Ion Diffusion in Super-ionic Conductors

Evaluating Machine-Learned Potentials for Quantifying Diffusional Properties

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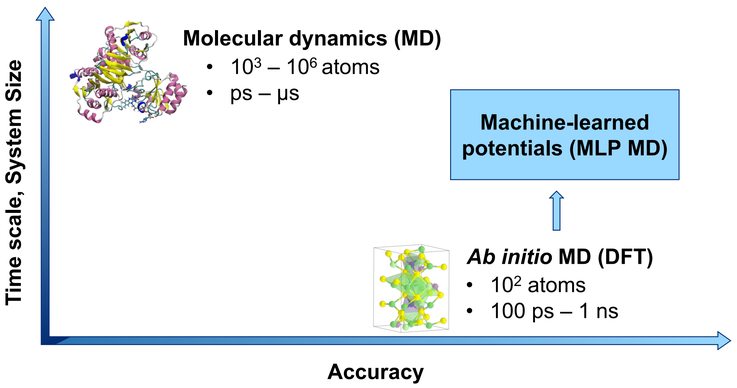
Abstract

Machine-learned potentials (MLPs) are a simulation method that utilize machine learning models to predict the energies and forces of atomistic structures. MLPs promise similar accuracy with a significant decrease in computational cost compared to well established *ab initio* molecular dynamics (AIMD) simulations used to reproduce physical phenomena. We evaluated the MLP M3GNet, a universal interatomic potential trained on structural relaxations from Materials Project. This study examines $Li_{10}GeP_2S_{12}$ (LGPS), $Li_9P_3S_{12}$ (LPS), $Li_{11}AlP_2S_{12}$ (LAPS), and lithium garnet $Li_7La_3Zr_2O_{12}$ (LLZO) and finds that there are discrepancies between M3GNet and AIMD for quantifying diffusional properties in super-ionic conductors.

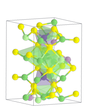
Comparison of Simulation Methods

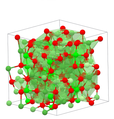


Ab initio molecular dynamics (AIMD) simulations utilizing density functional theory (DFT) calculations are widely used for studying diffusion mechanisms of materials but have computational limitations. Molecular dynamics simulations using machine-learned potentials address these limitations while promising similar accuracy.

Methods

lattice or atom position input → *calculate interactions* → *calculate energies and forces* → *reproduce physical phenomena (e.g. diffusion)*



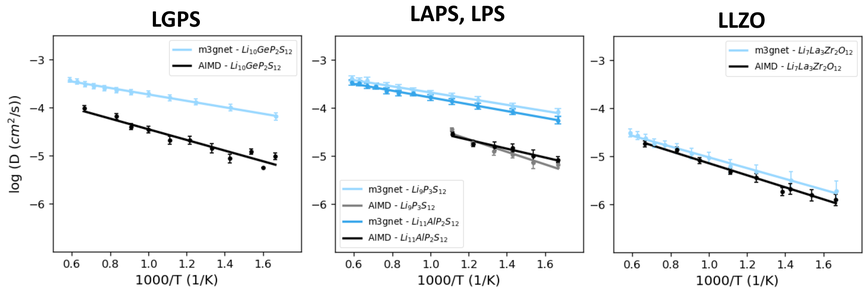


goal: evaluate M3GNet, a universal machine-learned interatomic potential → impact: if accurate, M3GNet could significantly reduce computational cost, accelerating materials discovery

motivation: understanding the diffusion mechanism in super-ionic conductors such LGPS and LLZO is key to improving their performance and gaining insight into designing new solid-state electrolytes

Results

MLP MD simulations were performed at a range of temperatures (600K – 1700K) to obtain diffusivity $\boldsymbol{D}$ and activation energy $\boldsymbol{E_a}$ from the Arrhenius relation: $\boldsymbol{D = D_0(-\frac{E_a}{kT})}$

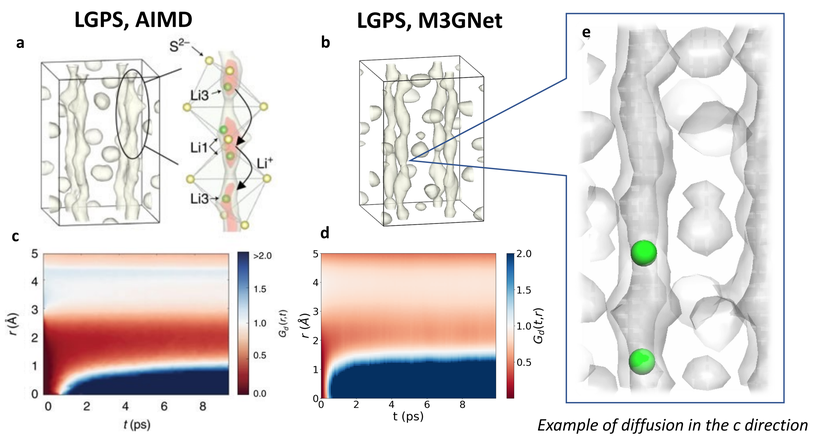


Arrhenius plot of Li^+ diffusivity D as a function of temperature T in $Li_{10}GeP_2S_{12}$ (LGPS), $Li_9P_3S_{12}$ (LPS), $Li_{11}AlP_2S_{12}$ (LAPS), and $Li_7La_3Zr_2O_{12}$ (LLZO) from AIMD and MLP MD simulations.

Table 1: Activation Energy for LGPS, LPS, LAPS, LLZO

	E_a AIMD (eV)	E_a m3gnet (eV)
$Li_{11}AlP_2S_{12}$	0.18 ± 0.06	0.14 ± 0.01
$Li_{10}GeP_2S_{12}$	0.23 ± 0.03	0.14 ± 0.01
$Li_9P_3S_{12}$	0.26 ± 0.09	0.13 ± 0.01
cubic-$Li_7La_3Zr_2O_{12}$	0.25 ± 0.02	0.23 ± 0.01

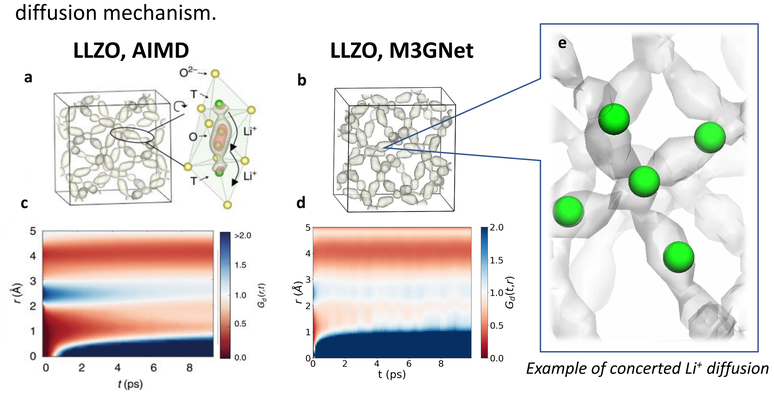
M3GNet achieves an ab initio level of accuracy in modeling diffusivity and E_a for LLZO. However, LGPS, LPS, and LAPS have different E_a values when comparing M3GNet to AIMD simulations. A possible explanation for these differences can be found in the diffusion mechanism. The aliovalent cation substitutions of Al^{3+} and P^{5+} for Ge^{4+} suggest that Li^+ concentration has little effect on E_a and diffusivity, which is consistent with AIMD results.



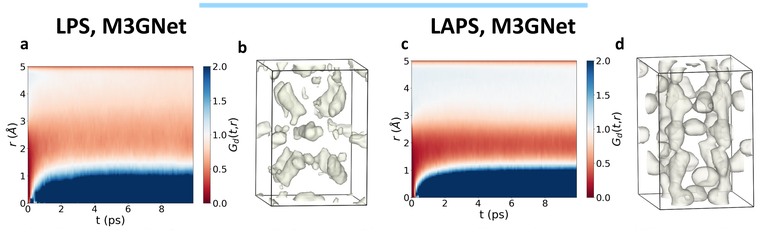
Example of diffusion in the c direction

(a-b) The probability density of Li^+ spatial occupancy during simulations. (c-d) The Van Hove correlation functions of Li^+ dynamics on distinctive Li^+ during simulations. (e) An example of Li diffusion.

The van Hove correlation function provides evidence for the concerted migration of Li^+ ions in super-ionic conductors. M3GNet reproduces this diffusion mechanism.



Example of concerted Li^+ diffusion



(a-d) $Li_9P_3S_{12}$ (LPS) and $Li_{11}AlP_2S_{12}$ (LAPS) show the effect of aliovalent (P^{5+} and Al^{3+}) cation substitutions on diffusivity in the LGPS structure.

Conclusions

M3GNet successfully reproduces diffusional properties for LLZO with an *ab initio* level of accuracy but there are discrepancies between M3GNet and AIMD when examining LGPS, LPS, and LAPS. Training on defected structures could improve M3GNet and further evaluation of other super-ionic conductors leaves room for future work.

Acknowledgments

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