Teaching Potentials to See the Interface: Machine-Learned Molecular Dynamics Across Solid Electrolyte Contacts

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Solid–solid interfaces govern the performance of all-solid-state batteries, which offer higher safety and energy density than traditional lithium-ion cells. Among solid electrolytes, halides and sulfides stand out due to their high ionic conductivity and ease of processing, but neither is stable against both electrodes. Stacking them, with halide (e.g., Li_3InCl_6) facing the cathode and sulfide (e.g., Li_6PS_5Cl) facing the anode, improves high-voltage resistance [1]. However, this internal interface is thermodynamically unstable [2, 3], and how the interphase forms or Li transport occurs remain unclear. Ab initio molecular dynamics (AIMD) captures the initial reaction steps but is not sufficient to study interphase evolution. We address this gap with a machine-learned interatomic potential (MLIP), investigating whether interfacial data must be explicitly included in training, and showing that the most commonly used validation practice fails to detect models that do not transfer across temperatures.

A MACE foundation model was fine-tuned through a committee-based active learning workflow, in which frames with the largest committee disagreement were labelled with DFT and added to the training set. Candidate configurations were selected from AIMD trajectories of crystalline bulk phases, surfaces, and explicit sulfide/halide interfaces (Figure 1). To test whether the computationally expensive interface AIMD is required, an additional dataset was created to replace explicit interfaces with amorphous Li–P–S–Cl–In mixtures and crystalline structures containing new environments that occur at the interface (In_2S_3, InP, $InPS_4$) (Figure 1).

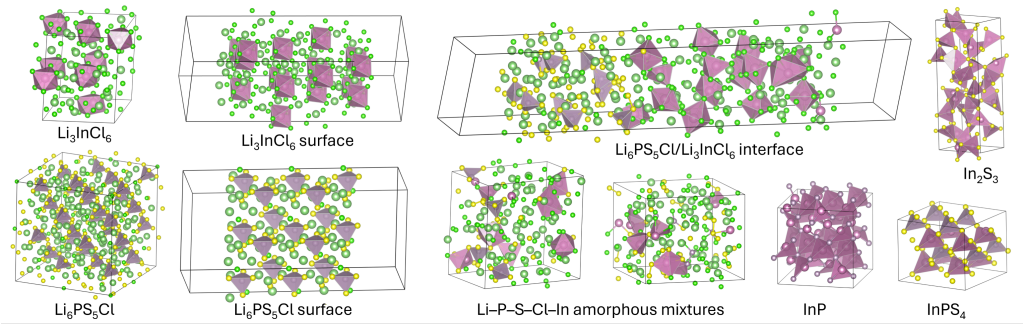

Figure 1: Bulk, surface, and interface configurations that were generated for MLIP training.

On held-out interface configurations, fine-tuning with explicit interfaces significantly reduced the energy and force RMSEs compared to the foundation model, while fine-tuning without interfaces improved only the energy RMSE. In MLIP-MD of the Li_6PS_5Cl/Li_3InCl_6 interface at 500 K, the foundation model produced an unphysical Li distribution, distorted radial distribution functions, and overestimated ionic mobilities, whereas both fine-tuned models agreed well with AIMD. However, in Arrhenius analysis at 350-550 K, the model trained with explicit interfaces underestimated the activation energy of Li diffusion. Surprisingly, the MLIP trained without interfaces matched the activation energy and AIMD diffusivities more closely. This is likely caused by the limited temperature coverage of the interface AIMD in the training set, which contained only 300 K and 1000 K trajectories, whereas the bulk and amorphous structures representing interfacial environments were sampled over a broader temperature range.

Our results indicate that explicit interface data can be replaced by computationally cheaper crystalline and amorphous structures representing interfacial environments. Moreover, MLIP validation requires testing target properties across multiple temperatures rather than relying on energy and force errors or a single-temperature comparison.

References

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