Bridging the gap between simulated and experimental ionic conductivities in lithium superionic conductors

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1. Introduction

Lithium superionic conductors (LSCs) are the critical enabling solid electrolyte component in next-generation all-solid-state rechargeable lithium-ion batteries [1–4]. Replacing the traditional flammable organic solvent electrolyte, ceramic LSCs exhibit superior safety and are also a potential pathway to higher energy densities, cell architectures and utilization of lithium metal anodes. As the name implies, a key property of LSCs is a high ionic conductivity, typically ranging from $10^{-1}$ to $10^1$ mS cm$^{-1}$ at room temperature. The anion chemistry of an LSC has a major influence on their properties. Sulfide LSCs, such as the Li$_2$GeP$_2$S$_4$ (LGPS) family [5–8], Li$_3$P$_5$S$_4$ [9–11] and Li$_3$PS$_4$ [12–14], tend to have very high ionic conductivities due to the large, polarizable $S^2^-$, but suffer from narrow electrochemical stability windows, air- and moisture-sensitivity. Oxide LSCs, such as the Li$_2$La$_2$Zr$_2$O$_{12}$ garnet family [15] and LISICONs [16–18], typically have lower ionic conductivities compared to the sulfides, but are much more electrochemically and chemically stable. Recently, a promising new class of halide LSCs, Li$_3$YCl$_6$ and Li$_3$YBr$_6$, has been discovered that exhibits a good compromise of ionic conductivities (0.51 mS cm$^{-1}$ for Li$_3$YCl$_6$ and 1.7 mS cm$^{-1}$ for Li$_3$YBr$_6$) and electrochemical stabilities between those of the sulfides and oxides [21].

Molecular dynamics (MD) simulations have been extensively used in the study of ion conduction in LSCs and other materials. In particular, ab initio MD (AIMD), i.e., simulations where the energies and forces are directly obtained by solving the Schrödinger equation via density functional theory (DFT), have emerged as a powerful tool in recent years as they can be transferably applied to the entire range of LSC chemistries [19,20–28]. However, the high cost of AIMD simulations means that they are usually performed at elevated temperatures to obtain sufficient diffusion statistics, sometimes far in excess of the melting points of some LSCs, and for relatively short simulation time frames (~ 100 ps). As a consequence, extrapolated room-temperature ionic conductivity and...
diffusivity have large error bars [30]. Further, there may be phase transitions or diffusion mechanisms occurring between room temperature and high simulation temperatures, invalidating the Arrhenius assumption used in extrapolation. Such non-Arrhenius behavior and phase transitions have been reported in many LSCs, including Li$_3$La$_{2/3-x}$TiO$_3$ [31,32], Li$_3$PS$_4$ [14], and LGPS [33]. Another source of error arises from the fact that most AIMD simulations of LSCs are performed in the NVT ensemble using the equilibrium volume from a 0 K density functional theory (DFT) relaxation calculation. The most common DFT functional used is the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) [34], which tends to overestimate the lattice parameters of solids and differ from experimental values by up to 2–3% [35,36]. These differences in lattice parameters can have a major effect on ion diffusion and activation barriers [23,37].

The net result of the mismatch in working temperatures and lattice parameters between simulations and experiments is that room-temperature ionic diffusivity and conductivity of LSCs computed from AIMD simulations often disagree substantially with those measured experimentally, e.g., via electrochemical impedance spectroscopy (EIS). For example, Chu et al. [13] previously predicted a room-temperature ionic conductivity of 57 mS cm$^{-1}$ for the Li$_3$P$_2$S$_7$ LSC using AIMD simulations, far in excess of the highest experimentally measured room-temperature ionic conductivity of 17 mS cm$^{-1}$ [10]. Similarly, Wang et al. [29] predicted an ionic diffusivity of 14 mS cm$^{-1}$ for the Li$_2$YCl$_6$ LSC, again in excess of the experimentally reported 0.51 mS cm$^{-1}$ [21].

Classical MD simulations using an interatomic potential (IAP) to parameterize the potential energy surface (PES) are a potential solution to enable low-temperature and long-timescale studies. In recent years, machine learning (ML) the PES as a function of local environment descriptors has emerged as an especially promising, and reproducible approach to develop IAPs with near-DFT accuracy in energies and forces [38–50]. However, most ML-IAPs that have been developed in the literature still rely on DFT calculations performed using the PBE functional; as such, their performance are still limited by the accuracy of the DFT training data.

In this work, we show that the gap between experimental and simulated ionic conductivities in LSCs can be bridged by developing ML-IAPs under the moment tensor potential (MTP) formalism [41,51] using training data from the optB88 van der Waals (vdW) DFT functional [36,52]. Three LSCs, Li$_{0.33}$La$_{0.67}$TiO$_3$ (LLTO), Li$_3$YCl$_6$ and Li$_3$P$_2$S$_7$ spanning a diversity of anion chemistries have been selected as the model systems for investigation, as shown in Fig. 1. These LSCs have been selected because of their major interest to the battery research community, as well as the fact that previous AIMD calculations have either yielded large disagreements with experimentally measured room-temperature ionic conductivities in energies and forces [38–50]. However, most ML-IAPs that have been developed in the literature still rely on DFT calculations performed using the PBE functional; as such, their performance are still limited by the accuracy of the DFT training data.

2. Material and methods

Fig. 2 summarizes the overall workflow for the construction of MTPs for the LSCs investigated in this work as well as the DFT functional choices investigated.

2.1. Structure construction

Supercells of LLTO, Li$_3$YCl$_6$ and Li$_3$P$_2$S$_7$ with lattice parameters greater than 10 Å were constructed to minimize interactions between periodic images. For LLTO, a $3 \times 3 \times 1$ supercell of LLTO, equivalent to $x = 0.11$ in the general formula of Li$_3$La$_{2/3-x}$TiO$_3$ [31,53,54], was initially generated to enumerate symmetrically distinct orderings of Li/La/Vacancy on the perovskite A site. These orderings were fully relaxed by DFT. The lowest energy ordering was then stacked along the c direction to obtain a $3 \times 3 \times 3$ supercell with 132 atoms. During relaxation, shifts of the lithium ion position from the A-sites of perovskite were observed (see Figure S1), which is consistent with previous theoretical studies on LLTO [55–57]. Li$_3$YCl$_6$ has previously been identified to be an isomorph of Li$_3$ErCl$_6$ (ICSD No. 50151, space group P$n3m$, No. 164) [21]. Starting from the experimentally reported disordered Li$_3$YCl$_6$ structure, the site occupancies were rounded to the nearest rational numbers based on a total of 3 formula units per unit cell (see Table S1) and enumeration of distinct orderings was performed. The lowest energy relaxed structure was then selected to construct a $1 \times 1 \times 2$ supercell with 60 atoms. A $1 \times 2 \times 1$ supercell of Li$_3$P$_2$S$_7$ with 84 atoms was constructed from the experimentally refined crystal structure [9]. The formation energies ($E_f$) and energy above the convex hull ($E_{\text{convex}}$) for all three LSCs calculated with the PBE and optB88 functionals are given in Table S2. All three LSCs are predicted to have $E_{\text{convex}} < 0.05$ eV/atom. The optB88 $E_f$ are 5–10% lower than the PBE values, which is consistent with the ~5% higher atomization energies predicted by optB88 for ionic solids [36].

2.2. DFT calculations and AIMD simulations

All DFT calculations were performed using the Vienna $ab$ initio simulation package (VASP) with the projector augmented-wave (PAW) approach [58,59]. For initial structural relaxations (Step 1 in Fig. 2), spin-polarized calculations were performed with an energy cutoff of 520 eV and a k-point density of at least 64/A$^3$, similar to those used in the Materials Project (MP) [60].

In Step 2, non-spin polarized $ab$ initio molecular dynamics (AIMD) simulations using NVT ensemble were carried out on the relaxed supercells with a plane-wave energy cutoff of 280 eV and a minimal Γ-centered $1 \times 1 \times 1$ k-mesh. A time step of 2 fs and the Nose–Hoover thermostat [61,62] were used. A similar protocol was followed as previous works [45,46,48], wherein simulations were performed at three strains (0, ±0.05) and four temperatures...
To (300 K–1200 K with 300 K intervals) to diversify the training structures. The initial structures were heated from 0 K to the target temperatures with a temperature gradient of 0.25 K/fs and equilibrated for at least 30 ps. Snapshots were then extracted from a production run of 15 ps at 0.1 ps intervals, i.e., 150 structures for each temperature and strain. Hence, for each LSC, a total of 1800 training structures (150 × 4 temperatures × 3 strains) were generated.

In Step 3, static self-consistent calculations were performed on the training structures to obtain accurate energies and forces for MTP training. These calculations were performed with a higher k-point density of at least 100/Å³, an energy cutoff of 520 eV and an electronic relaxation convergence condition of 5 × 10⁻⁵ eV/atom, which were consistent with those used in MP [60].

A main goal of this work is to evaluate the choice of the DFT functional on the training data and hence, the performance of the MTP generated. The initial structural relaxations and energy evaluations of symmetrically distinct LITTO and Li₇YCl₆ orderings were performed using the PBE [34] functional. Subsequent structural relaxations, AIMD simulations and static energy evaluations were performed using either the PBE functional or optB88 vdW functional [36,52], as shown in Fig. 2.

All DFT and AIMD simulations were carried out using fully-automated workflows [28] built on the Python Materials Genomics (pymatgen) [63] library and FireWorks scientific workflow package [64].

2.3 MTP: model training and verification

The moment tensor potential (MTP) formalism has been extensively discussed in earlier works [41,48,51] and successfully applied to many chemical systems, including metals [41,48,65], boron [68], alloys [51], gas-phase reactions [67] and cathode coating materials [49]. Briefly, the MTP describes the local environment around each atom in terms of moment tensors $M_{\mu\nu}$, defined as follows:

$$M_{\mu\nu}(\mathbf{r}_i) = \sum_{j=1}^{n} \sum_{\alpha} \xi_{\alpha} B_{\alpha}(\mathbf{r}_{ij}) \frac{\mathbf{r}_{ij} \otimes \mathbf{r}_{ij}}{\text{times}}$$

Here, $\mathbf{r}_i$ denotes the atomic types as well as the relative positions of the $i$th atom and all of its neighboring atoms, $z_i$ and $z_j$ represent the atomic types (integers from 0 to n-1 for a system with n different types of atoms) of the $i$th atom and its $j$th neighbor, respectively, and $\mathbf{r}_{ij}$ is the position vector of the $j$th neighbor to the $i$th atom. The radial part of the atomic environment is given by the $f_e$ term, and the angular part is encoded by the outer product (⊗) of the $\mathbf{r}_{ij}$ vectors, which is a tensor with rank $r_v$. The moment tensors $M_{\mu\nu}$ are then contracted to basis functions $B_{\alpha}$, which are intrinsically invariant to atomic permutations, rotations and reflections. The energy of the system $E_{\text{MTP}}$ is then expressed as a linear function of $B_{\alpha}$ as follows:

$$E_{\text{MTP}} = \sum_{\alpha=1}^{n} \sum_{\alpha} \xi_{\alpha} B_{\alpha}(\mathbf{r}_i)$$

where $n$ and $\alpha$ are the total number of atoms inside the system and the total number of basis functions for each atom, respectively, and $\xi_{\alpha}$ are the coefficients fitted in the training process implemented in the MLIP package. Similarly, the forces and stresses can be expressed as the first and second derivatives of the $E_{\text{MTP}}$ with respect to $\mathbf{r}_i$ [41,51]. An optimized MTP is then obtained by minimizing the errors in the predicted energies and forces with respect to the DFT training data. In this work, the energy and force data points are assigned weights of 100:1, similar to previous works [45–48].

Two key parameters control the performance trade-off of the MTP. The radius cutoff $R_{\text{cut}}$ determines the maximum interaction range between atoms. The larger the $R_{\text{cut}}$ the more the atomic interactions encoded in Equation (1). The completeness of the basis functions $B_{\alpha}$ is controlled by its maximum level ($\text{lev}_{\text{max}}$). The larger the $\text{lev}_{\text{max}}$, the larger the number of terms in the linear expansion in Equation (2), which in turn results in higher computational cost and a greater likelihood of over-fitting. In this work, the $R_{\text{cut}}$ was chosen to be 5.0 Å, a typical value used in previously reported MTPs [49,51,68], while the $\text{lev}_{\text{max}}$ were set as 18 for Li₇YCl₆ and Li₇P₃S₁₁ and 16 for LITTO based on our convergence tests (see Figure S2-S5). For the fitting, a training:test split of 90:10 was used. In total, seven MTPs were fitted for LITTO, Li₇YCl₆ and Li₇P₃S₁₁ according to the above discussed procedure. These MTPs are labeled with subscripts indicating the functionals used during the AIMD simulation (Step 2) and static energies and forces evaluations (Step 3). For instance, MTP$\text{PBE}_{\text{optB88}}$ refers to an MTP fitted using the snapshots extracted from AIMD simulations performed using the PBE functional, with energies and forces evaluated using the optB88 functional. It should be noted that MTP$\text{optB88}_{\text{optB88}}$ was fitted only for Li₇P₃S₁₁ as a test case and because the results were highly similar to MTP$\text{PBE}_{\text{optB88}}$ (see later Results section), only the latter was fitted for the other two LSCs. Previously, the current authors have also used an alternative approach in which the long-ranged electrostatic interactions were accounted for separately via an Ewald summation of the formal oxidation states prior to fitting the residual interactions via the ML-IAP [46]. A similar "electrostatic" MTP (eMTP) for the LITTO LSC was also developed but the performance was similar to the MTP without separate accounting of electrostatics. It can be concluded that there is significant screening in these materials, and the radius cutoff used above is already sufficient to account for most of the electrostatic interactions (see Figure S6).

All training, evaluations and simulations with MTP were performed using MLIP [41,51], LAMMPS [68] and the open-source Materials Machine Learning (maml) Python package [70].

![Flowchart of the stepwise construction of MTPs for LSCs.](image-url)
2.4. QHA thermal expansion

Phonon calculations were performed using the supercells (outlined in Section 2.1) at nine fixed volumes (80%–120% with 5% intervals of the equilibrium volume at 0 K from structural relaxations with PBE and optB88 functionals). Real-space force constants were calculated utilizing the density functional perturbation theory (DFPT) [71] method as implemented in VASP, while the real-space force constants from MTPs were generated with the theory (DFPT) [71] method as implemented in VASP, while the real-space force constants from MTPs were generated with the finite displacement approach implemented in the Phonopy [72] package. Phonon frequencies were then calculated from the force constants, and the thermal expansion from 0 K to 800 K was calculated under the quasi-harmonic approximation (QHA).

2.5. Diffusivity and conductivity calculations

Classical MD simulations for each LSC were performed using the trained MTPs. Taking advantage of the lower computational cost and linear scaling of MTP calculations with respect to system size, larger supercells with all lattice parameters over 20 Å were used for these simulations. Based on benchmarks of the convergence of the ionic conductivity with cell sizes (Figure S7), simulation cells of 3 × 3 × 2 (2,376 atoms), 2 × 2 × 3 (720 atoms) and 3 × 2 × 2 (1,008 atoms) AIMD supercells are utilized for LLTO, Li3YCl6 and Li7P3S11, respectively. The time step was set to 1 fs, and the total simulation time was at least 1 ns for all MD simulations.

The tracer diffusivity (D*) of Li ions was obtained by performing a linear fitting of the mean square displacement (MSD) of all diffusing Li ions with time, according to the Einstein relation [73]:

\[ D^* = \frac{1}{2DNt} \sum_{i=1}^{N} (\Delta r_i(t))^2 \]  

where \( d \) is the number of dimensions in which diffusion occurs (\( d = 3 \) for all three electrolytes), \( N \) is the total number of diffusing Li ions, and \( \Delta r_i(t) \) is the displacement of the \( i \)th Li ion at time \( t \).

The charge diffusivity (\( D_c \)) of Li ions was calculated from the square net displacement of all diffusing Li ions, as described below [73]:

\[ D_c = \frac{1}{2DNt} \left[ \sum_{i=1}^{N} (\Delta r_i(t))^2 \right]^2 \]  

The Haven ratio is then given by the following equation:

\[ H_R = D^*/D_c \]  

Finally, the ionic conductivity \( \sigma(T) \) at temperature \( T \) is given by the Nernst-Einstein equation [73]:

\[ \sigma(T) = \frac{\rho z^2 F^2}{RT} D_0(T) \]  

where \( \rho \) is the molar density of diffusing ions in the unit cell, \( z, F, R, \) and \( D_0 \) are the charge of Li ions (\( z = 1 \), the Faraday constant and the gas constant, respectively. Arrhenius plots were then generated to determine the temperature-dependent activation energies (Ea).

3. Results

3.1. MTP validation

Table 1 compares the mean absolute errors (MAEs) in energies and forces of the fitted MTPs. In all cases, the MAEs in energies are between 0.96 meV/atom and 2.07 meV/atom, while the MAEs in forces are below 0.20 eV/Å. These MAEs are similar to or lower than those of other MTPs fitted in the literature [48,49], and a substantial improvement over traditional IAPs. The training and test MAEs are generally very similar, indicating that there is little likelihood of overfitting. The MAEs in energies and forces are also uniformly distributed with respect to the different temperatures that training structures were extracted from (see Figure S5-S5), indicating consistently high accuracy of our MTPs to reproduce DFT energies and forces at different temperatures. These results are consistent regardless of the DFT functionals (PBE or optB88) used to generate the training data. Further analysis also found that the local environments sampled by nanosecond NPT MD simulations using the fitted MTP are similar with those sampled by the AIMD training data (Figure S8) and the MAEs in forces are consistently low regardless of local environment (Figure S9). It should be noted that while it is possible that MD simulations under more extreme conditions, e.g., above 1200 K, may sample local environments that are substantially different from the AIMD training data and possibly result in higher errors, such conditions are unlikely to be of interest for most applications of the fitted MTPs.

3.2. Lattice parameters

Table 2 compares the lattice parameters and volumes for the three LSCs from DFT and MTP relaxations with experimental values. It can be seen that the use of the optB88 functional significantly improves the predicted lattice parameters and densities over the PBE functional for Li3YCl6 and Li7P3S11 LSCs, while yielding smaller improvements for LLTO LSC. The PBE computed densities under-estimate the experimental densities by 3–6%, consistent with the well-known propensity of PBE to underbind. The optB88 computed densities are within 1–3% of the experimental densities due to the fact that optB88 functional is less repulsive at short interatomic separations [36]. As shown in Fig. 3, the MTPs are generally able to reproduce the DFT lattice parameters to within 1–2.5%. It should be noted that the errors with respect to DFT follows the order LLTO < Li3YCl6 < Li7P3S11. We hypothesize that this can be attributed to the difference in the potential energy landscapes, i.e., Li3YCl6 and Li7P3S11 have shallower potential energy landscapes, which leads to smaller energy changes with lattice parameter variations. This can be seen to some degree in the equation of state plots (see later Fig. 4), as the same percentage of change in volume leads to smaller changes in the total energies of Li3YCl6 and Li7P3S11.

3.3. Equations of state and thermal expansion

Fig. 4a–c shows the equation of state (EOS) curves of the three LSCs calculated from DFT and MTPs. In general, the MTP computed EOSs agree well with the corresponding DFT EOSs, further attesting
to the robustness of the MTP fitting procedure. In addition to the differences in equilibrium volumes discussed in the preceding section, we note that the optB88 DFT and MTP calculations predict a larger curvature for Li3YCl6 and Li7P3S11 LSCs, i.e., the optB88 functional predicts a higher bulk modulus than PBE. These results are consistent with the calculated QHA thermal volume expansion, plotted in Fig. 4d–f. The MTP QHA thermal expansion curves match closely with the corresponding DFT QHA thermal expansion curves. In general, the optB88 DFT and MTP volumes are much closer to the experimental volumes for respective temperatures between 0 and 800 K. LLTO has the smallest MTPPBE, optB88 vol expansion coefficient $(\beta_{\text{PBE, optB88}})$ of 1.08 K$^{-1}$, much closer to the 4 K$^{-1}$ that have been reported experimentally thus far. We further note that the MTPPBE, optB88 HT Ea are also consistent with those obtained from previous HT AIMD simulations for Li3YCl6 [29] and Li7P3S11 [13]. The Li3YCl6 LSC has only been experimentally studied at 230–360 K. Our MTPPBE, optB88 MD simulations predict that Li3YCl6 would undergo a transition to a lower phase at around 360 K.

### 3.4. Ionic conductivity

**Fig. 5** shows the Arrhenius plots for the three LSCs from MD simulations performed using the MTPs and a summary of the derived activation energies ($E_a$) and conductivities at room temperature ($\sigma_{300K}$) in comparison with experiments and previous AIMD simulations. From the MTPPBE, optB88 Arrhenius plots (filled markers and solid lines), it is immediately apparent that all three LSCs do not exhibit a single linear Arrhenius regime, which is the common assumption made when extrapolating high-temperature (HT) AIMD simulations to room temperature. Transitions between a HT quasi-linear regime with lower $E_a$ and a low-temperature (LT) quasi-linear regime with higher $E_a$ occur at ~450 K, 425 K and 360 K, respectively. In all cases, the MTPPBE, optB88 predicted $\sigma_{300K}$ and $E_a$ are in remarkably good agreement with previously reported experimental values for all three LSCs. In particular, while previous HT AIMD simulations predicted an extraordinarily high $\sigma_{300K}$ of 57 mS cm$^{-1}$ for Li3YCl6 and Li7P3S11, respectively. A slightly higher volume expansion is predicted for Li3YCl6 by optB88 compared to PBE.

### Table 2

Lattice parameters and densities of LSCs relaxed with the PBE and optB88 DFT functionals and the trained MTPs at 0 K, in comparison with experimental lattice parameters and densities at room temperature for LLTO [53], Li3YCl6 [21] and Li7P3S11 [9]. Values in brackets are the percentage differences between the computed values and the experimental measurements.

|                | a (Å)       | b (Å)     | c (Å)     | Density (g cm$^{-3}$) |
|----------------|-------------|-----------|-----------|-----------------------|
| **LLTO**       |             |           |           |                       |
| DFT PBE        | 3.96 (2.3%) | 3.89 (0.5%) | 3.91 (1.0%) | 4.84 (−3.0%)          |
| DFT optB88     | 3.95 (2.1%) | 3.88 (0.3%) | 3.90 (0.8%) | 4.88 (−2.2%)          |
| MTPPBE, PBE    | 3.96 (2.3%) | 3.89 (0.5%) | 3.90 (0.8%) | 4.85 (−2.8%)          |
| MTPPBE, optB88 | 3.95 (2.1%) | 3.87 (0.0%) | 3.89 (0.5%) | 4.90 (−1.8%)          |
| Experiment     | 3.87        | 3.87      | 3.87      | 4.99                  |
| **Li3YCl6**    |             |           |           |                       |
| DFT PBE        | 11.17 (−0.3%) | 11.17 (−0.3%) | 6.22 (3.2%) | 2.37 (−3.3%)          |
| DFT optB88     | 11.01 (−1.7%) | 11.01 (−1.7%) | 6.02 (−0.2%) | 2.52 (2.9%)          |
| MTPPBE, PBE    | 11.18 (−0.2%) | 11.18 (−0.2%) | 6.27 (4.0%) | 2.35 (−4.1%)          |
| MTPPBE, optB88 | 11.04 (−1.4%) | 11.04 (−1.4%) | 6.08 (0.8%) | 2.48 (1.2%)          |
| Experiment     | 11.20       | 11.20     | 6.03      | 2.45                  |
| **Li7P3S11**   |             |           |           |                       |
| DFT PBE        | 12.86 (2.9%) | 6.19 (2.7%) | 12.69 (1.3%) | 1.87 (−5.6%)          |
| DFT optB88     | 12.61 (0.9%) | 6.08 (0.8%) | 12.62 (0.7%) | 1.95 (−1.5%)          |
| MTPPBE, PBE    | 12.66 (1.3%) | 6.33 (5.0%) | 12.56 (0.2%) | 1.88 (−5.1%)          |
| MTPPBE, optB88 | 12.52 (0.2%) | 6.14 (1.8%) | 12.57 (0.3%) | 1.95 (−1.5%)          |
| Experiment     | 12.50       | 6.03      | 12.51     | 1.98                  |

**Fig. 3.** Comparison of the lattice parameters predicted via relaxation with the trained MTPs and the DFT-relaxed values. For each MTP, the relaxation was performed using 36 strained structures constructed by applying strains of −0.15 to 0.15 with 0.05 intervals in six different modes to the DFT relaxed ground-state structure to assess the numerical stability of MTP relaxation.
Li$_3$YCl$_6$ and Li$_7$P$_3$S$_{11}$, respectively. There are no existing reports of the Haven ratios for these LSCs to the authors' knowledge. However, LLTO has been experimentally reported to possess highly correlated motions at room temperature [75], consistent with the computed $H_R$ of 0.68. Further, our calculated $H_R$ for Li$_7$P$_3$S$_{11}$ also lies in between the AIMD simulated $H_R$ (0.42, 0.53) [76] and NMR measured $H_R$ (in the order of 1) [77] of Li$_{10}$GeP$_2$S$_{12}$, another sulfide LSC.

We also note that the MTPB, optB88 and MTPB, PBE yield fundamentally different results for Li$_3$YCl$_6$ and Li$_7$P$_3$S$_{11}$. In both cases, the MTPB, PBE simulations do not predict any transitions between quasi-linear Arrhenius regimes in the simulation temperature range of 300–600 K. The activation energies $E_a$ and room temperature ionic conductivities $\sigma_{300K}$ are also severely underestimated and overestimated, respectively, compared to experiments, similar to prior AIMD simulations using the PBE functional. The poor performance of the PBE-based MTP and AIMD simulations can be traced to the substantial overestimation of the lattice parameters by the PBE functional, which can lead to lower activation barriers and higher ionic conductivities [23,78]. It should be noted that we cannot rule out the possibility that the observed transitions between quasi-Arrhenius regimes are an artifact of the DFT functional used in generating the training data, i.e., optB88, but the generally improved agreement between the predicted room-temperature ionic conductivities and experimental values suggest that the transitions are a real phenomenon. It is our hope that future detailed experiments may shed further light on these predictions.

3.5. Transitions in diffusion mechanisms

To understand the reason behind observed transitions between quasi-linear Arrhenius regimes, we have extracted the trajectories from the MTPB, optB88 MD simulations of the three LSCs at room temperature and above the transition temperature and plotted them in Fig. 6 and Figure S10–S12. In all three LSCs, a substantial change in the number and variety of diffusion pathways is observed. For LLTO, Li diffusion at 300 K occurs primarily along $b$ and $c$ directions inside the La-poor layer, which agrees well with experimental observations at room temperature [79], but additional diffusion pathways between planes are activated above the transition temperature of 450 K (Fig. 6a). Similarly, Li$_3$YCl$_6$ exhibits quasi-1D diffusion at 300 K and 3D diffusion above the transition temperature of 425 K. For Li$_7$P$_3$S$_{11}$, Li diffusion is already 3D at 300 K but occurs along well-defined pathways. Above the transition temperature of 400 K, additional pathways are activated. The decrease in activation energies $E_a$ can be directly traced to the increase in the variety and dimensionality of diffusion in the three LSCs. The most significant reduction in $E_a$ (~ 0.25 eV) is observed for Li$_3$YCl$_6$, which transitions from a quasi-1D to 3D conductor at around 425 K.

4. Discussion

Briefly, the above results have shown that the discrepancy between computed and experimentally measured ionic conductivities in the literature can be traced to two effects. First, the choice of the DFT functional can lead to substantial errors in the lattice parameters, which can have a large effect on the predicted activation barriers and ionic conductivities. Second, most AIMD simulations of LSCs in the literature were performed at high temperatures in the NVT ensemble to obtain sufficient hop statistics. Not only does this lead to further errors in the lattice parameters, there is also a strong likelihood that these simulations do not capture transitions in quasi-linear Arrhenius regimes occurring at lower temperatures. These issues can be addressed through carefully-trained ML-IAPs. With a generalizable stepwise workflow for the construction of MTPs for LSCs (see Fig. 2), we have consistently generated training structures sampling a range of local environments (see Figure S8) and fitted MTPs to study LLTO, Li$_3$YCl$_6$ and Li$_7$P$_3$S$_{11}$ LSCs.
Our results suggest that the choice of DFT functional used in generating the initial and snapshot training structures is relatively unimportant, but the choice of the DFT functional used in the energy and force evaluations to generate the training data is critically important. Here, we show that the use of the optB88 vdW functional for static energy and force calculations and the ns-scale ML-IAP MD at lower temperatures significantly improve the agreement in lattice parameters, activation energies and room-temperature ionic conductivities of the LSCs with experiments.

These results have broad implications for ML-IAP development strategy. The typical approach in the literature thus far has been to use the same DFT functional in both the generation of training structures as well as energy/force evaluations to generate the training data. Here, we show that the use of the optB88 vdW functional for static energy and force calculations and the ns-scale ML-IAP MD at lower temperatures significantly improve the agreement in lattice parameters, activation energies and room-temperature ionic conductivities of the LSCs with experiments.

Our results also have significant implications for LSC development. For all three LSCs investigated, a transition between diffusive regimes is observed at relatively low temperatures (400–450 K). In most cases, the activation barriers and ionic conductivities that have been experimentally measured correspond to the low-temperature regime. One potential avenue for further enhancing the ionic conductivities of these and other LSCs is to attempt to stabilize the high-temperature, lower activation energy diffusion regimes at room temperature. This may be achieved by quenching from higher temperatures, compositional modifications (e.g., dopants or substitutions), or mechanical modifications (e.g., introducing strain). By developing ML-IAPs using the approach outlined in this work, MD simulations can provide critical guidance on potential pathways for further LSC optimization.

### 5. Conclusions

To conclude, we have shown that MTPs trained using optB88 energies and forces can successfully reproduce the experimental lattice parameters, activation energies and room temperature ionic conductivities of the LSCs with experiments. Our results suggest that the choice of DFT functional used in generating the initial and snapshot training structures is relatively unimportant, but the choice of the DFT functional used in the energy and force evaluations to generate the training data is critically important. Here, we show that the use of the optB88 vdW functional for static energy and force calculations and the ns-scale ML-IAP MD at lower temperatures significantly improve the agreement in lattice parameters, activation energies and room-temperature ionic conductivities of the LSCs with experiments.

Fig. 5. (Top) Arrhenius plot for LLTO, Li3YCl6 and Li7P3S11 from NPT/MD simulations using MTPPBE_PBE (open markers) and MTPPBE_optB88 (solid markers). The diffusivities were obtained by averaging the mean square displacements from five independent MD simulations at each temperature for at least 1 ns. (Bottom) Room temperature ionic conductivities (σ00K) and activation energies (Ea) for LLTO, Li3YCl6 and Li7P3S11, obtained from MD simulations using MTPPBE_PBE and MTPPBE_optB88. For MTPPBE_optB88, transitions between two quasi-linear Arrhenius regimes were observed for all three LSCs and the Ea for each regime are reported separately. Available AIMD derived values as well as experimental references are also listed.
conductivities of the LLTO, Li3YCl6 and Li7P3S11 LSCs. In all three LSCs, MD simulations using the trained MTP identify a transition between quasi-linear Arrhenius regimes occurring at relatively low temperatures. These results not only highlight the fundamental limitations in using high-temperature, short time scale AIMD simulations to predict room-temperature properties of materials, but also suggest a potential pathway and strategy to predictive LSC design through the use of machine learning interatomic potentials.

Data availability

The datasets generated and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mtphys.2021.100463.

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