

Supporting Information for

Probing Structure and Ionic Transport in Molten Lithium Carbonate

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Optimized hyperparameters

Table S1. Optimized hyperparameters for the neural equivariant interatomic potential (NequIP) model.

Hyperparameters	Value
Cut off radius (r_{cut})	5 Å
No of Interaction blocks (Convolutions)	5
Maximum “irrep” order of features (l_{max})	1
Channel size	32

Table S2. Optimized hyperparameters for the multi atomic cluster expansion (MACE) model.

Hyperparameters	Value
Cut off radius (r_{cut})	3.5 Å
No of Interaction blocks (Convolutions)	2
Order of symmetry of the messages	1
Channel size	32
Correlation (The order of the many-body expansion which creates basis functions of up to 4-body ($ijkl$) indices, for each layer)	3 (i.e., body order of 4)
Max_L (Angular resolution for the model)	3

Density Calculations

We evaluated the temperature-dependent density of molten Li_2CO_3 , over a 1010-1120 K range, using MACE-based molecular dynamics (MD) simulations in the isothermal-isobaric (NPT) ensemble. We used a $2 \times 2 \times 2$ supercell of the original 192-atom simulation cell of Li_2CO_3 , resulting in a simulation cell containing 1536 atoms. We performed MACE-MD runs at the target temperatures (1010 K, 1050 K, 1100 K, and 1120 K) and pressure of 0 bar using a time step of 2 fs. The thermostat and barostat damping parameters were set to 0.2 and 1.0 ps, respectively. At each temperature, the system was first equilibrated for 20 ps in the NPT ensemble, followed by a 20 ps NPT production run. During the production run, the instantaneous density was sampled once every 100 steps, corresponding to a sampling interval of 0.2 ps. Therefore, 100 density values were collected during each 20 ps production trajectory and averaged to obtain the time-averaged density over a single production run.

We performed three statistically independent simulations at each temperature using different initial velocity seeds. We obtained the final calculated density by averaging the time-averaged densities from the three independent production runs, which are reported in **Table S3**. We also estimated the uncertainty in the calculated density using the standard deviation among the three independent runs. Importantly, the predicted densities by MACE-MD show good agreement with experimental values [1] over the temperature range considered, with the relative deviations being 2.50 %, 1.86 %, 0.41 %, and 1.29 % at 1010, 1050, 1100, and 1120 K, respectively. Overall, the mean absolute percentage deviation of calculated densities is ~ 1.52 % compared to experiments, highlighting the generalizability of our optimized MACE model, which did not train on any AIMD data run with the NPT ensemble.

Table S3. Density (g/cc) of molten Li_2CO_3 computed using MACE-MD and compared with experimental values [1].

Temperature (K)	Calculated density (g/cc)	Experimental density (g/cc)
1010	1.87 ± 0.02	1.83
1050	1.84 ± 0.01	1.81
1100	1.78 ± 0.02	1.79
1120	1.76 ± 0.00	1.78

Time evolution in AIMD and MACE-MD

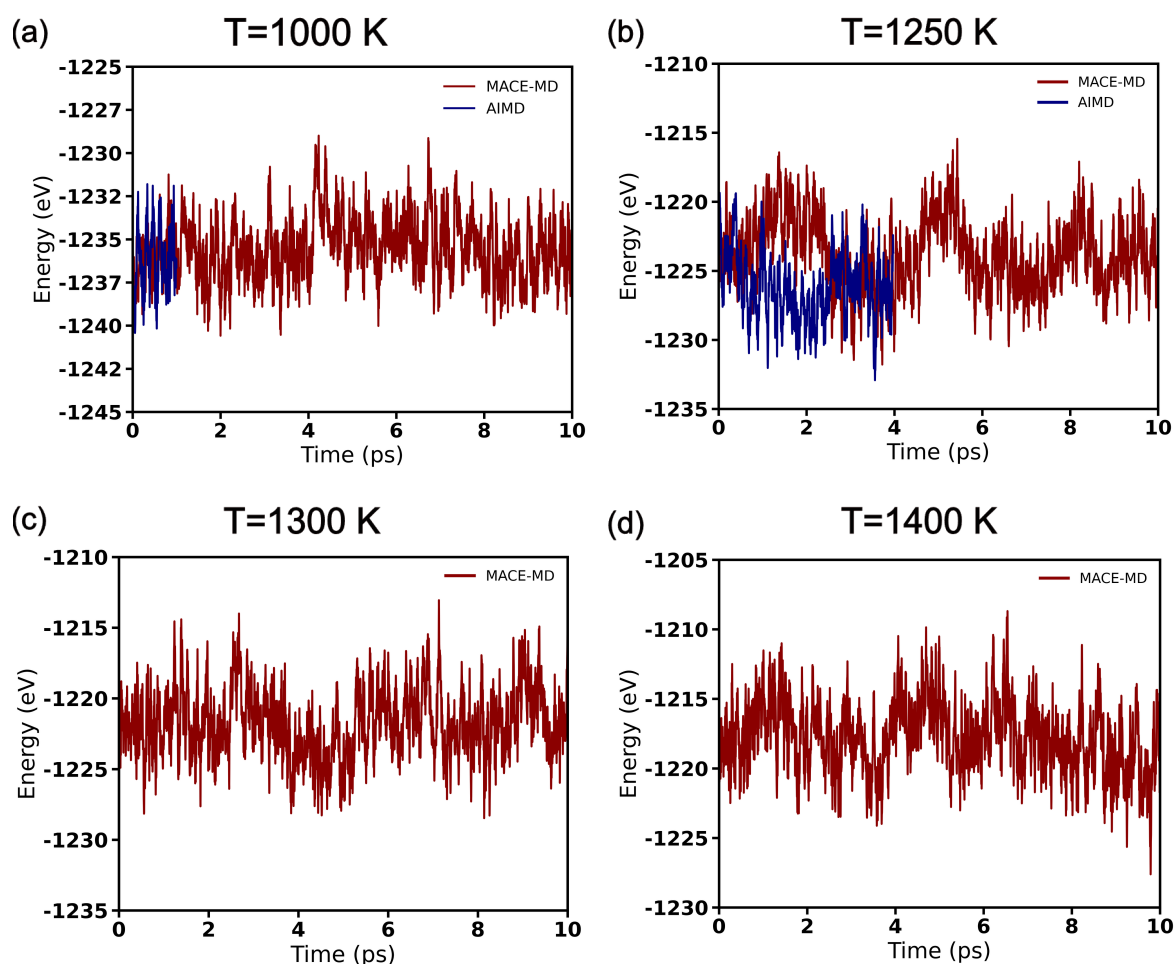


Figure S1. Variation of potential energy of Li_2CO_3 (in eV) calculated from AIMD (blue) and predicted by MACE (red) during the 10 ps equilibration at different temperatures.

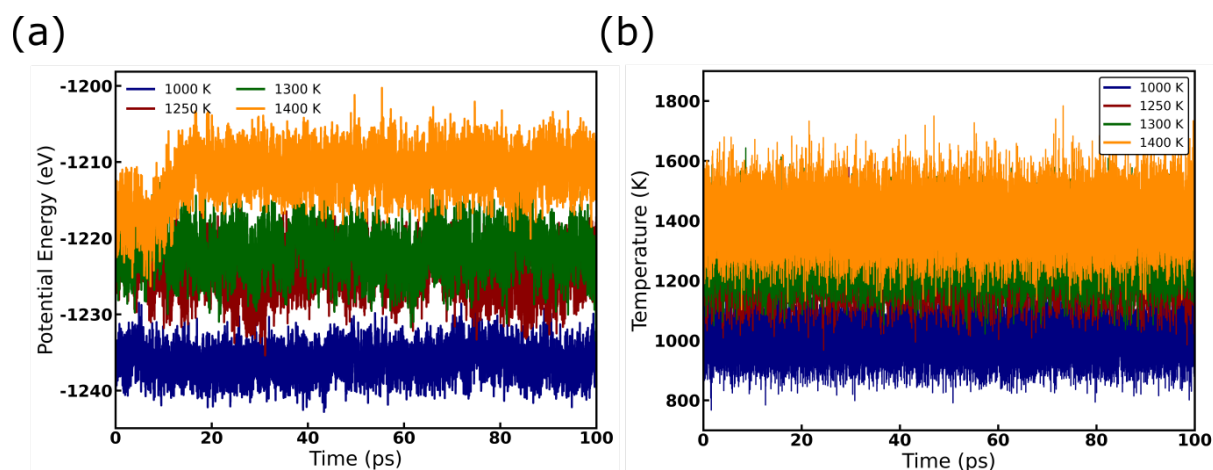


Figure S2. Time evolution of (a) potential energy and (b) temperature during 100 ps MACE-MD simulations of molten Li_2CO_3 at target temperatures of 1000, 1250, 1300, and 1400 K. The trajectories exhibit stable fluctuations around their corresponding equilibrium values after the initial equilibration period.

Table S4. Mean and standard deviation of potential energy (in eV) and temperature (in K), over 100 ps and 10 ps (equilibration) MACE-MD runs.

Temperature (K)	Mean±Standard deviation			
	Potential energy (eV) over 100 ps	Potential energy (eV) over 10 ps	Temperature (K) over 100 ps	Temperature (K) over 10 ps
1400	-1211.62 ± 3.01	-1217.80 ± 2.54	1400.11 ± 82.3	1397.18 ± 82.1
1300	-1221.79 ± 2.57	-1221.78 ± 2.40	1299.76 ± 76.6	1300.77 ± 75.5
1250	-1224.54 ± 2.73	-1223.77 ± 2.58	1249.84 ± 73.9	1251.84 ± 74.2
1000	-1236.22 ± 1.85	-1235.55 ± 1.795	1000.93 ± 59.5	1001.74 ± 60.0

Parity plots

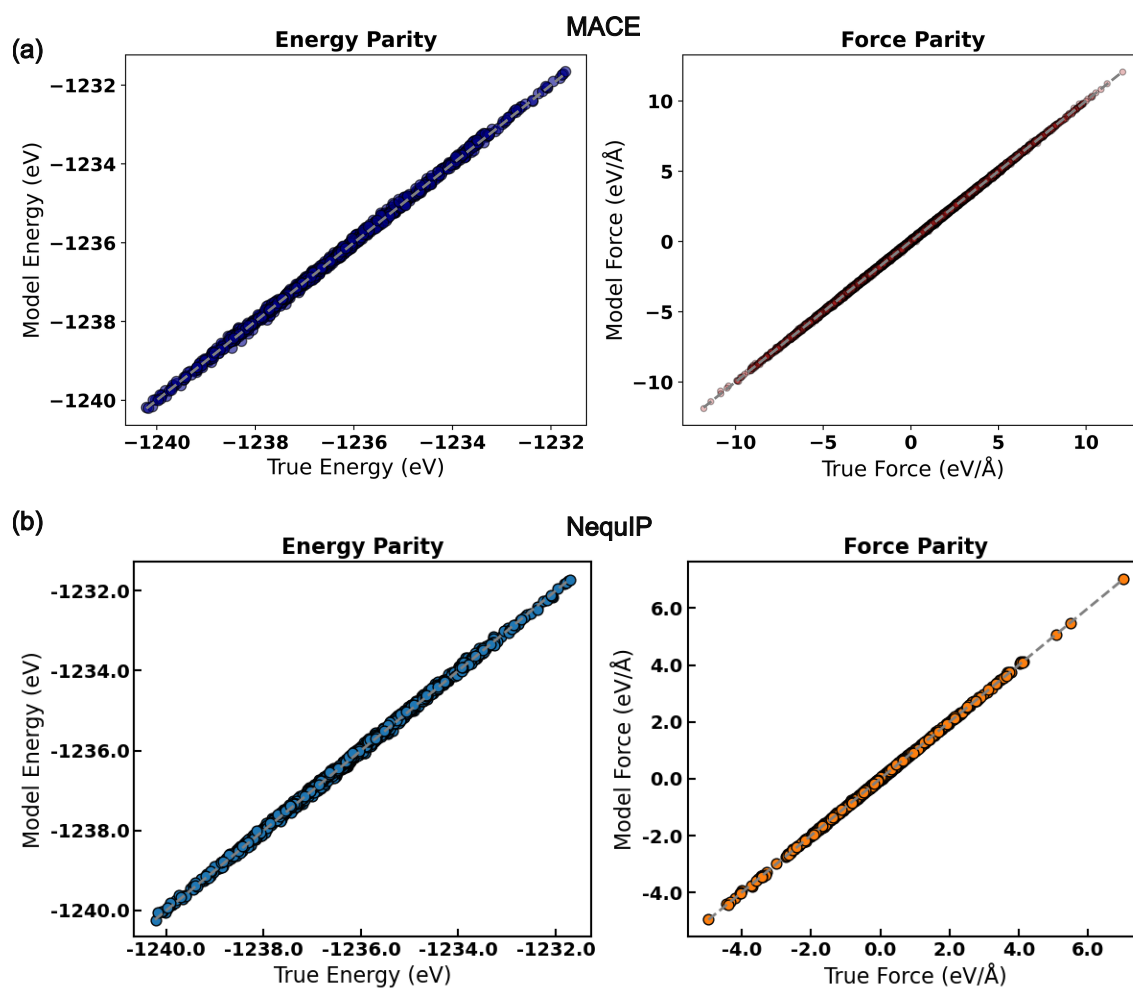


Figure S3. Parity plots for testing the performance of MACE and NequIP models using data at $T = 1000$ K. Model predicted versus ab initio molecular dynamics (AIMD) reference energies (in eV; left panels) and forces (in eV/Å; right panels) for MACE model (panel a) and NequIP (panel b).

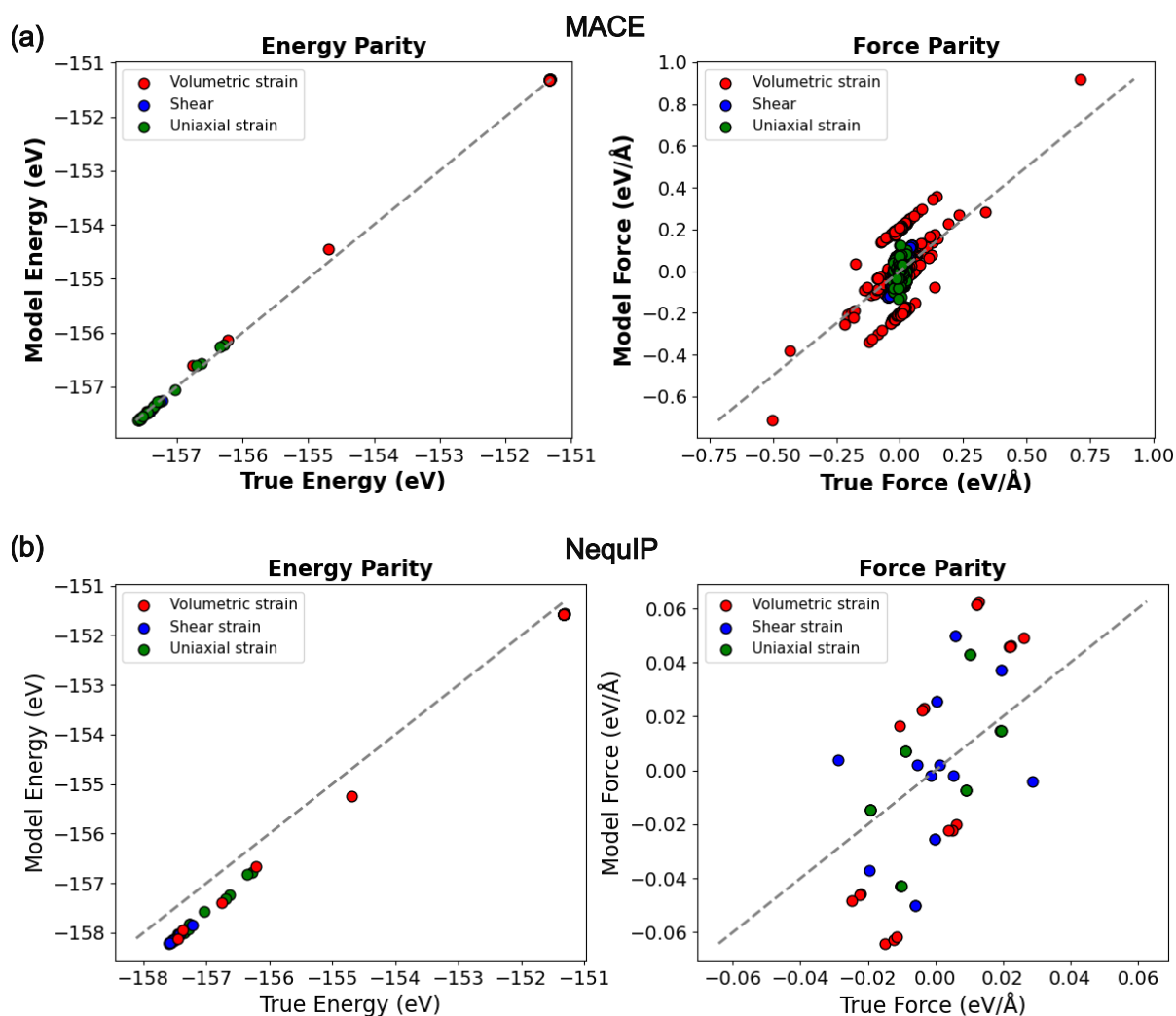


Figure S4. Parity plots for testing the performance of MACE and NequIP models on mechanically strained structures. The testing set includes homogeneous volumetric strain (red points; $\pm 2\%$, $\pm 5\%$, $\pm 10\%$), uniaxial strain (green points; $\pm 2\%$, $\pm 5\%$, $\pm 10\%$), and shear strain (blue points; 2%, 5%, 10%). Model predicted vs. AIMD reference energies (in eV; left panels) and forces (in eV/Å; right panels) for MACE (panel a) and NequIP (panel b).

Radial distribution functions

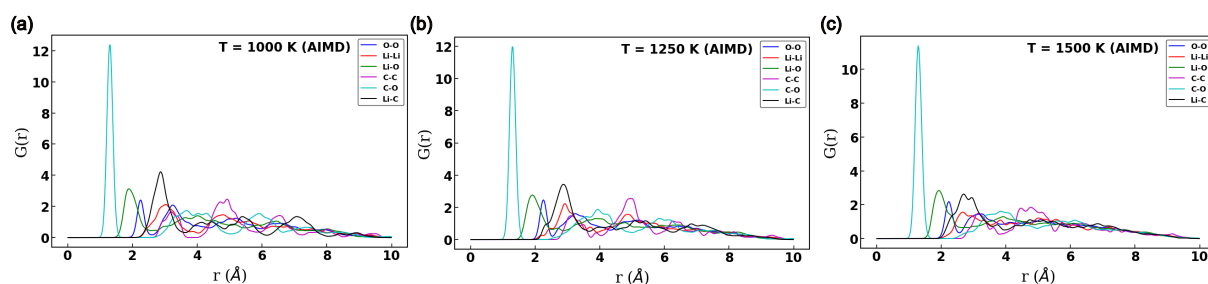


Figure S5. AIMD calculated radial distribution functions (RDFs) of Li_2CO_3 at 1000 K (panel a), 1250 K (panel b), and 1500 K (panel c) after 2 ps equilibration. The O–O, Li–Li, Li–O, C–C, C–O, and Li–C pair correlations are shown.

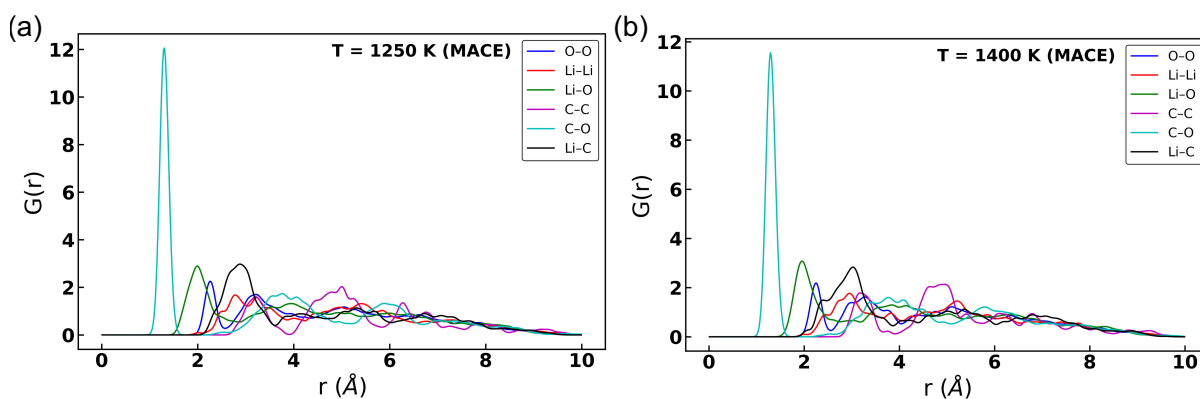


Figure S6. MACE calculated RDFs of Li_2CO_3 at 1250 K (panel a), and 1400 K (panel b) after 10 ps equilibration.

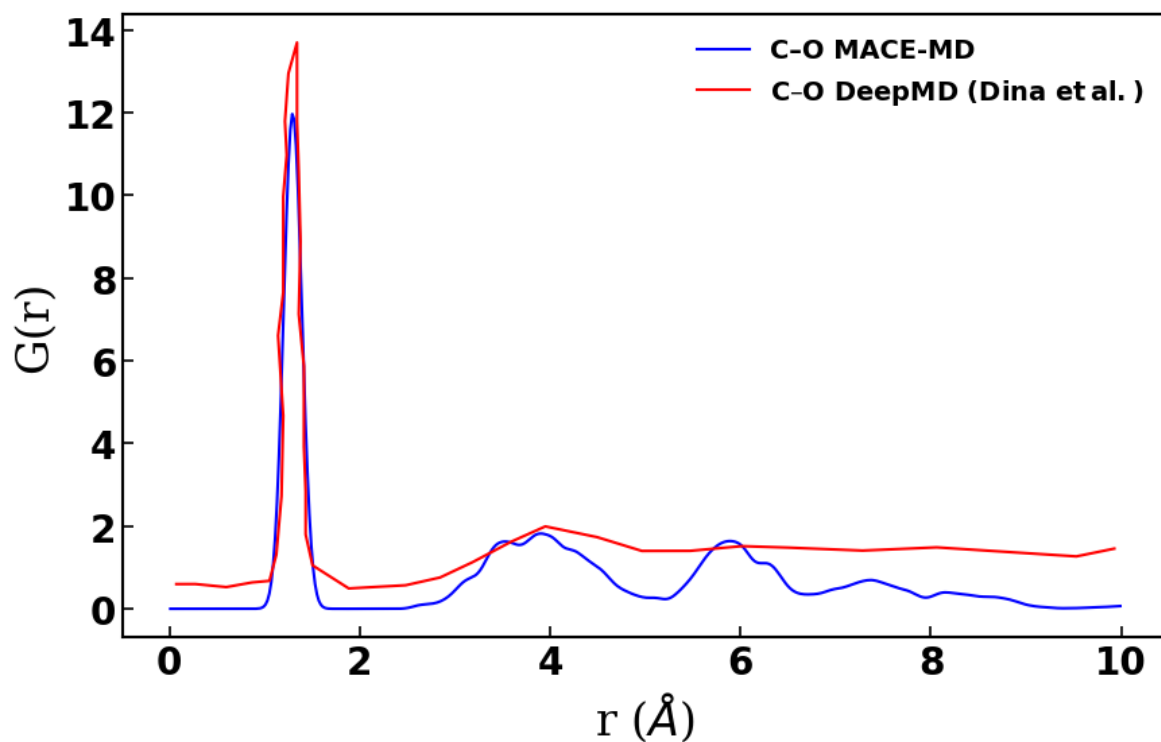


Figure S7. RDF of the C–O bond in Li_2CO_3 . The MACE model at 1000 K is shown in blue, while the deep potential model at 1043.15 K is shown in red [2].

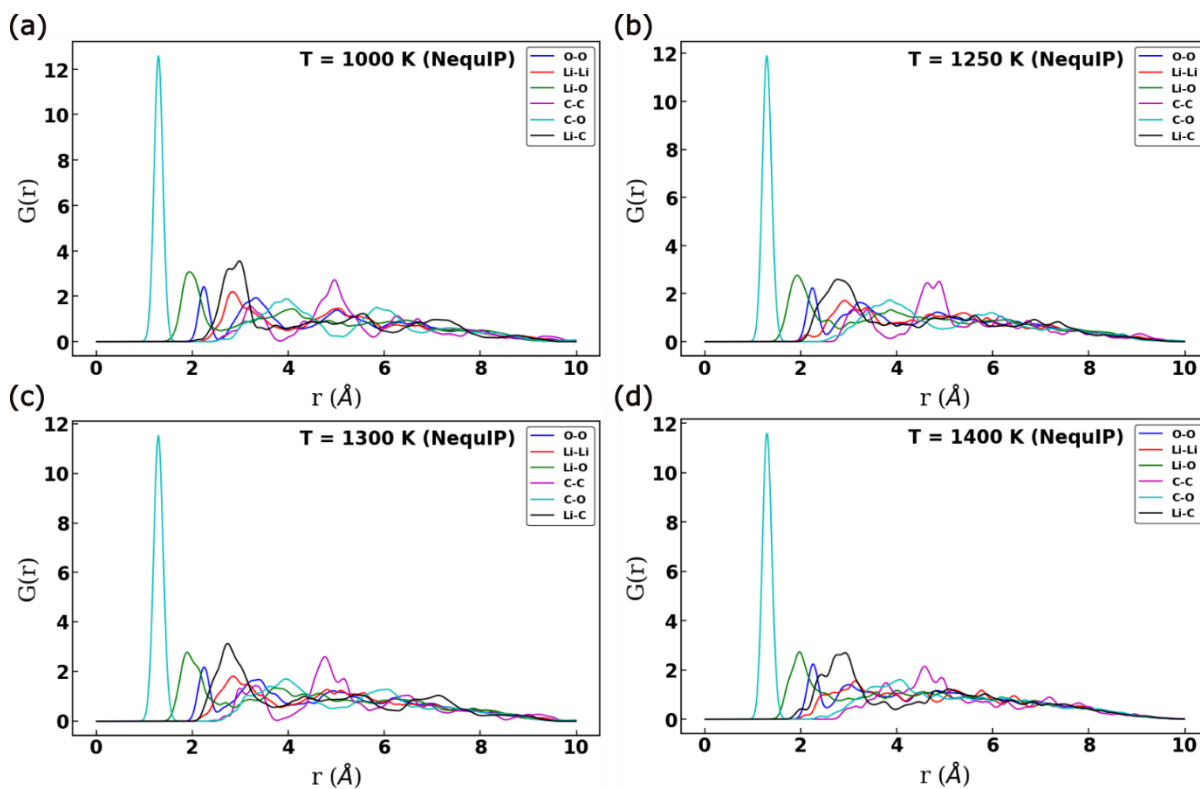


Figure S8. NequIP calculated RDFs of Li_2CO_3 at 1000 K (panel a), 1250 K (panel b), 1300 K (panel c), and 1400 K (panel d) after 10 ps of equilibration.

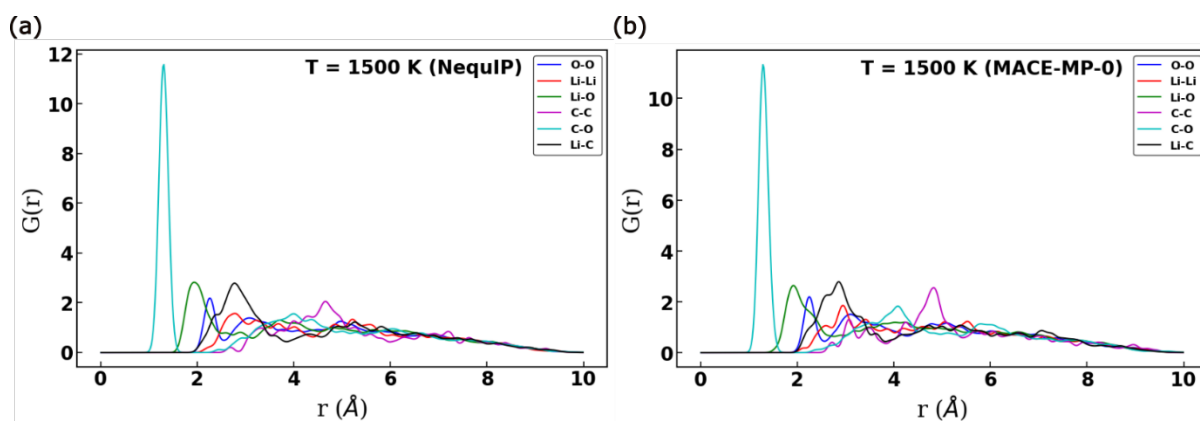


Figure S9. NequIP calculated (panel a) and MACE-MP-0 calculated (foundational potential; panel b) RDFs of Li_2CO_3 at 1500 K after 10 ps equilibration.

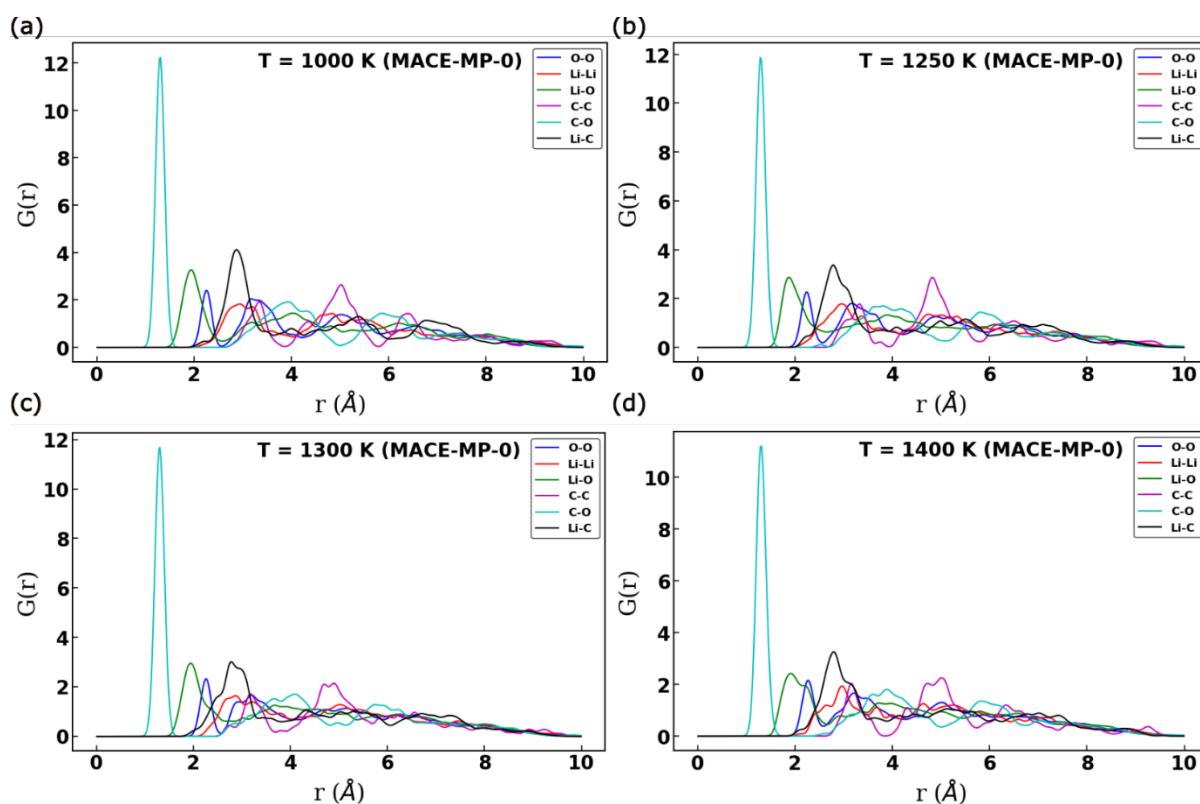


Figure S10. MACE-MP-0 calculated RDFs of Li_2CO_3 at 1000 K (panel a), 1250 K (panel b), 1300 K (panel c), and 1400 K (panel d) after 10 ps equilibration.

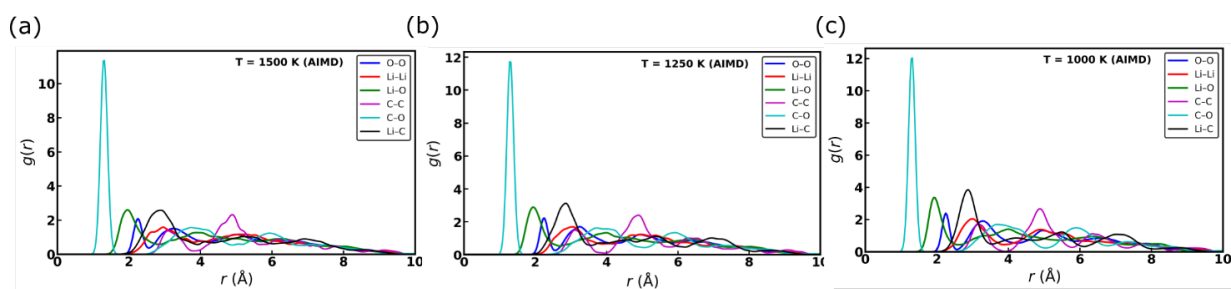


Figure S11. Time-averaged RDFs of molten Li_2CO_3 obtained from AIMD trajectories at (a) 1500 K, (b) 1250 K, and (c) 1000 K. The RDFs were averaged over 20 configurations extracted from AIMD trajectories for each temperature considered, using the vasppy package [3].

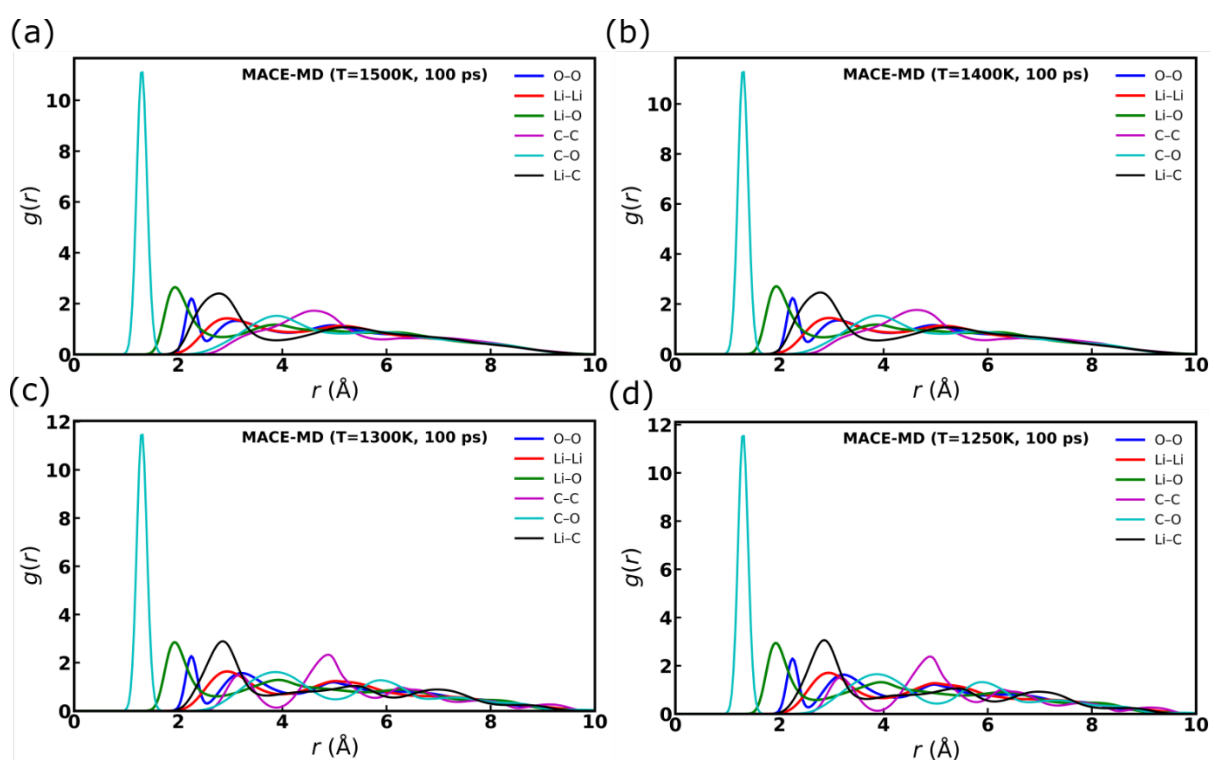


Figure S12. Time-averaged RDFs of molten Li_2CO_3 obtained from 100 ps MACE-MD trajectories at (a) 1500 K, (b) 1400 K, (c) 1300 K, and (d) 1250 K. The RDFs were averaged over 50 configurations sampled from the trajectory for each temperature, using the MDAnalysis package [4].

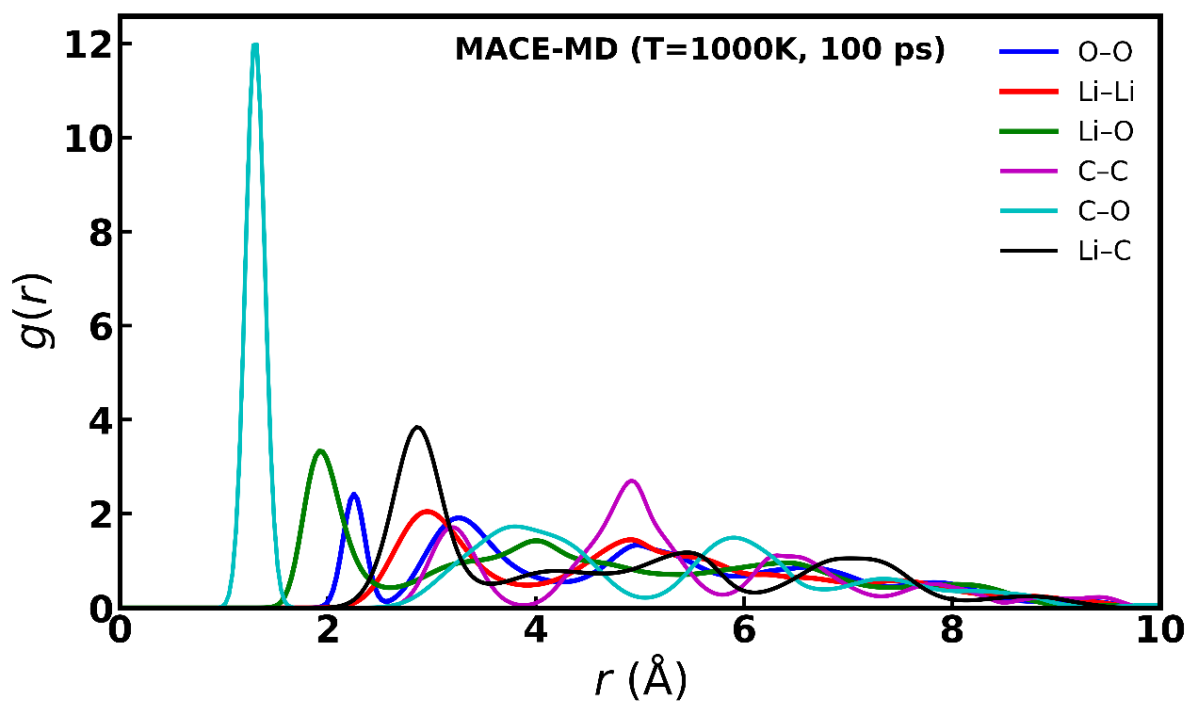


Figure S13. Time-averaged RDFs of molten Li_2CO_3 obtained from 100 ps MACE-MD trajectories at 1000 K. The RDFs were averaged over 50 configurations, using the MDAnalysis package [4].

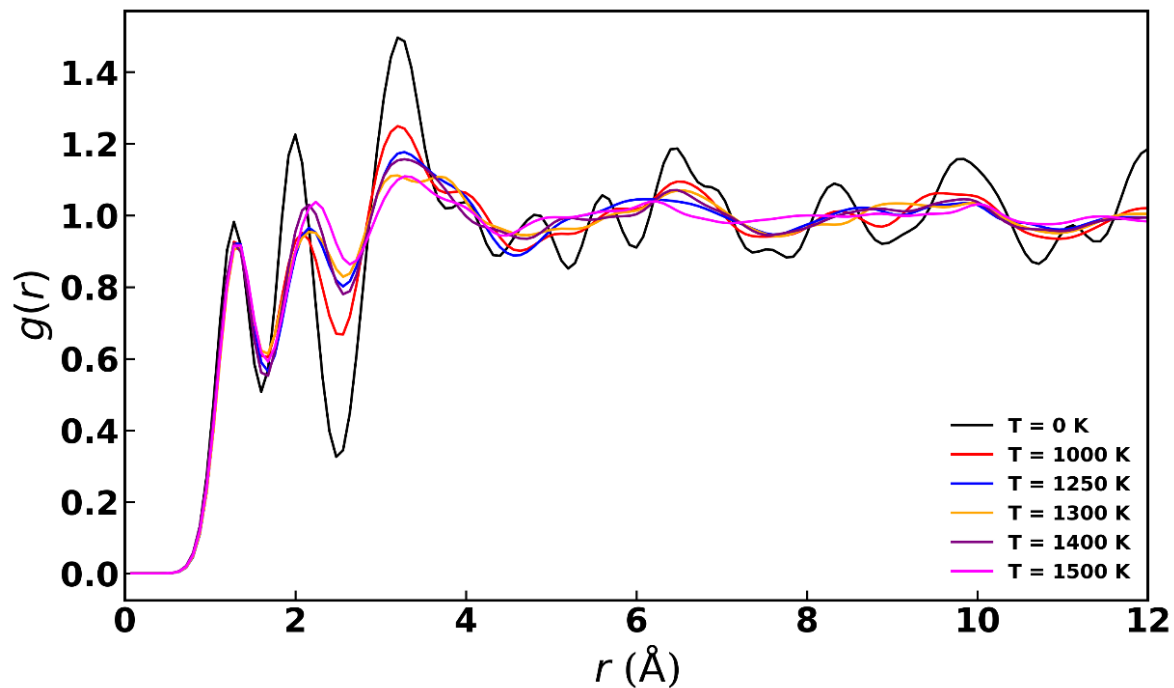


Figure S14. Total RDF ($g(r)$) of Li_2CO_3 calculated at different temperatures, namely 0 K (black), 1000 K (red), 1250 K (blue), 1300 K (orange), 1400 K (purple), and 1500 K (magenta).

Structure factor

Table S5. Molar fraction and atomic form factor ($q = 0$) used to calculate the static structure factor ($S(q)$) for Li_2CO_3 .

Elements	Molar fraction (C_a)	Atomic form factor (f_a) ($q=0$)
Li	0.33	2
C	0.167	6
O	0.5	8

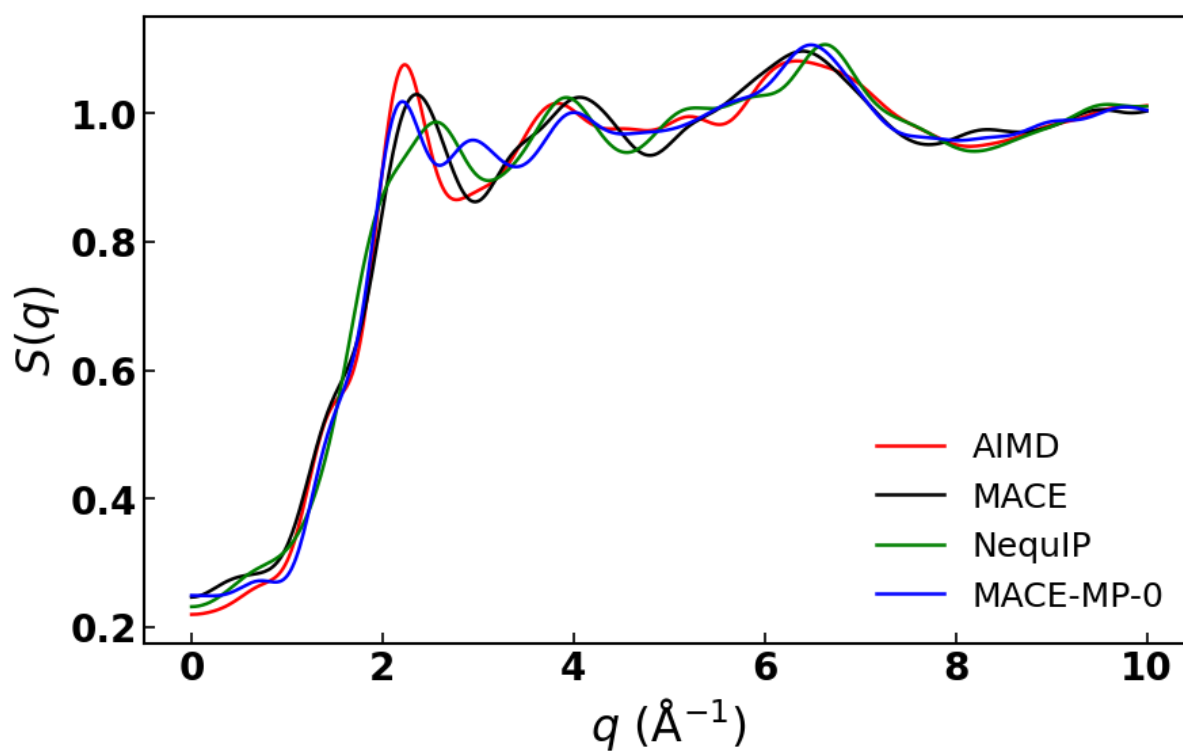


Figure S15. $S(q)$ of Li_2CO_3 as calculated by AIMD (red), MACE (black), NequIP (green), and MACE-MP-0 (blue) at 1500 K after equilibration.

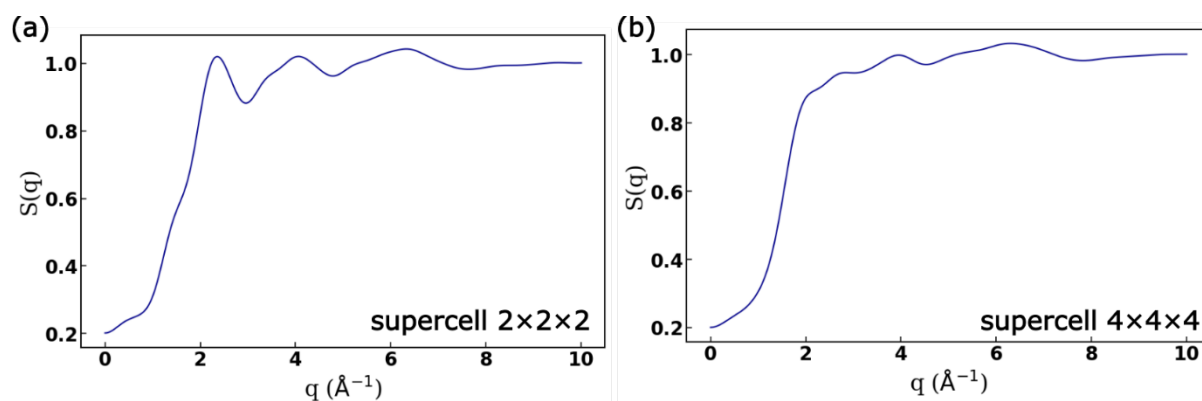


Figure S16. MACE-calculated $S(q)$ of Li_2CO_3 after 10 ps equilibration at 1500 K in a $2 \times 2 \times 2$ supercell and (b) a $4 \times 4 \times 4$ supercell.

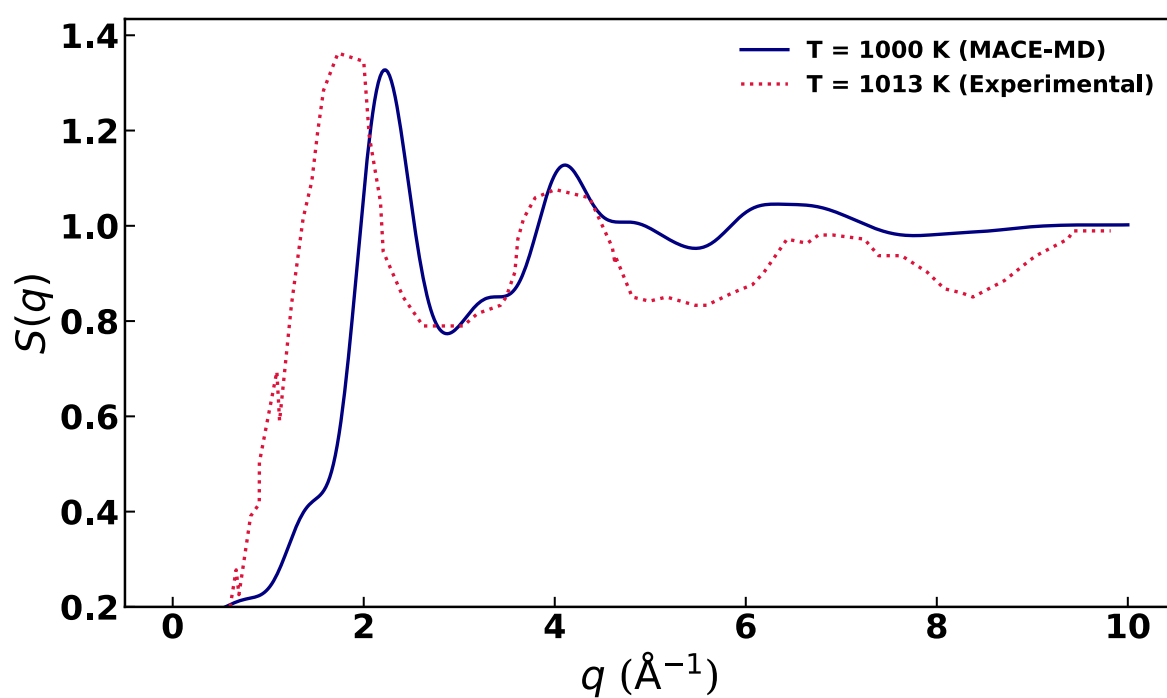


Figure S17. $S(q)$ of Li_2CO_3 , as predicted by MACE at 1000 K (blue solid line) and obtained from experimental neutron diffraction data at 1013 K (red dot line). The experimental data was extrapolated from Ref. [5], as done in Ref. [6].

Mean square displacement trajectories

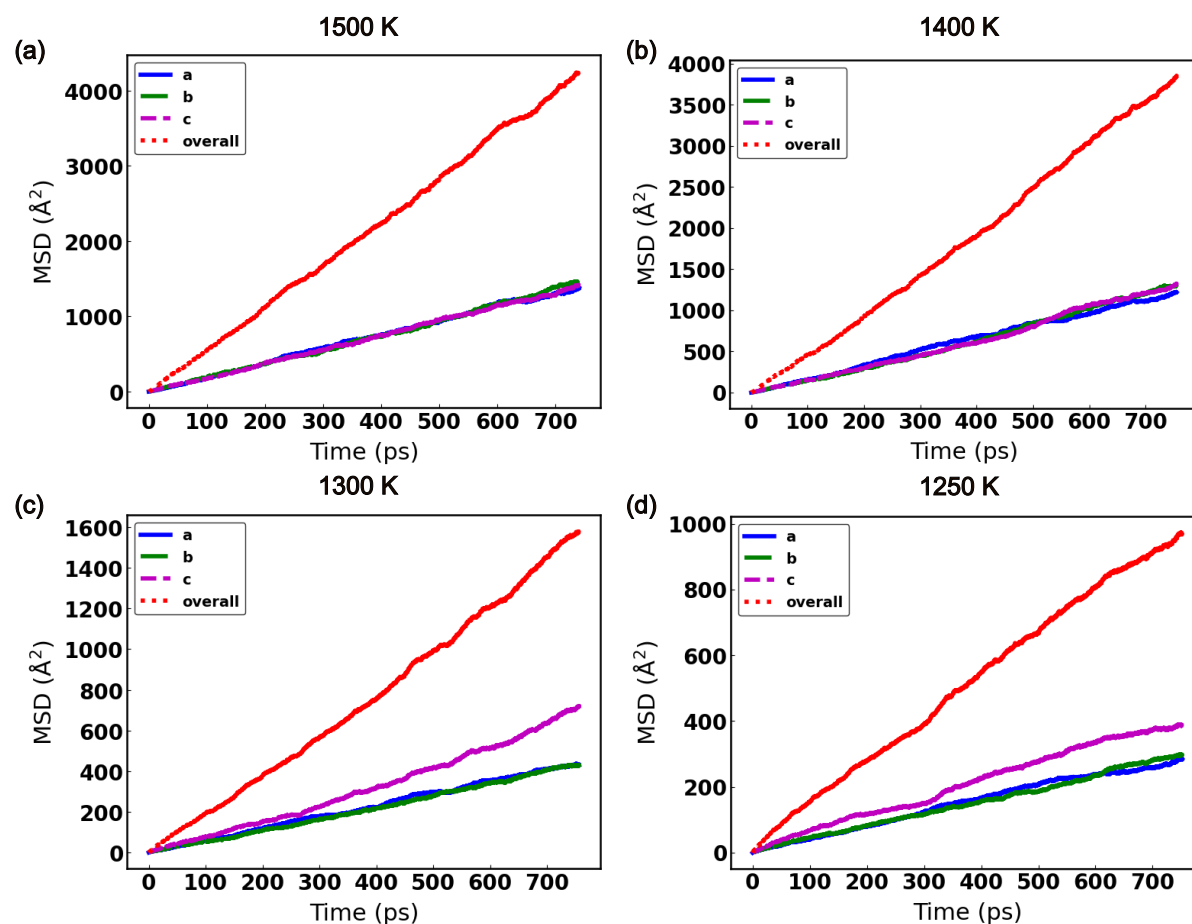


Figure S18. MACE-calculated mean squared displacement (MSD) vs. time (t) curves in $4\times4\times4$ Li_2CO_3 supercells over 700 ps at (a) 1500 K, (b) 1400 K, (c) 1300 K, and (d) 1250 K. Blue, green, and purple lines in each panel represent MSD along the a , b , and c lattice directions, respectively, within the Li_2CO_3 structure, with the red lines indicating the overall MSD.

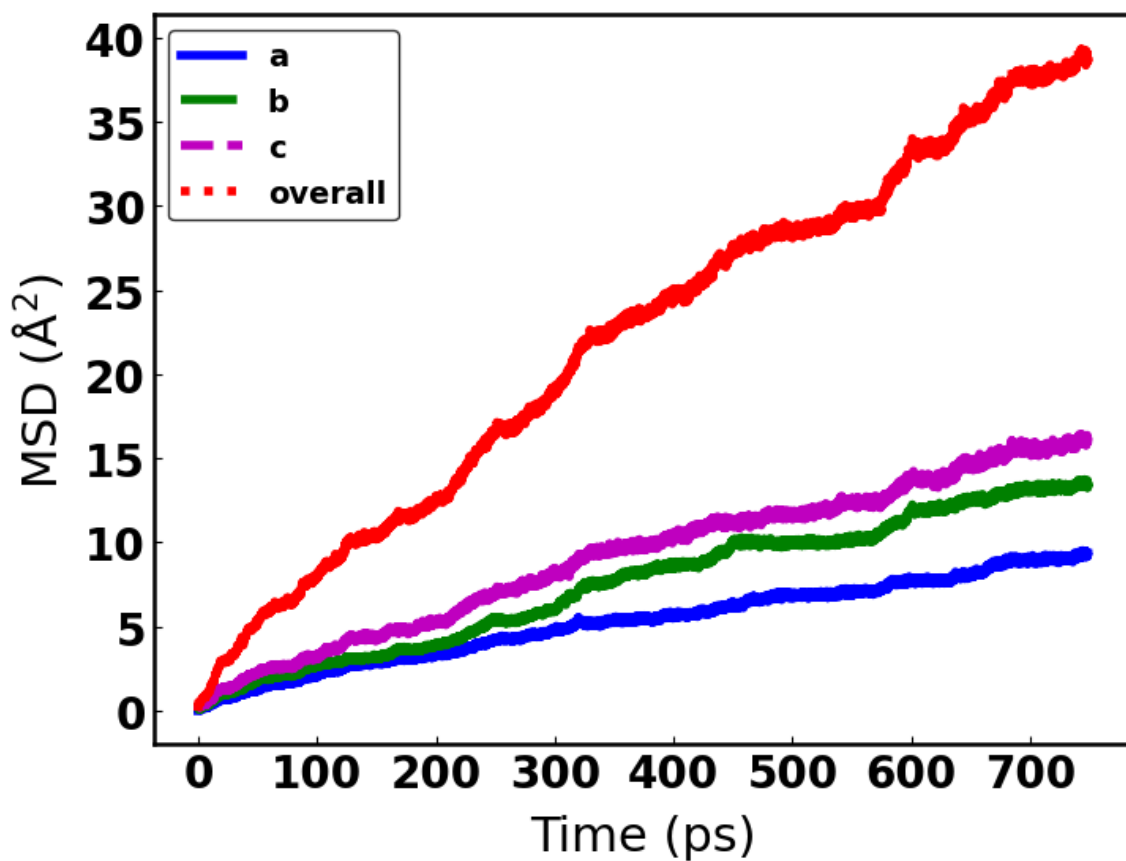


Figure S19. MACE-calculated MSD vs. t curves in $4 \times 4 \times 4$ Li_2CO_3 supercell over 700 ps at 1000 K. Notations used in each panel are identical to **Figure S18**.

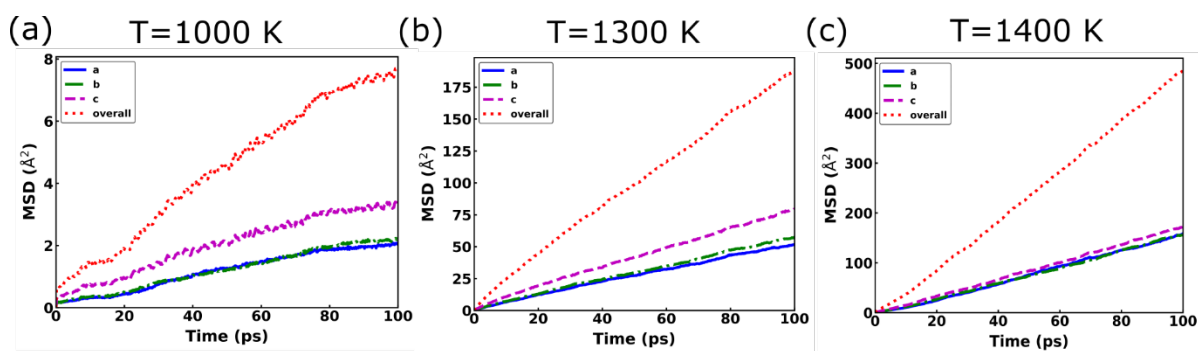


Figure S20. MACE-calculated MSD vs. t curves in $6 \times 6 \times 6$ Li_2CO_3 supercells over 100 ps at (a) 1000 K, (b) 1300 K, and (c) 1400 K. Notations used are identical to **Figure S18**.

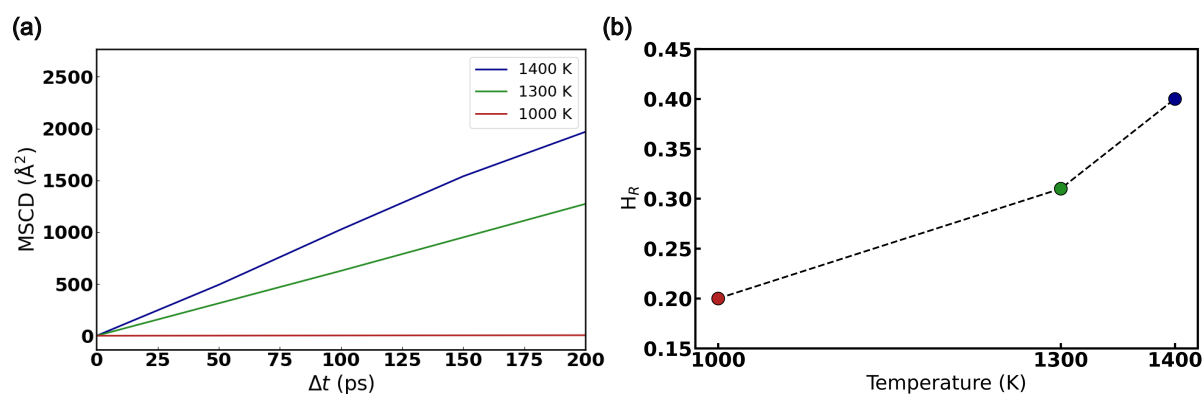


Figure S21. a) MACE-calculated mean squared centre-of-mass displacement (MSCD) as a function of time step size (Δt) for molten Li_2CO_3 , obtained from simulations over 700 ps, at 1400 K (blue), 1300 K (green) and 1000 K (red). (b) Variation of calculated Haven's ratio (H_R) with temperature, with color notations being identical to panel a.

Viscosity and diffusivity

Table S6. Calculated viscosity (cP) for molten Li_2CO_3 .

Temperature (K)	Viscosity (cP)
1300	2.09 ± 1.02
1200	2.20 ± 0.49
1100	5.80 ± 0.70
1050	6.05 ± 0.64
1000	7.35 ± 0.16

Table S7. Temperature-dependent Li-ion tracer diffusivity and its standard deviation ($D^* \pm \sigma$) in molten Li_2CO_3 calculated from raw MSD data (i.e., MSD vs t) for a $4 \times 4 \times 4$ supercell.

Temperature (K)	Li-ion diffusivity (cm^2/s)
1500	$(9.48 \pm 0.61) \times 10^{-5}$
1400	$(8.51 \pm 1.30) \times 10^{-5}$
1300	$(3.13 \pm 0.18) \times 10^{-5}$
1250	$(2.06 \pm 0.33) \times 10^{-5}$
1000	$(8.01 \pm 2.34) \times 10^{-7}$

Table S8. Temperature-dependent tracer diffusivity and its standard deviation ($D^* \pm \sigma$) in molten Li_2CO_3 calculated from raw MSD data (i.e., MSD vs t) for a $6 \times 6 \times 6$ supercell. The right column reports the percentage deviation in calculated D^* between $6 \times 6 \times 6$ and $4 \times 4 \times 4$ supercells.

Temperature (K)	Li-ion diffusivity (cm^2/s)	$\frac{D^*(6 \times 6 \times 6) - D^*(4 \times 4 \times 4)}{D^*(4 \times 4 \times 4)} \times 100$
1400	$(8.31 \pm 0.28) \times 10^{-5}$	2.35
1300	$(3.00 \pm 0.21) \times 10^{-5}$	4.15
1000	$(1.20 \pm 0.05) \times 10^{-6}$	49.80

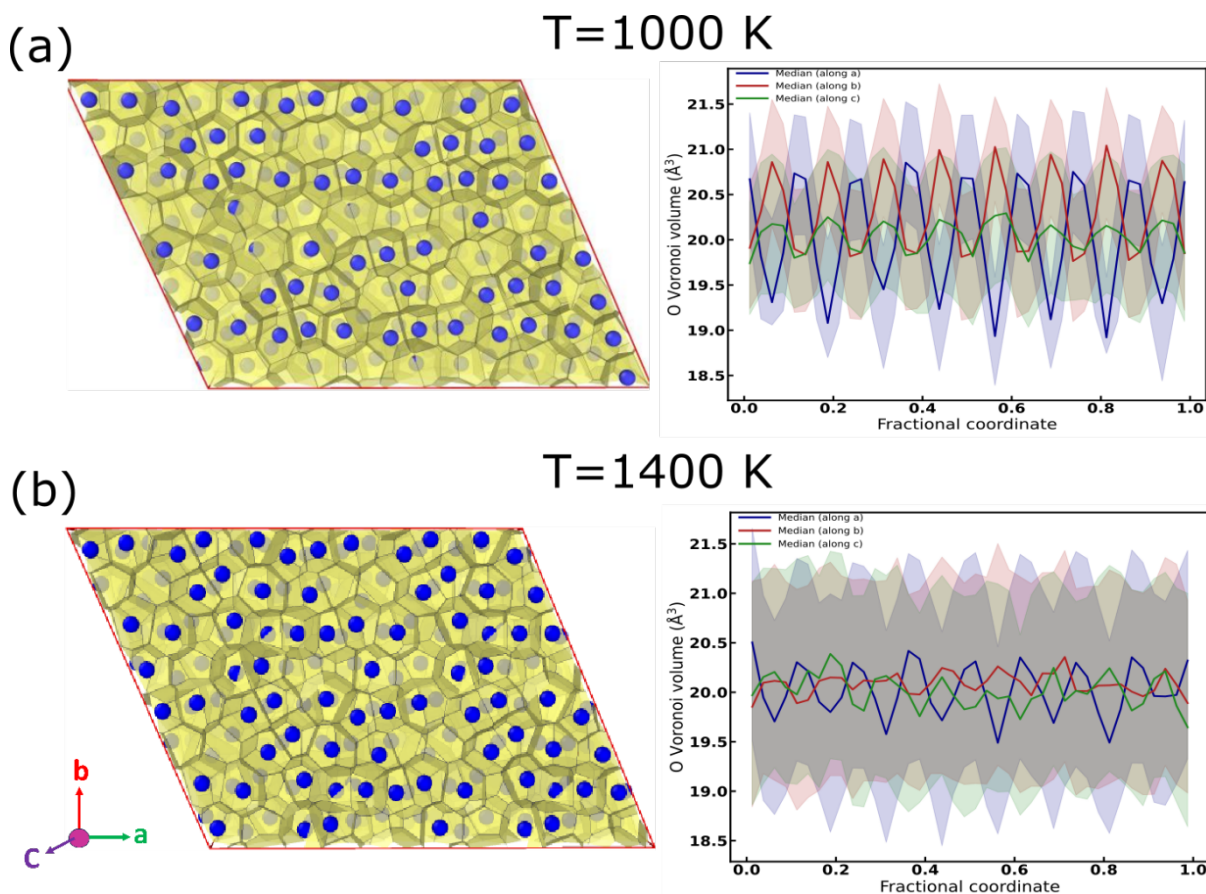


Figure S22. (a) Representative snapshots of molten Li_2CO_3 from MACE-calculated molecular dynamics (MD) trajectories at 1000 K (panel a) and 1400 K (panel b), showing the O-centered Voronoi cages (yellow) and Li ions (blue). Voronoi tessellation is performed using O atoms as seeds to capture the transient carbonate cages through which Li ions migrate (left panels). Direction-resolved O-centered Voronoi cage volumes are plotted as a function of the fractional coordinate along the crystallographic a , b , and c axes (right panels). Solid curves denote the median cage volumes while the shaded regions represent the interquartile range (25–75%), indicating the magnitude of cage-volume fluctuations sampled over the trajectories. Different colors indicate different directions within the structure.

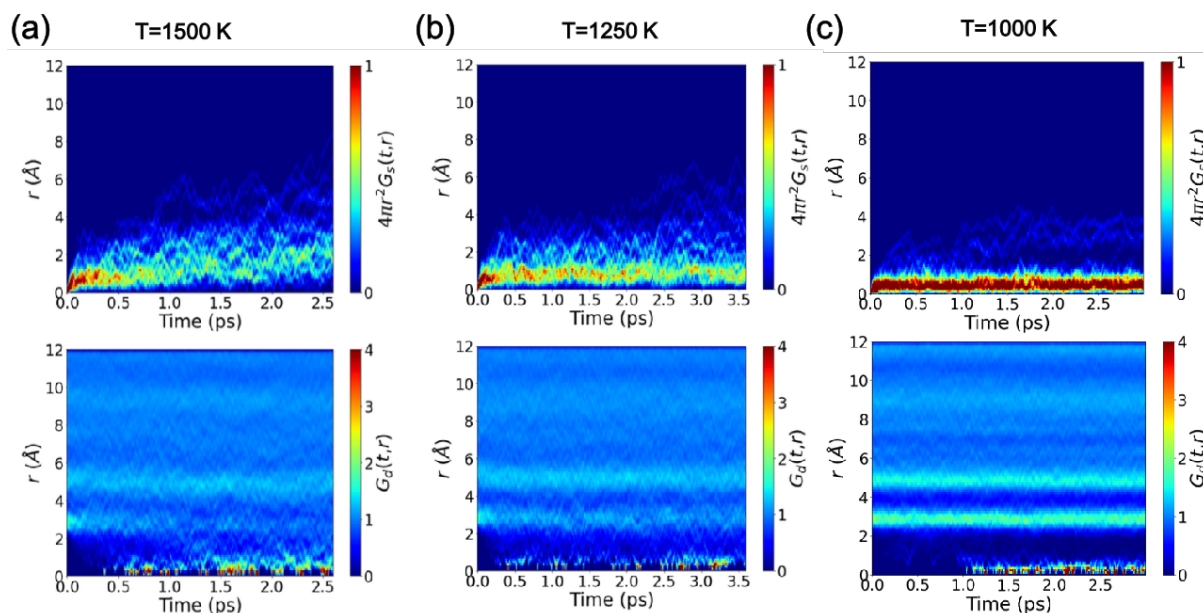


Figure S23. Temperature-dependent ion dynamics in molten Li_2CO_3 at 1500 K (panel a), 1250 K (panel b), and 1000 K (panel c) from the self ($G_s(r, t)$; top row) and distinct ($G_d(r, t)$; bottom row) parts of the van Hove correlation function. Dark blue regions indicate a low probability of finding a different atom at distance r from the reference atom's initial position after time t , while bright red regions mark the most probable positions of neighboring atoms relative to the reference ion.

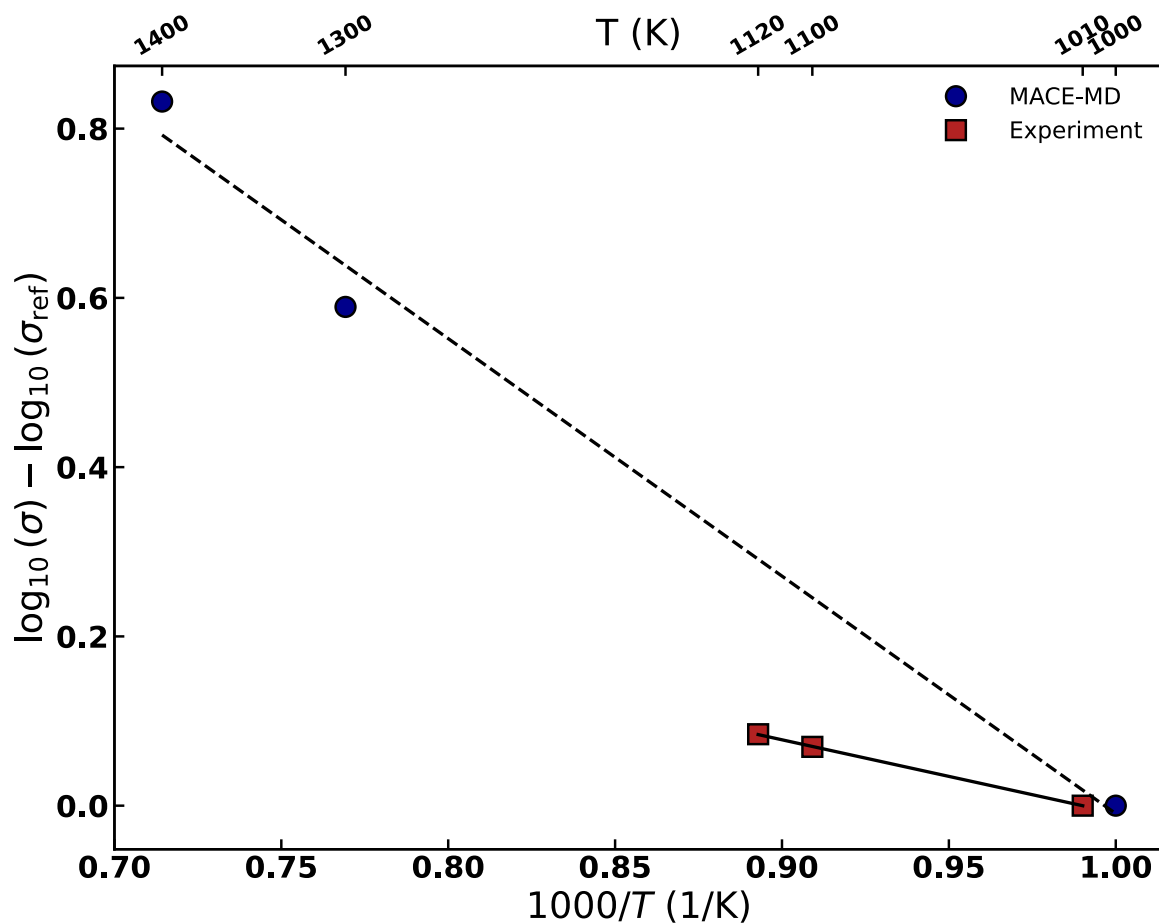


Figure S24. Arrhenius fit of the ionic conductivity of molten Li_2CO_3 , plotted as $\log_{10}(\sigma) - \log_{10}(\sigma_{ref})$ versus $1000/T$. MACE-MD results (blue circles) are compared against experimental conductivity data (red squares). Linear fits yield activation energies (E_a) with MACE = 0.557 eV ($R^2 = 0.99$) and E_a with experiments = 0.172 eV ($R^2 = 0.99$). Temperatures corresponding to each data point are indicated on the top x -axis. Conductivity values are vertically shifted by subtracting $\log_{10}(\sigma_{ref})$, where σ_{ref} corresponds to 1000 K (for MACE-MD) and 1010 K (for experiments), to enable comparison of Arrhenius slopes. The experimental values are reported in [7].

Accuracy comparison

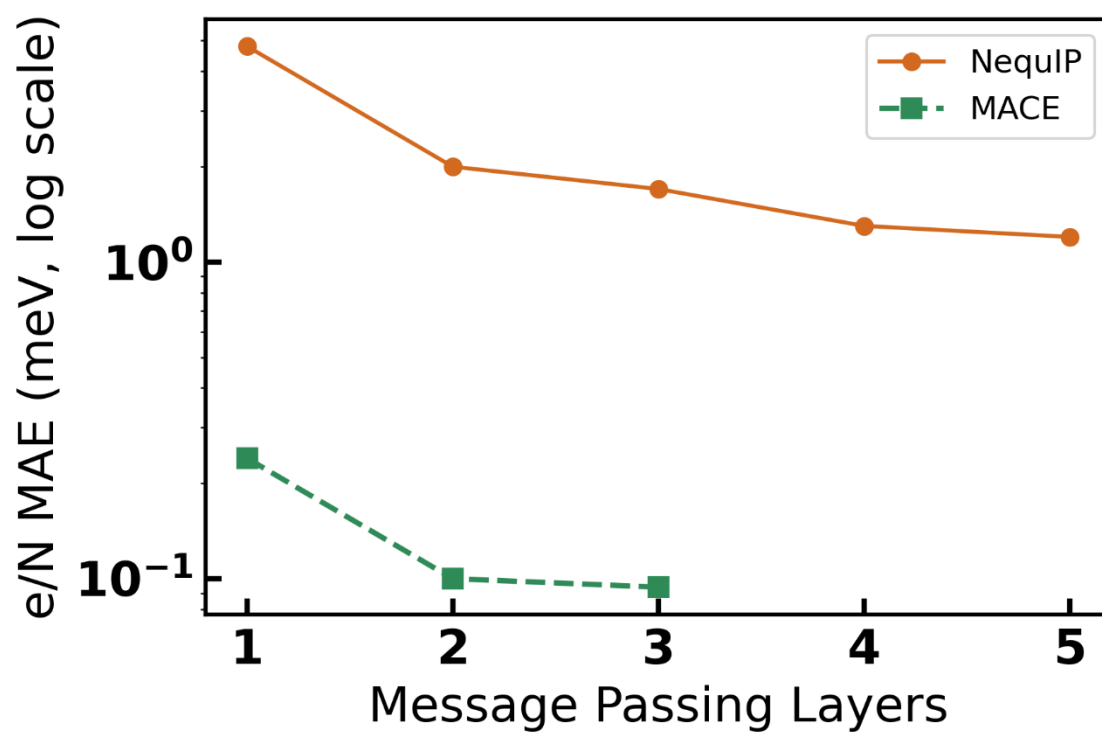


Figure S25. Comparison of accuracy on energy predictions, per the mean absolute error (MAE in meV) metric between MACE (green) and NequIP (orange). MACE achieves higher accuracy with fewer message passing layers compared to NequIP.

Computational speed benchmarking

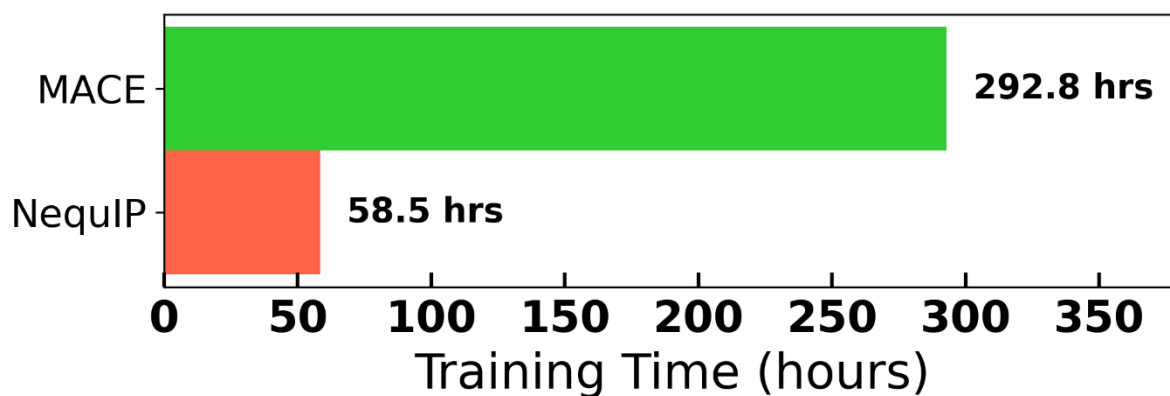


Figure S26. Comparative benchmark of training times for MACE (green) and NequIP (red) on our datasets using a single NVIDIA V100 GPU.

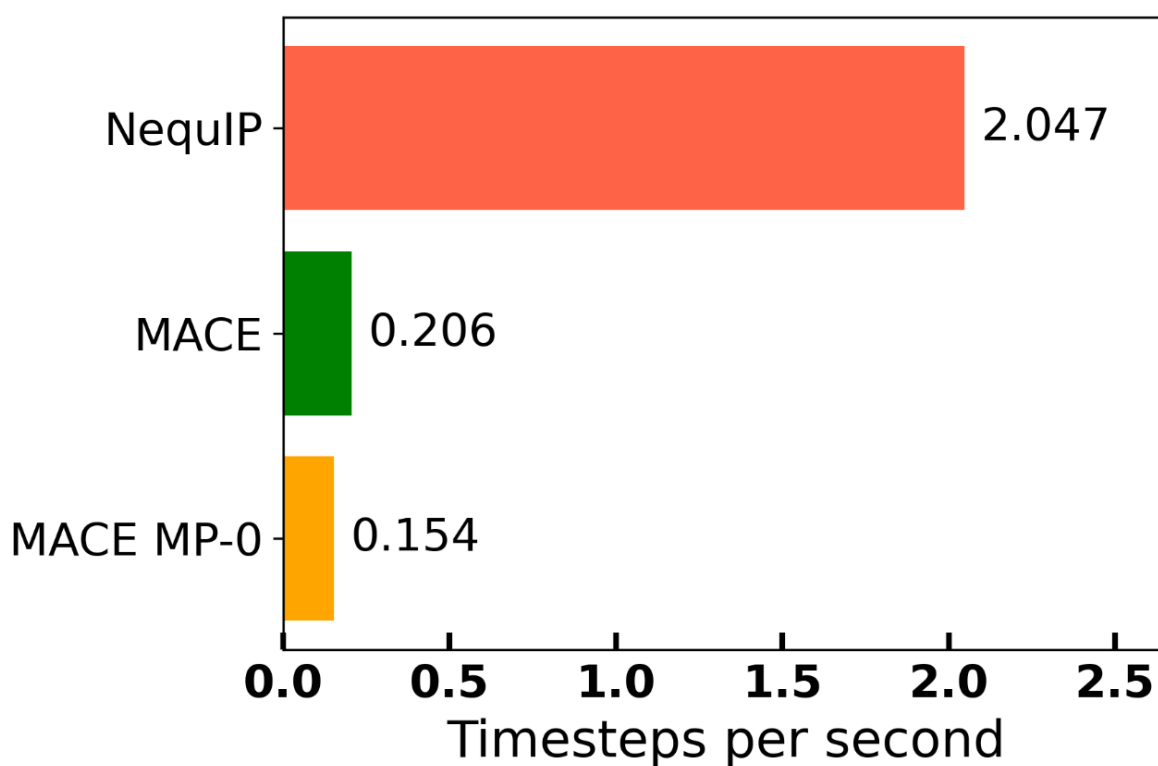


Figure S27. CPU-based MD simulation speed comparison for a 192-atom system using 16 threads on a single CPU core for NequIP (red), MACE (green), and MACE-MP-0 (orange). The calculations were performed using one MPI process and 16 CPU threads on a single compute node equipped with Intel® core i7 10th generation CPU without cuEquivariance. All models were executed using their PyTorch implementation with double precision, namely mace-torch (for MACE and MACE-MP-0) and PyTorch-based v0.6.1 for NequIP.

References:

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