with the experimental density of 2.1 g/cm³.^{91,92}

Energies of Amorphous Bulk Materials and Interfaces. To calculate the energies of bulk amorphous materials and interfaces, the initial atomic structure of each amorphous phase at room temperature was obtained using the melt-quench procedures described in the Methods Section. To examine the progress of energy minimization and geometry optimization over time, we took snapshots evenly selected from the trajectories of the initial AIMD (150 fs time interval), LOTF-MD equilibration (10 ps time interval), and production periods (10 ps time interval) and recalculated their energies by DFT to make a comparison with AIMD. We note that across all systems, the mean absolute validation error between DFT and MTP is about 4 meV/atom (Figure 6) and 0.24 eV/Å (Figure S4) for energies and forces, respectively. To understand the evolution of the structure over time, we also calculate the Global Instability Index (GII) of these snapshots. The GII represents the mean deviation of the bond valence sums from the formal valences.⁹³ It has been previously used to evaluate the stability of crystalline structures,^{94,95} and here, we use it as a measure of atomic order in amorphous structures. The procedure of calculating the GII can be found in Section 2 of the Supporting Information.

From MD trajectories of bulk glasses and the amorphous interface structures, we found a substantial correlation between GII and the DFT energy, which continuously decreased over the course of the initial AIMD period and the LOTF-MD equilibration period. In Figure 7, we illustrate this trend for the solid–solid amorphous interface structure, which possesses the highest degree of complexity among the systems that we studied. During the initial 15 ps AIMD simulation, the energy decreased from -5.74 eV/atom to -5.99 eV/atom, and the

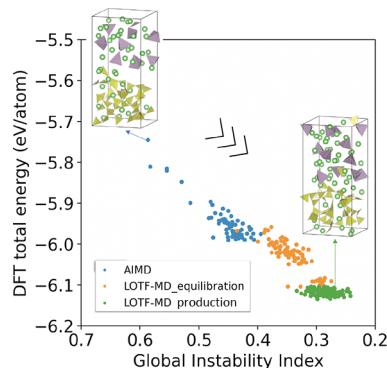


Figure 7. DFT energy per atom of an interface structure plotted against the global instability index (GII) for 13 ps AIMD started from randomly initialized structure (blue), 100 ps LOTF-MD equilibration (orange), and 1 ns LOTF-MD production (green). The configurations at the first step of AIMD and the last step of LOTF-MD production are shown on the plot.

GII decreased from 0.6 to 0.4. In the subsequent 100 ps LOTF-MD equilibration, the total energy further decreased by 0.1 eV/atom. This suggests that inadequate equilibration time (e.g., tens of picoseconds) could yield structures trapped in unrealistically high energy states. In the final LOTF-MD production, the GII ranged from 0.24 to 0.33 and the total energy fluctuated between -6.11 and -6.13 eV/atom, which suggests the convergence of energy. As a reference, it has generally been found that stable crystalline structures are characterized by $\text{GII} \leq 0.2$,^{93,96,97} suggesting that the amorphous structures exist just outside this range.

The energies of bulk Li_3PS_4 , bulk $\text{Li}_3\text{B}_{11}\text{O}_{18}$, and the interface are determined by taking the ensemble average of structures in the LOTF-MD production period for each

composition. Based on the DFT energies of amorphous Li_3PS_4 and $\text{Li}_3\text{B}_{11}\text{O}_{18}$ with reference to their crystalline counterparts, we calculated the amorphization energies to be 36.7 and 42.0 meV/atom, respectively. These values are on the lower end of the range of amorphization energies reported in a systematic study of 41 binary amorphous systems by AIMD.⁹² This is consistent with the strong glass forming tendency of these materials and the long equilibration times enabled by LOTF-MD. The relatively slow cooling rate allowed the structures to relax into low-energy amorphous configurations that may be impractical to achieve with AIMD, ultimately yielding more physically plausible and representative models for subsequent structural and dynamic analyses.

The interfacial energy between the two amorphous phases (eq 4) was calculated to be 620 mJ/m^2 ($38.5 \text{ meV/}\text{\AA}^2$). To our knowledge, this is the first time the interfacial energy between two amorphous ionic compounds has been reported. This is just above the range of a typical semicoherent interface (200 – 500 mJ/m^2) and comparable to that of a low-energy incoherent interface.⁹⁸ For comparison, the computationally predicted interfacial energies of crystalline $\text{LiCO}_2/\beta\text{-Li}_3\text{PS}_4$ and $\text{Li}/\gamma\text{-Li}_3\text{PO}_4$ ⁵² have been reported to be 2466 and 624 mJ/m^2 , respectively.

Li-Ion Conductivity of Bulk and Interfacial Amorphous Systems. To accurately characterize the transport properties of lithium ions in the glass materials and minimize finite-size effects, we constructed supercells of over 2 nm in each dimension for bulk Li_3PS_4 and $\text{Li}_3\text{B}_{11}\text{O}_{18}$. Figure 8a,b shows the calculated total Li^+ temperature-dependent diffusivities of the sulfide and borate glasses, where the Arrhenius relationship is fitted to statistics collected from multiple uncorrelated amorphous phases. The error bar on each averaged diffusivity data point is derived from hundreds of nanoseconds MD trajectories using the method of He *et al.*

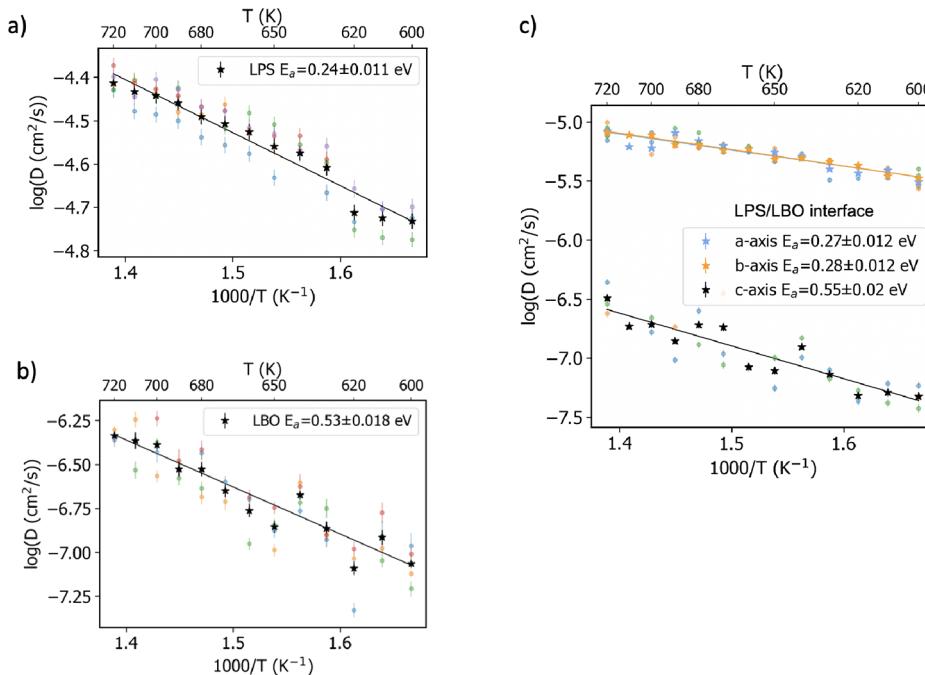


Figure 8. Arrhenius plots of Li^+ temperature-dependent diffusivities and activation energies (E_a) for bulk (a) Li_3PS_4 , (b) $\text{Li}_3\text{B}_{11}\text{O}_{18}$, and (c) $\text{Li}_3\text{PS}_4/\text{Li}_3\text{B}_{11}\text{O}_{18}$ diffusion along the three main axes. Each series of colored dots represents an independently simulated glass structure. At each temperature, an average diffusivity is calculated across all of these structures as shown by the black stars with corresponding error bars. The weighted Arrhenius fit to the diffusion data is denoted by the black lines.

al.⁷³ At intermediate temperatures for systems with activation energies over 0.5 eV, a nano-to-microsecond timescale is essential to obtain results with high statistical quality. While there are varying diffusivities at the same temperature among the different samples (especially in the borate), the average diffusivities exhibit good linear dependence on reciprocal temperature for both the fast-conducting sulfide electrolyte and the intermediate-conducting borate coating. The statistical quality is enhanced by the extensive sampling of the configuration space by nanosecond timescale LOTF-MD production.

The calculated bulk Li_3PS_4 conductivity is 16.4×10^{-3} S cm⁻¹ at 300 K, in good agreement with 19×10^{-3} S cm⁻¹ from a comprehensive study of Li_3PS_4 using AIMD.³⁷ The theoretical predicted ionic conductivities are higher than experimentally characterized values by about two orders of magnitude.^{32,99,100} It has been speculated that ionic-impeding impurity/residues such as Li_2S , $\text{P}_2\text{S}_6^{4-}$, and $\text{P}_2\text{S}_7^{4-}$ raised the apparent Li-ion diffusion barrier in the synthesized amorphous Li_3PS_4 .³⁷

The conductivity for $\text{Li}_3\text{B}_{11}\text{O}_{18}$ calculated using LOTF-MD is 1.38×10^{-4} S cm⁻¹ at 300 K with a predicted diffusion activation energy of 0.53 eV. We have not found any reported experimentally determined ionic conductivity for this specific borate glass in the literature. For comparison, the experimental activation energy for the composition 0.2Li₂O·0.8B₂O₃ with a lower Li content is 0.8 eV.¹⁰¹

To probe the impact of the interface on the ionic conductivity across the cell, we analyze diffusivities along axes parallel and perpendicular to the interface plane, as shown in Figure 8c. The lateral isotropic diffusion barrier represents the total resistance of bulk sulfide glass, borate glass, and the interface connected in parallel. The apparent activation energy is dominated by the component with the highest ionic conductivity. In the direction normal to the interface, lithium ions encounter the resistance of the bulk sulfide glass, the interface, and the borate glass connected in series. In this direction, the activation energy is dominated by the component that has the lowest ionic conductivity.

To ensure sufficient sampling of all three types of diffusions, we analyzed the displacement of each individual lithium ion along interface normal, as shown in Figure 9. The distance between neighboring interfaces in the simulation cell is ~ 14 Å. The histogram shows that within 1 ns MD production, most lithium ions were bouncing within the bulk phases and few

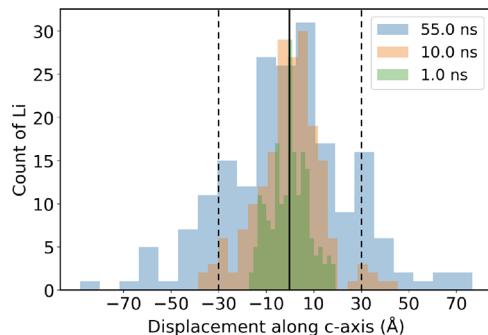


Figure 9. Histogram showing the displacement of lithium ions along the c axis perpendicular to the interface averaged over four individual interface structures simulated at 700 K for durations of 1, 10, and 55 ns.

diffusion hops across the interface were sampled. During the long MD simulation of 55 ns, over 25% of the lithium ions in the simulation cell have displaced from their original location by at least 30 Å in the direction normal to the interface, which means that they have traveled across an interface at least two times.

To determine the extent to which the amorphous–amorphous interface may hinder lithium ion conductivity in a solid-state battery, we compare diffusion across the interface to diffusion in the bulk materials. If the interface was a significant barrier to diffusivity, we would expect to see a significantly higher activation energy for diffusion in the direction normal to the interface. However, the calculated activation energy in this direction (0.55 ± 0.02 eV) is very similar to the calculated activation energy for diffusion through the bulk borate glass (0.53 ± 0.02 eV), giving evidence that diffusion across the interface does not reduce the rate of Li-ion conduction. These findings are in line with previous studies, demonstrating that the local Li-ion environment has minimal impact on Li-ion diffusivity.^{35,88} Our results indicate that lithium ions experience negligible additional impedance when diffusing between amorphous sulfide and borate anion sublattice. This might not be the case with crystalline systems due to lattice mismatch at the interface.

To investigate the diffusion pathways across the amorphous interface, we calculated an isosurface of Li-ion probability density for the LPS/LBO interface at 700 K (Supporting Information Figure S4a). In addition, we calculated the distribution of lithium ions moving across the interface by keeping track of lithium ions coordinated by both S (from Li_3PS_4) and O (from $\text{Li}_3\text{B}_{11}\text{O}_{18}$) atoms, excluding those coordinated by both S and O atoms in the snapshot taken 1 ps earlier. The spatial distribution plots in Figure 10 and Figure

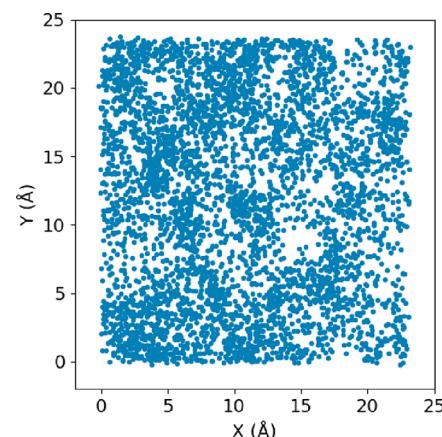


Figure 10. Trajectory of interface-crossing Li atoms projected onto the x - y plane.

S5 provide evidence for a homogeneous distribution of Li diffusion events within the interface region, with some fluctuations in density at the angstrom scale that are likely due to the host atomic structure.

CONCLUSIONS

Machine-learned interatomic potentials trained on-the-fly with DFT can give new insights into the kinetic behavior of amorphous materials and interfaces. Through realistic large-scale MD simulations using a highly accurate machine-learned

interatomic potential model, we investigated the interface morphology, thermodynamic properties, and Li-ion diffusion rates in amorphous battery materials. We found that the amorphous structures obtained by simulated melt-and-quench are critically affected by the cooling rate, and AIMD in particular may be insufficiently fast to obtain a reasonable approximation of the amorphous structure. With MD simulations of tens of nanoseconds enabled by the machine-learned potential model, we obtained structures with amorphization energies significantly lower than those obtained by sub-nanosecond quenching. The structural stability of these amorphous structures as measured by the global instability index is just above the range of crystalline materials. The interfacial energy between the sulfide solid electrolyte and borate protective coating was calculated to be 620 mJ/m², which to our knowledge, is the first calculation of the interfacial energy between two amorphous materials from first principles. The calculated activation energies for lithium-ion diffusion across the interface provide quantitative evidence that the interface between amorphous Li₃PS₄ and amorphous Li₃B₁₁O₁₈ does not impede Li-ion diffusion. The method introduced in this study is generalizable to model a variety of interfaces involving amorphous materials, which can help to reduce experimental efforts of synthesizing and characterizing these systems.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.3c00993>.

Details of statistical error analysis and weighted Arrhenius fitting; global instability index calculation method; radial distribution function analysis of S–S pairs in the glass structure simulated by two different cooling rates; snapshots of simulated glasses; density evolution over 30 ps AIMD simulation of amorphous Li₃PS₄; mean absolute errors for predictions of forces by MTP with reference to DFT; and isosurfaces of the Li-ion probability density distribution from the LOTF-MD simulation at 700 K for the LPS/LBO interface and spatial distribution of interface-crossing Li atoms ([PDF](#))

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Notes

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