

Probing Structure and Ionic Transport in Molten Lithium Carbonate

Debsundar Dey, Abhirup Patra,* Anand Narayanan Krishnamoorthy, and Gopalakrishnan Sai Gautam*

Cite This: <https://doi.org/10.1021/acsaem.6c02035>

Read Online

ACCESS |



Metrics & More



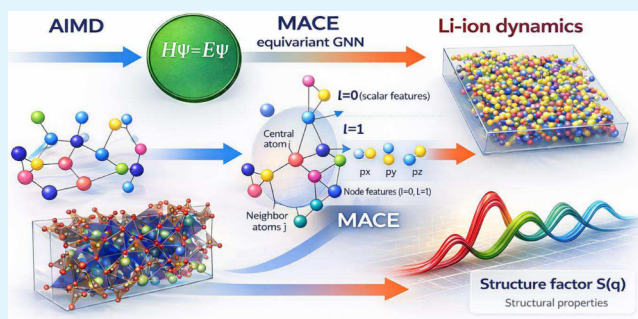
Article Recommendations



Supporting Information

ABSTRACT: Lithium carbonate (Li_2CO_3) is an important material for high-temperature molten carbonate fuel cells, electrochemical carbon capture, and lithium-based energy-storage technologies. However, understanding its molten-state structure and ionic transport remains challenging because of the limited time and length scales accessible to ab initio molecular dynamics (AIMD) and the accuracy limitations of classical force fields. Here, we employ equivariant machine-learned interatomic potentials (MLIPs) trained on AIMD data to investigate the structure and transport properties of molten Li_2CO_3 over extended time and length scales. Our MLIP-driven simulations agree with the experimentally measured static structure factor and shear viscosity and accurately describe the characteristic short- and medium-range structural correlations of molten- Li_2CO_3 . Importantly, we find that Li^+ diffusion is governed by strongly correlated and cooperative ionic motion rather than independent uncorrelated motion. At 1000 K, Li^+ transport is anisotropic and highly concerted because the ions remain constrained within persistent oxygen-centered coordination environments. With increasing temperatures, the faster rearrangement of the local oxygen environments facilitates more isotropic and less correlated Li^+ diffusion, leading to a distinct change in the transport mechanism by 1400 K. Our results establish a direct connection between the temperature-dependent dynamics of the local oxygen environment, which contributes to the local structure of Li_2CO_3 and the macroscopic Li^+ transport. Our findings provide fundamental insights into ionic conduction in molten alkali carbonates and demonstrate the utility of equivariant MLIPs for investigating molten salts and ionic liquids relevant for energy applications.

KEYWORDS: lithium carbonate, molten salts, equivariant machine-learned interatomic potentials, ionic transport, concerted diffusion



1. INTRODUCTION

Molten alkali carbonates represent a critically important class of ionic liquids with wide-ranging technological applications in clean energy systems.¹ For example, the high-temperature ionic melts serve as electrolytes in molten carbonate fuel cells (MCFCs), which operate at temperatures of 600–700 °C and achieve electrical efficiencies approaching 60%, with combined heat and power efficiencies reaching 85%.^{2,3} Among the alkali carbonates, lithium carbonate (Li_2CO_3) plays a particularly prominent role due to its superior ionic conductivity compared to sodium and potassium carbonates.^{4,5} Standard MCFC electrolytes typically contain 62–68 mol % Li_2CO_3 mixed with K_2CO_3 or Na_2CO_3 , with the lithium component providing enhanced ionic transport while the secondary carbonate reduces corrosion and improves gas solubility.^{6,7} Beyond fuel cells, molten Li_2CO_3 has emerged as a promising medium for electrochemical CO_2 capture and subsequent conversion to valuable carbon nanomaterials, including carbon nanotubes and graphene nanocarbons, offering a pathway for large-scale decarbonization.^{8,9}

Despite their technological importance, achieving a fundamental, atomistic understanding of the structure and dynamics of molten carbonates remains challenging. The extreme

chemical reactivity of these melts at elevated temperatures, combined with their corrosive nature, presents significant obstacles for experimental characterization of atomic structures and transport properties.^{10,11} Experimental techniques such as X-ray and neutron scattering can provide structural information through the static structure factor ($S(q)$) and radial distribution functions (RDFs, denoted by $G(r)$ or $g(r)$), while electrochemical methods and pulsed-field gradient nuclear magnetic resonance can probe transport coefficients.^{12,13} However, these measurements are technically demanding and provide limited insight into the microscopic mechanisms governing ionic transport, particularly the nature of correlated ionic motion that deviates from the ideal Nernst-Einstein behavior. Resolving whether ionic transport in these melts follows a traditional, independent random-walk model or a more complex,

Received: June 22, 2026

Revised: September 14, 2026

Accepted: September 15, 2026

many-body correlated mechanism, and the local structural motifs that influence macroscopic conductivity are essential for the optimal design of high-performance electrolytes that enhance ionic conductivity and reduce interfacial resistance.

Beyond their importance in molten carbonate systems, lithium carbonates are also technologically relevant in Li-ion batteries.^{14–16} Li_2CO_3 is one of the dominant inorganic constituents of the solid electrolyte interphase (SEI), where it forms crystalline and amorphous domains that govern Li^+ transport across the electrode-electrolyte interface.^{17–19} The SEI stabilizes the anode by preventing continuous electrolyte decomposition, but it also introduces additional interfacial resistance, making Li^+ mobility through Li_2CO_3 -rich domains a critical determinant of fast-charging performance and long-term cycling stability.^{20–22} The contrasting Li^+ conductivities of crystalline and amorphous Li_2CO_3 , as well as the mixed-phase and polydomain character of realistic SEIs, highlight the broader importance of understanding Li ionic transport in Li_2CO_3 across both solid and molten regimes.

Atomistic simulation provides a powerful complementary approach for elucidating the structure–property relationships in molten salts. Classical molecular dynamics (MD) simulations based on empirical force fields, such as rigid-ion or polarizable shell models, have been widely employed to study molten carbonates.^{23,24} While computationally efficient, these classical potentials often struggle to accurately capture the complex many-body interactions and polarization effects that are critical in ionic systems. Ab initio molecular dynamics (AIMD) based on density functional theory (DFT) offers quantum mechanical accuracy but is computationally prohibitive for accessing the long time scales (hundreds of picoseconds to nanoseconds) and large system sizes (thousands of atoms) required for converged transport properties and proper sampling of the liquid structure.^{25,26} This fundamental trade-off between accuracy and computational efficiency has motivated the development of machine learned interatomic potentials (MLIPs) that can achieve near-DFT accuracy at a fraction of the computational cost of AIMD simulations.

Various MLIP architectures have been successfully applied to molten salts and related systems, including neural network potentials, Gaussian approximation potentials (GAP), moment tensor potentials (MTP), and deep potential molecular dynamics (DeepMD).^{27–30} Similar successes have been reported for diverse molten salt chemistries relevant to energy conversion, nuclear applications, and high-temperature electrochemical technologies.^{30–32} Recently, MLIPs have also been used for characterizing ionic transport across amorphous materials and their interfaces in battery systems.^{33,34} So far, equivariant MLIPs have not been used to probe the transport and local structure motifs in molten Li_2CO_3 .

Recent advances in equivariant neural network architectures have further improved the accuracy and data efficiency of MLIPs. For example, $E(3)$ -equivariant graph-based neural networks, which explicitly include the symmetries of three-dimensional space (i.e., translations, rotations, and reflections), along with message passing, provide a better representation of atomic environments compared to invariant neural networks.^{35,36} Specifically, the neural equivariant interatomic potential (NequIP) architecture employs $E(3)$ -equivariant convolutions to describe geometric tensors, achieving high accuracy with remarkable data efficiency that outperforms invariant approaches with up to three orders of magnitude fewer training

data.³⁷ Building upon NequIP, the multi atomic cluster expansion (MACE) architecture introduces higher body-order message passing, enabling the capture of many-body interactions (typically up to four-body terms). By explicitly accounting for such many-body interactions, MACE is uniquely positioned to resolve the subtle, concerted ion–ion interactions that govern transport in molten carbonates—features that are often missed by traditional invariant potentials.^{38,39} Given the utility in incorporating equivariance, message passing and many-body interactions (in MACE), both NequIP and MACE have been successfully applied to challenging systems, such as, ionic liquids, water, amorphous solids, and complex molecular systems.^{34,40–42}

In this work, we construct and assess equivariant MLIPs and subsequently probe the structural and transport properties in molten Li_2CO_3 . We construct the MLIPs based on AIMD training data, with training configurations sampling melt–quench trajectories at 1500 and 1250 K, resulting in 3600 and 1988 structures, respectively. To assess model fidelity against AIMD and available experimental data, we use RDFs and $S(q)$ as metrics. We train both the MACE and NequIP architectures on our dataset, from scratch, and identify MACE to be the best model based on the train and test mean absolute errors (MAEs) across energies and forces. Additionally, we evaluate the medium-sized MACE-MP-0 model,⁴³ a foundational pre-trained MLIP without fine-tuning, to benchmark structural accuracy. Using the best-performing potential, i.e., MACE architecture trained from scratch, simply referred to as MACE in the remainder on the text, we perform long time-scale MD simulations to compute macroscopic transport properties, including the shear viscosity and Li^+ self-diffusion coefficients.

Importantly, we find the apparent diffusion activation energy of Li^+ diffusion (E_a), calculated based on an Arrhenius fit of Li^+ diffusivities over temperatures to be 1.287 eV, which is consistent with prior molten-salt literature.²² Our analysis of ionic trajectories reveals distinct temperature-dependent diffusion mechanisms. For example, at 1400 K, Li^+ exhibit continuous migration through the molten carbonate network, while at 1000 K transient trapping events emerge, wherein Li^+ oscillate between nearby carbonate coordination cages before escaping. Large-scale simulations enabled by the optimized MACE potential further show that Li-ion transport in molten Li_2CO_3 is fundamentally collective, with Haven's ratio (H_R) values significantly below unity ($H_R \sim 0.20$ – 0.40). Finally, we identify a temperature-driven transition from anisotropic transport at 1000 K to isotropic diffusion at 1400 K, demonstrating the ability of equivariant MLIPs to resolve complex transport behavior across different molten carbonate regimes. We hope that our work is a useful contribution in the optimal design of molten salt electrolytes for MCFCs and related applications.

2. COMPUTATIONAL DETAILS

2.1. Dataset Generation and Optimized MLIPs

Figure 1 summarizes the overall workflow of this study, including AIMD-based data generation, MLIP training and validation, and subsequent molten-phase simulations performed using the optimized model. To develop and evaluate MLIPs for molten- Li_2CO_3 , we generated a dataset using AIMD melt-quench simulations^{44,45} on a $2 \times 2 \times 2$ supercell (192 atoms) of the crystalline Li_2CO_3 structure that was obtained from the

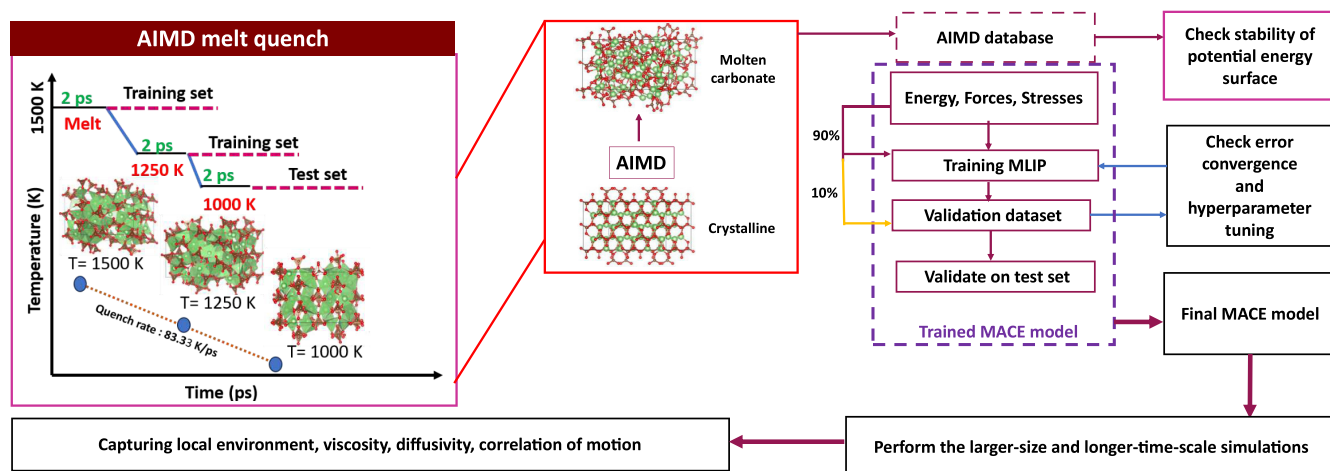


Figure 1. Workflow for dataset generation and MLIP training (for MACE) employed in this work. We employ AIMD melt-quench simulations both for training and hyperparameter optimization. The accuracy and transferability of the trained MLIP are evaluated using independent test configurations. After validation, the optimized MACE model is deployed for long time-scale and large system-size MD simulations to characterize transport properties of molten- Li_2CO_3 .

inorganic crystal structure database (ICSD).⁴⁶ We applied step-wise heating initially from 0 to 500 K, subsequently from 500 to 1000 K, and finally from 1000 to 1500 K, with each heating step conducted over 5 ps followed by 2 ps of equilibration. The choice of 1500 K as the highest temperature in our heating simulations is motivated by the fact that Li_2CO_3 melts at 996 K.⁴⁷ Subsequently, we quenched the equilibrated structure at 1500 K to 1000 K, in steps of 250 K at a quench rate of 83.33 K/ps. For training, we sampled configurations from AIMD trajectories at 1500 K (accounting for 3600 structures sampled over 7.2 ps) and at 1250 K (1988 structures sampled over 3.98 ps), with the training data collected after the initial 2 ps of equilibration at each temperature.

We trained both NequIP and MACE models using the dataset generated from the AIMD melt-quench simulations. We performed training and hyperparameter optimization on the AIMD-derived training dataset, by creating a 90:10 train:validation split of the dataset. The list of optimal hyperparameters that were chosen to minimize errors on the validation set for both models are listed in Tables S1 and S2 of the supporting information (SI). To ensure a fair comparison, we set the equivariance level of both models to one (i.e., vectors are treated equivariantly). We evaluated the performance of both models using MAEs across both total energies and atomic forces. We used two separate test datasets to evaluate the transferability of the trained MLIPs: (i) configurations from AIMD, post quench, at 1000, 500, and 250 K, and (ii) mechanically strained structures of crystalline- Li_2CO_3 , including homogeneous volumetric strain (± 2 , ± 5 , $\pm 10\%$), uniaxial strain (± 2 , ± 5 , $\pm 10\%$), and shear strain (2, 5, 10%). To verify that the sampled configurations correspond to the molten phase of Li_2CO_3 , we computed the RDFs for all relevant atomic pairs ($G(r)$), namely O–O, Li–Li, C–O, Li–O, C–C, and Li–C.

2.2. DFT and MD Calculations

We utilized the Vienna ab initio simulation package^{48,49} with projector augmented wave potentials⁵⁰ to perform all spin-polarized DFT and AIMD calculations. We used the Perdew–Burke–Ernzerhof functionalization of the generalized gradient approximation⁵¹ to account for the electronic exchange and

correlation. We selected the PBE functional since it has provided reliable descriptions of the structural, thermodynamic, reactive, and transport properties in molten alkali carbonate systems, as reported by prior studies.^{52,53} We applied a kinetic energy cutoff of 520 eV, and sampled the irreducible Brillouin zone using Γ -centered Monkhorst–Pack k -point meshes with a density of at least $32/\text{\AA}^3$.⁵⁴ We relaxed the as-obtained crystalline Li_2CO_3 structure (from the ICSD) by optimizing the cell volume, cell shape, and atomic positions without imposing symmetry constraints before performing AIMD simulations and generating the strained structure dataset. We set the convergence criteria for total energy and atomic forces to 10^{-5} eV and $[0.03]$ eV/ $\text{\AA}$, respectively. For generating the strained structure dataset, we deformed the DFT-relaxed Li_2CO_3 lattice with the corresponding amount of strain and evaluated the total energy using a single self-consistent field calculation (with energy convergence set to 10^{-5} eV) without any further relaxation of the structure.

We performed AIMD simulations on a $2 \times 2 \times 2$ supercell of Li_2CO_3 , corresponding to 192 atoms, using a 2 fs time step to ensure accuracy and efficiency. We did classical MD simulations with our trained MACE model using the large scale atomic/molecular massively parallel simulator (LAMMPS).⁵⁵ We employed a 2 fs time step for the classical MD simulations and used a $4 \times 4 \times 4$ supercell containing 1536 atoms. All AIMD and MD runs employed the NVT ensemble with a Nosé–Hoover thermostat,⁵⁶ the ‘SMASS’ tag set to 0, and the velocity-Verlet integration scheme.⁵⁷ The AIMD melt–quench configurations used for MLIP training were also generated in the NVT ensemble at a fixed simulation-cell volume, thus neglecting any temperature-dependent density variations. Subsequent evaluations of equilibrium densities using MACE-MD simulations in the NPT ensemble do agree well with available experimental data (see Table S3 and SI for details).

For MD simulations with the MACE model trained from scratch, we equilibrated the structures in the NVT ensemble for 10 ps, followed by 700 ps of production runs to estimate diffusivities at 1500, 1400, 1300, 1250, and 1000 K. The evolution of the potential energy during the 10 ps equilibration period is

presented in Figure S1 alongside limited-time AIMD runs at 1000 and 1250 K. The variations in potential energy (in eV) and temperature (K), as estimated with MACE-MD during a 100 ps period are shown in panels a and b of Figure S2, respectively, for 1000, 1250, 1300, and 1400 K. The mean and standard deviation in the potential energy and temperature during MACE-MD production runs are tabulated in Table S4, highlighting minimal variations around the target mean value.

2.3. Estimation of Diffusivity, Ionic Correlation, and Viscosity

In molten Li_2CO_3 , ionic conductivity (σ) and diffusivity ($D(c)$) of any species, such as Li^+ , are connected through the Nernst–Einstein (NE) relation as,

$$\sigma = \frac{q^2 c D(c)}{k_B T} \quad (1)$$

where q , c , k_B , and T represent the ion's charge (+1 in case of Li^+), the ion's concentration, the Boltzmann constant, and temperature, respectively. While the NE relation provides an estimate of σ assuming uncorrelated ionic motion, molten salts generally exhibit strong many-body interactions, leading to significant correlations. Therefore, the calculated σ from NE can systematically deviate from the true σ , with the correlation effects requiring further quantitative analysis, such as using H_R .⁵⁸ $D(c)$ in the NE framework describes the ionic flux according to Fick's first law⁵⁹ and can be expressed as $D_c = \Theta D_j$, where Θ is the thermodynamic factor. The jump diffusivity (D_j)^{60,61} measures the mean squared displacement of the center-of-mass of the mobile ions (denoted as 'MSCD' in our work), thus capturing cross-correlations among individual ionic hops over time. Mathematically, D_j is defined as

$$D_j = \lim_{t \rightarrow \infty} \left[\frac{1}{2dt} \frac{1}{N} \left(\sum_{i=1}^N \mathbf{r}_i(t) \right)^2 \right] \quad (2)$$

where d , t , and N represent the dimensionality of the diffusion process, time, and number of mobile ions, respectively. $\mathbf{r}_i(t)$ indicates the displacement of the i th ion over t .

On the other hand, the tracer diffusivity (D^*) tracks the motion of individual ions thereby not accounting explicitly for any cross-correlations among their motion. Specifically, D^* quantifies the mean squared displacement (MSD) that is averaged over N and t and is mathematically defined as,

$$D^* = \lim_{t \rightarrow \infty} \left[\frac{1}{2dt} \frac{1}{N} \sum_{i=1}^N [\mathbf{r}_i(t)]^2 \right] \quad (3)$$

Note that D_j and D^* can be obtained from the slopes of the linear regimes of MSCD and MSD values, respectively, with respect to t .⁶⁰ Finally, H_R is defined as the ratio of D^* and D_j as,

$$H_R = \frac{D^*}{D_j} \quad (4)$$

Thus, H_R provides insight into how cross-correlations alter the overall ionic mobility. If a system exhibits completely uncorrelated ionic motion, $H_R = 1$. In systems with significant ion–

ion interactions, H_R deviates from 1, indicating the presence of cross-correlation. Note that in molten Li_2CO_3 , we do expect cross-correlation effects to be significant since Li^+ transport does not occur in isolation and is often influenced by the rearrangements in the carbonate network and the local charge neutrality.

Due to the limited total simulation time (t_{tot}) in both AIMD and classical MD, MSD data often exhibits noise, leading to fluctuations in the estimated slope versus t . To reduce this statistical variability, we employed the total mean-squared displacement (TMSD, eq 5), which averages the MSD over multiple time intervals (Δt), following the approach of He et al.⁶⁰

$$\text{TMSD}(\Delta t) = \sum_{i=1}^N \left[\frac{1}{N_{\Delta t}} \sum_{t=0}^{t_{\text{tot}}-\Delta t} |\mathbf{r}_i(t+\Delta t) - \mathbf{r}_i(t)|^2 \right] \quad (5)$$

Here, $N_{\Delta t}$ denotes the number of possible time intervals of duration Δt . D^* is subsequently determined from the slope of MSD versus Δt , subject to ranges of Δt values for which MSD behaves linearly.

$$D^* = \frac{\text{MSD}(\Delta t)}{2d\Delta t} \quad (6)$$

where $\text{MSD}(\Delta t) = \text{TMSD}(\Delta t)/N$. A similar approach can be used for estimating D_j as well.⁶⁰ In this work, we set $\Delta t = 50$ ps for all diffusivity calculations because it provides a sufficiently long window to access diffusive behavior while maintaining adequate averaging statistics within the total trajectory length ($t_{\text{tot}} = 700$ ps). Also, the MSD exhibits linear scaling with Δt in this regime. We used the DiffusionAnalyzer class of pymatgen⁶² for post-processing our AIMD and classical MD calculations and determining D_j , D^* and H_R .

Finally, in an ideal transport regime, where ionic hops occur with uniform frequency and are unaffected by local compositional fluctuations or structural heterogeneity, the overall diffusion coefficient (D_j or D^* , denoted as D below) takes the Arrhenius form,

$$D = D_0 \exp\left(-\frac{E_a}{k_B T}\right) \quad (7)$$

The pre-exponential factor D_0 encapsulates parameters such as the hop distance, the atomic vibrational frequency, the available diffusion-carrier concentration, the correlation factor (which describes deviations from random walk), and the geometric factor (connectivity of pathways). The activation energy (E_a) for migration, a material-specific property, governs D exponentially and can be extracted from the slope of $\ln D$ versus $1/T$. Although D may depend on correlation and geometric factor, E_a is typically the dominant rate-limiting parameter and therefore a key quantity for assessing ionic transport performance.

For the calculation of the shear viscosity (η), we equilibrated the Li_2CO_3 system in the NVT ensemble for 50 ps, and collected the stress components collected during a 30 ps production run. Note that the viscosity is related to the time integral of the autocorrelation function of the off-diagonal stress–

tensor components, within the Green-Kubo formalism,^{63,64} as

$$\eta = \frac{V}{3k_B T} \int_0^\infty \left[\langle P_{xy}(0)P_{xy}(t) \rangle + \langle P_{xz}(0)P_{xz}(t) \rangle + \langle P_{yz}(0)P_{yz}(t) \rangle \right] dt. \quad (8)$$

Here, V is the simulation cell volume, k_B is the Boltzmann constant, T is the temperature. $P_{\alpha\beta}$ represent the off-diagonal components of the pressure or stress tensor, where $\alpha\beta = xy$, xz , or yz . The angular brackets denote averaging over time. To improve the statistical reliability of the calculated viscosity, multiple independent simulations were performed at each temperature, with up to five independent runs. The reported viscosity values correspond to the mean of these independent runs, while the associated uncertainties are represented by their standard deviations.

3. RESULTS AND DISCUSSION

3.1. Model Comparison

To compare the performance of the NequIP and MACE models, we evaluated their energy and force prediction errors on the training, validation, and independent test datasets. The parity plots obtained using MACE (panel a) and NequIP (panel b) for the AIMD test dataset at 1000 K are presented in Figure S3. For MACE, the training and validation energy MAEs are both 0.1 meV/atom, while the corresponding force MAEs are 2.4 and 3.3 meV/Å, respectively. For NequIP, the training and validation energy MAEs are 1.3 and 0.3 meV/atom, respectively, whereas the corresponding force MAEs are 22.4 and 21.3 meV/Å.

Further, we evaluated the models using independent AIMD test datasets at 1000, 500, and 250 K. At 1000 K, MACE yields energy and force MAEs of 0.25 meV/atom and 31.80 meV/Å, respectively, while NequIP yields corresponding values of 0.27 meV/atom and 16.71 meV/Å. At 500 K, the energy and force MAEs are 0.26 meV/atom and 21.72 meV/Å for MACE and 1.30 meV/atom and 16.83 meV/Å for NequIP. At 250 K, MACE gives energy and force MAEs of 0.60 meV/atom and 20.04 meV/Å, respectively, whereas NequIP gives corresponding values of 0.20 meV/atom and 16.61 meV/Å. While MACE exhibits lower training and validation errors and provides lower test energy MAEs at 1000 and 500 K, NequIP produces lower force MAEs for all three independent test datasets and a lower energy MAE at 250 K.

For the mechanically strained test structures, MACE achieves energy and force MAEs of 6.8 meV/atom and 13.16 meV/Å, respectively. In comparison, NequIP yields higher MAEs of 21.08 meV/atom and 24.49 meV Å⁻¹. The corresponding energy and force parity plots are shown in Figure S4. Based on its lower training and validation errors, its accurate energy predictions over the temperature range relevant to the present study, and accurate estimations of density with respect to experimental data (Table S3), we employed the optimized MACE model for the subsequent large-scale and long-timescale MD simulations of molten Li₂CO₃.

3.2. Structural Properties of Molten Li₂CO₃

We used RDFs and $S(q)$ to characterize the structural properties of molten Li₂CO₃. Note that $S(q)$ plays a particularly important role, as it is directly accessible via experimental

techniques such as X-ray and neutron scattering. We examine the RDFs of all atomic pairs to resolve the short- and medium-range structural ordering within Li₂CO₃, as compiled in Figure 2. Note that we compiled RDFs of crystalline Li₂CO₃ (calculated with DFT), and molten Li₂CO₃ (above 1000 K, calculated with MACE) in Figure 2, with some complimentary RDF data generated by AIMD and MACE compiled in Figures S5–S7. The predicted RDFs by the NequIP and MACE-MP-0 models are provided in Figures S8–S10.

For crystalline Li₂CO₃ (Figure 2a), the DFT-calculated RDFs exhibit sharp and well-defined peaks, with distinct peaks appearing over long distances reflecting the presence of long-range periodicity in the lattice. After melt-quench to 1000 K and subsequent heating to 1500 K (with MACE, panels b–d of Figure 2), the RDF peaks progressively broaden and decrease in intensity with increasing temperature, indicating a gradual loss of long-range structural order and increased configurational disorder in the molten state. Indeed, the atomic configurations reveal a distinct progression from a periodic network of well-defined Li–O polyhedra in the crystalline phase (Figure 2a) to a fully disordered molten structure (Figure 2d), wherein the Li-centered coordination environments become increasingly distorted and non-uniform. We observe an exception to the trend of broadening RDF peaks for the C–O pair (cyan peak), where we find only a marginal reduction in the height of the first coordination peak, even at 1500 K. The lack of significant changes in the C–O peak highlights the strong covalent character of the C–O bond that preserves the planar carbonate geometry irrespective of temperature. Note that although the carbonate units remain locally intact across all temperatures, their orientations become progressively random with increasing temperature, resulting in the loss of medium- and long-range structural order.

At 1000 K (Figures 2b and S5a), both MACE and AIMD calculations show pronounced ordering in Li₂CO₃, with a strong C–O peak at ~1 Å, followed by additional peaks at ~4 and ~6 Å, although these higher-order peaks are significantly reduced in intensity compared to the crystalline state. Beyond ~6 Å, no sharp peaks are observed, consistent with the loss of long-range periodicity. The Li–O pairs (green) also show significant peak broadening beyond ~2 Å, while Li–C pairs (black) retain some medium-range ordering. Further, we compare the C–O RDF predicted by the DeepMD model of Dina et al.⁵² at 1043.15 K with our MACE data at 1000 K, and find that we accurately reproduce the peak positions and broadening observed by the authors at ~1.5 and ~4 Å (see Figure S7). This agreement with literature data demonstrates that both models capture the local structural features of molten Li₂CO₃ reasonably well.

Upon increasing the temperature to 1300 K (Figure 2c, the Li–C, C–O, C–C (magenta), and Li–O peaks begin to develop shoulders and further broaden, particularly beyond ~3, ~6, ~5, and ~4 Å, respectively. This progressive broadening confirms that the melt structure becomes increasingly disordered with temperature. At 1500 K (Figures 2d and S5c), the Li–O peak at ~2 Å, and the Li–C peak at ~3 Å show reduced intensity accompanied by pronounced shoulder formation. We do not observe any discernible peaks beyond ~6 Å, confirming the complete loss of long-range order and the molten state of Li₂CO₃.

Compared to AIMD data at 1500 K (Figure S5c), the MACE model exhibits similar RDFs (Figure 2d) except a marginally

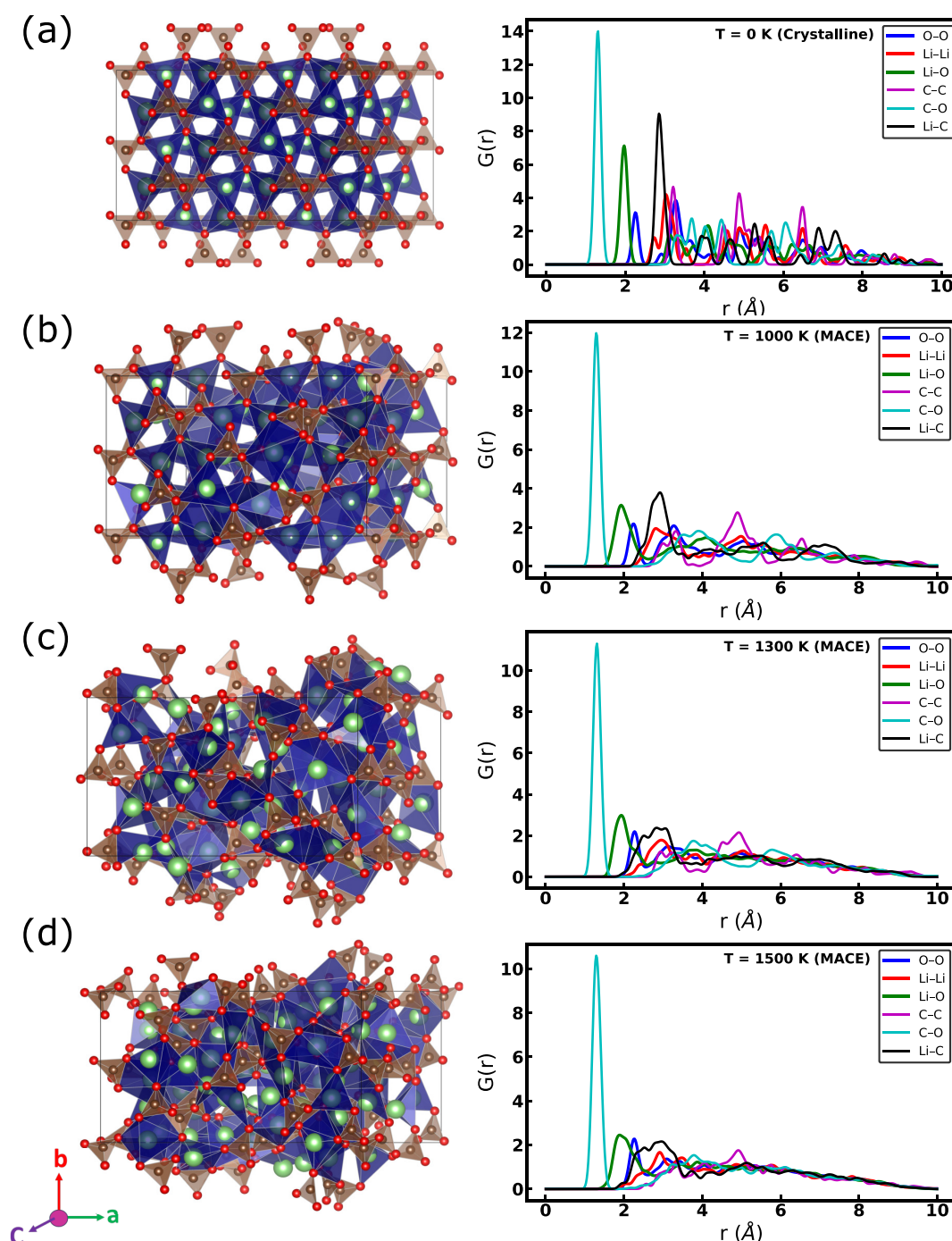


Figure 2. Representative atomic configurations (left panels) and corresponding radial distribution functions, $G(r)$ (right panels), of Li_2CO_3 at different temperatures. (a) Crystalline Li_2CO_3 at 0 K, relaxed using DFT. Molten Li_2CO_3 configurations generated using the optimized MACE potential at (b) 1000 K, (c) 1300 K, and (d) 1500 K. The blue, red, green, magenta, cyan, and black curves represent the O–O, Li–Li, Li–O, C–C, C–O, and Li–C pair correlations, respectively.

more pronounced shoulder broadening for the Li–C peak at ~ 3 Å and a reduced broadening for the C–O and C–C peaks at ~ 4 and ~ 5 Å, respectively. On the other hand, the NequIP and MACE-MP-0 models correctly identify the peak positions in their predicted RDFs but fail to accurately reproduce the extent of peak broadening observed in AIMD across all temperatures (Figures S8–S10). Nevertheless, both NequIP and MACE-MP-0 successfully capture the melting of Li_2CO_3 above 1000 K, as evidenced by the complete loss of structural ordering

beyond ~ 6 Å. For further validation of MACE-MD derived structures compared to AIMD, we calculate time-averaged RDFs from both AIMD and MACE-MD trajectories at different temperatures (see Figures S11–S13), where MACE-calculated RDFs show good agreement with AIMD calculations at the same temperatures.

We calculated the total RDF ($g(r)$) for molten Li_2CO_3 at different temperatures to further examine the evolution of the Li_2CO_3 structure, as compiled in Figure S14. In the range of

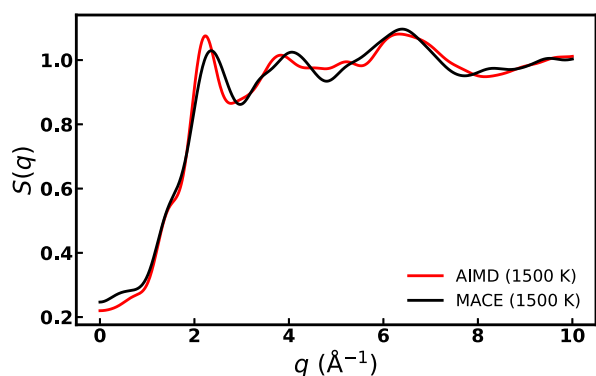


Figure 3. $S(q)$ for molten Li_2CO_3 at 1500 K, as calculated using AIMD (red) and MACE (black).

2–4 Å, the peaks exhibit a gradual shift and reduced peak intensity towards larger r values with increasing temperature, indicating a loss of short-range order in the structure. At distances beyond ~ 6 Å, the peaks become progressively broad and diminished at high temperatures (e.g., 1500 K), ultimately converging to $g(r) \approx 1$, which signifies the complete loss of long-range order in the molten state.

As an additional validation of the structures generated by our MACE model, we calculate the $S(q)$ at 1500 K and compare that with the AIMD data in Figure 3. The $S(q)$ predictions from the NequIP and MACE-MP-0 models at 1500 K are provided in Figure S15. The detailed methodology used to compute $S(q)$ follows previous studies,¹² with the necessary parameters compiled in Table S5. To further test the scalability and the accuracy of the MACE model, we benchmark the predictions by MACE at 1500 K in $2 \times 2 \times 2$ and $4 \times 4 \times 4$ supercells of the Li_2CO_3 structure (Figure S16).

Importantly, the high degree of overlap between the AIMD (red) and the MACE (black) $S(q)$ curves in Figure 3 indicates that the MACE model successfully reproduces $S(q)$ and accurately captures the correct peak intensities as well. Additionally, we compare the MACE prediction for molten Li_2CO_3 at 1000 K with the experimental $S(q)$ measured at 1013 K (see Figure S17).^{13,65} The calculated profile reproduces the overall oscillatory behaviour and the approximate positions of the major structural features observed experimentally, with the deviations between experiments and computations attributable to differences in temperature and density of the melt. In the case of NequIP and MACE-MP-0, both models mostly capture the correct peak positions and peak broadening in $S(q)$ compared to AIMD, with deviations in the regions of ~ 2.5 , 4.5 , and 6 Å^{-1} , whereas MACE only shows deviations around 6 Å^{-1} .

3.3. Transport Properties in Li_2CO_3

Given the crucial role that η plays in the flow of any molten medium, we compare the MACE-computed η at different temperatures with those from experimental⁵ and computational^{52,66} studies in Figure 4. We also summarize the MACE computed mean η and their standard deviation, as obtained via five independent MACE-MD runs at different temperatures, in Table S6. Importantly, the η values predicted by our MACE model (green diamonds in Figure 4) closely match the experimental trends (orange triangles),⁵ and significantly outperform the DeepMD model (blue squares)⁵² in terms of reproducing

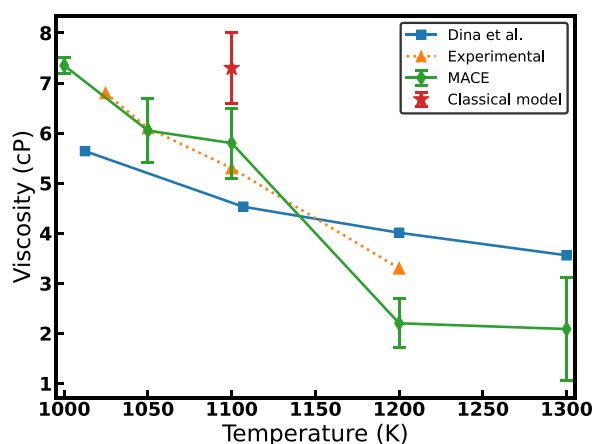


Figure 4. Viscosity of Li_2CO_3 (in units of centipoise or cP) as a function of temperature. Values predicted by the MACE-model (green) are compared with experimental data (orange), DeepMD model results (blue), and a classical force field (pink). The MACE values represent the mean viscosities averaged over five independent MD runs at each temperature, while the error bars indicate the corresponding standard deviations.

experimental observations. Also, predictions from a classical parameterized force field⁶⁶ overestimates the experimental η at 1100 K. Thus, our optimized MACE model is able to reproduce experimental trends in η accurately compared to other computational models.

We obtain the D^* of Li^+ in Li_2CO_3 using long time-scale and large-system MD simulations, done with the MACE potential at various temperatures, and plot the results in Figure 5. The overall averaged MSD of individual Li^+ combining the ionic displacements along all three Cartesian directions, as a function of Δt , is presented in Figure 5a, with the yellow, blue, green, pink, and red curves indicating 1500, 1400, 1300, 1250, and 1000 K, respectively. Figure 5b plots the D^* (denoted simply as ' D ' in the figure) at individual temperatures, obtained from the MSD- Δt slopes in panel a, with the color of the dots matching the colors used in panel a. The bottom and top x-axes of Figure 5b correspond to $1000/T$ and T , respectively, with the slope (dashed black line) proportional to the E_a . The raw MSD- t curves containing the direction-dependent MSD of Li, at different temperatures, are compiled in Figures S18 and S19.

At all temperatures, the MSD increases linearly with Δt , indicating diffusive behavior. Based on the MSD data, we calculate the $\text{Li}^+ D^*$ in molten Li_2CO_3 to be $8.38 \times 10^{-7} \text{ cm}^2/\text{s}$ at 1000 K, $2.13 \times 10^{-5} \text{ cm}^2/\text{s}$ at 1250 K, $3.47 \times 10^{-5} \text{ cm}^2/\text{s}$ at 1300 K, $8.51 \times 10^{-5} \text{ cm}^2/\text{s}$ at 1400 K, and $9.53 \times 10^{-5} \text{ cm}^2/\text{s}$ at 1500 K, as plotted in Figure 5b. The Arrhenius fit of D^* with T yields an apparent diffusion activation energy of $E_a = 1.287 \text{ eV}$, with an R^2 score of 0.98. We refer to E_a as the apparent activation energy here since the interpretation of an activation barrier in a molten state does not correspond to a single ion migration event that is typically observed in crystalline solids. For a baseline reference, earlier studies reported $E_a \sim 1.34 \text{ eV}$ ²² in molten Li_2CO_3 , while diffusion studies in bulk crystalline phases reported migration barriers (i.e., based on single ion-migration events) in the range of 0.23–0.49 eV.⁶⁷ The estimated statistical uncertainty, $D^* \pm \sigma$, as obtained via block-averaging of MSD-based diffusivities is summarized in Table S7.

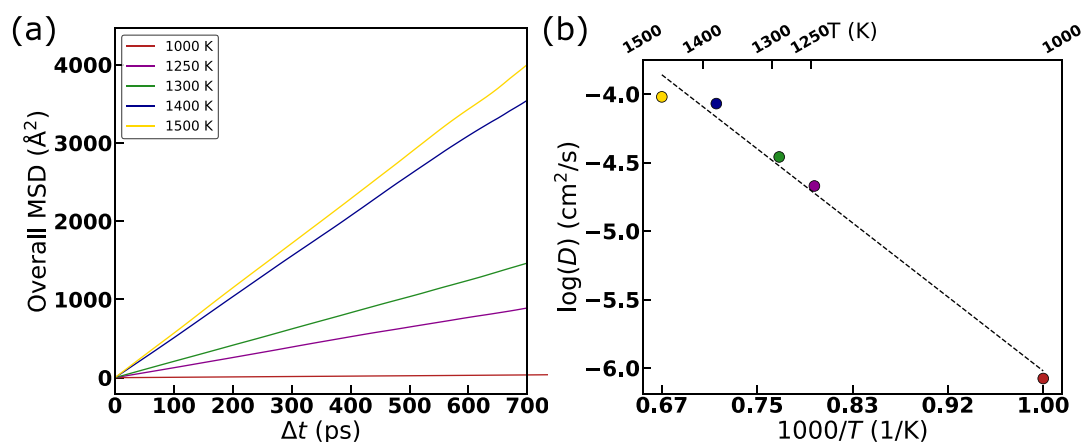


Figure 5. (a) Mean-squared displacement (MSD) as a function of Δt , obtained from 700 ps MACE-MD simulations. Data are shown for five temperatures: 1500 K (yellow), 1400 K (blue), 1300 K (green), 1250 K (pink), and 1000 K (red). (b) Arrhenius representation of the diffusion coefficient, plotted as $\log D$ (with D in cm^2/s) versus $1000/T$. Symbols are color-coded according to panel (a), and the dashed black line indicates the linear fit.

To assess the influence of the simulation cell size, we additionally calculated D^* using MACE in a $6 \times 6 \times 6$ supercell (5184 atoms) of Li_2CO_3 , as shown in Figure S20. Importantly, we observe only minor deviations in Li^+ D^* between the $6 \times 6 \times 6$ and $4 \times 4 \times 4$ supercells (~ 2.35 – 4.15% deviation, see Table S8) at 1300 and 1400 K, suggesting that our MD simulations using the $4 \times 4 \times 4$ supercell should be reliable enough. We do observe a significant deviation in calculated D^* at 1000 K across the supercell sizes ($\sim 49.80\%$, Table S8), but this can be largely attributed to the low absolute value of D^* , resulting in limited sampling of migration events and consequently larger errors.

Figure S21 shows the temperature-dependent MSCD data, as a function of Δt for molten Li_2CO_3 (panel a) and the corresponding H_R (panel b), as extracted from MACE MD simulations on a $4 \times 4 \times 4$ supercell over 200 ps at 1000, 1300, and 1400 K. Importantly, H_R remains well below unity even at high temperatures, with values of 0.40 at 1400 K, 0.31 at 1300 K, and 0.20 at 1000 K, indicating that Li-ion transport in molten Li_2CO_3 is fundamentally strongly correlated. Particularly, a H_R of 0.20 (at 1000 K) indicates a significant departure from the ideal Nernst–Einstein behavior, signifying concerted migration as the dominant transport mechanism compared to uncorrelated site-to-site hopping of Li-ions. Note that the extent of correlated Li^+ motion in molten Li_2CO_3 is not immediately apparent from D^* estimates of Figure 5a and requires explicit calculations of MSCD and H_R . Within the ionic diffusion framework proposed by He et al.,⁶⁸ such concerted migration events typically arise when ions in high-energy sites hop downhill, thereby causing a possible reduction in the effective energy barrier for neighboring ions that move uphill.

Additionally, we find that molten Li_2CO_3 exhibits pronounced directional anisotropy in Li^+ D^* , as revealed by the direction-dependent MSD curves at lower temperatures (Figures S18 and S19). For example, at 1000 K, the c -axis of molten Li_2CO_3 supports faster Li transport ($D_c^* > D_b^* > D_a^*$, Figure S19), whereas at 1400 K the three components converge to similar values (Figure S18b), reflecting a transition towards isotropic diffusion at elevated temperatures. Our analysis of the transient oxygen-centered Voronoi cages (i.e., regions of space closer to oxygen than other ions) in molten Li_2CO_3 ,

through which Li^+ migrate (Figure S22), also supports the notion of anisotropic Li^+ motion at lower temperatures. For instance, at 1000 K (Figure S22a), the c -axis displays markedly smaller fluctuations in the oxygen-centered Voronoi cage volumes, compared to the a and b axes, which indicates a more persistent local topology that preferentially facilitates Li^+ transport along the c -axis. On the other hand, at 1400 K (Figure S22b), the cage volume fluctuations are similar along all three crystallographic directions consistent with isotropic Li^+ transport.

To further understand the concerted nature of Li^+ motion, we visualize the unwrapped trajectories of representative Li^+ motion in molten Li_2CO_3 in Figure 6, over 350 ps, at 1400 K (panel a) and at 1000 K (panel b). We unwrap the trajectory of motion across periodic images to improve visualization and interpretation of ionic motion. We employ a rainbow color map as a temporal marker, where blue and red denote the initial ($t = 0$ ps) and final ($t = 350$ ps) positions, respectively, of the ions. Importantly, the continuous nature of the Li^+ trajectories at 1400 K (Figure 6a) reflects the extensive migration of ions through the molten carbonate environment and signifies lower correlation among Li^+ motion. In contrast, the black circles at 1000 K (Figure 6b) highlight regions where Li^+ temporarily oscillate between nearby carbonate coordination sites (or cages), indicating transient trapping events before continuing its migration through the molten environment. Thus, the nature of the Li^+ concerted motion undergoes a significant change from 1000 to 1400 K, which is also reflected in the increase in H_R from 0.2 at 1000 K to 0.40 at 1400 K (Figure S21b) and the increasing isotropy of Li^+ motion (Figures S18b and S19) with increasing temperatures.

The MACE-calculated RDFs further support our observations on the transient trapping of Li^+ at lower temperatures. For example, we observe pronounced Li–C peaks at ~ 3 and ~ 5 $\text{\AA}$, while the Li–O exhibits a strong peak at ~ 3 $\text{\AA}$ at 1000 K (Figure 2b). Notably, both the Li–C and Li–O peaks appear sharper at 1000 K than at 1400 K (Figure S5b), indicating a more ‘ordered’ local coordination environment and lower thermal disorder at 1000 K compared to 1400 K. Also, the sharper Li–C and Li–O peaks at 1000 K (than at 1400 K) suggest that Li^+ experience stronger coordination with nearby

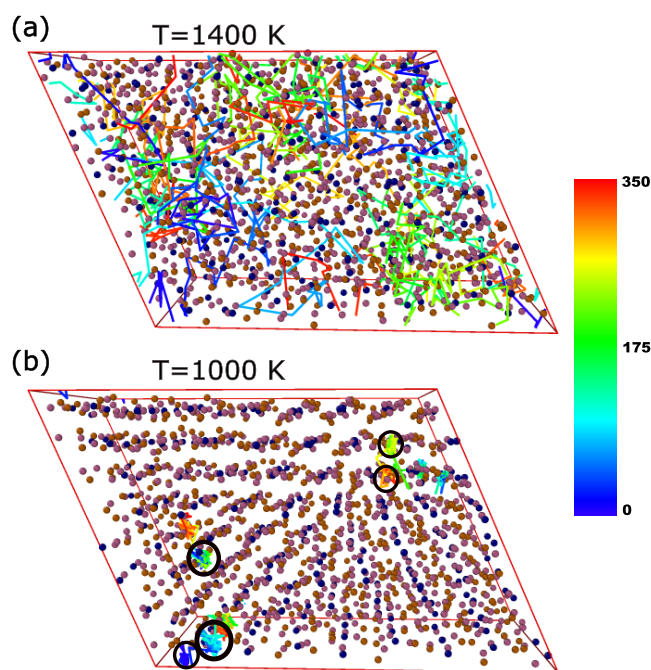


Figure 6. Unwrapped diffusion trajectories of representative Li^+ in molten Li_2CO_3 at 1400 K (panel a) and at 1000 K (panel b) over 350 ps. The rainbow color map traces an ion's motion from blue ($t = 0$ ps) to red ($t = 350$ ps), depicting the temporal evolution of its path. The black circles at 1000 K mark regions of localized Li motion due to transient trapping by neighboring carbonate groups.

carbonate groups, reflecting the possibility of (transient) trapping of Li^+ by the neighboring carbonate groups.

For elucidating the dynamic correlation among the Li-ions, we analyze the self ($G_s(r, t)$) and distinct ($G_d(r, t)$) parts of the van Hove correlation function at 1500, 1250, and 1000 K (Figure S23). While $G_s(r, t)$ characterizes the displacement statistics of individual ions and is directly related to the MSD, $G_d(r, t)$ probes the relative motion and spatial correlations between distinct ions. At 1500 K, we observe bright horizontal bands in $G_d(r, t)$ that rapidly decay in intensity over a 2.5 ps window, consistent with liquid-like motion. In contrast, the horizontal bands at 1250 and 1000 K remain sharper and persist for longer timescales, particularly in the 2–6 Å range, indicating stronger transient order and more concerted motion, consistent with our previous observations in Figures 6, S5, S6, S18, and S19. We further calculate the ionic conductivity (σ), as obtained from the Nernst–Einstein relation, plot it as a function of temperature in Figure S24, and compare the resultant activation energy with experimental data.⁵

3.4. Discussion

In this work, we employed two equivariant graph-based MLIPs, NequIP and MACE, to understand the structure and Li-ion dynamics in molten Li_2CO_3 , with broad applications in MCFCs and batteries. We trained both MLIPs on ab initio melt-quench trajectories consisting of 3600 structures at 1500 K and 1988 structures at 1250 K (Figure 1). Notably, we found MACE to be the best-performing model, given its low errors on the test set (Figures S3 and S4), as quantified by energy and force errors of 0.2 meV/atom and 0.17 meV/Å,

respectively, on the 1000 K trajectory test set. Notably, our trained MACE model exhibited better performance than the foundational MACE-MP-0 model (without any fine-tuning) on our dataset. While fine-tuning MACE-MP-0 is a feasible strategy to accelerate MD simulations of specific systems, we trained the MACE architecture from scratch in our work to bias the model towards maximal accuracy towards the Li_2CO_3 system. Although the ‘local’ MLIPs considered in our work do not explicitly account for long-range Coulombic interactions, their description is expected to be adequate for the homogeneous, charge-neutral molten Li_2CO_3 system, where the electrostatic interactions arising from distant ions are partially screened by the surrounding ionic environment.⁶⁹ Note that the absence of explicitly including long-range interactions within MACE and NequIP remains a limitation of the architectures so far.

Remarkably, our best-performing MACE model requires only two message-passing layers, while the best-performing NequIP model requires five layers (Figure S25), indicating the efficiency of the MACE model in learning the contributions of local bonding features to the overall potential energy surface.⁴¹ In our benchmarking, we fixed the equivariant message-passing order to $L_{\text{max}} = 1$ for both models to ensure a consistent comparison. However, NequIP did not achieve our optimal MACE model's accuracy even when increasing the equivariant order to $L_{\text{max}} = 2$, indicating the superior featurization of the local geometry and the utility of including higher body-order interactions by the MACE architecture.

Given that training both models typically requires GPU acceleration, we trained the models using a single NVIDIA V100 GPU. Subsequently, the optimized MACE model was able to simulate 760 ps of molten Li_2CO_3 containing 1536 atoms within 24 h on a NVIDIA A100 GPU. For comparison, our previous study showed that the invariant MTP model, which is not based on graph networks, was easier to train and remained more computationally efficient for MD simulations on CPUs.^{33,70} Although MACE achieved higher accuracy than NequIP in our benchmarking, it was approximately five times slower to train than NequIP with a single GPU (Figure S26). In CPU-based MD simulations of a 192-atom system using 16 CPU processes on a single compute node, MACE was also significantly slower ($\approx 10\times$) than NequIP, highlighting the superior CPU performance of NequIP for production-scale MD (Figure S27). Thus, our computational speed benchmarks on both CPUs and GPUs is further indicative of the speed-accuracy trade-off that users have to optimize for in training equivariant models, which also depends on the choice of hyperparameters and the specific system itself.

We characterized the structural properties of molten Li_2CO_3 using RDFs and $S(q)$ across multiple temperatures (Figures 2 and 3). AIMD simulations reveal a progressive loss of medium- and long-range structural order with increasing temperature, while the strong covalent C–O bonding motif remains intact throughout the melt. The MACE model reproduces both the RDFs and $S(q)$ with high fidelity, against both AIMD and experimental data (Figures S5, S15, and S17) by accurately capturing the temperature dependence of peak positions and widths, and remains consistent upon scaling to larger system sizes. Furthermore, we computed the shear viscosity using MACE, which closely matches with available experimental measurements (Figure 4), demonstrating that the model can faithfully recover critical properties of molten Li_2CO_3 .

Analysis of Li^+ transport indicated that Li-ion diffusion in molten Li_2CO_3 proceeds via highly correlated motion, as evidenced by $H_R \ll 1$ over all temperatures (Figure S21). While the extent of correlated motion is not immediately apparent from D^* estimates (Figure 5), the resultant E_a are in agreement with previous simulations.²² Notably, direction-dependent decomposition of Li^+ MSDs (Figures S18 and S19) reveal a pronounced transport anisotropy at 1000 K (with Li^+ diffusion preferred along the c -axis) and subsequent transition to a fully isotropic regime at 1400 K. Our visualization of the unwrapped Li^+ trajectories over 350 ps supports the notion of concerted motion and directional anisotropy, as indicated by transient trapping of Li^+ by carbonate cages at 1000 K (Figure 6). The directional anisotropy of Li^+ motion can also be linked to fewer oxygen-centered Voronoi cage fluctuations along the c -axis at 1000 K (reflecting persistent topologies that favor directional Li^+ transport) compared to 1400 K (Figure S22). Further, analysis of the van Hove correlation function points to a higher degree of dynamic correlation at 1000 K compared to liquid-like uncorrelated motion at 1500 K (Figure S23). Thus, it is clear that the extent of correlation among Li^+ motion in molten Li_2CO_3 is highly temperature dependent and tends to reduce with increasing temperatures. Although longer simulations and additional temperature sampling would improve statistical accuracy, our calculated MACE MD trajectories already exhibit clear temperature-dependent diffusion regimes, enabling reliable estimation of transport properties.

4. CONCLUSIONS

In summary, we have performed a comprehensive atomistic investigation of the structure and transport properties of molten Li_2CO_3 using equivariant MLIPs, namely MACE and NequIP. Our initial benchmarking demonstrated that the MACE model provided superior accuracy and transferability compared to NequIP and the foundational MACE-MP-0 models, based on independent test set evaluations. The structural properties predicted by our optimized MACE model, such as the persistence of the C–O pair correlation even upon melting based on RDFs and $S(q)$, show remarkable agreement with experimental and *ab initio* data. Also, our shear viscosity estimates in molten Li_2CO_3 are closer to experimental values than previous computational estimates. A central finding of our study is our prediction that Li^+ transport in molten Li_2CO_3 is fundamentally governed by highly correlated, concerted motion rather than simple, uncorrelated random hopping, as evidence by our H_R estimates that point towards a substantial deviation from the ideal Nernst-Einstein behavior. Apart from the transient trapping of Li^+ by neighboring carbonate cages contributing to the correlated motion, we also observe a high degree of directional anisotropy in Li^+ transport at lower temperatures, as characterized by the fluctuations in oxygen-centered Voronoi cage volumes and computed van Hove correlation functions. Thus, our results represent a unique temperature-dependent transition in Li^+ transport in molten Li_2CO_3 , from highly correlated and anisotropic diffusion at lower temperatures to less correlated and isotropic diffusion at higher temperatures. Our work also demonstrates the utility of equivariant graph-based MLIP architectures, such as MACE, which can effectively scale to systems containing thousands of atoms and reach nanosecond time-scales while maintaining near-DFT accuracy, for modelling molten systems. We hope that the insights gained in this work are

useful in the optimization of MCFCs and for understanding Li^+ transport in amorphous Li_2CO_3 -based SEIs.

■ ASSOCIATED CONTENT

Data Availability Statement

All computed data and models constructed in this work are available freely for all via our [GitHub](#) repository.

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsaem.6c02035>.

Model hyperparameters, energy and force parity plots, energy fluctuations during equilibration, radial distribution functions, static structure factors, viscosity data, mean-squared-displacement and Li-ion diffusivity analysis, oxygen-centered Voronoi cage-volume analysis, van Hove correlation function calculations, ionic conductivity estimates, and computational efficiency benchmarks (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Abhirup Patra – Shell International Exploration & Production Inc., 200 N Dairy Ashford Rd, Houston, Texas 77079, United States; orcid.org/0000-0002-2446-8017; Email: abhirup.patra@shell.com

Gopalakrishnan Sai Gautam – Department of Materials Engineering, Indian Institute of Science, Bengaluru 560012, India; orcid.org/0000-0002-1303-0976; Email: saigautam@iisc.ac.in

Authors

Debsundar Dey – Department of Materials Engineering, Indian Institute of Science, Bengaluru 560012, India

Anand Narayanan Krishnamoorthy – Shell India Markets Pvt. Ltd. (Shell Projects & Technology), Mahadeva Kodigehalli, Bengaluru, Karnataka 562149, India

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acsaem.6c02035>

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

G.S.G. acknowledges financial support from the Science and Engineering Research Board (SERB), of the Department of Science and Technology, Government of India, under sanction number IPA/2021/000007. D.D. acknowledges the Indian Institute of Science for academic support and the Shell fellowship for financial support. A.P. and A.N.K. acknowledge the support and resources provided by Shell International Exploration & Production Inc. and Shell India Markets Pvt. Ltd. A portion of the density functional theory calculations and molecular dynamics simulations showcased in this work was performed with the computational resources provided by the Supercomputer Education and Research Center, Indian Institute of Science. The authors thank Sharan Shetty, Neha Solanki, and Jason Williams at Shell for their support.

REFERENCES

- (1) Watanabe, M.; Thomas, M. L.; Zhang, S.; Ueno, K.; Yasuda, T.; Dokko, K. Application of ionic liquids to energy storage and conversion materials and devices. *Chem. Rev.* **2017**, *117*, 7190–7239.
- (2) McPhail, S.; Moreno, A.; Bove, R. *International Status of Molten Carbonate Fuel Cells Technology*; ENEA, Rome, **2008**.
- (3) Ghezal-Ayagh, H. Advances in MCFC Technology for Power Generation. *ECS Trans.* **2017**, *75*, 77–85.
- (4) Kojima, T.; Miyazaki, Y.; Nomura, K.; Tanimoto, K. Density, surface tension, and electrical conductivity of ternary molten carbonate system $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3\text{--K}_2\text{CO}_3$ and methods for their estimation. *J. Electrochem. Soc.* **2008**, *155*, F150.
- (5) Janz, G. J. *Thermodynamic and transport properties for molten salts: correlation equations for critically evaluated density, surface tension, electrical conductance, and viscosity data*; Journal of physical and chemical reference data. Supplement; **1988**; vol 17.
- (6) Barckholtz, T. A.; Elsen, H.; Kalamaras, P. H.; Kiss, G.; Rosen, J.; Bove, D.; Audasso, E.; Bosio, B. Experimental and modeling investigation of $\text{CO}_3^{2-}/\text{OH}^-$ -equilibrium effects on molten carbonate fuel cell performance in carbon capture applications. *Front. Energy Res.* **2021**, *9*, 669761.
- (7) McPhail, S. J.; Hsieh, P.-H.; Selman, J. R. *Materials for High-Temperature Fuel Cells*; Wiley-VCH, **2013**, pp 341–371.
- (8) Licht, S.; Wang, B.; Ghosh, S.; Ayub, H.; Jiang, D.; Ganley, J. A new solar carbon capture process: solar thermal electrochemical photo (STEP) carbon capture. *J. Phys. Chem. Lett.* **2010**, *1*, 2363–2368.
- (9) Licht, G.; Hofstetter, K.; Wang, X.; Licht, S. A new electrolyte for molten carbonate decarbonization. *Commun. Chem.* **2024**, *7*, 211.
- (10) Bini, R.; Bortolini, O.; Chiappe, C.; Pieraccini, D.; Siciliano, T. Development of cation/anion “interaction” scales for ionic liquids through ESI-MS measurements. *J. Phys. Chem. B* **2007**, *111*, 598–604.
- (11) Zhadan, A.; Sarou-Kanian, V.; Del Campo, L.; Cosson, L.; Malki, M.; Bessada, C. Transport properties in molten carbonates: self-diffusion and conductivity measurements at high temperature. *Int. J. Hydrogen Energy* **2021**, *46*, 15059–15065.
- (12) Wilding, M. C.; Wilson, M.; Alderman, O. L. G.; Benmore, C. J.; Weber, J. K. R.; Parise, J. B.; Tamalonis, A.; Skinner, L. Low-Dimensional Network Formation in Molten Sodium Carbonate. *Sci. Rep.* **2016**, *6*, 24415.
- (13) Ohata, H.; Takeuchi, K.; Ui, K.; Koura, N. The Structure of Molten Lithium Carbonate Calculated by DFT and MD Simulations. *ECS Trans.* **2007**, *6*, 57.
- (14) Heiskanen, S. K.; Kim, J.; Lucht, B. L. Generation and evolution of the solid electrolyte interphase of lithium-ion batteries. *Joule* **2019**, *3*, 2322–2333.
- (15) Jagger, B.; Pasta, M. Solid electrolyte interphases in lithium metal batteries. *Joule* **2023**, *7*, 2228–2244.
- (16) Adenusi, H.; Chass, G. A.; Passerini, S.; Tian, K. V.; Chen, G. Lithium batteries and the solid electrolyte interphase (SEI)—progress and outlook. *Adv. Energy Mater.* **2023**, *13*, 2203307.
- (17) Wang, A.; Kadam, S.; Li, H.; Shi, S.; Qi, Y. Review on modeling of the anode solid electrolyte interphase (SEI) for lithium-ion batteries. *npj Comput. Mater.* **2018**, *4*, 15.
- (18) Xu, K. Electrolytes and interphases in Li-ion batteries and beyond. *Chem. Rev.* **2014**, *114*, 11503–11618.
- (19) Peled, E.; Menkin, S. SEI: past, present and future. *J. Electrochem. Soc.* **2017**, *164*, A1703.
- (20) Baba, T.; Sodeyama, K.; Kawamura, Y.; Tateyama, Y. Li-ion transport at the interface between a graphite anode and Li_2CO_3 solid electrolyte interphase: ab initio molecular dynamics study. *Phys. Chem. Chem. Phys.* **2020**, *22*, 10764–10774.
- (21) Ma, X.-X.; Shen, X.; Chen, X.; Fu, Z.-H.; Yao, N.; Zhang, R.; Zhang, Q. The origin of fast lithium-ion transport in the inorganic solid electrolyte interphase on lithium metal anodes. *Small Struct.* **2022**, *3*, 2200071.
- (22) Benitez, L.; Seminario, J. M. Ion diffusivity through the solid electrolyte interphase in lithium-ion batteries. *J. Electrochem. Soc.* **2017**, *164*, E3159.
- (23) Tosi, M.; Fumi, F. Ionic sizes and born repulsive parameters in the NaCl-type alkali halides—II: The generalized Huggins-Mayer form. *J. Phys. Chem. Solids* **1964**, *25*, 45–52.
- (24) Mondal, A.; Young, J. M.; Barckholtz, T. A.; Kiss, G.; Koziol, L.; Panagiotopoulos, A. Z. Genetic algorithm driven force field parameterization for molten alkali-metal carbonate and hydroxide salts. *J. Chem. Theory Comput.* **2020**, *16*, S736–S746.
- (25) Car, R.; Parrinello, M. Unified approach for molecular dynamics and density-functional theory. *Phys. Rev. Lett.* **1985**, *55*, 2471.
- (26) Marx, D.; Hutter, J. *Ab initio molecular dynamics: basic theory and advanced methods*; Cambridge University Press, **2009**.
- (27) Behler, J.; Parrinello, M. Generalized neural-network representation of high-dimensional potential-energy surfaces. *Phys. Rev. Lett.* **2007**, *98*, 146401.
- (28) Tovey, S.; Narayanan Krishnamoorthy, A.; Sivaraman, G.; Guo, J.; Benmore, C.; Heuer, A.; Holm, C. DFT accurate interatomic potential for molten NaCl from machine learning. *J. Phys. Chem. C* **2020**, *124*, 25760–25768.
- (29) Bartók, A. P.; Payne, M. C.; Kondor, R.; Csányi, G. Gaussian approximation potentials: The accuracy of quantum mechanics, without the electrons. *Phys. Rev. Lett.* **2010**, *104*, 136403.
- (30) Sivaraman, G.; Guo, J.; Ward, L.; Hoyt, N.; Williamson, M.; Foster, I.; Benmore, C.; Jackson, N. Automated development of molten salt machine learning potentials: application to LiCl. *J. Phys. Chem. Lett.* **2021**, *12*, 4278–4285.
- (31) Lam, S. T.; Li, Q.-J.; Ballinger, R.; Forsberg, C.; Li, J. Modeling LiF and FLiBe molten salts with robust neural network interatomic potential. *ACS Appl. Mater. Interfaces* **2021**, *13*, 24582–24592.
- (32) Nguyen, M.-T.; Rousseau, R.; Paviet, P. D.; Glezakou, V.-A. Actinide molten salts: a machine-learning potential molecular dynamics study. *ACS Appl. Mater. Interfaces* **2021**, *13*, 53398–53408.
- (33) Choyal, V.; Dey, D.; Sai Gautam, G. Exploration of Amorphous V_2O_5 as Cathode for Magnesium Batteries. *Small* **2025**, *21*, e05851.
- (34) Seth, A.; Kulkarni, R. P.; Sai Gautam, G. Investigating Ionic Diffusivity in Amorphous LiPON using Machine-Learned Interatomic Potentials. *ACS Mater. Au* **2025**, *5*, 458–468.
- (35) Geiger, M.; Smidt, T. e3nn: Euclidean neural networks. **2022**, *arXiv preprint arXiv:2207.09453*.
- (36) Batzner, S.; Musaelian, A.; Kozinsky, B. Advancing molecular simulation with equivariant interatomic potentials. *Nat. Rev. Phys.* **2023**, *5*, 437–438.
- (37) Batzner, S.; Musaelian, A.; Sun, L.; Geiger, M.; Mailoa, J. P.; Kornbluth, M.; Molinari, N.; Smidt, T. E.; Kozinsky, B. E (3)-equivariant graph neural networks for data-efficient and accurate interatomic potentials. *Nat. Commun.* **2022**, *13*, 2453.
- (38) Batatia, I.; Kovacs, D. P.; Simm, G.; Ortner, C.; Csányi, G. MACE: Higher order equivariant message passing neural networks for fast and accurate force fields. *Adv. Neural Inf. Process. Syst.* **2022**, *35*, 11423–11436.
- (39) Batatia, I.; Batzner, S.; Kovács, D. P.; Musaelian, A.; Simm, G. N.; Drautz, R.; Ortner, C.; Kozinsky, B.; Csányi, G. The design space of E (3)-equivariant atom-centred interatomic potentials. *Nat. Mach. Intell.* **2025**, *7*, 56–67.
- (40) Goodwin, Z. A.; Wenny, M. B.; Yang, J. H.; Cepellotti, A.; Ding, J.; Bystrom, K.; Duschatko, B. R.; Johansson, A.; Sun, L.; Batzner, S., et al. Transferability and accuracy of ionic liquid simulations with equivariant machine learning interatomic potentials. *J. Phys. Chem. Lett.* **2024**, *15*, 7539–7547.
- (41) Kovács, D. P.; Batatia, I.; Arany, E. S.; Csányi, G. Evaluation of the MACE force field architecture: From medicinal chemistry to materials science. *J. Chem. Phys.* **2023**, *159*, 044118.
- (42) Musaelian, A.; Batzner, S.; Johansson, A.; Sun, L.; Owen, C. J.; Kornbluth, M.; Kozinsky, B. Learning local equivariant representations for large-scale atomistic dynamics. *Nat. Commun.* **2023**, *14*, 579.

- (43) Batatia, I.; Benner, P.; Chiang, Y.; Elena, A. M.; Kovács, D. P.; Riebesell, J.; Advincula, X. R.; Asta, M.; Avaylon, M.; Baldwin, W. J., et al. A foundation model for atomistic materials chemistry. *J. Chem. Phys.* **2025**, *163*, 184110.
- (44) Nayak, G. K.; Srinivasan, P.; Todt, J.; Daniel, R.; Nicolini, P.; Holec, D. Accurate prediction of structural and mechanical properties on amorphous materials enabled through machine-learning potentials: A case study of silicon nitride. *Comput. Mater. Sci.* **2025**, *249*, 113629.
- (45) Scopel, W. L.; da Silva, A. J.; Fazzio, A. Amorphous HfO_2 and $\text{Hf}_{1-x}\text{Si}_x\text{O}$ via a melt-and-quench scheme using ab initio molecular dynamics. *Phys. Rev. B* **2008**, *77*, 172101.
- (46) Hellenbrandt, M. The inorganic crystal structure database (ICSD)—present and future. *Crystallogr. Rev.* **2004**, *10*, 17–22.
- (47) Yan, Q.; Wang, C.; Liu, C.; Zhang, J. Wearable Human Motion Monitoring Using Vertical Contact Separation Mode Triboelectric Nanogenerator. *IOP Conf. Ser.: Mater. Sci. Eng.*, **2020**, *729*, 012031.
- (48) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **1996**, *6*, 15–50.
- (49) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, *54*, 11169.
- (50) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, *59*, 1758.
- (51) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- (52) Kussainova, D.; Panagiotopoulos, A. Z. Molecular simulation of lithium carbonate reactive vapor–liquid equilibria using a deep potential model. *J. Chem. Eng. Data* **2023**, *69*, 204–214.
- (53) Kussainova, D.; Panagiotopoulos, A. Z. Chemical Reactions in Molten Lithium Carbonates and Hydroxides with Deep Potential Molecular Dynamics. *J. Phys. Chem. B* **2025**, *129*, 7282–7292.
- (54) Monkhorst, H. J.; Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B* **1976**, *13*, 5188.
- (55) Thompson, A. P.; Aktulga, H. M.; Berger, R.; Bolintineanu, D. S.; Brown, W. M.; Crozier, P. S.; In't Veld, P. J.; Kohlmeyer, A.; Moore, S. G.; Nguyen, T. D., et al. LAMMPS—a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales. *Comput. Phys. Commun.* **2022**, *271*, 108171.
- (56) Hoover, W. G. Canonical dynamics: Equilibrium phase-space distributions. *Phys. Rev. A* **1985**, *31*, 1695.
- (57) Verlet, L. Computer “experiments” on classical fluids. I. Thermodynamical properties of Lennard-Jones molecules. *Phys. Rev.* **1967**, *159*, 98.
- (58) Marcolongo, A.; Marzari, N. Ionic correlations and failure of Nernst-Einstein relation in solid-state electrolytes. *Phys. Rev. Mater.* **2017**, *1*, 025402.
- (59) Fick, A. V. On liquid diffusion. *London, Edinburgh Dublin Philos. Mag. J. Sci.* **1855**, *10*, 30–39.
- (60) He, X.; Zhu, Y.; Epstein, A.; Mo, Y. Statistical variances of diffusional properties from ab initio molecular dynamics simulations. *npj Comput. Mater.* **2018**, *4*, 18.
- (61) Gautam, G. S.; Canepa, P. In *Magnesium Batteries: Research and Applications*; Fichtner, M., Ed.; Royal Society of Chemistry, **2019**; pp 79–113.
- (62) Mo, Y.; Ong, S. P.; Ceder, G. First principles study of the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ lithium super ionic conductor material. *Chem. Mater.* **2012**, *24*, 15–17.
- (63) Plumari, S.; Puglisi, A.; Scardina, F.; Greco, V. Shear viscosity of a strongly interacting system: Green-Kubo correlator versus Chapman-Enskog and relaxation-time approximations. *Phys. Rev. C* **2012**, *86*, 054902.
- (64) Desmaele, E.; Sator, N.; Vuilleumier, R.; Guillot, B. Atomistic simulations of molten carbonates: thermodynamic and transport properties of the Li_2CO_3 – Na_2CO_3 – K_2CO_3 system. *J. Chem. Phys.* **2019**, *150*, 094504.
- (65) Sessa, F.; Della Pietra, M.; Mataloni, S.; Muñoz-García, A. B.; Pavone, M. Structure and dynamics of $\text{Li}_{1.24}\text{K}_{0.76}\text{CO}_3$ molten carbonate electrolyte from molecular simulations with explicit polarization. *Phys. Chem. Chem. Phys.* **2024**, *26*, 14420–14429.
- (66) Mondal, A.; Young, J. M.; Barckholtz, T. A.; Kiss, G.; Koziol, L.; Panagiotopoulos, A. Z. Genetic algorithm driven force field parameterization for molten alkali-metal carbonate and hydroxide salts. *J. Chem. Theory Comput.* **2020**, *16*, 5736–5746.
- (67) Iddir, H.; Curtiss, L. A. Li ion diffusion mechanisms in bulk monoclinic Li_2CO_3 crystals from density functional studies. *J. Phys. Chem. C* **2010**, *114*, 20903–20906.
- (68) He, X.; Zhu, Y.; Mo, Y. Origin of fast ion diffusion in super-ionic conductors. *Nat. Commun.* **2017**, *8*, 15893.
- (69) Lanning, O. J.; Madden, P. A. Screening at a charged surface by a molten salt. *J. Phys. Chem. B* **2004**, *108*, 11069–11072.
- (70) Choyal, V.; Sagar, N.; Sai Gautam, G. Constructing and evaluating machine-learned interatomic potentials for Li-based disordered rocksalts. *J. Chem. Theory Comput.* **2024**, *20*, 4844–4856.