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Sabiha Rustam

Combining Artificial Intelligence With Physics Based Simulations in Understanding and Design of Interfaces

Sabiha Rustam

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Reading Committee:

Jim Pfaendtner, Chair

David Beck

Jenna Pope

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Abstract

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Sabiha Rustam

Chair of the Supervisory Committee:

Jim Pfaendtner

Chemical Engineering

Interfaces play a critical role in chemical engineering processes, where understanding their behavior and properties is essential for process optimization, material design, and technological advancements. However, interfacial problems are inherently complex, characterized by intricate intermolecular interactions and a multitude of influencing factors. To advance our understanding and design of complex interfacial systems, the integration of computational simulations with advanced techniques like machine learning (ML) and data-driven approaches is crucial. This dissertation investigates the challenges and opportunities associated with utilizing simulation and ML techniques to study interfacial phenomena and design chemically patterned surfaces with specific interfacial properties. The research projects presented in this dissertation concentrate on electrode/electrolyte interfaces in lithium-ion batteries, interfacial heat transfer optimization at the Si/Al interface, and the practical application of machine learning potentials (MLPs) for structural relaxation of ternary transition metal dichalcogenides (TMDs). Through these projects, valuable insights are gained into the interplay between surface chemistry and electrolyte dynamics, the optimization of interfacial heat transfer, and the challenges and strategies involved in applying MLPs to custom datasets. This work contributes to the development of an integrated computational workflow, opening avenues for exploring a broader range of interfacial systems, uncovering novel phenomena,

and optimizing interfacial properties.

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DEDICATION

to my Mom and Dad, for supporting all my crazy dreams. to my beloved husband,
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Chapter 1

INTRODUCTION

Interfaces exhibit distinct properties compared to the bulk phase and play a vital role in diverse chemical engineering processes.[1, 2, 3, 4] The understanding of interfacial phenomena encompasses a wide range of areas, including the interface between electrodes and electrolytes in electrochemical systems, which is crucial for battery development, fuel cells, and electrochemical sensors.[5, 6, 7, 8] Understanding and optimization of interfacial heat transfer is another fundamental aspect of chemical engineering, playing a crucial role in applications like heat exchangers[9], cooling systems[10], boilers[11], and thermal management of electronic devices.[12] By delving into the behavior and properties of interfaces, researchers can uncover fundamental insights into the underlying mechanisms and processes that govern interfacial interactions, leading to development of new theoretical models[13, 14], computational methods[11, 15, 16], and experimental techniques[17, 18] that can better predict and control interfacial behavior. This knowledge can then be applied to optimize chemical processes, design new materials, and develop innovative technologies. Most interfacial problems of scientific interest are inherently complex due to the intricate nature of intermolecular interactions and the multitude of factors influencing interfacial behavior.[3, 4, 13] The complexity arises from factors such as the diverse composition and structure of the interface, the presence of multiple phases, the dynamics of molecular rearrangements, and the coupling between different physical and chemical processes[1, 19]. Furthermore, interfacial phenomena often occur at different length and time scales, requiring a multi-scale approach to capture the intricate details and dynamics involved.[1, 20] Experimental studies can be challenging due to limited access to interfaces, and the difficulty of directly observing molecular-level

details.[21]

Molecular dynamics (MD) simulation is a powerful tool for studying interfacial phenomena. MD simulation allows researchers to observe and analyze the behavior, interactions, and dynamics of individual molecules at interfaces.[22, 23, 24, 25] This level of detail provides insights into the underlying mechanisms governing interfacial phenomena, which may not be easily accessible through experimental techniques alone.[25] MD simulation enables exploration of interfacial phenomena across various length and time scales, providing insights into transient dynamics.[22, 24] With high degree of flexibility and control over the simulated system, researchers can manipulate various parameters, such as temperature, pressure, composition, and surface properties, to investigate their effects on interfacial phenomena. This allows for systematic studies and the exploration of a wide range of conditions that may be challenging or time-consuming to achieve experimentally.

The ability to engineer surface patterns, such as grooves, ridges, or hierarchical structures, grants control over various interfacial phenomena.[26, 27, 28] This tailoring of the surface structure opens up new possibilities for developing advanced materials with improved functionality in diverse fields.[29, 30] Designing specific surface patterns with desired interfacial properties presents a formidable challenge, especially considering that molecular surfaces are far from simple terminations of bulk structures. Instead, they encompass vast combinatorial spaces, further adding to the complexity of the task. Computational modeling and simulations, including MD and machine learning (ML) techniques, play a crucial role in predicting and optimizing the interfacial properties of patterned surfaces.[27, 31, 32] ML can assist in system selection by analyzing existing data, identifying patterns, and suggesting promising systems for investigation. ML models trained on simulation data can predict interfacial properties for new systems, enabling quick assessment of parameter combinations.[33] ML optimization algorithms efficiently explore the system design space and find optimal parameter combinations.[34, 35] Additionally, ML techniques can analyze large simulation datasets to extract valuable insights about interfacial interactions, uncover hidden relationships, and guide the design of effective simulation systems.[27] By leveraging ML, researchers

can reduce reliance on intuition, screen potential systems, and guide experimental efforts, ultimately enhancing the understanding and exploration of interfacial phenomena.

While MD simulation offers a powerful approach for studying interfacial phenomena, computational studies of interfacial phenomena face challenges such as accurately capturing the complexity of the systems and the need for validated force fields or potential models to describe intermolecular interactions.[22, 23, 24] In past decade, ML techniques also contributed immensely to enhancing the accuracy, efficiency, and predictive capabilities of MD simulations. From the 1) construction of interatomic potentials[36, 37, 38, 39, 40, 41, 42, 43, 44] to efficiently perform MD simulations that can incorporate quantum effects, and 2) the construction of coarse-grained[45, 46, 47, 48] descriptions of molecular interactions to learn effective models at reduced resolution, to 3) the accelerated sampling of rare events through enhancement of MD sampling by learning bias potentials[49, 50, 51, 52] or selecting starting configurations by active learning[53, 54], the impact of ML on MD simulation engines has been transformative. This enables tackling of complex problems, explore new phenomena and leading to breakthroughs in the understanding of molecular systems and interfacial phenomena.

The primary thrusts of my graduate research have been dedicated to tackling a set of relevant interfacial challenges through a computational lens whilst taking advantage of various ML methods. This dissertation presents three unique research projects that contribute differently towards advancement of interfacial studies. In Chapter 2, model electrode/electrolyte interfacial system, multi-component electrolyte with varying species compositions combinatorically paired with four different graphitic surfaces, is simulated to explore the interplay between surface chemistry and electrolyte dynamics at electrode/electrolyte interfaces. In Chapter 3, Bayesian optimization is used with MD simulations to solve the complex problem of interfacial heat transfer optimization that involve massive combinatorial space. A transferrable and easily scalable framework, seamlessly incorporating MD simulations with ML algorithms, is built to enable parallel evaluation of candidate structures with MD simulations and expedite the optimization process. In Chapter 4, a state-of-the-art ma-

chine learning potentials (MLPs) model is used to perform structural relaxation of ternary transition metal dichalcogenides. Thorough analysis on impact of the training data and testing criteria shed light to the practicality of MLPs outside the contexts of benchmark criteria. Additional strategies are explored to enhance the reliability and applicability of MLPs with incorporation of domain knowledge. Finally, Chapter 5 concludes with discussion of significance and perspective.

Chapter 2

EFFECT OF GRAPHITIC ANODE SURFACE FUNCTIONALIZATION ON THE STRUCTURE AND DYNAMICS OF ELECTROLYTES AT THE INTERFACE ¹

2.1 *Abstract*

Surface termination on a graphitic surface and the type of electrolytes in lithium-ion batteries (LIBs) play an important part in determining the structure, composition, and thus, the quality of the emergent solid electrolyte interphase (SEI). In this paper, we analyze the structure and dynamics of electrolyte molecules in multi-component electrolyte with varying species compositions combinatorically paired with four different graphitic surfaces terminated with hydrogen, hydroxyl, carbonyl, and carboxyl to explore the interplay between surface chemistry and electrolyte dynamics at electrode/electrolyte interfaces. Addition of dimethyl carbonate and fluoroethylene carbonate brought substantial changes in the ethylene carbonate (EC) and LiPF_6 surface population density for hydroxyl and carbonyl surfaces. Strong density oscillation and drastic slowing of the dynamics of the electrolyte molecules at the interface are reported for all the systems. While these observations are universal, carboxyl surface has the strongest local and long-range effects. Characterization of the average dipole direction at the interface shows strong orientational preferences of ethylene carbonate molecules. EC molecules are preferred to be oriented either almost parallel or perpendicular to the hydroxyl surface, are tilted between parallel and perpendicular with a higher angle of incidence of the dipole vs surface normal on the carbonyl surface than on the hydroxyl surface, and are oriented perpendicularly against the carboxyl surface. These differences

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highlight the significant effect of graphite surface termination on the dynamics of the electrolytes and provide insights into the complex interplays between electrolyte species and graphite anode in LIBs.

2.2 Introduction

Lithium-ion batteries (LIBs) have become one among the most widely used energy technologies, spanning diverse uses including portable electronic devices to potential applications in large scale static and transportation energy storage. Traditionally, a LIB is comprised of a graphitic anode, a metal oxide cathode, a separator, and an electrolyte. The typical electrolyte used in the commercial LIBs consists of a mixture of cyclic ethylene carbonate (EC) solvent and Li-based salts in a 1:1 molar ratio, another linear carbonate species, and a small fraction of additives. However, electrolyte selection for LIB applications remains a complicated task, with competing requirements to have an optimized mixture for high conductivity, good electrochemical and thermal stability, low flammability, volatility, and toxicity. To add to the complexity, the electrolyte also needs to readily promote the formation of a stable solid electrolyte interphase (SEI) layer.[56]

SEI is a passivation layer that is formed as the electrolyte molecules decompose during the operation of LIBs at the surface of electrodes. SEI allows Li^+ transport and blocks electrons in order to prevent further electrolyte decomposition and ensure continued electrochemical function. It is generally accepted that the SEI layer is critical to the performance of LIBs and has been directly linked to its initial capacity loss, cycle life, rate capability and safety.[57, 58, 59] Although the presence of the SEI layer is vital for the performance of LIBs, SEI formation and stability are still regarded as, "the most important, but least understood" component of LIBs[58] due to the complexity of the chemical structure and electrochemical reactions involved, as well as lack of experimental tools for direct measurement. For example, it is still difficult for current experimental methods to characterize the SEI (beyond chemical composition). This is especially true for understanding the thermodynamics and kinetics associated with the process.

The stability and the quality of the SEI formed are intimately connected to the choice of the electrolyte used. Favorable electrolyte pairings also lead to the formation of a stable SEI with smoother and a more uniform lithium deposition.[60] EC-based electrolytes are known to form a stable SEI on graphitic anodes, which helps in preventing further electrolyte decomposition and provides good reversibility for lithium intercalation/deintercalation.[61] For the Li-based salts, LiPF_6 is the most common choice due to its high ion dissociation and conductivity.[62] The addition of linear carbonate such as dimethyl carbonate (DMC) and diethyl carbonate (DEC) lowers the viscosity of the electrolyte, which in turn further improves the conductivity. Furthermore, the addition of additives such as fluoroethylene carbonate (FEC) and vinylene carbonate (VC) in small amounts has been shown to improve a battery's performance; it is proposed that this marked improvement is due to the mechanisms by which additives modulate the growth mechanisms and resulting composition of the SEI layer.[63, 64] These additives are found to polymerize at the surface of the anode that leads to the formation of a compact and thin SEI layer,[65, 66] which in turn prevents runaway solvent decomposition and ever-growing SEI formation.[67]

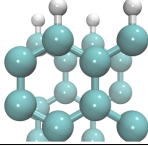
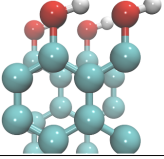
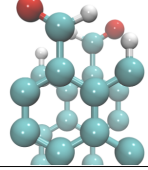
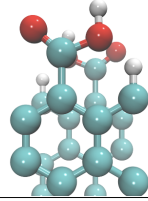
However, even slight changes in the electrolyte composition have been found to remarkably affect the properties of the SEI formed. These effects can be extremely subtle. For example, many of the carbonate electrolytes used in LIBs such as EC, DMC, FEC, and propylene carbonate (PC) are very similar in structures. For example, both EC and PC are cyclic carbonates, with the only difference in the structures of EC and PC is one methyl group.[68] When used as solvents in LIBs, lithium intercalation into the electrodes is reversible in EC,[69] but irreversible in PC.[70] The irreversibility of the lithium intercalation process in PC leads to exfoliation of the graphite anode, which eventually damages the battery.

In addition to the electrolyte choice, the initial rate of formation of SEI and its properties are also heavily affected by the types of electrodes and their surface terminations.[71] In battery studies, the electrodes' surface chemistry is rarely mentioned as the surface is quickly covered by SEI during the initial cycling period. However, surface termination plays

a substantial role in the initial SEI formation process.[66, 72] In the case of the graphite-based anode, the surface is commonly terminated by oxygen-based functional groups: hydrogen ($-H$), hydroxyl ($-OH/-H$), carboxyl ($(=O)-OH$), and carbonyl ($(=O)-H$).[73] Many studies have been devoted to understanding the effect brought by different surface terminations on initial SEI formation. For example, a more facile EC molecule decomposition was observed at the graphite edge with hydroxyl ($C-OH$) and carbonyl ($C=O$) terminated functional groups as they provide larger driving force for EC reduction.[72] Furthermore, functional groups with $C=O$ bonds such as carboxyl and carbonyl were found to improve the capacity of LIBs.[74, 75, 76] On the other hand, $LiPF_6$ salt is more stable at the H-terminated graphite surface than at the oxygenated graphite surface.[77]

Although it has been established that the type of surface termination on the graphitic surface and the type of electrolytes in LIBs play an important part in determining the structure, composition, and thus, the quality of the SEI, the effect of the surface termination on the structure and dynamics of the liquid electrolyte at the uncycled interface has yet to be discussed in detail. Furthermore, the complex interplay between individual constituents within the electrolyte formulation and their role in interfacial phenomena are also not yet known. These phenomena are important to study to provide new information about the role of surface functionalization and electrolyte composition in promoting early phases of electrolyte decomposition while the SEI is being formed. In this paper, we study the effect of different graphite surface terminations on the structure and dynamics of different electrolyte species pairings. Using electrolyte species commonly found in commercial LIBs on oxygenated zigzag edged graphite surfaces, we employ molecular dynamics (MD) simulations to investigate the effect of different graphitic termini: hydrogenated, hydroxyl, carboxyl, and carbonyl on the structure and dynamics of four different electrolyte mixtures, which contain one or more of the following species: EC, $LiPF_6$, DMC, and FEC. Following an introduction of the computational methods, the results introduce a range of characterization of the static structure and dynamic properties of the electrolyte/graphite interface. We will then discuss the impact of these observed behaviors on the initial formation of SEI at the surface of the

Table 2.1: Systems of interest. Top: four electrolyte boxes with names and composition listed accordingly. Bottom: four different surfaces and snapshot of the unit-cell.

Electrolytes	names	EC	ESS	MIX_1	MIX_2
	Composition	pure EC	1.2 M LiPF ₆ in EC	1.2 M LiPF ₆ in EC with 10 mol% FEC	1.2 M LiPF ₆ in 45:45:10 mol% EC: DMC: FEC
Surfaces	names	H	OH	NYL	XYL
	figure				

graphitic anode.

2.3 Computational Methods

2.3.1 Model systems

Model graphite anodes were modeled as periodic slabs comprised of $16 \times 10 \times 6$ of graphite unit cells[78] to make up slabs with the dimensions of $38.440 \times 24.966 \times 40.176 \text{Å}^3$. The surface consisted of two layers of graphite in the c direction, which were fully capped by four different oxygen functionals, hydrogen ($-\text{H}$), hydroxyl ($-\text{OH}$), carbonyl ($-\text{C}(-\text{H})=\text{O}$), and carboxyl ($-\text{C}(-\text{OH})=\text{O}$), and were labeled as H, OH, NYL, and XYL, respectively. For each termination, electrolyte boxes of size $38.440 \times 75 \times 40.176 \text{Å}^3$ were placed on top graphitic slabs that contain four different electrolyte mixtures: a) pure EC, b) 1.2 M LiPF₆ in EC, c) 1.2 M LiPF₆ in EC with 10 mol% FEC, and d) 1.2 M LiPF₆ in 45:45:10 mol% EC: DMC: FEC, which are labeled as EC, ESS, MIX_1, and MIX_2, respectively. Dimensions of equilibrated electrolyte boxes were obtained from separate NPT simulations (Table A.1 in the Supporting Information). All surfaces and electrolyte combinations are listed in Table 2.1.

2.3.2 *Molecular dynamics simulations*

MD simulations were carried out using the LAMMPS software package.[79] The generalized AMBER force field (GAFF)[80] was employed to describe bonded and nonbonded interactions. Periodic boundary conditions were implemented in all three dimensions. Partial charges for the terminal functional groups were determined with restrained electrostatic potential (RESP) using the CP2K program package. Molecularly optimized double zeta valence polarized basis set with shorter range Goedecker-Teter-Hutter pseudopotentials (DZVP-MOLOPT-SR-GTH) is used with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional[81, 82, 83, 84, 85, 86] and are shown in Figure A.1. The Nosé-Hoover thermostat[87, 88] and barostat[88, 89] were implemented to control the temperature and pressure, respectively. The cut-off distance for long range contributions to the potential energy was set to 10 Å for both the pairwise and electrostatic interactions. The contributions of long-range interactions were calculated via the tail correction and the particle–particle–particle–mesh (pppm) solver.[90] Newton’s equations of motion were integrated using a 1 fs time-step throughout all simulations. Energy minimization using the steepest descent algorithm was conducted to remove unfavorable contacts. After the energy minimization, all systems were equilibrated for 10 ns in the canonical ensemble (NVT) using the Nose-Hoover thermostats at 300 K followed by 20 ns of production run. As discussed in the following text, the relevant liquid behaviors we are investigating converge extremely fast (timescales of ~ 5 ns), making the 20 ns production runs more than sufficient for this study. Simulation trajectories were visualized by using Visual Molecular Dynamics (VMD)[91] software, and were analyzed by using MDAnalysis[92] open-source software augmented by in-house python scripts.

2.4 *Results*

2.4.1 *Interfacial probability density*

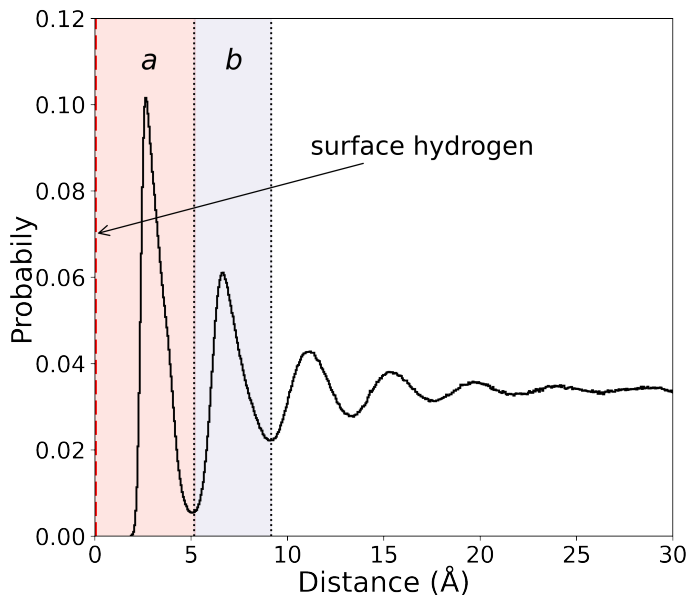


Figure 2.1: Probability density of EC at the H-surface and depiction of the interface and intermediate regions. The surface hydrogen position is marked with red dashed lines: (a) interface region and, (b) intermediate region.

To determine the electrolyte structure in the vicinity of the electrode surface, first, we compute the layer density profiles of the systems to identify the different layers of the electrolyte. For comparison, the surface is represented by the average position of hydrogen in the surface termination groups, and the x-axis indicates the center of mass (COM) of the molecule orthogonal to the surface. Figure 2.1 shows the density profile of the EC molecule at the H-terminated graphite surface. The electrolyte behavior is identical whether viewed after 5, 10, or 20 ns of production simulation

(Figure A.2). We define two areas of interest for studying the structure and dynamics of the electrolyte molecules based on the distance of the COM of the molecules to the surface. Shown as shaded region a, and b, we identify the interface area as the first adsorption layer and the intermediate area as the second adsorption layer. As we show below, electrolyte mixtures in contact with graphitic surfaces universally display strong surface-induced ordering and layering effects up to 2 nm into the bulk fluid. Even with the simplest H-terminated surface, the probability density increases nearly three times in comparison to that of the bulk. Meanwhile, the strong density oscillations of the fluid molecules in the vicinity of solid surfaces is a universal phenomenon.

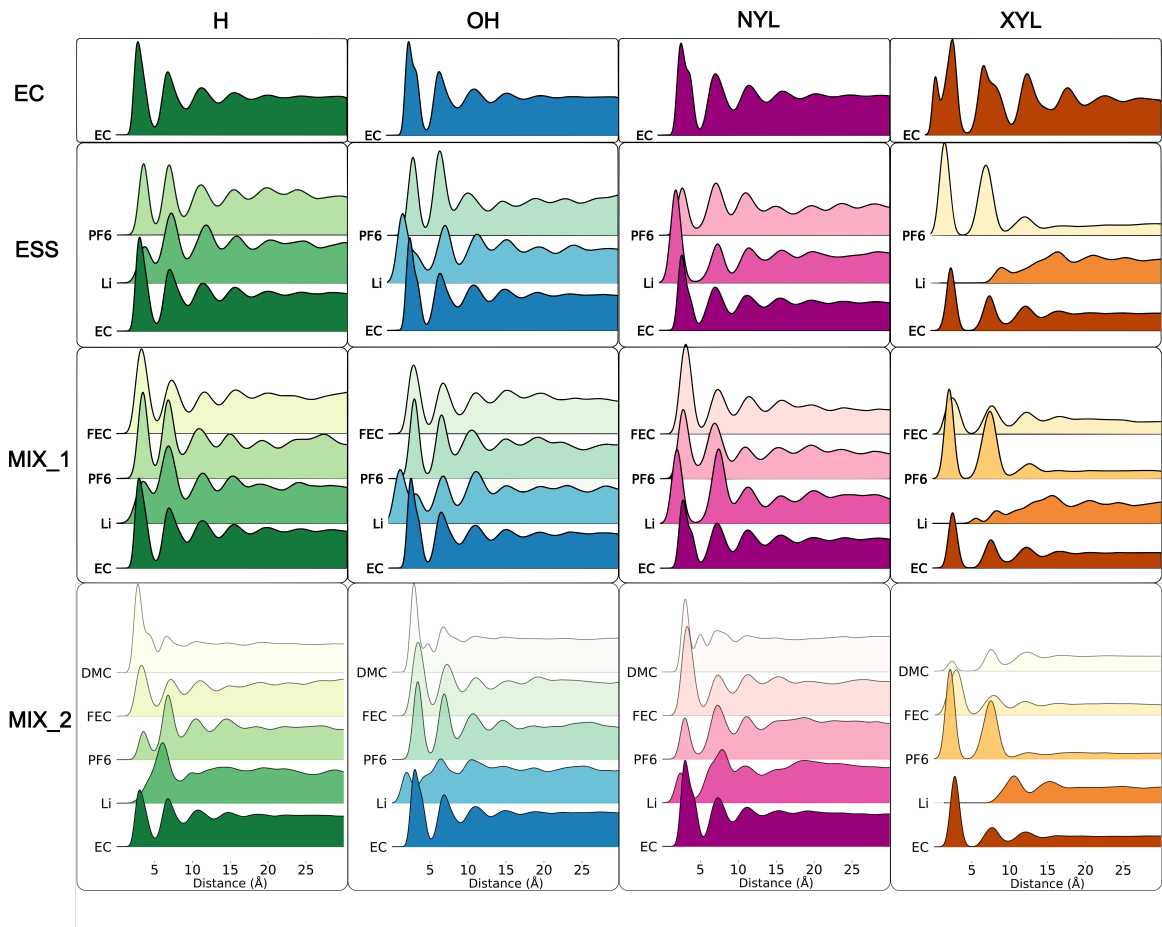


Figure 2.2: Density profiles across surface chemistry and variation in the electrolyte composition. Left to right: comparison of the same electrolyte composition on various surfaces. Top to bottom: comparison of four electrolyte systems on the same surface. The intensity of the peaks is relative to each system.

To enable easy comparison between all the systems, the number density of each electrolyte molecule is plotted as a ridgeline plot as shown in Figure 2.2. Each surface is represented with the same color scheme from left to right to study the effect of the surface termination, while four electrolyte combination is plotted top to bottom to examine the variation of each electrolyte constituent across surfaces. Intensities of the peaks are relative to each system and for visualization purpose we did not set a global axis limitation. We note that for H, OH, and NYL surfaces, the first solvation peak position of EC is identical, with both OH and

NYL showing no appreciable changes with the addition of lithium salt and other additives (Figure A.3).

For pure EC, the first peak position is identical for H, OH, and NYL surfaces with a slight shoulder in both OH and NYL surfaces. The intensity of the first peak has increased 15% from H to OH, but it did not change the density profile of the EC and rest of the peaks align nicely. As we show below, this behavior arises from a mixture of orientations near the surface, leading to two broad, overlapping peaks. The shoulder on the first peak of the density profile appears as the result of interactions between EC molecules of different layers (first and second adsorption layers). These interactions cause the EC molecules in the first layer to point away from graphite surfaces in a perpendicular fashion against the surface normal. As the COM of the EC molecules moves farther away from the surface, it resulted in the presence of the shoulder in the density profiles. While the first peak is wider for the NYL, it leads to the even wider second peak with rest of the peak shifted right. In the case of XYL, EC molecules are found to fill small open pockets that form on the graphite surface as the result of reorientation of the carboxyl group (Figure A.4). It can then be found that on the XYL surface the first solvation layer has bifurcated into two sharp peaks with the first peak much closer to the interface, and stronger density oscillations further into the bulk. This is especially pronounced in broader peaks with higher peak intensity for the second and third layers on the XYL surface.

On the other hand, the addition of both DMC and FEC results in surfaces that are highly populated by these two molecules. In the case of DMC, the addition of DMC into the electrolyte mixture seems to dampen the intensity of both Li^+ and PF_6^- peaks on all but the XYL surface. A similar but subtler trend can also be observed with FEC addition. Additionally, the addition of FEC for OH and XYL surfaces indicates a scenario in which Li^+ is closer to the surface. In comparison to ESS, the Li average peak position in MIX_1 is nearer to the surface (x-axis) (Figure A.5). This effect is not seen for H and NYL surfaces, where the intensity and distance from the surface of other electrolyte species are similar to those without FEC. However, the addition of DMC on the XYL surface seems to cancel out

the effect brought by FEC on Li^+ . It can thus be concluded that DMC acts as a passivation layer on oxygenated graphitic surfaces.

In terms of the effect of different surface terminations for association of the salt with the surface, in general, the first peak of PF_6^- has the strongest intensity for all mixtures on the XYL surface in comparison to other surfaces and is closest to the XYL surface. This is due to the larger concentration of positive partial charges that were fixed on surface carbon atoms on the XYL surface (and thereby stronger electrostatic interactions) in comparison to those on OH and NYL surfaces (Figure A.1). As the result, the XYL surface has a stronger intrinsic electron withdrawing properties than OH and NYL surfaces. This behavior of the XYL surface was also observed in density functional theory (DFT)-based simulations.[93] As the consequence of the cumulative effects of the Coulombic and Lennard-Jones forces, the positively charged Li^+ ions are driven farther away from the XYL surface. On the other hand, the total partial charges of surface carbon atoms on both OH and NYL surfaces are not as positive as those on XYL,[93] are reflected in the high intensity of Li^+ first peaks on both OH and NYL surfaces, and are especially pronounced for ESS and MIX_1 systems on the NYL surface.

2.4.2 *Survival probability and residence time*

Survival probability (SP) is an important quantity in characterizing the relaxation dynamics of molecules in contact with an interface. SP is the probability that a group of particles remain in a specified region for a certain amount of time.[94] At given timestep τ , the SP is given by:

$$P(\tau) = \frac{1}{T} \sum_{t=1}^T \frac{N(t, t+\tau)}{N(t)}$$

where T is the maximum time of interest for the calculation, $N(t)$ is the number of particles at time t , and $N(t, t+\tau)$ is the number of particles that remain in the selection at time $t+\tau$.[95]

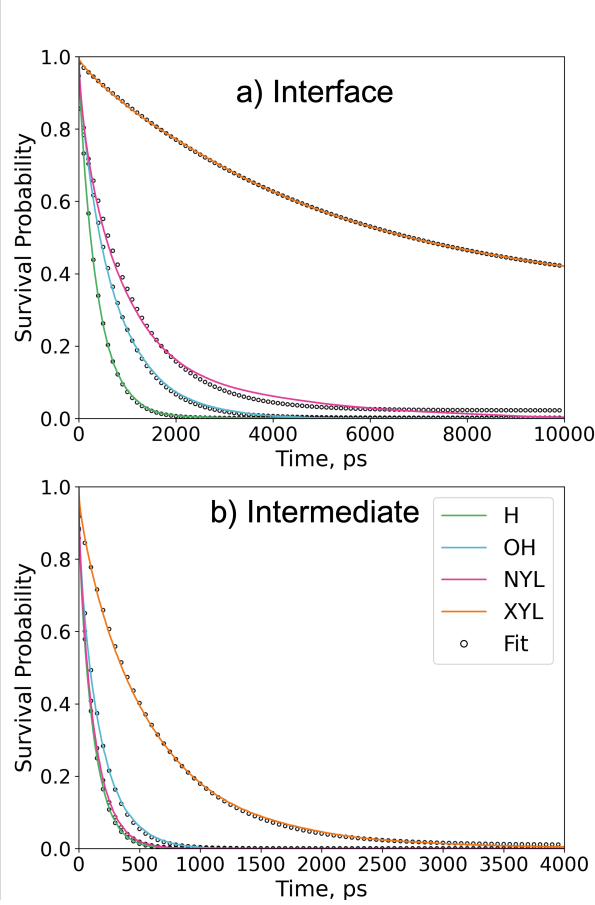


Figure 2.3: Survival probability of the EC molecule in the (a) interface, and (b) intermediate layers of the four surfaces. The red circles show the fitted data. The residence times obtained from the data fitted to a biexponential are shown in Table 2.2

residence time of 31 ps,[96] indicating a drastic slowing down of the EC molecule crossing the layers near the surface.

As discussed above the density profile of EC is similar for H and OH surfaces with the slight increase and shoulder on the first peak which we described as the result of interactions between EC molecules of different layers (first and second adsorption layers). Indeed, the residence time of EC in the second adsorption layer of the OH surface is greater than that of the H surface because of these interactions. Although this shoulder peak is also observed for the NYL surface, we noted the shift in the following peaks. Thus, the increase in residence

After identifying the interface and intermediate regions in the same manner as described in Figure 2.1 (i.e., the first and second density peaks), we evaluated the SP over a duration of 10 ns (sampling frequency of 1 ps). Normalized SP data are then fit to the following biexponential function to quantify the residence time:

$$P(\tau) = \beta \exp\left(-\frac{t}{\tau}\right) + y_0$$

The time evolution of the normalized survival probability of pure EC on four different graphitic surfaces for the interface, intermediate layers and their fit is shown in Figure 2.3. The corresponding residence times which are given in Table 2.2 reveal a significant increase in residence time from intermediate to the interface for all systems that compare to the experimentally reported bulk

time for the NYL system is not as profound. This increase is more drastic for the XYL system, presumably due to the significantly stronger ordering of EC near the XYL interface, which is discussed later in this manuscript.

Table 2.2: Residence time for the EC interface and intermediate layer (Fig. 2.1) of four graphitic surfaces in the pure EC system. The residence time of EC increased for all systems from intermediate to interface. Correlation coefficients for all the fittings are > 0.99 .

Area	System	β	$\tau(\text{ps})$
Interface	H	0.95 ± 0.01	388.9 ± 2
	OH	0.92 ± 0.01	754.3 ± 4
	NYL	0.83 ± 0.01	1099 ± 20
	XYL	0.66 ± 0.02	5115 ± 20
Intermediate	H	0.88 ± 0.01	118.97 ± 0.05
	OH	0.85 ± 0.01	180.60 ± 0.20
	NYL	0.88 ± 0.01	129.44 ± 0.35
	XYL	0.91 ± 0.01	602.69 ± 10

The difference in the interfacial survival probability between different oxygenated surfaces follows the extent of electrostatic interactions originating the surface group. The H interface that has the lowest survival probability is neutral, followed by the OH surface that has single charge. Both NYL and XYL with surficial oxygen double bond have larger magnitude point charges, which corresponds to higher survival probability of EC. As the survival probability of EC on the XYL surface is highest in both interface and intermediate layers, it also suggests that the effect of the XYL surface is able to penetrate farthest into the electrolyte, thus implying that the effect brought by the XYL surface on electrolyte is the strongest out of the four surfaces considered here.

2.4.3 Orientation of EC

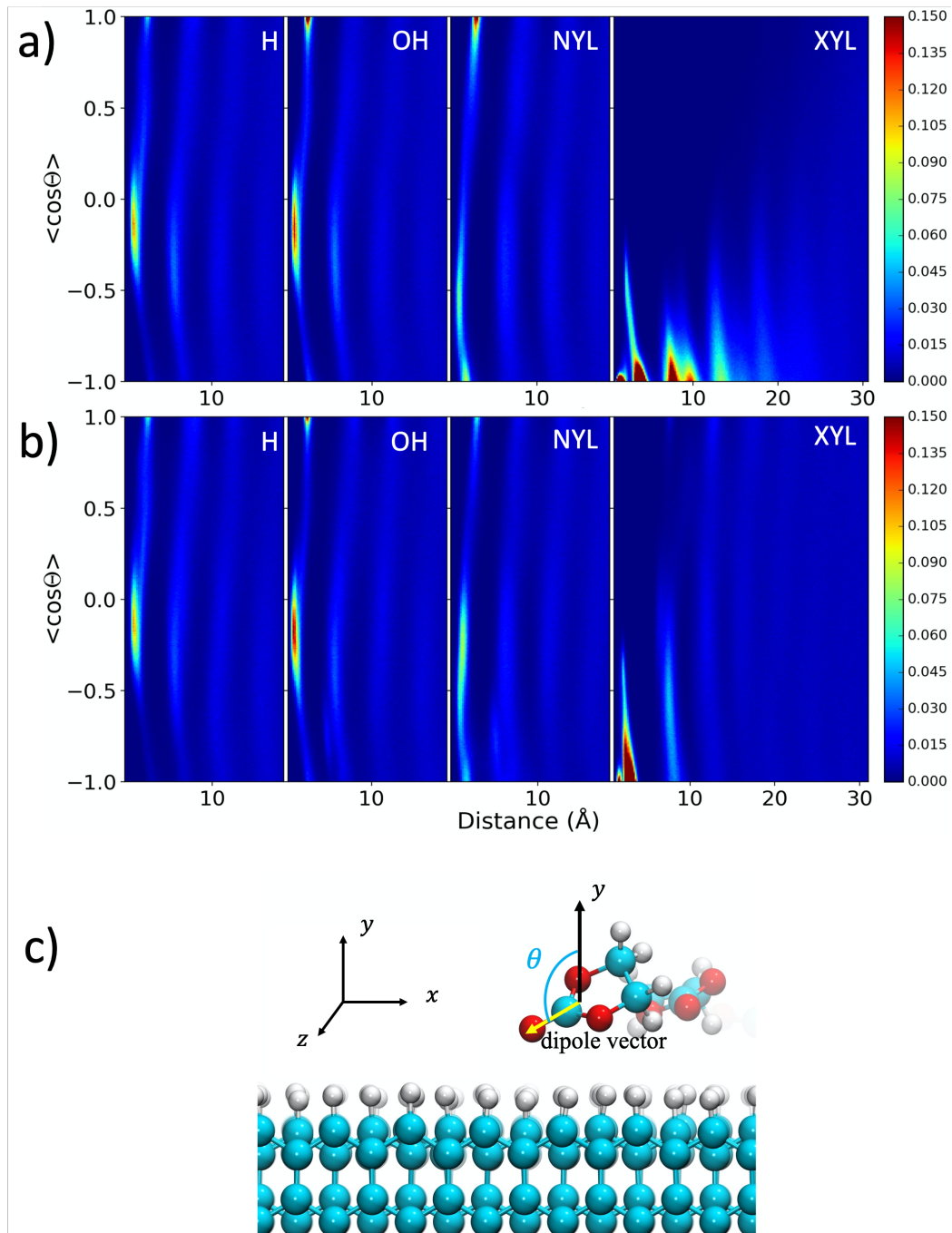


Figure 2.4: Probability density map for the average ethylene carbonate dipole orientation (from surface normal) on H, OH, NYL, and XYL graphitic surfaces with panel (c) for the illustration. (a) EC, (b) ESS, and (c) depiction of calculation of theta using the ethylene carbonate dipole vector and surface normal vector (y-axis denotes the direction of the surface normal).

Analysis of different orientational preferences induced by variation in the surface chemistry was performed through characterization of the average angle between the EC dipole and the surface normal as shown in Figure 2.4. Snapshots of the trajectories showing the preferred orientation of the EC molecules are provided in Figure 5 to assist the interpretation. Figure 2.5 shows that EC molecules are preferentially oriented mostly in almost parallel [$\cos(\theta) = 0$], with a small fraction in almost perpendicular [$\cos(\theta) = 1$] direction to the OH surface, which could possibly provide an avenue for future investigation into the underlying origins of why EC has such a low angle of incidence of the dipole vs surface normal on graphite surfaces.

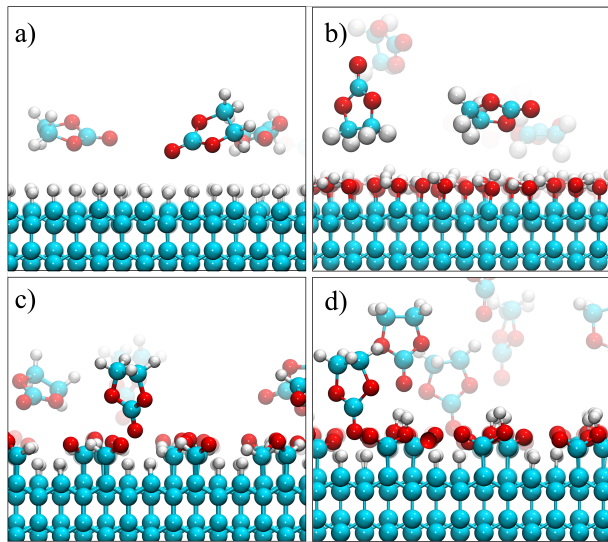


Figure 2.5: Snapshot of EC molecules at the interface of a) H, b) OH, c) NYL, and d) XYL surface.

On the NYL surface, EC molecules prefer to be oriented between parallel and perpendicular to the NYL surface with a high angle of incidence of the dipole vs surface normal [$\cos(\theta) \approx 0.5$]. Meanwhile, EC molecules show strong preference for perpendicular orientation to the XYL surface. The strong preference of EC molecules to be on perpendicular orientation to the XYL surface can be seen to not only apply to the first interface layer, but also apply to the subsequent interface and intermediate layers. This observation of a high degree of molecular ordering within the subsequent layers further helps in explaining the EC high sur-

vival probability in both interfacial and intermediate layers on the XYL surface described above. The orientational preference of EC molecules in the second layer that can be seen on OH and NYL surfaces is significantly less pronounced in comparison to the first layer. In general, we observe a trend that the strength of ordering in the second layer is strongly

correlated with that of the first layer. For example, the NYL surface shows a wide diffuse trough in the first layer orientation density plot and nearly no orientation preference for the second layer. The overall ranking of strength of molecular dipole ordering decreases as $XYL > OH > H > NYL$, presumably due to the collective effects of the H-bonded network between EC molecules between the surface, first and second layers.

The addition of Li-salt into the electrolyte makes the orientation preference of EC molecules even more pronounced on oxygenated OH, NYL, and XYL graphitic surfaces as shown in Figure 2.4(b). Furthermore, nearly all of the second layer orientation effects are completely removed on all surfaces with the addition of Li-salt. This interesting effect is likely due to the constituents of the salt disrupting the well-ordered hydrogen bonding network that provides driving force for the multi-layer ordering described above.

2.5 Discussion

These findings provide a framework for gaining new insight into the mechanistic connection between surface chemistry and electrolyte formulation, their role in the emergent liquid structure, orientation, and dynamics, and ultimately the way in which these affect factors connected to initial stage SEI formation. In terms of the effect of electrolyte species on the initial SEI formation, the decomposition of EC and linear carbonate lead to lithium ethylene decarbonate (LEDC) formation, which is coupled with alkoxide species regeneration,[97, 98] and various gaseous species such as H_2 , CO , and CO_2 . [99, 100, 101] The formation of LEDC results in the formation of an SEI layer, while alkoxide regeneration reinforces SEI build up at the electrode/electrolyte interface. On the other hand, accumulation of gaseous species that are trapped inside LIBs may result in batteries explosion.[102] The addition of additives such as FEC stabilizes the battery as it helps to suppress the uncontrollable SEI build-up. Additionally, FEC decomposition leads to the formation of various oligomers[103] on the surface of the graphitic anode, which results in a more uniform, thinner, and a more flexible SEI.[60]

The decomposition reaction of the EC molecule has been subject to many computational

studies. *ab initio* molecular dynamics (AIMD) based study revealed that EC decomposition may happen through either a one-electron or a two-electron ring opening mechanism[104] in which the different carbon-ethylene oxygen bond(s) were broken.[72] In one-electron mechanism, decomposition of EC leads to the formation of alkoxide species, which may oligomerize on the electrode surface. On the other hand, the two-electron mechanism also generate ethylene decarbonate (EDC^{2-}) and carbonate (CO_3^{2-}) anions and various gas species (C_2H_4 , CO , CO_2) in addition to alkoxide species. Previous AIMD + DFT based work from our group on the same oxygenated graphite surfaces has reported that the type of surface oxygen groups at the edge sites of a graphitic anode can determine the products of electrolyte decomposition reactions at the interface.[66] For example, one electron reduction of an EC molecule on pristine and hydroxyl surfaces leads to the formation of linear oligomers, while the same reaction on both carbonyl and carboxyl surfaces results in cyclic oligomer species. The preferred parallel orientation of EC molecules on the OH surface shown in Figure 2.4 thus suggests that the decomposition of cyclic carbonate molecules (including EC and FEC)[60, 72] could proceed more readily on the OH surface. This finding thus validates the importance of additives in LIBs and adds further molecular scale insight to prior findings. For example, previous work reporting OH rich graphite anode surfaces can suppress runaway SEI formation.[105] Based on our results in Figure 2.2, strong FEC peaks on H, OH, and NYL surfaces thus suggest that FEC is highly stabilized near these surfaces, which could promote decomposition reactions to occur more readily. Furthermore, the first peak of FEC is the most prominent on the NYL surface out of all electrolyte species in all mixtures. We thus speculate that the NYL terminated surfaces will have the most superior SEIs in comparison to other surfaces. This hypothesis is further supported by the high angle of incidence of the dipole vs surface normal between interfacial EC molecules and the NYL surface shown in Figure 2.4, which makes the decomposition reactions harder to proceed. However, future investigations in these directions will help to further establish the important link between the early-stage chemical reactions that are critical in SEI formation and the prevalent orientation and structure that arises within a particular electrolyte formulation.

Looking beyond the role of the electrolyte structure and dynamics, there are well known effects of different graphite terminations that also have different effects on the lifetime of LIBs. For example, the OH rich surface is found to assist in additive decomposition on the anode, while the presence of NYL and XYL surfaces leads to higher rates of gaseous species formation.[106] Meanwhile, the presence of NYL and XYL surfaces is found to enhance the reversible capacities of LIBs, which leads to LIBs with higher energy density and cyclabilities.[107, 108] The contrasting effects brought by NYL and XYL thus suggest the importance of careful fine tuning of the graphitic anode surface to bring improvement to both cyclability and stability of current LIBs.[109] This finding open the possibility of a new rational design approach for achieving much higher control over the design of SEIs by modifying the electrode surface to tailor the mobility and concentration of the electrolytes at the electrode/electrolyte interface. Our work begins to provide some underlying molecular scale explanation for these interesting studies and motivates further studies making use of molecular simulations.

2.6 Conclusion

This study has highlighted the importance of surface chemistry of graphite anodes on the structure and dynamics of electrolyte molecules, specifically strong interaction between electrolytes and the surface even without the presence of the electric field. Analysis of the probability density of electrolyte molecules in a multi-component electrolyte with varying species compositions combinatorically paired with four different graphitic surfaces terminated with hydrogen, hydroxyl, carbonyl, and carboxyl shows that the presence of both DMC and FEC out-populates EC on the surfaces of the oxygenated graphite anode. We observe that the addition of FEC into the electrolyte mixture brings Li^+ ions closer to the surface on OH and XYL surfaces. This effect is not seen in the H or NYL surfaces. On the other hand, the addition of DMC into the electrolyte mixture seems to dampen the intensity of both Li^+ and PF_6^- peaks. Calculations of survival probability of EC molecules on four different oxygenated surfaces conclude that the XYL surface has the strongest effect that

can penetrate farthest into the electrolyte bulk. This result is supported by EC dipole orientation density map, in which the dynamic behavior of the EC molecules in the layers farther away from the XYL surface is similar to those molecules on the first interfacial layer. This behavior is not observed on other surfaces considered in this study. Furthermore, the EC dipole orientation density map also reveals that EC molecules: 1) are oriented either almost parallel or perpendicular to the OH surface, 2) are tilted between parallel and perpendicular with a higher angle of incidence of the dipole vs surface normal on the NYL surface than on the OH surface, and 3) have strong preference towards perpendicular orientation against the XYL surface.

2.7 Acknowledgements

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2.8 Data Availability

The data that support the findings of this study are available from the corresponding author upon request. LAMMPS input files used in this study are available on github repository (<https://github.com/UWPRG/Electrolyte-at-interface>).

Chapter 3

OPTIMIZATION OF THERMAL CONDUCTANCE AT INTERFACES USING MACHINE LEARNING ALGORITHMS¹

3.1 *Abstract*

Optimization of thermal transport across the interface of two different materials is critical to micro/nanoscale electronic, photonic, and phononic devices. Although several examples of compositional intermixing at the interfaces having positive effect on interfacial thermal conductance (ITC) have been reported, optimum arrangement has not yet been determined due to the large number of potential atomic configurations and the significant computational cost of evaluation. On the other hand, computation-driven materials design efforts are rising in popularity and importance. Yet, the scalability and transferability of machine learning models remain as challenges in creating a complete pipeline for the simulation and analysis of large molecular systems. In this work we present a scalable Bayesian optimization framework, which leverages dynamic spawning of jobs through the Message Passing Interface (MPI) in order to run multiple parallel molecular dynamics simulations within a parent MPI job, to optimize heat transfer at silicon and aluminum (Si/Al) interface. We found maximum of 50% increase in the ITC when introducing a two layer intermixed region that consists of higher percentage of Si. Due to the random nature of the intermixing, the magnitude of increase in the ITC varies. We observed that both homogeneity/heterogeneity of the intermixing as well as the intrinsic stochastic nature of molecular dynamics simulations account for the variance

¹This chapter was reproduced with permission from S. Rustam, M. Schram, Z. Lu, A. Chaka, W. Rosenthal and J. Pfaendtner. Optimization of Thermal Conductance at Interfaces Using Machine Learning Algorithms. Applied Materials & Interfaces, 14(28), 32590-32597 (2022). Copyright 2022 American Chemical Society.[110]

in ITC.

3.2 Introduction

As the size of electronic devices decreases, controlling heat transfer becomes a critical issue. For some devices such as thermoelectrics, retention of heat is a desirable characteristic to improve the figure-of-merit.[111, 112] In contrast, for the majority of micro- and nanoscale devices as well as cryogenic detectors and quantum information systems, heat dissipation is important to maintain function.[113, 114] For nanoscale devices in particular, when the surface-to-volume ratio is high, maximizing heat transfer across solid-solid interfaces is essential. This corresponds to maximizing phonon transport across interfaces. Hence, identifying ways to vary interfacial phonon scattering that can lead to controlling the thermal conductivity (Kapitza conductance) in nanosystems can provide necessary insights for tailoring thermal performance in devices and guidance for materials synthesis.[115]

In macroscopic devices, interfacial thermal transport depends primarily on the interfacial structure and contact areas (vibrational and lattice mismatch of the two materials are nanoscale factors). At the atomic level, however, roughness at the interface has been demonstrated to influence thermal transport.[115, 116, 117, 118, 119, 120, 121] “Roughness” can entail a wide range of phenomena, including compositional intermixing, nano-patterning, amorphous structures, and defects such as impurities, vacancies, and dislocations. Typically, roughness at an interface has been demonstrated to decrease thermal transport, both experimentally[115, 116, 117] and computationally.[118, 119, 120, 121] Hopkins and colleagues used high-vacuum thin-sputter deposition to demonstrate that at a Cr/Si boundary, thermal conductivity varies as a function of the thickness of the intermixing layer as well as the rate of compositional change.[116] Duda and Hopkins found that chemical etching can be used to control roughness between thin aluminum films and silicon substrates, and the impact on thermal conductivity measured by time-domain thermo-reflectance was exponential with respect to the root-mean-square roughness of the interface.[117] In some computational models, Kapitza conductance was found to be reduced by amorphous or disordered regions[119]

or by large mass impurities.[121] Other computational models, however, have determined that the thermal conductance can be increased by bridging the phonon mismatch between two materials. This bridging can occur by several methods such as intermixing,[122, 123] introduction of impurity atoms of an intermediate mass,[121, 124] or deposition of an interfacial film with median properties.[125] Increasing thermal conductance across an interface requires precise control of the interfacial structure, which is becoming increasingly attainable due to advanced synthetic methods such as molecular beam epitaxy. Despite these examples of atomic arrangements increasing thermal conductance, an optimum arrangement has not yet been determined due to the large number of potential atomic configurations and the significant computational cost of evaluation.

With current technological advances in the field of machine learning (ML) and computing science, the accessibility of ML methods for molecular simulations has increased significantly in the past decade [126, 127, 128]. Despite the variety of ML tools that have been applied to molecular simulation, there are still significant challenges in creating a complete pipeline for the simulation and analysis of atomistic systems. In particular, improvements in scalability and transferability are necessary for closing this gap, especially for large computational systems.

We developed an efficient and scalable framework to explore a large number of atomistic configurations to optimize thermal conductivity at the silicon and aluminum (Si/Al) interface. Silicon and aluminum were chosen as the materials because of their widespread use in micro- and nano-electronics, detectors for dark matter and high energy physics,[129] and resonator applications in quantum computing devices.[130] In addition, high-quality Si/Al interfaces can be grown using techniques such as molecular beam epitaxy and ultrahigh-vacuum evaporation, where the abruptness of the interface and degree of intermixing can be controlled.[131] Only phonon transport was considered in this study as the interfacial electronic effects can either be separated from phonons [132, 133], or can be neglected in nano-sized thin films [134]. We used a single objective Bayesian optimization technique to optimize heat transfer at the semiconductor: metal interface by tuning the depth and fraction

of compositional intermixing. A Gaussian process-based ML algorithm was used to search the configuration space, and non-equilibrium molecular dynamics (NEMD)[135] was used to evaluate the thermal conductance.[136]

Bayesian optimization has been used extensively to optimize a scalar figure-of-merit or property of interest—such as isotropic thermal conductance—when at any set of input parameters the property remains uncertain and therefore can only be known up to some distribution. [137, 138, 139] The distribution of the property as a function of the input parameter is referred to as the response function. An upper confidence bound (UCB)[140] approach is called for when the purpose is to identify a subset of possible parameters which maximizes the response function. However, it is computationally expensive to use molecular dynamics (MD) simulations to estimate thermal conductance, so a parallel batch sampling variation is developed for the present study in which several choices for the input parameters are evaluated simultaneously in a high-performance computing (HPC) environment. Typically, in statistical sampling, as the number of parameters tested increases, the knowledge of the thermal conductance distribution improves. A standard learning rate is applied to the UCB cutoff so that as the number of parameters tested increases, the level of confidence in the UCB likewise increases, and the uncertainty in the optimal material parameters decreases.

3.3 Methodology

3.3.1 Simulation domain

MD is a powerful technique to simulate heat transfer processes, as it intrinsically includes all lattice vibrations with well-developed inter-atomic potentials. In its classical limits, MD is an ideal method for predicting thermal boundary resistance[141, 142]. We chose the Large-Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package [143] for integration with ML due to its high-efficiency computation parallelization and high customizability. We used the modified embedded atomic method (MEAM) potential of Jelinek *et al.*, which has been reported to reproduce Al and Si properties with high accuracy for all pair-wise atomic

interactions [144].

System setup

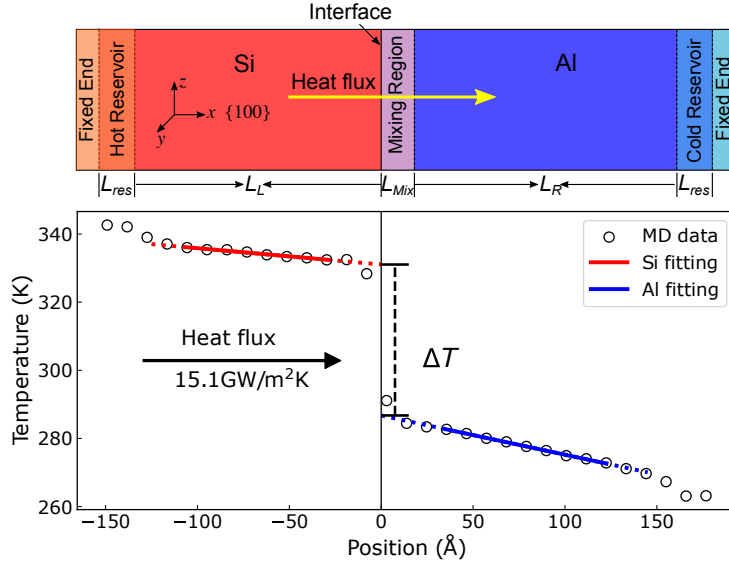


Figure 3.1: Schematic of the simulation cell (top) and example of fitted temperature profile (bottom). Solid lines are the fitting to actual data points and dashed lines are the extrapolation of the fitted lines. Each point on the temperature profile is obtained through kinetic energy of the group of atoms in 1.1 nm cross-sectional bin in the heat transfer direction averaged over the number of atoms in the bin, over the data collection period.

with the mixing region that consists of 3 unit cells of Al, forming a single interface parallel to the (100) crystallographic plane. The cross-sectional area of the simulation box, which is parallel to the interface, consists of 6×6 Si unit cells and 8×8 Al unit cells, such that the lattice mismatch is small (0.56%) to minimize interfacial strain. As the bulk of the materials were fully relaxed prior to NEMD simulations, the straining effects are assumed to be negligible. Therefore, we omit the investigation of straining effect on interfacial thermal transport properties. The mixing region bounds the optimization space to 6 atomic layers

The schematic of the periodic simulation cell is shown in Figure 3.1. The system consists of hot/cold reservoirs and fixed boundaries at both ends to break periodicity in the heat transfer direction, while maintaining periodic boundary conditions in the y and z directions. The reservoirs have the same composition and periodicity as the sample. The sample region is defined as everything except for the reservoirs and fixed boundary regions. The Si region is 30 unit cells in length (lattice constant $a_{\text{Si}} = 5.43 \text{ \AA}$), and the Al region is 45 unit cells in length ($a_{\text{Al}} = 4.05 \text{ \AA}$). The two regions are in contact

of Al, with mixing ratio defined as the ratio of Si to Al. For an intermixing arrangement of $[l, r]$, where l is the mixing depth (atomic layers) and r is the mixing ratio, the initial configuration is produced by obtaining the indices of all Al atoms in the mixing region l and randomly selecting $r\%$ of indices to replace the atom type with Si atom. A unity mixing fraction means that all atoms in the mixing region have been swapped from Al to Si while still initially in an FCC configuration. Minimum mixing fraction is set to 0.01 to ensure there are at least 1-2 Si atoms intermixed into the Al structure, while the maximum mixing fraction is set to 0.99 to ensure there are at least 1-2 Al atoms present in the mixing region.

Direct method

The NEMD heat transfer simulation is set up using the direct method [136], where a fixed amount of energy $\Delta\epsilon$ is added to atoms in the hot reservoir in the Si substrate and the same energy is subtracted from atoms in the cold reservoir in the Al substrate, creating a heat flux $J = \Delta\epsilon/A_c\Delta t$ (A_c is the cross-sectional area, Δt is the timestep of MD). This establishes a temperature gradient in the system, which when combined with knowledge of the energy transfer rate enables us to compute the interfacial thermal conductance (ITC) as the inverse of the Kapitza resistance[145]:

$$G = \frac{1}{R_k} = \frac{J}{\Delta T} \quad (3.1)$$

where J is the heat flux (in W/m²) and ΔT is the interfacial temperature gradient. The interface has a variable thickness due to atomic intermixing; thus, we treat the maximum Si/Al mixing region as the interfacial region and evaluate ΔT at its boundaries, so that G can manifest all the influence from intermixing and represent the overall thermal performance of the system when the length is fixed. The method of applying heat flux involves scaling the velocities of the atoms in each of the reservoirs to add or remove a desired amount of kinetic energy. We defined thickness of the reservoirs to consist of four unit cells in each material such that a sufficient number of atoms are present in the reservoirs, reducing the energy scaling per atom.

Data collection and analysis

During MD simulations, the sample and reservoirs are initially equilibrated at a uniform temperature of 300 K by randomly generating the atomic velocities according to a Gaussian distribution. This is followed by a constant number of atoms, volume, and energy (NVE, microcanonical) simulation, where a heat flux of 15.1 GW/m² is applied. The magnitude of the heat flux is large enough to create a distinct temperature profile along the substrate without developing nonlinearities throughout the sample due to the temperature dependence of the thermal conductivity[123]. Immediately after the heat flux is applied, the simulation runs for a period of 4 ns with 1 fs-timesteps (four million steps) to allow the sample to reach a steady-state condition. Atomic energies are then collected at every timestep for an additional 2 ns (two million steps), which are averaged to obtain the temperature profile along the x -axis. Considering that the mixing regions of the systems have different thicknesses, the temperature change at the interface is evaluated by extrapolating the linear part of the temperature profile in each material to the interface, where ΔT is taken as the difference of the two values, as shown in Figure 3.1(b). We found that the distribution of temperature drops across the mixing region was sensitive to the choice of regions supporting each linear fit. From a preliminary dataset, the endpoints for each linear region were optimized to ensure the fitting function works for all the systems with various intermixing arrangements while maintaining the quality of the linear fit (with $R^2 \geq 0.98$). For a given heat flux, the change in the ITC is monitored by keeping track of ΔT .

Uncertainty in MD simulations

Small deviations can have large effects during high-throughput optimization over a large sample space. With randomness and uncertainties in MD simulations, assessing the uncertainty upfront is important. Previous studies have demonstrated that the MD-predicted thermal boundary resistance (R_k) depends on the size of the system L_s , where $L_s = L_L + L_{\text{mix}} + L_R$, and the thermal reservoir (L_{res}) used in the simulation [136, 142, 123]. Therefore, we kept

L_s and L_{res} constant over all simulations. We indeed found that L_s changes slightly during the simulation with varying intermixing depth and percentage. However, the magnitude of this change is less than 0.5% in all cases, which is sufficiently small and can be neglected. The size dependence of R_k on L_s , which in principle can only be eliminated when the system is infinitely large, still exists and can potentially affect the optimization of intermixing. According to the study of Schelling *et al.*, for the same interface there is a linear correlation between R_k and $1/L_s$ [136]; thus, it was expected that in our systems, each distinct intermixing ratio or pattern warrants a new interface with a different linear correlation. However, by conducting a convergence study we find that the linear correlation is consistent for the same intermixing ratio and region regardless of the random atomic arrangement (Figure B.1). Therefore, linear extrapolation can still be applied to extend our results to systems of varied lengths. Still, a convergence study is needed for the size effect on the optimization of intermixing, which is introduced in the Results Section.

Significant progress in simulation methodology and computing power has enabled simulations of increasingly large systems and long time scales[126, 127, 128, 146, 147]. However, the accuracy of these simulations in predicting physical observables remains variable and relies on both accurate energy functions and effective sampling. With accurate energy functions, adequate sampling of a desired phase-space is essential in achieving low associated error of estimated thermodynamic and kinetic properties. Simulations generally consist of equilibration and production phases, where the systems evolve during equilibration to be representative of the desired ensemble before data is collected during production run to derive physical properties. It is necessary to thoroughly investigate the effect of equilibration and data collection periods to determine the appropriate timescale to ensure both the accuracy and efficiency of the simulations while comparing the results of independent MD in a self-consistent manner. To isolate the effect of intermixing, both pristine and intermixed interfaces are examined in this particular study. We chose 15 different combinations of $[\tau_{ss}, \tau_{av}]$ to examine the sensitivity of ITC to the simulation time, where τ_{ss} is the time allowed for the temperature to reach steady state after introducing the heat flux and τ_{av} is the time used

for collecting and averaging atomic energies to obtain the temperature profiles.

3.3.2 Machine learning domain

Bayesian optimization

Bayesian optimization is a sample-efficient and gradient-free approach to global optimization black-box functions. The goal of this technique is to bound the maxima of the random objective function, $f(\mathbf{x}; \xi)$ (where ξ represents the random input upon which f depends) using the fewest number of samples that satisfy the accuracy requirement or the computational budget [139, 148, 149].

Bayesian optimization[150] consists of two main components: 1) a Bayesian statistical model for modeling the objective function, and 2) an acquisition function to decide the next point to sample. The statistical model provides a Bayesian posterior probability distribution that describes potential values for $\mathbf{x}$ at a candidate point x . Each time we observe f at a new point, this posterior distribution is updated. The acquisition function measures the value that would be generated by evaluation of the objective function at a new point x , based on the current posterior distribution over f .

Gaussian process (GP) is a generalization of the Gaussian probability distribution. It is a convenient and powerful prior distribution on functions and are used in majority of the Bayesian optimization work. GPs are defined by their mean ($\mathbf{m}$) and covariance/kernel functions ($k(x_i, x_j)$). $\mathbf{m}$ is almost always assumed a constant value (often assumed 0) which simplifies the necessary equations for conditioning. We parameterized the covariance kernel as a composite of a two-dimensional radial basis function and added a white noise kernel to account for the noise from MD simulations. Specifically,

$$k(x_i, x_j) = C \left(\exp \left[\frac{-d(x_i, x_j)^2}{2l_1^2} \right] + \exp \left[\frac{-d(x_i, x_j)^2}{2l_2^2} \right] \right) + \delta(x_i - x_j) \quad (3.2)$$

Here we define C as a constant term, $d = x_i - x_j$, and l_i is the parameter that sets the characteristic length-scale of the process for each dimension.

The second component of Bayesian optimization is an acquisition function, which defines how to explore/exploit the parameter space for a defined figure-of-merit. Normally, the high values of acquisition functions correspond to potentially high values of the objective function, whether for high predicted mean value, the greater uncertainty, or both[151]. Upper confidence bound (UCB) is a popular acquisition function, it calculates the most optimistic improvement at a given point, weighted by a scalar multiplier, β , of the noise estimation, as shown below:

$$UCB(\mathbf{x}) = \mu(\mathbf{x}) + \beta\sigma(\mathbf{x}) \quad (3.3)$$

The value of β balances between exploiting the supposed location of the maximum where the posterior mean $\mu(\mathbf{x})$ is high, and exploring uncertain regions where the posterior variance $\sigma(\mathbf{x})$ is high. In sequential optimization, $\text{argmax } UCB(\mathbf{x})$ is then taken as the next sampling point. Since the time consuming nature of the MD simulations necessitates batch evaluation to achieve optimization within a reasonable time frame, we implemented a quantile-based adaptive sampling algorithm based on UCB, as described in Algorithm 1, to select a batch of sampling points. As opposed to using the maximum UCB value to determine the next sampling point, we randomly sampled a batch of test points from the quantile of the GP above the UCB, hereafter called the quantile region. As the optimization proceeds, we restrict the quantile region further to the upper P_Q percent of heat transfer rate values, $1/\Delta T$, in the quantile region by evaluating the threshold $\mathcal{Q}$ which is the lower bound on the heat transfer rate value in this restricted region. Considering higher variance in ΔT values acquired from the MD simulations for the intermixed cases, $\beta = 5$ is taken to ensure the GP regions with high uncertainties are not excluded from the reduced sampling region at the earlier stage of the optimization.

Algorithm 1: Quantile-based adaptive sampling

Input: f: function to be optimized
 $\mathcal{X}$: sampling space
 $\mathcal{D}$: initial dataset $\{(x_1, y_1), \dots, (x_n, y_n)\}$
 T: number of iterations
 b: batch size
 P_Q : percentage of the quantile region //starts with 100%
 Q : quantile threshold value
 ε : decay rate
 GP = model_init($\mathcal{D}$)
for t in $1, \dots, T$, **do**
 $UCB(x) = \mu_{t-1}(x) + \beta \sigma_{t-1}(x)$ // Calculate UCB using full sampling space ;
 Q = lower bound of the top P_Q quantile of $UCB(x)$;
 $\mathcal{R} = \{x \in \mathcal{X} | UCB(x) \geq Q\}$ // Update quantile region ;
 for i in $1, \dots, b$, **do**
 $x_i = \text{random.choice}(\mathcal{R})$ // randomly select sampling points from quantile
 region ;
 Query x_i to obtain y_i ;
 end
 $\mathcal{D} = \mathcal{D} \cup \{(x_1, y_1), \dots, (x_b, y_b)\}$;
 GP.update_model;
 $P_Q = P_Q \times \varepsilon$;
end

MPI assisted parallel optimization framework

Although Bayesian optimization is an efficient technique, the computational cost of MD is still comparatively high. In order to accelerate the exploration/exploitation process, we developed a Message Passing Interface (MPI) based framework that can execute multiple

concurrent LAMMPS simulations and update a central Bayesian optimization model, as shown in Figure 3.2. Child processes are created with the MPI spawning function. The spawned processes have their own **MPI_COMM_WORLD** consisting of identical copies of the MPI program specified by the command, and in addition they have a predefined intercommunicator **MPI_COMM_PARENT**[152]. Open-source Python library—OpenAI Gym[153]—is used in this work for creating environment instances and interacting with them. It provides standard application programming interface to communicate between Bayesian optimization algorithm and the environment in which sampling points are queried by building the intermixing structure, obtaining temperature profile with LAMMPS and performing post-simulation analyses to evaluate ΔT . A more detailed description of the OpenAI Gym environment is included in Supporting Information.

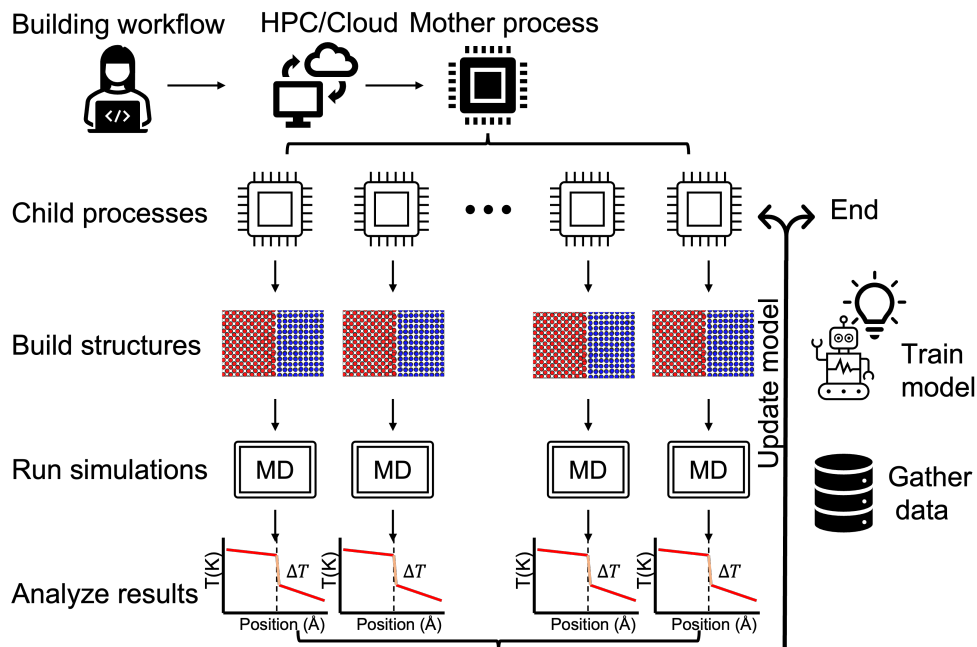


Figure 3.2: Schematic diagram of the MPI-based framework used to achieve batch optimization. Each of the child processes is initiated with **MPI Spawn** and interfaces with LAMMPS using the OpenAI gym environment.

3.4 Results and Discussion

As detailed in the methodology section, we used a GP model as the probabilistic surrogate for the black-box objective function we seek to optimize which describes the relationship between intermixing and ITC. ITC is calculated as $G = J/\Delta T$. For systems with mixing regions no larger than two atomic layers, we obtained ITC between 0.35–0.48 GW/m²K, which fall in the range predicted by mismatch models and similar simulations[154]. These theoretical values are higher than experimental measurements[155], likely due to the ideal conditions in simulations without oxidation. In addition to the idealized interfaces, the choice of the interatomic potentials as well as the finite system size effect can also lead to the discrepancy between experiment and simulations. Since we fixed the heat flux J for all systems, we defined the figure-of-merit for the optimization as the inverse of the temperature drop across the interface, $1/\Delta T$, which is used as an analogue for thermal conductivity. Snapshots of GP-UCB hyper-surface throughout the optimization are shown in Figure 3.3. Throughout the optimization, the shape of the GP hyper-surface evolves and converges while the quantile region continues to shrink with each iteration. Batch of 10 sampling point selected from evolving quantile region is evaluated (with NEMD simulation) per iteration to accelerate the exploration/exploitation process. Resulting $1/\Delta T$ values obtained from these simulations show large variance especially at early iterations of the optimization, as shown in Figure B.2(a), due to the fact that we are evaluating the points in the quantile region with low a quantile threshold value. With each iteration of the optimization, as the quantile region shrinks, points with higher predicted GP values are evaluated and mean $1/\Delta T$ value of the batch also increases. GP predicted max $1/\Delta T$ values for each iteration plotted in Figure B.2(b) shows the convergence of the GP model only after six iterations with minimal variance. A convergence study shows that optimizations of systems with different lengths tend to reach the same intermixing percentile region (Figure B.3). This, together with the applicability of linear extrapolation of our results, suggests that our current data set is capable of representing a wider range of Si/Al systems of varying lengths. In following

paragraphs we will look into the sources of the large variance from MD data and discuss the significance of the intrinsic uncertainties to the model training and evaluation.

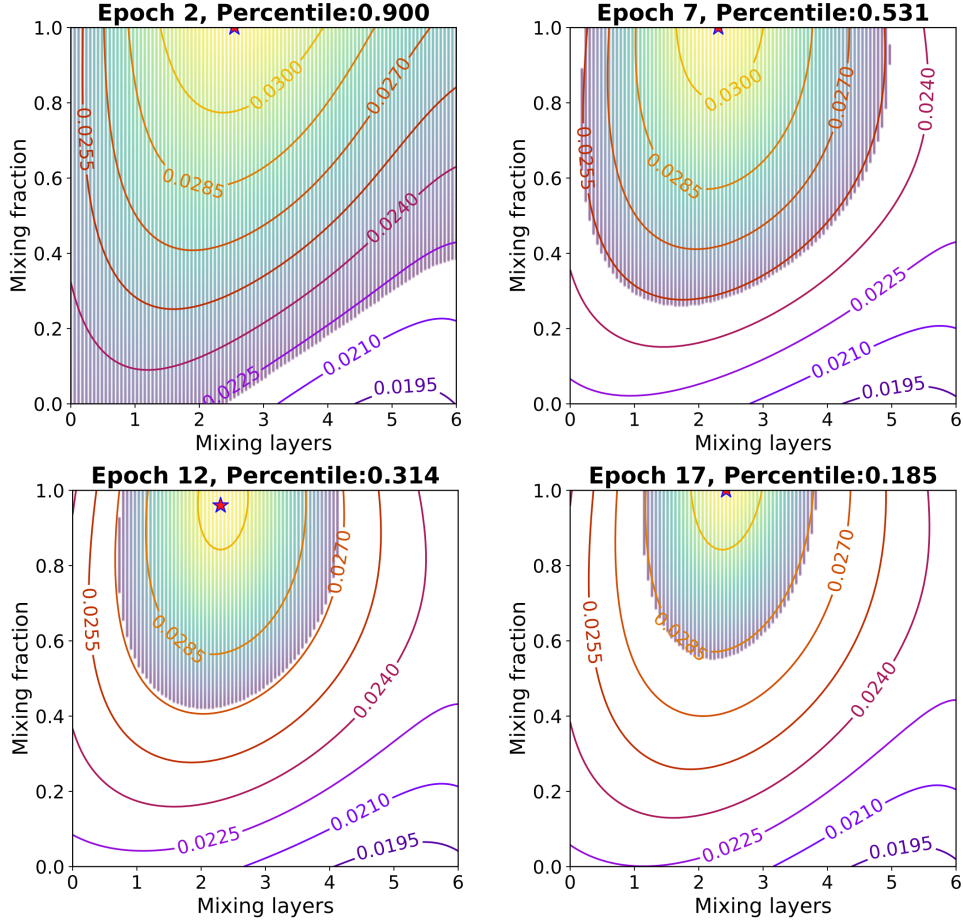


Figure 3.3: Illustration of the GP-UCB surface evolution throughout the optimization. The contours indicate the topography of the GP-UCB surface in terms of the heat transfer rate, $1/\Delta T$. The shaded region is the quantile region at a given epoch, which shrinks during optimization as the learning rate forces P_Q to decrease (called "Percentile" in each subplot), and consequently the heat transfer rate threshold Q to increase.

A snapshot comparison of three mixing profiles (pristine, optimal, negative impact) is shown in Figure 3.4. The results from the optimization scan show that the ITC increases by as much as 50% relative to the pristine interface with a mixing region of two atomic layers

at 93% intermixing. Previous work based on atomistic Green's function has demonstrated that interfacial atomic intermixing can enhance the elastic phonon transmission by providing a region with bridging phonon density of states that overlaps with both materials, thus increasing the ITC [122], while more recent work based on classical MD suggests that enhanced inelastic phonon transport contributes significantly at such deformed interfaces [156]. We attribute the ITC enhancement in our study to both factors, considering the similarity between our modeling environment and that of Lu *et al.* [156]. However, further increasing the size of the mixing region beyond the apex values reduces the ITC. This can be explained by increased Anderson localization in the disordered mixing region [157, 158], which negates the increase introduced by enhanced elastic and inelastic phonon transport. It is noteworthy that even with 50% increase, the ITC does not reach the value predicted by acoustic mismatch model[154].

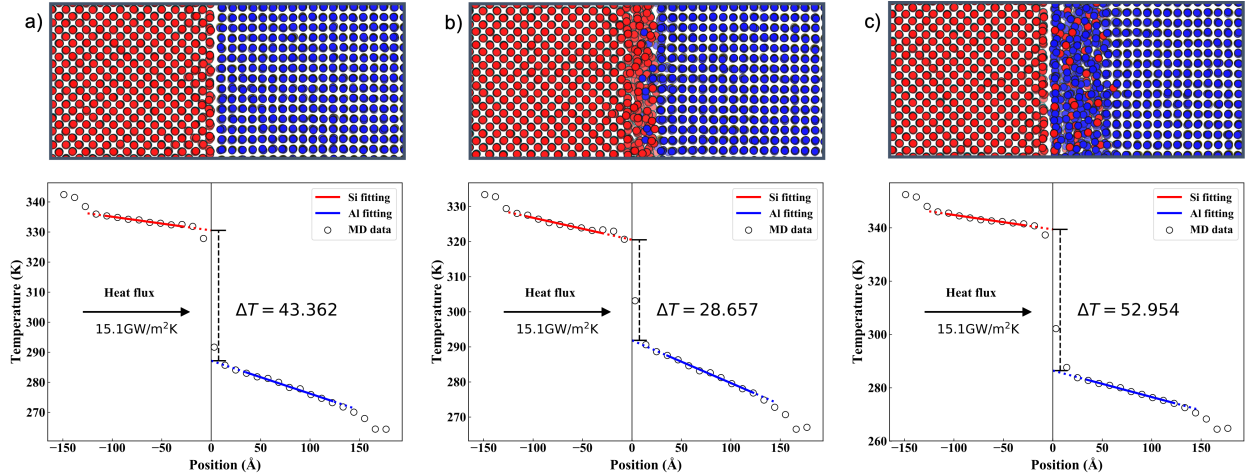


Figure 3.4: Temperature profiles of three interfacial mixing configurations: a) pristine interface, b) two layer intermixing at 93%, c) six layer intermixing at 50%.

50% increase of the ITC, despite the significance, is not always guaranteed. This can be attributed to two factors. One is the intrinsic errors from the MD simulations which can be minimized but cannot be eliminated. The other is the random positioning of the intermixed atoms leading to different intermixed structures for the same intermixing length and ratio.

NEMD is a powerful technique to simulate heat transfer processes. Still, no single method is perfect. With systematic and random sources of errors accruing in MD simulations, assessing the uncertainties is important to support active-learning strategies. In our work, we carefully evaluated the system design, parameterization and analysis of simulation result to minimize the variation in the results to be less than the quantity of interest. As stated in setup section, with length of the system and thermal reservoir kept constant over all simulations, resulting ITCs are directly comparable. Simulation duration is another important parameter. We examined 15 different combinations of $[\tau_{ss}, \tau_{av}]$ for both pristine and intermixed structures, and the distributions of the resulting ΔT values are plotted in Figure 3.5. Additional figure with different ordering (varying τ_{av} for τ_{ss}) is included in Supporting Information (Figure B.4).

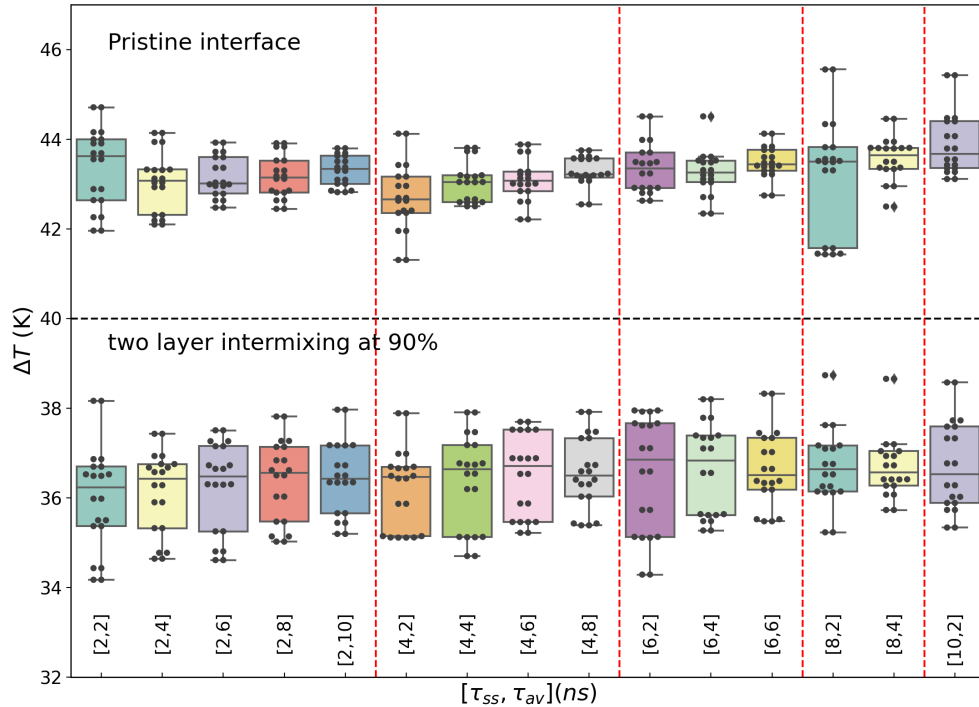


Figure 3.5: Various run times and distribution of resulting ΔT for pristine and intermixed interfaces. Each box plot contains 20 data points. Vertical dashed red lines are used to separate each set of τ_{ss} .

Relative variance (variance divided by mean) of ΔT ranges from 0.27% to 4.0% for the pristine interface and 1.69% to 4.72% for the intermixed cases. Detailed statistical description of each entry is listed in Supporting Information (Table B.1). For a fixed τ_{ss} , the variance of ΔT decreases with increasing data collection time τ_{av} . In theory, the uncertainties can be reduced to a certain degree (the intrinsic uncertainty of MD from its stochastic nature) with increased computational time. However, this increases the cost of the simulation significantly and the low cost-effectiveness destroys the ML workflow. For our system, each additional ns of NVE integration adds ~ 256 core hours to the simulation. Increasing the $[\tau_{ss}, \tau_{av}]$ from [4 ns, 2 ns] to [4 ns, 8 ns] doubles the computational cost from ~ 1700 core hours to ~ 3400 core hours, while lowering the relative variance roughly from 1.37% to 0.27% for the pristine interface and only from 2.21% to 1.82% for the intermixed case. Considering the trade-off between computational cost and accuracy, and that each data point requires a separate MD simulation, we equilibrate the systems for 4 ns before collecting data for an additional 2 ns to calculate the temperature gradient.

Comparing the pristine interface with the intermixed, we observed greater variance in ΔT for the intermixed cases. Since the positions of the swapped atoms in the intermixing layers are assigned randomly when generating the intermixed structure, homogeneity/heterogeneity of the intermixed region is not controlled. Lu *et al.* [156] also found the distribution of disorder to affect the ITC. Swapping atoms at the boundary layer rather than in layers further from the interface improves ITC enhancement, as this provides better atomic intermixing and more inelastic scattering sites at the interface. Introducing changes away from the interface has a reduced effect on ITC and introduces extra inelastic scattering in the bulk phase of the material, which hinders phonon transport.[156] It is important to highlight that despite the greater variation in results, there is no overlap between the temperature gradients of intermixed vs. pristine interfaces, clearly indicating the improvement of thermal conductivity with intermixing. We note that the percentage of enhancement also depends on the total length of the system, as is indicated by the size effect on ITC (Fig. B.1); thus, a 50% increase is not guaranteed for systems of sizes other than those used in the current

study.

3.5 Conclusions

This study highlights the advantages of Bayesian optimization technique with built-in uncertainties leveraging the errors from MD to yield statistically robust and reproducible results. We pushed the model to explore more in the higher confidence region using an adaptive quantile-based confidence interval approach (1) to prevent early lock-in on local maxima, (2) to increase the confidence in the result, (3) to generate multiple non-overlapping plausible query points to expedite the optimization. Parallel evaluation of candidate structures with MD simulations, made possible by dynamic spawning of jobs through the Message Passing Interface (MPI), ensured viability of optimization within a reasonable time frame. This framework—seamlessly incorporating MD simulations with ML algorithms—is easily transferable to any system with well-developed interatomic potentials. GP model suggests that the ITC of the Si/Al junction can be enhanced by introducing an intermixed region that consists of three or fewer atomic layers containing 80% or higher ratio of Si. Further extending the intermixing region increases Anderson localization in the disordered mixing region and negatively impacts the ITC. Due to the random nature of intermixing, the magnitude of increase in the ITC varies. Further efforts are ongoing to better understand the relationship between ITC and distribution of the intermixing.

3.6 Acknowledgement

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Chapter 4

PRACTICAL APPLICATION OF MACHINE LEARNING POTENTIALS FOR STRUCTURAL RELAXATION¹

4.1 *Abstract*

The accurate determination of atomic structures plays a fundamental role in understanding and predicting the properties and behavior of materials. Traditionally, this task has been tackled using computationally intensive methods, such as density functional theory (DFT), which accurately describe the electronic structure and energetics of materials. However, the growing demand for high-throughput calculations and the need for efficient exploration of complex energy landscapes have spurred the development of alternative approaches. Machine learning potentials (MLPs) have emerged as a promising tool for accelerating structure relaxation processes, offering a balance between computational efficiency and accuracy. Here, we present a comprehensive study on the practical application of MLPs for structure relaxation, aiming to evaluate their performance, reliability, and potential impact across different domains. By harnessing the power of machine learning algorithms, we aim to unlock new opportunities for accelerated materials design and exploration.

¹This chapter is a draft of an article titled "Practical Application of Machine Learning Potentials for Structure Relaxation", and was reproduced with permission from S. Rustam, J.A. Bilbrey, S. Muller, and J. Pfaendtner.

4.2 Introduction

Transition metal dichalcogenides (TMDs) are a class of materials with unique structural and electronic properties, making them highly attractive for various applications in optoelectronics[159, 160], catalysis[161, 162], and energy storage[163, 164, 165]. Accurate determination of the atomic configurations of TMDs is essential for a comprehensive understanding and prediction of their material properties and behavior[166, 167]. However, performing efficient and reliable structural relaxations in TMDs is a challenging task, often requiring computationally intensive calculations based on first-principles methods, such as density functional theory (DFT).

In recent years, machine learning approaches have emerged as powerful tools for accelerating structural relaxation processes. Machine learning models, such as machine learning potentials (MLPs), approximate the potential energy surface (PES) of the material system, enabling more efficient search for low-energy configurations compared to traditional methods[168]. Significant advancements have been made in the development of high-accuracy MLPs to capture the complex interactions and energy landscapes of materials, enabling reliable predictions of atomic configurations and material properties[39, 40, 41]. Notably, graph neural networks (GNNs), which have the ability to capture equivariant representations of atomic environments, have shown effectiveness in modeling the complex PES of materials[42, 43, 44, 169, 170, 171].

However, practical application of MLPs for structure relaxation of TMDs comes with inherent challenges. While most MLPs are typically evaluated based on their accuracy in reconstructing forces across popular benchmark datasets like MD17[42, 43, 44], these standard benchmarks may obscure the specific challenges that arise when applying MLPs to custom datasets. A key challenge is the acquisition of a sizable dataset that adequately represents the atomic configurations and relevant properties of the specific TMD system under study, while ensuring the reliability and consistency of the data. Additionally, MLP models often have complex architectures and numerous hyperparameters that must be carefully optimized.

Finding the optimal architecture and hyperparameter values requires extensive experimentation and computational resources. The lack of clear guidelines or best practices for model selection and optimization adds to the challenge. Furthermore, MLPs can introduce unstable dynamics during structure relaxation, necessitating thorough validation procedures to guarantee their reliability and accuracy.

In this study, we apply Neural Equivariant Interatomic Potentials (NequIP), a state-of-the-art MLP architecture, to perform structural relaxation of 1T ternary TMDs. We explore the capabilities and limitations of MLPs in accurately predicting atomic structures while optimizing computational efficiency. Through a series of experiments and analyses, we detail workflows for curating training data and selecting evaluation criteria to obtain reliable and reproducible results. We also explore strategies for incorporating domain knowledge to enhance the reliability and applicability of MLPs. We further show that a training set with structural similarity, but not energetic similarity (due to size extensive nature of the potential energy) can provide geometrically accurate relaxed structures, even when the MLP shows a systematic error in energy prediction. Finally, we provide our perspective for MLPs to become a method capable of reliably generating minimized structures at high throughput without compromising accuracy. As such, MLPs represent an essential step towards fully computational materials design.

4.3 Computational Methods

4.3.1 Dataset

The dataset utilized in this study is a subset of a larger dataset generated by Muller et al.[172] that contains structural relaxations of bulk TMDs computed using plane-wave DFT. Specifically, we focus on the 1T ternary structures of $\text{VS}_{2-\delta}\text{Te}_\delta$, where δ represents the ratio of Te atoms to S atoms. The chalcogenide stoichiometric ratio δ ranges from 0 to 2, with a minimum step size of 0.0625 (corresponding to the replacement of one chalcogenide atom in the simulation cell), resulting in a total of 23 unique stoichiometries in the dataset.

Due to the different arrangements of chalcogenide atoms within a single ternary TMD structure, the number of computed structures can vary for each stoichiometry. Figure C.1 presents a histogram illustrating the distribution of total energies for all relaxed structures in the dataset. Moreover, it provides the total number of computed structures and the mean total energy for each chalcogenide stoichiometric ratio δ .

4.3.2 Curation of training data

In our study, we conduct a series of experiments to establish best practices for curating training data for MLPs, aiming to enhance accuracy, robustness, generalization, and reproducibility. We train a series of MLPs on training sets of different sample sizes and stoichiometric compositions to examine the impact on the MLP predictions. First, we train the network exclusively using DFT trajectories of VS_1Te_1 ($\delta = 1.0$) with a chalcogenide ratio of 1:1. Subsequently, we evaluate the trained model on other chalcogenide stoichiometric ratios to assess its generalizability. Second, we selectively control the representation of stoichiometries and size of the training data while comparing the performance of the trained models. We define the sampling frequency of the chalcogenide stoichiometric ratio δ to control the representation of various potential energies in the training data. Furthermore, we vary the sample sizes to strike a balance between accuracy and data efficiency, considering the trade-off between a comprehensive dataset and computational efficiency.

Figure 4.1 provides a visual representation of the curated training datasets used in this study. Each colored block in the figure represents a specific stoichiometry along with the corresponding sample size in the training data. Stoichiometries that are missing from the dataset are marked with a cross. The training data exclusively containing VS_1Te_1 is labeled with its chemical symbol. For the training data that encompass multiple chalcogenide stoichiometries, we adopt the notation fxny , where "x" can take values 1, 2, or 3. A value of 1 signifies the inclusion of all stoichiometries in the training data, while values of 2 and 3 represent sampling of stoichiometric ratios with frequencies of 0.125 and 0.25, respectively, and the inclusion of only those samples in the training data. The parameter "y" denotes

δ	0.000	0.125	0.250	0.375	0.500	0.625	0.750	0.875	1.000	1.125	1.250	1.375	1.500	1.625	1.750	1.875	2.000	
VS_1Te_1						X	X	X		X	197	X		X	X	X		
f1n30	30	30	30	30	30	30	30	30	X	30	X	30	X	30	X	X	30	30
f1n10	10	10	10	10	10	10	10	10	X	10	X	10	X	10	X	X	10	10
f2n30	30		30		30		30	X	X	30	X	30	X	30	X	X	30	
f2n10	10		10		10		10	X	X	10	X	10	X	10	X	X	10	
f3n30	30			30			30	X	X	30	X		X	30	X	X	30	
f3n10	10			10			10	X	X	10	X		X	10	X	X	10	
f3n5	5			5			5	X	X	5	X		X	5	X	X	5	
f3n2	2			2			2	X	X	2	X		X	2	X	X	2	
f3n1	1			1			1	X	X	1	X		X	1	X	X	1	

Figure 4.1: Visual representation of the curated training datasets. Total number of structures and mean total energy is given each δ values.

the number of structures chosen to represent each stoichiometry in the training data. To ensure consistency, we curate the training data by selecting a fixed number of structures for each stoichiometry, regardless of the varying lengths of the DFT trajectories. Supporting Information Figure C.2 illustrates the variability of trajectory lengths in the dataset.

4.3.3 Model training

Specific details of model hyperparameters and testing of its impact are discussed in the original NequIP paper[44]. Here we use 6 interaction blocks, an initial learning rate of 0.005, and a batch size of 32. It is noteworthy that the use of small batch sizes is found to be an important hyperparameter in the NequIP model. However, in our preliminary experiments, we determined that for structural relaxation, when incorporating DFT in the first few steps of the relaxation, the impact of the batch size is negligible (Supporting Information Figure C.3, Figure C.4). A learning rate scheduler is implemented with decay factor of 0.8 whenever the loss is not improved for 50 epochs. Training is halted when any of the following conditions are met: (a) the maximum training time of 96 hours is reached, (b) the maximum number of 1,000 epochs is reached, or (c) the learning rate falls below 10^{-6} . All models were trained with a tensor rank of $l = 1$ and 64 features.

4.3.4 Structural relaxation using MLPs

The `nequip-deploy`[44] command is used to deploy the result of a training session into a model that can be stored and used for inference. A Python-based Atomic Simulation Environment (ASE)[173] calculator can be built directly from the deployed model to run structure optimization. The BFGS algorithm is used as an optimizer to relax a given structure, which relies on the forces on each atom obtained from the associated calculator object and the Hessian matrix to guide atom movement at each step. The convergence criterion for the optimization is that the magnitude of the force acting on each individual atom should be below a specified threshold, denoted as `fmax`. To match the DFT settings, `fmax` is set to 0.01 for the ASE optimizer.

4.3.5 Model evaluation

The fundamental principle of model evaluation involves assessing the ability of a specific model to generate structurally and energetically accurate relaxed structures, which aligns with the intended purpose of its development. Thus, structural optimization performed with the ASE calculator built from the MLP is directly compared to the initial DFT calculations. Specifically, final structures obtained from DFT- and MLP-based optimization are compared in terms of energetic and structural similarities.

The ASE provides a "`get_potential_energies()`" function to obtain potential energies associated with the atom object[173]. This feature enables direct access to the total potential energy of structures in MLP-based structure relaxation performed in ASE. Similarly, by reading DFT output files into ASE atom objects, the total energy of DFT-optimized structures can be accessed in a similar manner, allowing for convenient analysis and comparison of energies. To assess the energetic similarity between a DFT and MLP optimized structures, we define the energy difference as $\Delta E = E_{DFT} - E_{MLP}$. A positive value of ΔE indicates that the total energy of the MLP optimized structure is lower than that of the DFT optimized structure, while a negative value suggests the opposite. This energy difference provides a

metric for comparing the energetics of the two optimization methods and evaluating their agreement.

Root Mean Square Deviation (RMSD) is widely recognized as the most commonly used quantitative measure to assess the similarity between two superimposed structures. However, it should be noted that RMSD is sensitive to the initial alignment of the compared structures, which can pose challenges, particularly when dealing with flexible or highly symmetric structures. In order to address this issue, we employed a method that involved generating sorted lists of metal-metal distances for each structure. Subsequently, we computed the RMSD of these metal-metal distances to account for the structural similarity between the two structures.

In order to validate the different models, we have developed a validation protocol that enables a direct and concise comparison of their performance. Each model is evaluated by the coefficient of determination (R^2) for the total energy, which is defined as:

$$R^2 = 1 - \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2}$$

where y_i is the observed values, $\hat{y}_i$ is the predicted values, $\bar{y}$ is the mean of the observed values, and n is the total number of data points. Values usually ranges between 0 and 1 where a higher value means better fitting performance. If the goal is to minimize the energy differences between optimized structure generated with MLP and DFT, R^2 can be used to score different model to provide direct comparison.

4.4 Results and Discussion

4.4.1 Efficacy of MLP-based structure optimization

As described in the Methods section, the deployed MLP model is utilized to build an ASE Calculator for conducting structure optimization. The relaxation process based on MLP is fast, with each optimization step taking less than a second and the total time averaging between one to three minutes. We use the MLP model trained on f1n30 to demonstrate the effectiveness of the MLP model in accurately performing structural relaxation. The results

obtained from the MLP-based relaxation process are compared against the corresponding DFT reference structures.

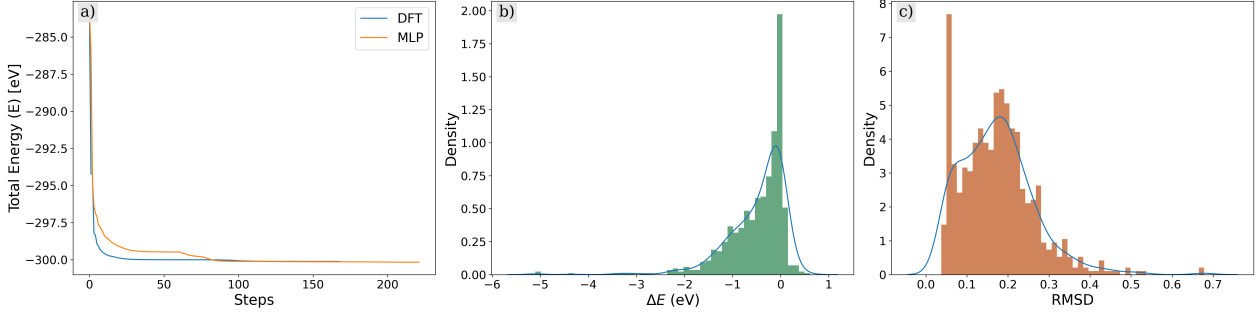


Figure 4.2: Evaluation of the MLP model trained on VS_1Te_1 . a) An example energy minimization trajectory. b) Histogram of ΔE after relaxation, where ΔE equals to total energy differences between DFT and MLP optimized structures. c) Histogram of RMSD between MLP and DFT optimized structures.

Notably, the MLP model successfully reproduces the structural and energetic features of the DFT-optimized structures, as evidenced by the high degree of agreement in terms of total energy and interatomic distances. Figure 4.2 (a) illustrates the convergence of the total energy for an example structure during DFT and MLP-based relaxation, shedding light on the effectiveness of the MLP-based relaxation process. Furthermore, the distribution of ΔE values (Figure 4.2 (b)) and RMSD values (Figure 4.2(c)) across all structures further emphasizes the consistent agreement between the DFT and MLP relaxed structures, consolidating the reliability and accuracy of the MLP model in capturing the essential characteristics of the system. However, MLP produced unstable dynamics for some of the structures during structural relaxation process, presumably due to the under representation of configuration space in training data, which is discussed later in this manuscript.

4.4.2 Potential synergies between MLP and DFT

To enhance the reliability and practical applicability of MLP-based methods in providing accurate minimized structures, it is essential to explore synergies between MLPs and DFT.

By harnessing the strengths of MLPs and the high accuracy of DFT calculations, we strive to improve the overall performance of structure relaxation processes and enable more robust and precise predictions of atomic configurations, which are crucial for a comprehensive understanding and prediction of material properties and behavior.

First, we examined the use of MLPs as an initial guess or starting point for DFT-based structure optimizations. We randomly selected 10 structures from each stoichiometry and performed structural relaxation with MLP (trained on fln30). Output structure is then further relaxed in DFT and compared with corresponding structure relaxed with standalone DFT. We found that utilizing MLP-relaxed structures as the initial input for DFT calculations significantly reduced the computational cost and improved the convergence of the optimization process. An example trajectory of the relaxation presented in Figure 4.3 (a) shows that the MLP provided an effective approximation of the potential energy surface, allowing the DFT calculations to focus on fine-tuning the structures towards more accurate energy minima. For all 210 structures calculated, average DFT steps are cut in roughly 1/3 after using MLP to provide starting structure as shown in Figure 4.3 (b). Structures obtained from both standalone DFT and the combined approach exhibit remarkable energetic and structural similarity, as demonstrated by the exceptionally narrow distribution of ΔE and RMSD values centered around zero (Figure 4.3 c)). The combined approach demonstrated comparable accuracy to standalone DFT optimizations, while significantly reducing the computational resources needed for the calculations.

Furthermore, we investigated the possibility of iterative refinement by alternating between MLP-based relaxation and DFT. Specifically, for each value of N in the range of 10, we employed the Nth DFT trajectory as the initial structure for MLP-based structure relaxation. The resulting output structure was then evaluated against the corresponding DFT-optimized structure in a similar manner. Figure 4.4 illustrates the distribution of ΔE and RMSD values for the relaxed structures obtained using the same MLP model, highlighting the impact of each initial DFT step on the subsequent relaxation process. Notably, even without additional training, the MLP model demonstrates improved accuracy in structural relaxation when

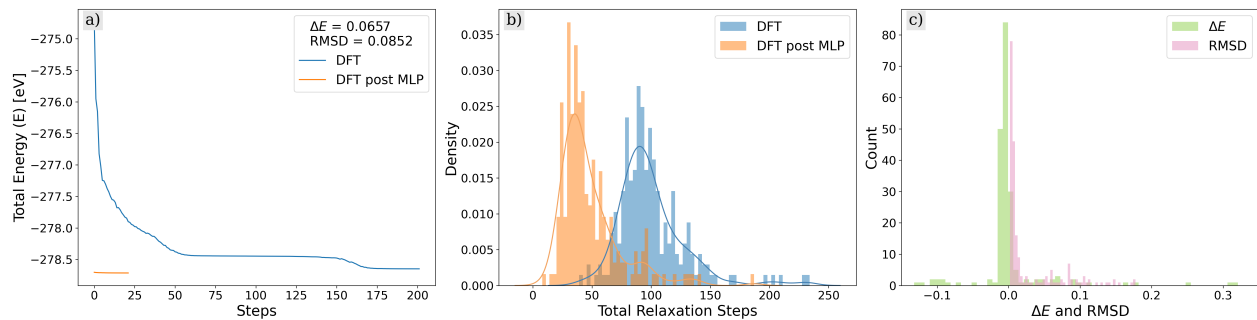


Figure 4.3: a) An example energy minimization trajectory. b) Histogram of ΔE after relaxation, where ΔE equals to total energy differences between DFT and MLP optimized structures. c) Histogram of RMSD between MLP and DFT optimized structures.

only a few initial DFT steps are incorporated. This observed improvement in structural relaxation accuracy with the inclusion of a few initial DFT steps is consistent across all the MLP models investigated in this study (Figure C.5). Furthermore, by incorporating initial DFT relaxation, the previously observed unstable dynamics for certain configurations were completely eliminated. A more detailed discussion on this topic will be presented in the subsequent sections focusing on data efficiency and model accuracy.

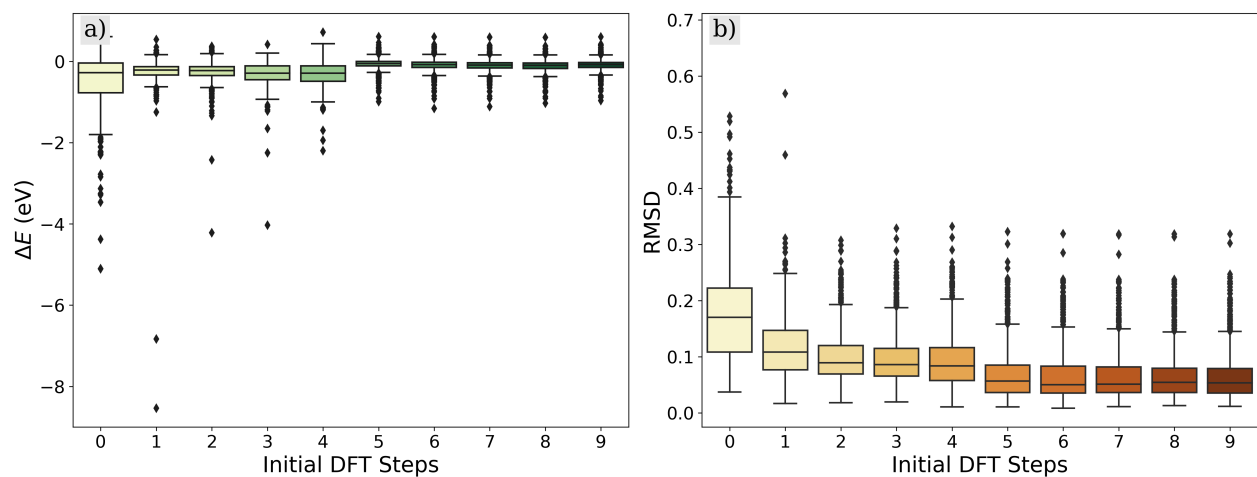


Figure 4.4: Distribution of ΔE (a) and RMSD (b) values with respect to initial DFT steps.

The iterative approach holds great potential for enhancing the accuracy and efficiency of structure relaxation. By refining the structures using MLPs and subsequently further refining them with more computationally intensive techniques, we can combine the strengths of these methods. This allows us to overcome the limitations of each individual technique and achieve more reliable and computationally feasible results.

4.4.3 Data Efficiency Vs Model Accuracy

ML algorithms rely on diverse and high-quality training data to effectively learn and make accurate predictions[174]. It is crucial for the training data to encompass a wide range of configurations and properties that the MLP aims to capture[175, 176, 174]. This necessitates meticulous sampling from the relevant parameter space, including diverse examples that cover various scenarios and variations. As mentioned previously, some configurations can exhibit unstable dynamics during the process of structural relaxation. Figure 4.5 illustrates an example of such instability observed for certain structures. This failure can be partially explained by examining Figure 4.2 (a), which shows the total energy of the structure during energy minimization. Typically, the optimization process starts with higher-energy initial configurations. During the early stages of optimization, the structure undergoes significant rearrangements to reach a more energetically favorable conformation. The convergence to the global or local minima, depending on the system, occurs gradually over multiple steps as the structure settles into a stable configuration.

During the training of MLP models using DFT trajectories, a data imbalance arises in the population distribution among different energy states. This imbalance poses a challenge for the model to accurately learn the PES for higher-energy configurations characterized by relatively low density. The incorporation of initial DFT relaxation, as observed, helps eliminate the unstable dynamics and further supports the claim of data imbalance as a contributing factor.

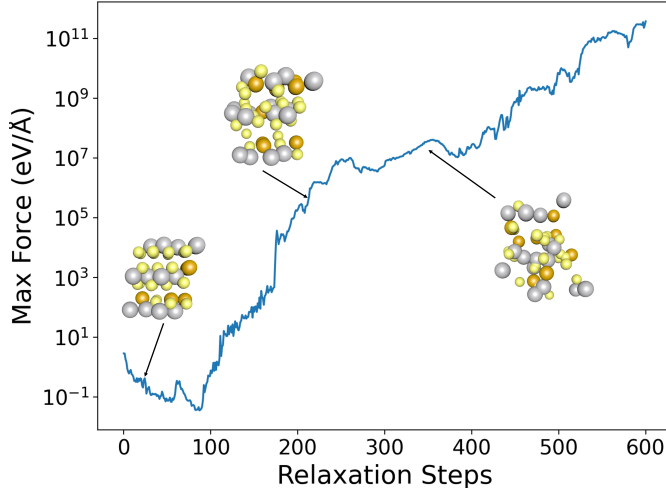


Figure 4.5: An example of energy minimization blowing up when applying MLP to initial TMD structure. The y-axis shows the maximum force observed on any atom in the system at a certain time step. Notable nonphysical regions are observed in the visualized time steps after force blowout.

able conformations, and another for further refining these structures. This two-step approach can help achieve more accurate and reliable results by leveraging the strengths of each model in the optimization process.

Apart from the evident impact of data imbalance on the high-energy unstable configurations, there is another important consideration regarding the robust extrapolation of MLPs to the under-sampled configuration space. This consideration can be further divided into two questions: 1) how finely you need to sample the chalcogenide stoichiometric ratio δ to be able to capture the energetics of $\text{VS}_{2-\delta}\text{Te}_\delta$, 2) how many configurations should be considered for each stoichiometry in order to adequately capture the variability of the energetic and structural properties? Addressing these questions will provide valuable insights into the sampling requirements for accurately representing the energetics and structural properties of different stoichiometries in the TMDs.

To address this issue, a potential solution is to intentionally incorporate distorted and off-equilibrium geometries in the training data[177]. By including such configurations, the model can learn to capture a wider range of atomic arrangements and enhance its robustness. This approach helps the model adapt to diverse structural variations and improves its ability to handle systems with non-equilibrium geometries. Alternatively, another approach is to train two separate MLP models: one for performing the initial minimization to obtain more energetically favorable conformations, and another for further refining these structures.

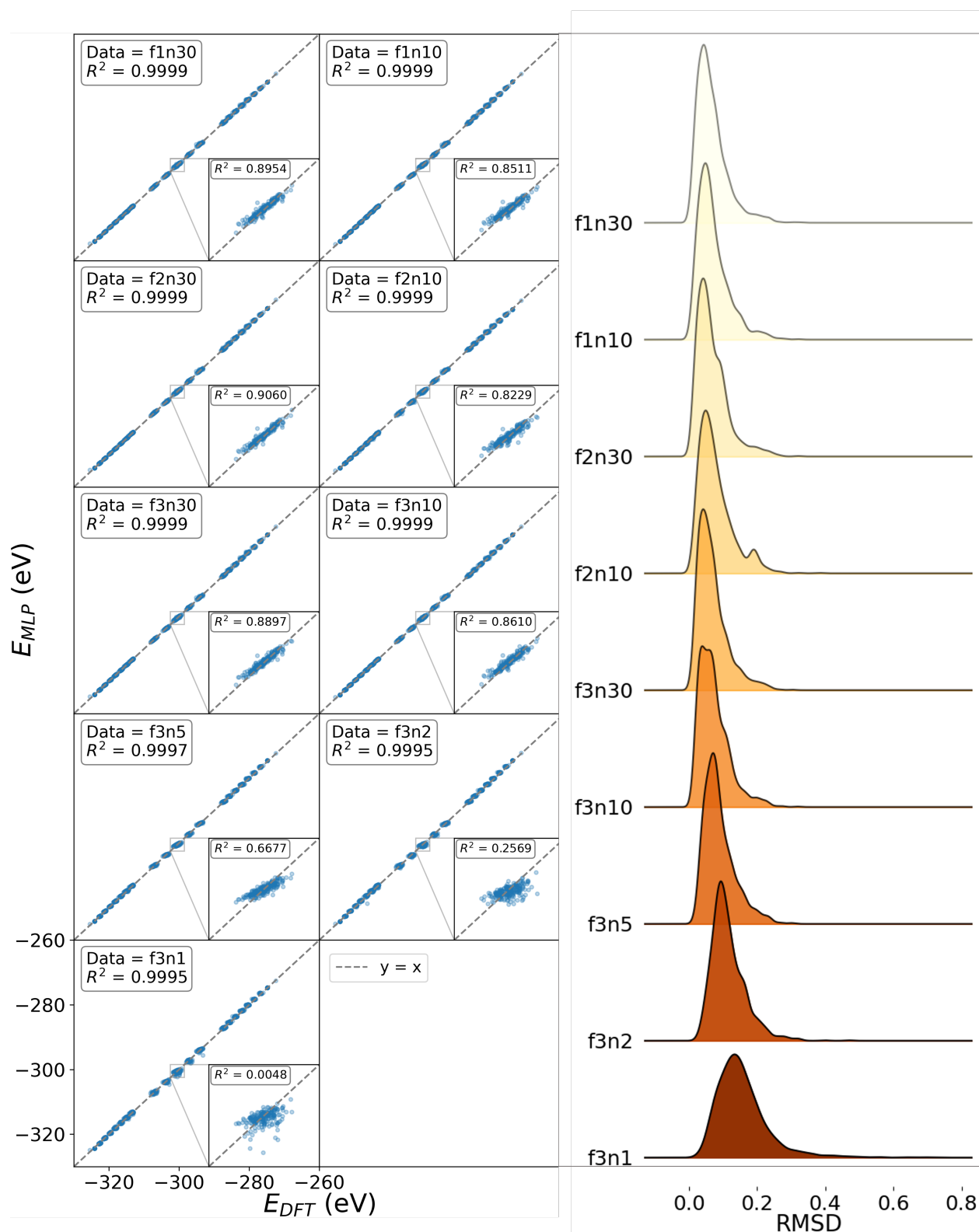


Figure 4.6: (Caption on next page.)

Figure 4.6: (Previous page.) Left: parity plot comparing the total energy of DFT and MLP optimized structures for various MLP models. To exclude the unstable dynamics, we employed the 5th DFT trajectory as the initial structure for MLP-based structure relaxation. The diagonal line represents perfect agreement between the energy values obtained from both methods. R^2 value quantifies the degree of correlation. Zoomed axes plots the VS_1Te_1 which contains most sample for the same stoichiometry to better illustrate the capacity of the MLP in capturing the variability within the samples. Right: Joy plot illustrating the distribution of RMSD values between structures obtained from DFT and various MLPs.

We utilized a series of carefully curated training datasets, as described in the methods section, to investigate the impact of sampling resolution on capturing the energetics of $\text{VS}_{2-\delta}\text{Te}_\delta$. To exclude the unstable dynamics, the 5th DFT trajectory was used as the initial structure for MLP-based structure relaxation. The total energy comparison between the resulting output structure and DFT-optimized structure is depicted in the parity plot presented in Figure 4.6 (left). In order to better visualize the MLP’s ability to capture the variability within each stoichiometry, a zoomed-in axis is included for VS_1Te_1 , which represents the largest sample for a given stoichiometry. Additionally, a joy plot (Figure 4.6, right) showcases the distribution of RMSD values between structures obtained from DFT calculations and the MLPs. This plot provides a comprehensive visualization of the range and density of RMSD values, allowing for a thorough assessment of the agreement and consistency among different MLPs. All MLP models demonstrated the capability to capture the desired energetics as the sampling frequency was reduced from including all 23 unique stoichiometry to 15 and further down to only 9 unique stoichiometry. However, upon closer examination using zoomed axes, it became apparent that a sample size greater than 10 was necessary to effectively capture the variability within each stoichiometry.

4.4.4 Generalizability of MLP

The ternary structures of $\text{VS}_{2-\delta}\text{Te}_\delta$ consist of the same atom types, namely V, S, and Te. These structures exhibit structural similarity with a polytype of 1T, while their energies vary

due to the size-extensive nature of potential energy. We trained the MLP model exclusively using VS_1Te_1 ($\delta = 1.0$) to evaluate its generalizability to other ternary structures in the system. The resulting model exhibited satisfactory performance on the structure relaxation of VS_1Te_1 , with a compact distribution of ΔE and RMSD values observed in Figure C.6.

When performing structural relaxation on other ternary structures of $\text{VS}_{2-\delta}\text{Te}_\delta$ with different chalcogenide stoichiometric ratios δ , an interesting observation emerges. The MLP model, trained exclusively on VS_1Te_1 , shows a systematic energy error in the relaxed structures, as depicted in Figure 4.7(a). Notably, this energy error aligns precisely with the outline of the total energy distribution for the various stoichiometries (Figure C.1 in Supplementary Information). In contrast, the distribution of RMSD values shown in Figure 4.7(b) reveals a remarkable level of structural similarity between the MLP-relaxed structures and the corresponding DFT-relaxed structures, despite the presence of a systematic energy error. In the NequIP model, the total potential energy is calculated by summing the atomic potential energies. Subsequently, the forces acting on the atoms are determined by taking the gradients of the predicted total potential energy with respect to the atomic positions[44]. Due to the size-extensive nature of the energy function, the scalar component representing the total energy is not effectively learned by the model, as it has only been exposed to a single ratio. However, the systematic error in the energy predictions is mitigated when taking the derivative, as the scalar component does not contribute to the derivative calculation. Consequently, the model is still able to accurately learn the forces, which are the derivatives of the energy, leading to successful relaxation of the atomic structures.

4.5 Conclusions

This study emphasizes the significance of carefully curated training data in MLP-based structure optimization for accurately capturing the energetics and structural properties of ternary structures in the $\text{VS}_{2-\delta}\text{Te}_\delta$ system. MLPs may exhibit unstable dynamics due to their limited ability to robustly extrapolate to the under-sampled configuration space. However, by leveraging the complementary strengths of MLPs and DFT calculations, potential synergies

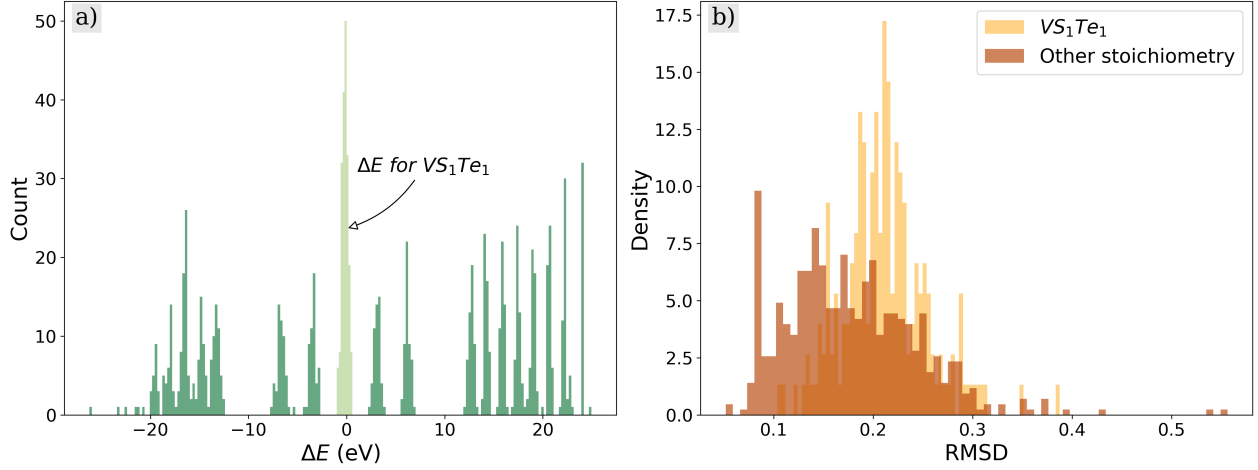


Figure 4.7: Distribution of ΔE values between the ternary TMD structures relaxed using the MLP model trained exclusively on VS_1Te_1 and their corresponding DFT-optimized structures. Interestingly, the pattern of the systematic energy error aligns precisely with the outline of the total energy distribution for various stoichiometries.

have been identified to enhance the practicality of MLPs in structure relaxation. Utilizing MLP-relaxed structures as initial inputs for DFT-based relaxation reduces computational costs and improves convergence. Incorporating a few initial DFT relaxation steps followed by MLP refinement enhances accuracy and efficiency in structure relaxation, eliminating unstable dynamics without additional training. The generalizability of the MLP model to other ternary structures in the $VS_{2-\delta}Te_\delta$ system was also evaluated. While the MLP model trained exclusively on VS_1Te_1 exhibited systematic energy errors, the structural similarity between MLP-relaxed structures and corresponding DFT-relaxed structures remained high.

In conclusion, this study highlights the potential of MLP-based methods in accurately capturing the energetics and structural properties of ternary systems. The findings provide valuable insights into the optimization process, data efficiency, and model accuracy, contributing to the development of efficient and reliable computational techniques for material science research. Further investigations are warranted to explore the applicability of MLP-based methods to other material systems and optimize the training process for enhanced

performance. Ongoing advancements in machine learning and computational methods hold promise in facilitating the understanding and prediction of material properties, enabling accelerated materials design and discovery.

4.6 Acknowledgement

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4.7 Data Availability

Primary database of TMDs is openly available at <https://doi.org/10.6084/m9.figshare.21308157>. Scripts used to collate the subset of the dataset used in this study is included in the open source implementation <https://github.com/sabiharustam/MLP-for-structure-relaxation>.

4.8 Code Availability

All scripts are written in Python (v3.9) and the usage examples are detailed in the jupyter notebook files. All files are available at <https://github.com/sabiharustam/MLP-for-structure-relaxation>.

Chapter 5

SIGNIFICANCE AND PERSPECTIVE

Interfacial problems of scientific interest are inherently complex and challenging due to the intricate nature of intermolecular interactions and the multitude of factors influencing interfacial behavior. Over the course of several decades, researchers from various disciplines around the world have made significant contributions towards gaining fundamental insights into the underlying mechanisms and processes governing interfacial interactions. Their efforts have led to the development of new theoretical models, computational methods, and experimental techniques that better predict and control interfacial behavior. To further advance our understanding and design of complex interfacial systems, it is essential to establish a complete workflow that integrates computational simulations with advanced techniques like machine learning and data-driven approaches. This integration allows leveraging existing experimental data for further breakthroughs in understanding and designing chemically patterned surfaces. Throughout my graduate research, I had the opportunity to work on three distinct projects, each addressing a different interfacial problem. Together, these projects form integral pieces of the larger puzzle, contribute to the development of a simulation and machine learning-integrated computational workflow aimed at designing chemically patterned surfaces with specific interfacial properties.

The work described in Chapter 2 highlights the importance of surface chemistry of graphite anodes on the structure and dynamics of electrolyte molecules, particularly the strong interaction between electrolytes and the surface even without the presence of an electric field. This study addresses the lack of detailed understanding regarding the effect of surface termination on the structure and dynamics of the liquid electrolyte at the uncycled interface in LIBs. Additionally, it investigates the complex interplay between individual con-

stituents within the electrolyte formulation and their role in interfacial phenomena. By systematically comparing 16 model systems with different electrolyte compositions and graphitic surface terminations, our work provides new insights into the role of surface functionalization and electrolyte composition in promoting early phases of electrolyte decomposition during SEI formation, filling this knowledge gap. Furthermore, our findings align with previous studies and open up the possibility of a new rational design approach for achieving much higher control over the design of SEIs by modifying the electrode surface to tailor the mobility and concentration of the electrolytes at the electrode/electrolyte interface. For example, previous AIMD + DFT based work from our group on the same oxygenated graphite surfaces has reported that the type of surface oxygen groups at the edge sites of a graphitic anode can determine the products of electrolyte decomposition reactions at the interface.[66] The preferred orientation of EC molecules observed in this study on the hydroxyl surface thus suggests that the decomposition of cyclic carbonate molecules (including EC and FEC) could proceed more readily on the hydroxyl surface. This finding thus validates the importance of additives in LIBs and adds further molecular scale insight to prior findings. Importantly, we have demonstrated the capability of MD simulations to capture the diverse impact of solvent composition and surface chemistry on interfacial properties. This serves as a proof of concept, showcasing the effectiveness of MD in an integrated workflow for assessing the interfacial properties of various chemically patterned surfaces.

In the work detailed in Chapter 3, ML algorithm is integrated with MD simulations to create a fully autonomous workflow that can build, test, optimize in a closed loop to achieve optimization of interfacial heat transfer at Si/Al interface. Previous studies lacked a definitive optimum arrangement due to the computational challenges associated with evaluating the large number of potential atomic configurations. Using our computational framework, we successfully identified an intermixing solution within a reasonable timeframe. This solution led to a significant 50% increase in the ITC compared to the pristine Si/Al interface. Moreover, significant challenges arise in incorporating ML algorithms directly with physics-based simulation tools and converging into a complete pipeline for the simulation and analysis of

molecular systems. These challenges stem from the complexities and intricacies of molecular systems, as well as the unique requirements and considerations of ML algorithms. MD simulations of complex interfaces can be computationally demanding, often requiring hours to days to complete. ML algorithms on the other hand, thrive on large datasets to achieve accurate learning and prediction. Consequently, computational challenges arise when guiding the optimization of interfacial composition to tailor the interfacial properties using ML methods, which typically involve multiple iterations. The scalable MPI-based framework developed in this work overcomes this challenge by enabling the execution of multiple concurrent MD simulations and updating a central Bayesian optimization model. Furthermore, the developed computational framework relies fully on Python codes to interface with MD engines. The Python interface handles everything from managing dynamic processes, generating input files, running MD simulations, to analyzing simulation results and updating ML algorithms. It provides an easy solution to the complex problem of ensuring efficient communication and seamless interaction between ML models and existing simulation codes. Additionally, our study includes a thorough assessment of the influence of system design, parameterization, and analysis of simulation results on the quality of training data. We also quantify the uncertainties associated with ML predictions, allowing for an evaluation of the robustness and confidence of the obtained results. These aspects serve as valuable best practice guidelines for integrating ML and MD in the design of chemically patterned surfaces.

Finally, the work described in Chapter 4 sheds light on the importance of tailored approaches and strategies when utilizing MLPs for custom datasets. This study provides valuable insights into the specific challenges that arise in the practical application of machine learning potentials. It emphasizes the need to address issues related to dataset acquisition, ensuring data reliability and representativeness, tuning model architecture and hyperparameters, and tackling the interpretability of MLP models. By identifying and discussing these challenges, this research contributes to a better understanding of the complexities involved in achieving practical and reliable applications of machine learning potentials. Furthermore,

the study explores the synergies between MLPs and DFT, enabling us to overcome the limitations of each individual technique and achieve more reliable and computationally feasible results. The findings from this study pave the way for the integration of MLPs with MD simulations, enabling the exploration of a wider range of interfacial systems and conditions, facilitating the discovery of novel phenomena and the optimization of interfacial properties.

While I have made significant progress in developing a simulation and machine learning-integrated computational workflow for designing chemically patterned surfaces with specific interfacial properties, it is important to acknowledge that there is still much work ahead. The complexity of interfacial systems and the multitude of factors influencing their behavior present ongoing challenges and opportunities for further exploration. The integration of simulation and machine learning techniques has opened new avenues for understanding and optimizing interfacial phenomena, but there is still a need for advancements in modeling approaches, data acquisition, and algorithm development. Continued research and collaboration in this field will contribute to the development of more robust and reliable computational tools for designing and tailoring interfacial properties. The journey towards achieving practical and effective applications of simulation and machine learning in this context is an ongoing process that requires continued dedication and innovation.

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Appendix A

SUPPORTING INFORMATION FOR: CHAPTER 2. EFFECT OF GRAPHITIC ANODE SURFACE FUNCTIONALIZATION ON THE STRUCTURE AND DYNAMICS OF ELECTROLYTES AT THE INTERFACE

A.1 *Simulation Details & Setup*

Each surface and electrolytes are parameterized using the Generalized AMBER force field (GAFF)[80] is employed to describe bonded and nonbonded interactions. RESP charges were calculated by the CP2K program package at the DZVP-MOLOPT-SR-GTH level with type GTHPBE potential.[81, 82, 83, 84, 85, 86] All atoms, except for the edge carbons and termination groups were fixed during the course of the simulation. A cutoff of 10 Å is implemented to calculate electrostatic interactions and LJ interactions. The solid slab which has thickness greater than two times the cutoff is enough so that there are no interactions between the upper and lower faces of the slab.

Table A.1: Electrolyte boxes setup with ethylene carbonate (EC), lithium salt, fluoroethylene carbonate (FEC) and dimethyl carbonate (DMC).

Electrolyte systems	EC	Li ⁺	PF ₆ ⁻	FEC	DMC	Box length
EC	867	0	0	0	0	60.2 Å
ESS	867	58	58	0	0	63.7 Å
MIX1	780	58	58	79	0	63.7 Å
MIX2	390	58	58	79	309	63.4 Å

Composition and dimension of each electrolyte box is listed in Table 1. Although cyclic

solvents are often used together with linear solvent ingredients such as DEC or DMC to modify viscosity, it was found that when EC contributes more than 50 % by weight of the electrolyte, EC becomes, to good approximation, the exclusive "inner member" of the Li+ solvation sheath.[179] Hence, we considered only EC (and FEC) molecules for the simplified model but also included DMC for more realistic setup. The molecules were initially packed randomly in a cubic box of size $38.440\text{\AA} \times 100\text{\AA} \times 40.176\text{\AA}$ periodic in the X Y Z direction using PACKMOL.[178] The initial configuration was minimized by conjugated-gradient energy minimization scheme employing a convergence criterion of 1.0×10^{-4} . The systems were equilibrated for 10.5 ns in the isothermalisobaric ensemble (constant NPT) using the Nose-Hoover thermostats and barostats to maintain a pressure of 1 bar and a temperature of 300 K with a time constant of 1 fs. An annealing process was conducted to further guarantee that all systems are melted and to avoid local configuration confinement. All systems were heated from 300 K to 500 K for 5 ns, and maintained at 500 K for 5 ns, and subsequently annealed from 500 to 300 K in 5 ns. Finally, the production runs of 20 ns were conducted to obtain the electrolyte box dimension. TCL scripts used with VMD[91] to align electrolyte boxes with the surface slab and generate the LAMMPS input file.

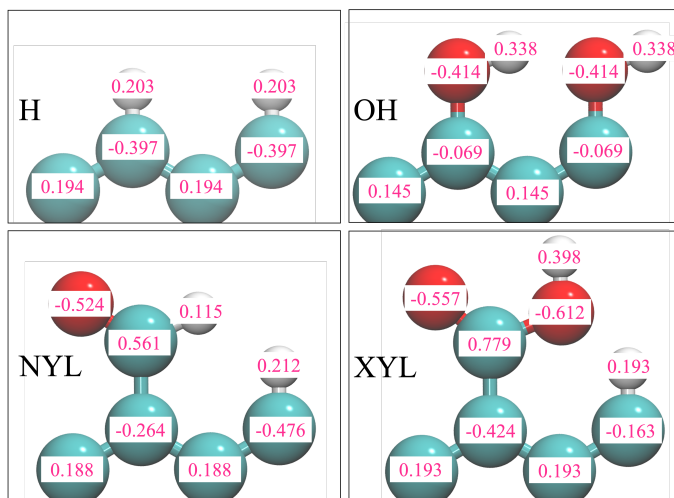


Figure A.1: RESP charges of the surface atoms obtain from CP2K.

A.2 Simulation Convergence

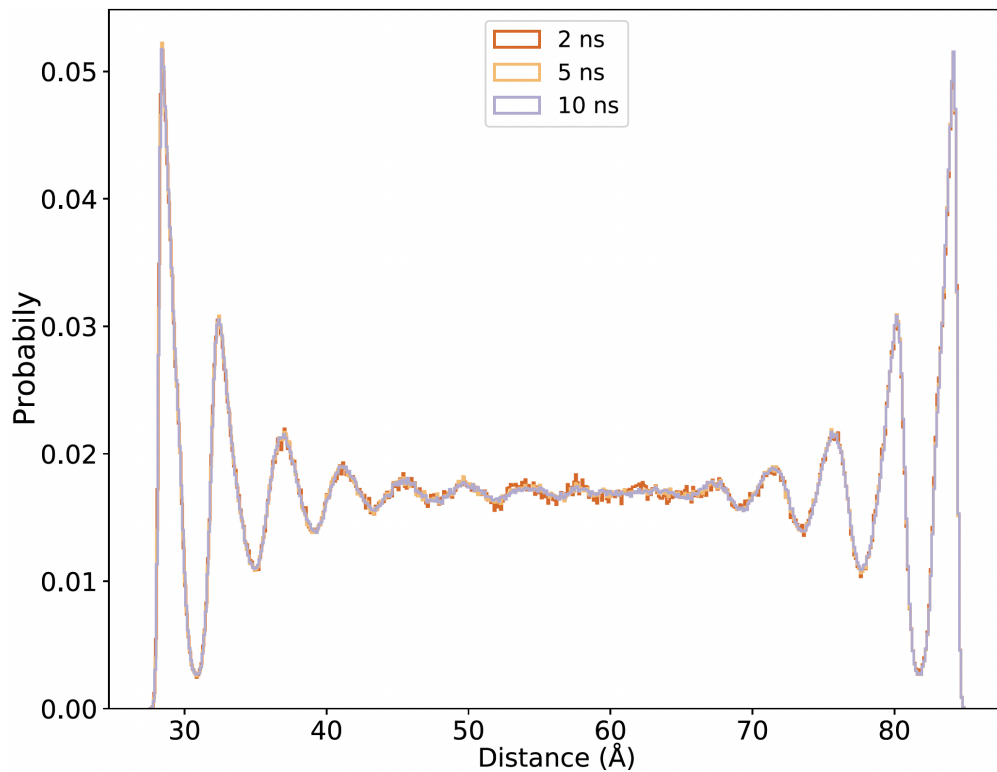


Figure A.2: Time averaged EC density profile as a function of distance from surfaces; The bin size used to calculate the density was $0.1 \text{ \AA}$, and we note that the first solvation states do not change appreciably with bin sizes between $0.05 \text{ \AA}$ - $0.5 \text{ \AA}$. We have not subtracted the thickness of the surface; the interface begins at approximately $25.7 \text{ \AA}$.

A.3 Probability Density Profile

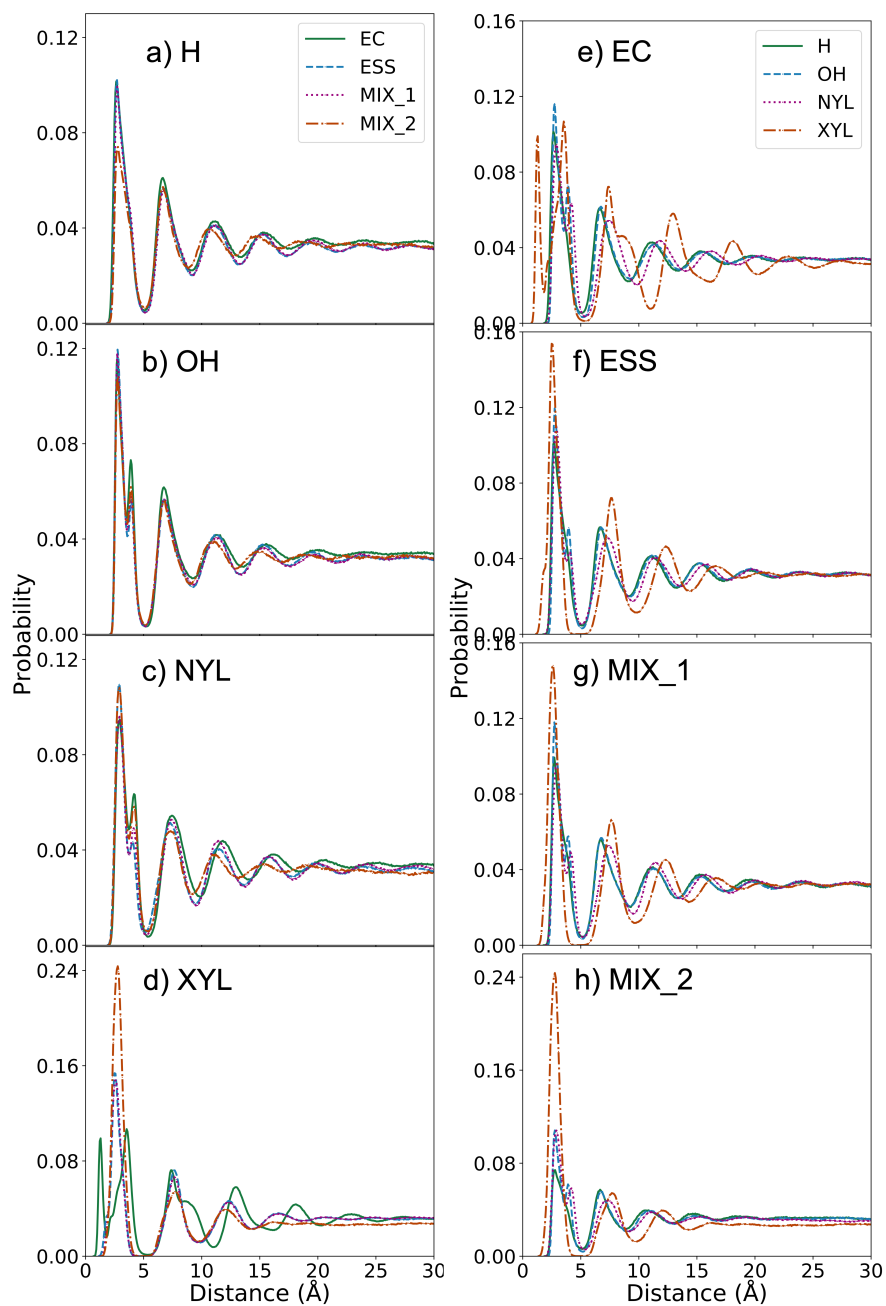


Figure A.3: Probability density of EC molecule in various systems. Comparison of the EC in four different electrolyte solutions on a same graphitic surface (left). Comparison of the same electrolyte on four different graphitic surfaces (right).

A.4 Trajectory Snapshot

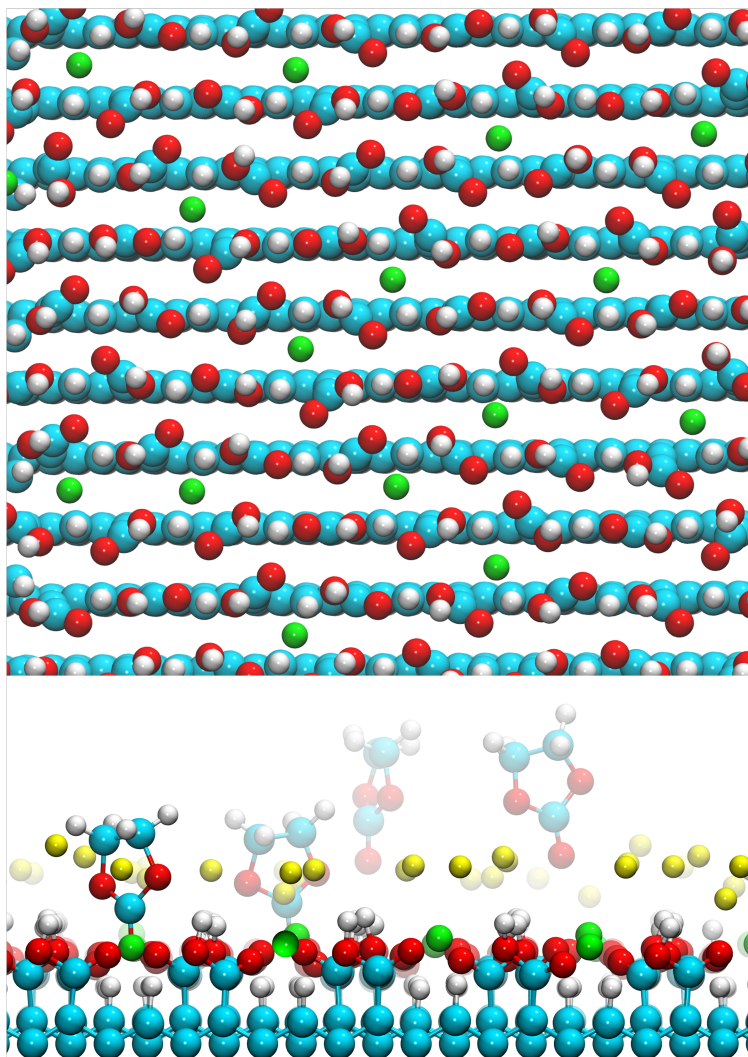


Figure A.4: Snapshot of MD trajectory top and side views highlighting the positions of EC in the first adsorption layer relative to the XYL surface. Green dots and yellow dots are the position of EC head oxygen corresponds to the two bifurcated peaks in the COM probability density plot.

A.5 Density Profile

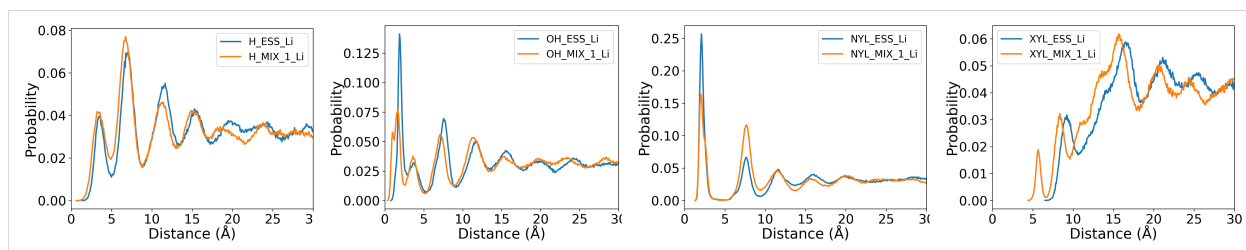


Figure A.5: Density profile of Li^+ with/without addition of FEC (comparing ESS and MIX.1) References

Appendix B

SUPPORTING INFORMATION FOR: CHAPTER 3. OPTIMIZATION OF THERMAL CONDUCTANCE AT INTERFACES USING MACHINE LEARNING ALGORITHMS

B.1 System size effect

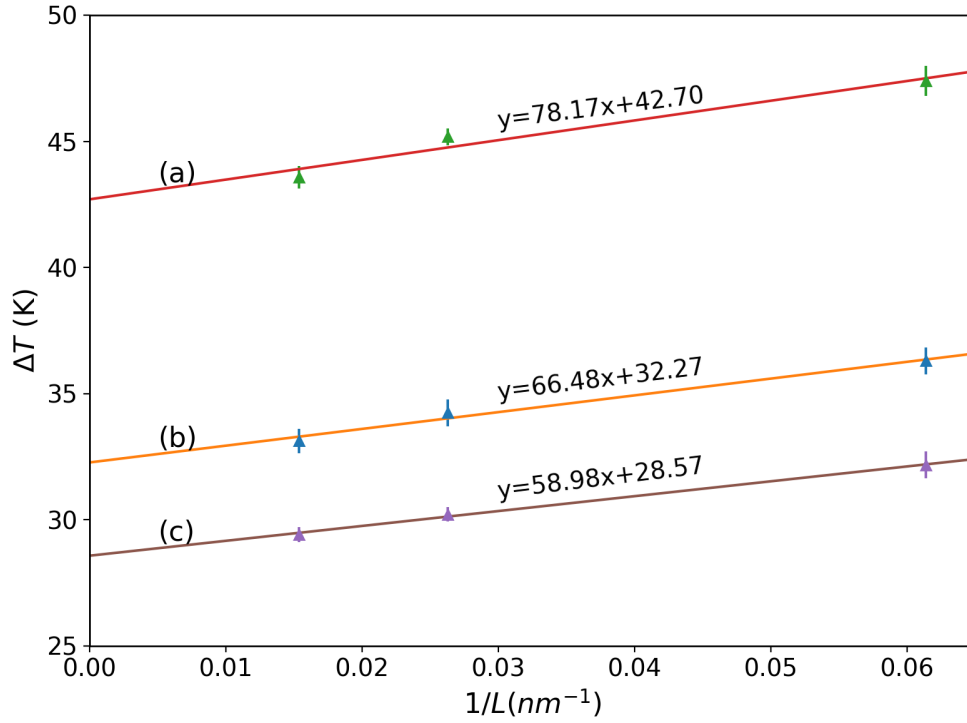


Figure B.1: System size dependence of ΔT on $1/L$ (L is the length of the Si substrate). Data are shown for three different mixing arrangement: (a) 6-layer at 50%, (b) 2-layer at 90%, (c) 2-layer at 99%. We note that the rate of change of ΔT with $1/L$ for different intermixing arrangements appears to be only slightly dependent on the intermixing arrangements. Note: Four random atomic arrangements are used for each entry point with triangles showing the mean and error bars showing the std of the resulting ΔT values.

B.2 Description of the OpenAI Gym environment

OpenAI Gym is a toolkit built for developing and comparing reinforcement learning algorithms. However, we can take advantage of its shared interface with various environments that are versioned, to create a general algorithm and allow for comparisons when changes are made. In this work, we created separate Python environments, registered with OpenAI Gym, for testing the simulation configurations and for optimizing the interfacial thermal conductance. Each environment includes custom python function to generate input files for the LAMMPS as well for analyzing the LAMMPS output to obtain the interfacial temperature gradient. Driver functions are created to tailor the interaction between Bayesian optimization agent and gym environments for various test cases. We compiled LAMMPS as a shared library and Python wraps LAMMPS through its library interface with the wrapper functions included with LAMMPS distribution. This enables creation of one or more instances of LAMMPS and launching one or more simulations directly from Python by importing “lammeps” module in the Python script. MPI for Python package is used to run LAMMPS in parallel from Python.

B.3 GP model convergence test

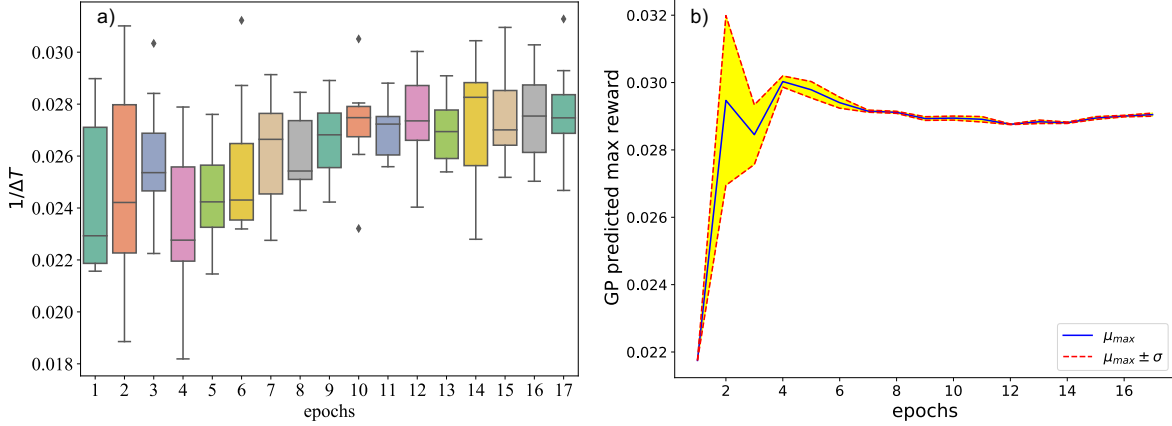


Figure B.2: Sample and GP predicted $1/\Delta T$ values for each iteration: a) box plot of actual $1/\Delta T$ values returned from ten parallel simulations for that iteration. Note that each simulation has a unique intermixing depth and percentage randomly sampled from the evolving quantile region. b) GP predicted max $1/\Delta T$. μ_{max} is the mean of ten predicted GP max values from the parallel models and $\sigma_{\mu_{max}}$ is the standard deviation of those max values.

For Figure B.2(a), we used boxplot to display the distribution of the $1/\Delta T$ values obtained from the MD simulations for each iteration. Interquartile range (IQR) in colored box represents 25th percentile (Q1) to 75th percentile (Q3) of the data points, whiskers connect IQR to the minimum ($Q1-1.5IQR$) and maximum ($Q3+1.5IQR$) with outliers. In this study, we defined a quantile region which is a reduced sampling region above the quantile threshold value, and randomly sampled a batch of data points per iteration. With that, you are likely not sampling points corresponding to highest interfacial thermal conductance. Figure B.2(a) thus shows a wide spread of batch $1/\Delta T$ values. As shown in Figure 3 in main paper, quantile region is still relatively large at the end of the optimization, this means that we are sampling from a region where expected ITC is at top 18%, thus, the values obtain from the MD simulations, although high, will be unlikely to reach the expected max GP values (0.029) as shown in Figure B.2(b).

B.4 GP results for the smaller length system

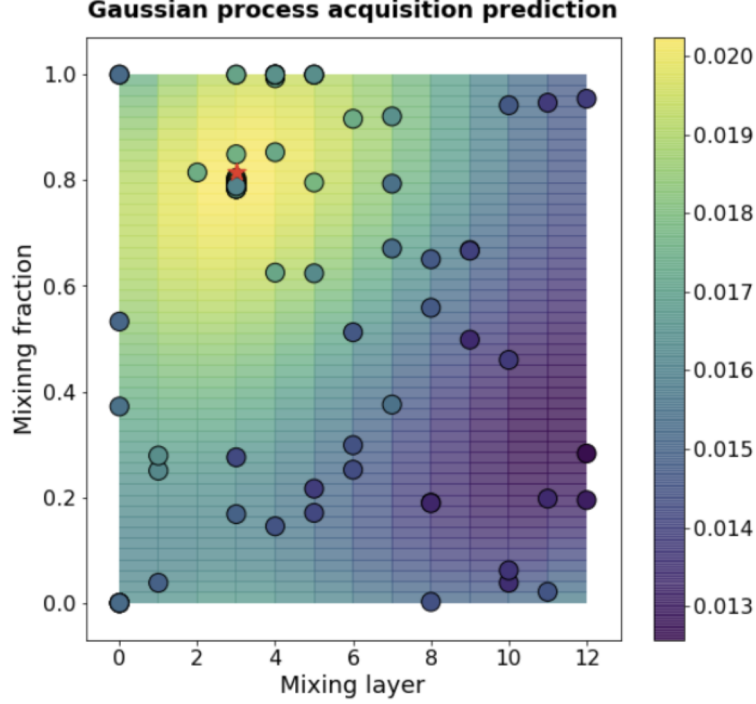


Figure B.3: GP-UCB hypersurface at the end of the optimization.

Initial optimization study with smaller system is shown in Figure B.3. It results in similar region of interest while the value of the $1/\Delta T$ differs from final results. There are several differences between two optimization setups: 1) In the initial study we have the Si substate that is roughly $1/3$ of the system used in the final setup. 2) Equilibration and production runtime is the fraction of the runtime used in the final setup. 3) We did not implement quantile-based adaptive sampling in the initial study. As a result of the different simulation setup, interfacial temperature gradient (ΔT) resulting from the initial study is larger compared to the systems with longer length, also the evaluation is noisier. Initial study points to the optimal region of 3-layer intermixing at 80%, and without the random sampling from the quantile region, model exploits the UCB max region thus did not explore 2-layer intermixing at higher mixing percentage, therefore a slight variance from the optimization

results at the current setup. Nonetheless, both optimization results points to the region of 2 3 layers of intermixing at 70% or above to have improved ITC compared to the pristine interface.

B.5 Various run times and distribution of resulting ΔT

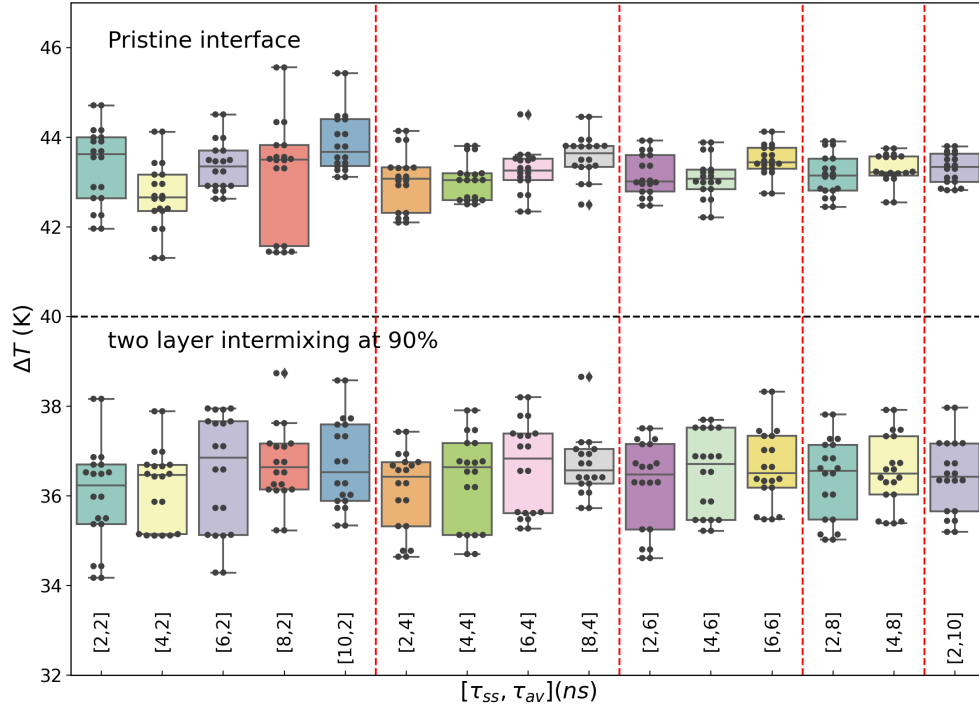


Figure B.4: Various run times and distribution of resulting ΔT for the pristine and intermixed interfaces. Each box plot contains 20 data points. Vertical dashed red lines are used to separate each set of τ_{av} .

Table B.1: Statistical description of the sample points in above figure

	$[\tau_{ss}, \tau_{av}](\text{ns})$	mean	std	variance	sem	variance/mean (%)
Pristine interface	[2, 2]	43.376	0.871	0.759	0.195	1.749
	[2, 4]	43.039	0.676	0.457	0.151	1.063
	[2, 6]	43.148	0.470	0.221	0.105	0.513
	[2, 8]	43.161	0.478	0.228	0.107	0.529
	[2, 10]	43.306	0.343	0.117	0.077	0.271
	[4, 2]	42.702	0.763	0.583	0.171	1.365
	[4, 4]	43.033	0.453	0.205	0.101	0.477
	[4, 6]	43.090	0.477	0.227	0.107	0.528
	[4, 8]	43.289	0.341	0.116	0.076	0.269
	[6, 2]	43.364	0.572	0.327	0.128	0.755
	[6, 4]	43.284	0.564	0.318	0.126	0.734
	[6, 6]	43.485	0.369	0.136	0.082	0.313
	[8, 2]	43.203	1.314	1.726	0.294	3.996
	[8, 4]	43.545	0.534	0.285	0.119	0.654
	[10, 2]	43.886	0.696	0.485	0.156	1.105
Two-layer intermixing at 90%	[2, 2]	36.022	1.164	1.354	0.260	3.759
	[2, 4]	36.132	0.917	0.841	0.205	2.327
	[2, 6]	36.259	1.003	1.007	0.224	2.777
	[2, 8]	36.386	0.919	0.845	0.206	2.321
	[2, 10]	36.454	0.837	0.700	0.187	1.921
	[4, 2]	36.242	0.895	0.801	0.200	2.209
	[4, 4]	36.377	1.048	1.099	0.234	3.021
	[4, 6]	36.508	0.917	0.841	0.205	2.303
	[4, 8]	36.562	0.816	0.665	0.182	1.820
	[6, 2]	36.513	1.313	1.723	0.294	4.720
	[6, 4]	36.641	1.040	1.082	0.233	2.953
	[6, 6]	36.669	0.863	0.745	0.193	2.030
	[8, 2]	36.768	0.938	0.879	0.210	2.392
	[8, 4]	36.748	0.788	0.621	0.176	1.690
	[10, 2]	36.727	1.018	1.035	0.228	2.819

Appendix C

SUPPORTING INFORMATION FOR: CHAPTER 4. PRACTICAL APPLICATION OF MACHINE LEARNING POTENTIALS FOR STRUCTURAL RELAXATION

C.1 Dataset

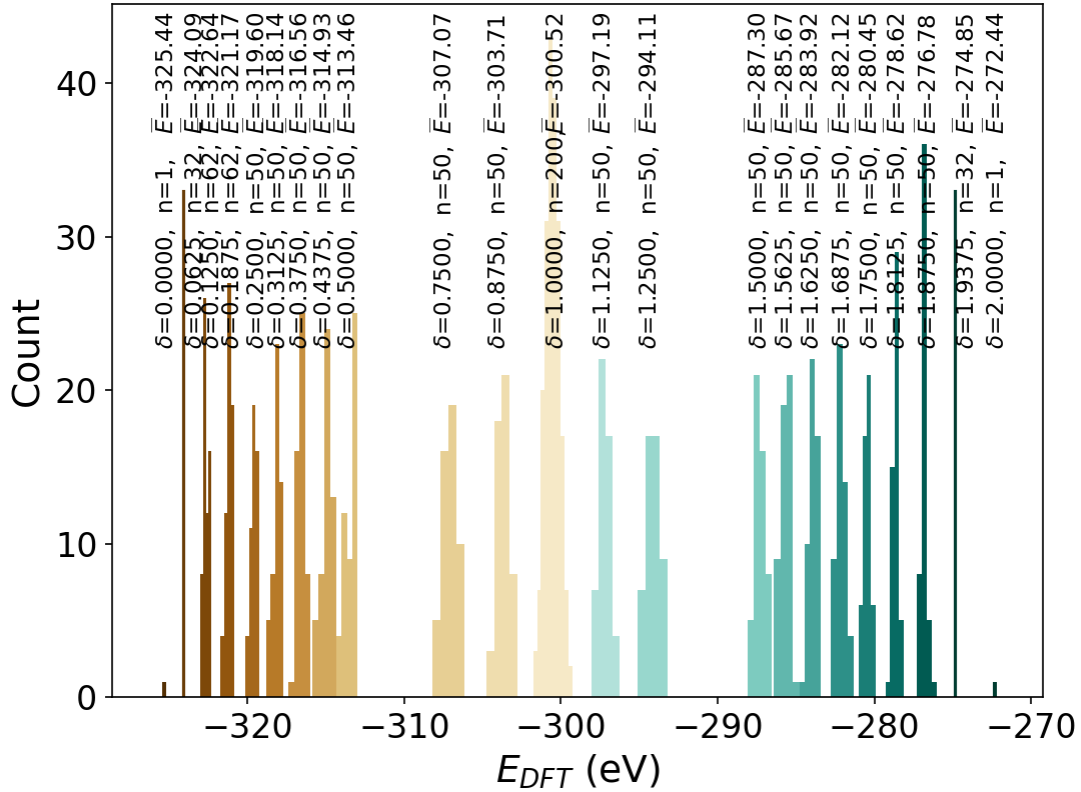


Figure C.1: Histogram of the total energy of the relaxed structures for each stoichiometries. Total number of structures and mean total energy is given each δ values.

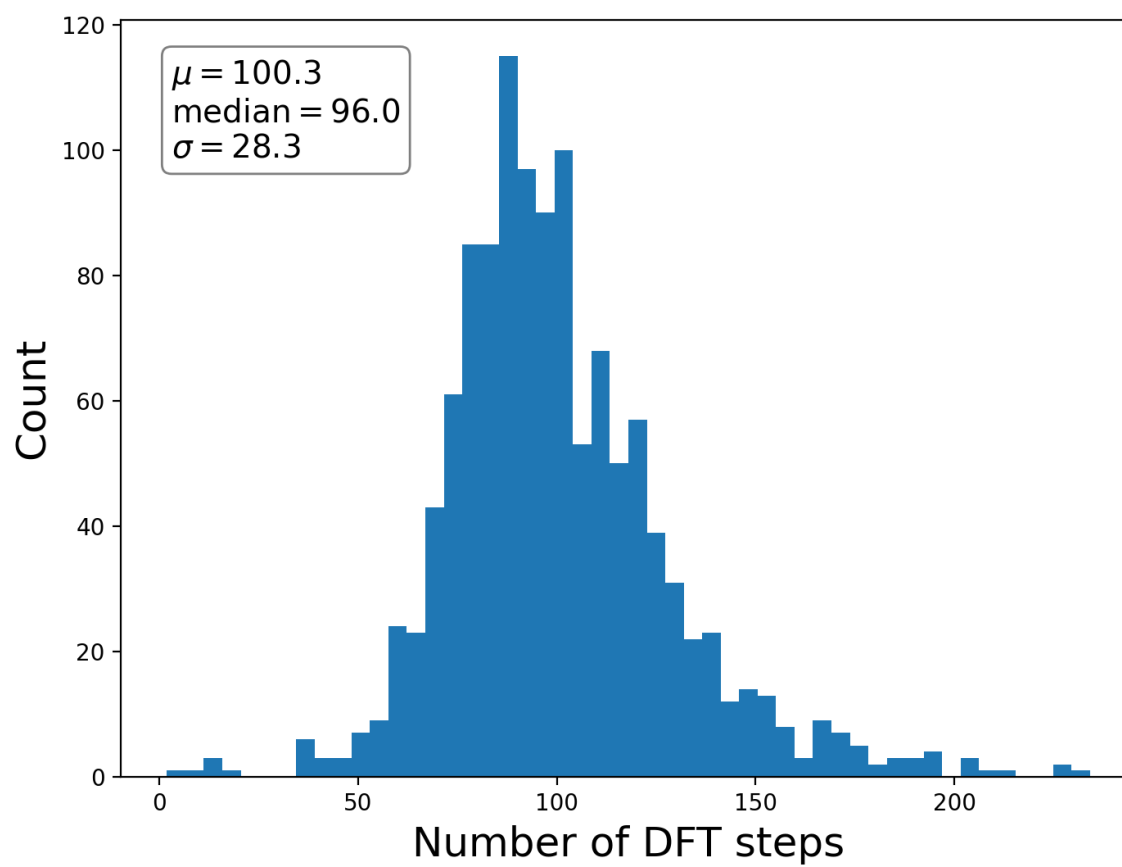


Figure C.2: Distribution of the total number of DFT steps for relaxation of TMD structures.

C.2 *Impact of the initial DFT steps*

We investigated the possibility of iterative refinement by alternating between MLP-based relaxation and DFT. Specifically, for each value of N in a range of 10, we employed the N th DFT trajectory as the initial structure for MLP-based structure relaxation. When incorporating initial DFT steps, the MLP model demonstrates improved accuracy in structural relaxation.

C.2.1 *Batch size*

For the MLP trained on VS_1Te_1 with batch sizes of 1, 32, and 128, same improved accuracy is observed (Figure C.3). For clearer Figure C.4 shows the parity plot comparing the total energy of DFT and MLP relaxed structures for the initial DFT steps equal to 0 (left) and 5 (right). The top of each sub-figure provides the number of successful MLP relaxations without unstable dynamics for all 197 structures of VS_1Te_1 . When no DFT initial steps are included, the MLP trained with a batch size of 1 demonstrates a higher rate of successful relaxations compared to the batch size of 32. However, the MLP trained with a batch size of 128 exhibits the highest rate of successful relaxations among all three. After incorporating 5 initial DFT steps, the influence of the batch size becomes negligible.

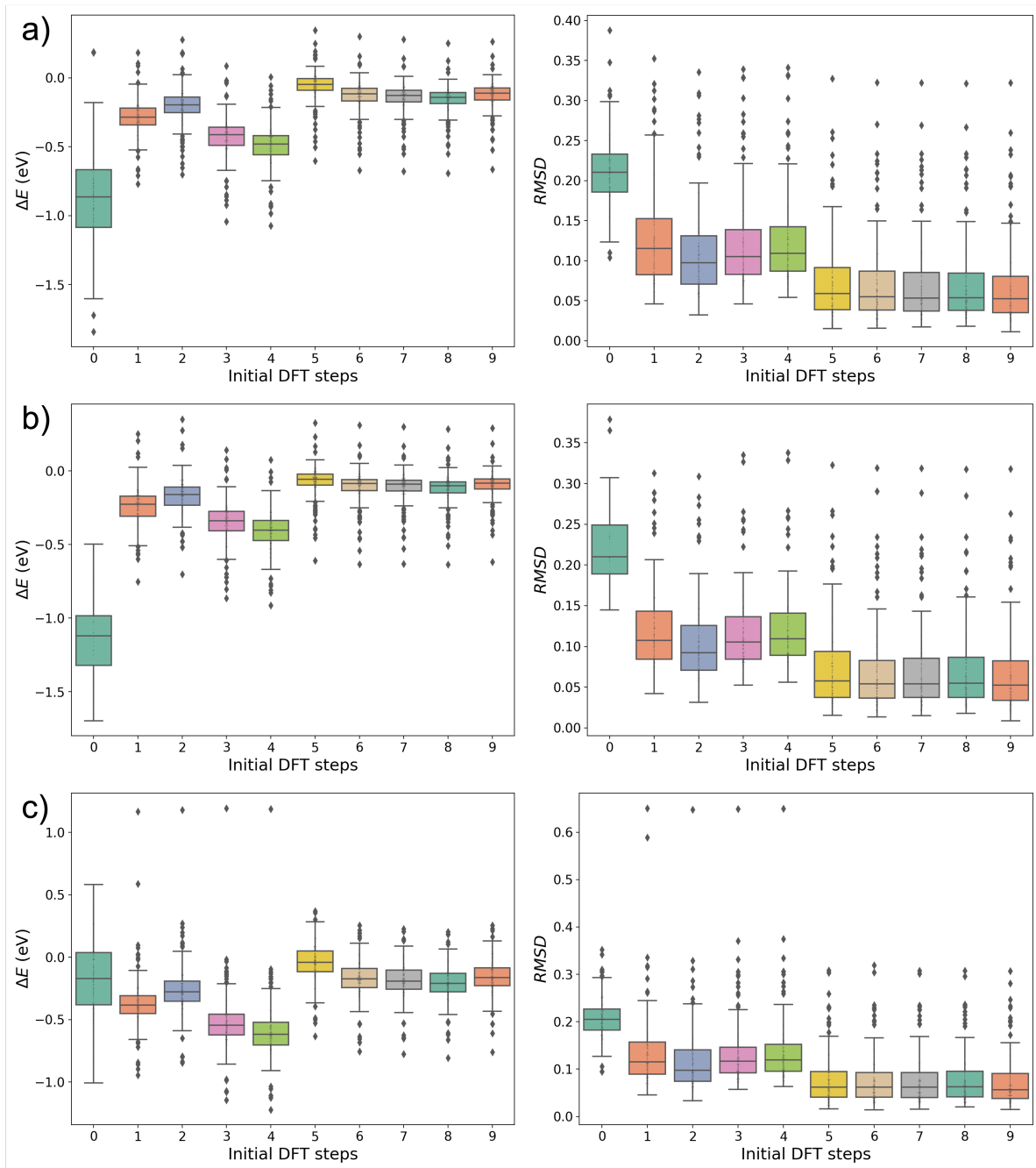


Figure C.3: Evaluation of the MLP trained on VS_1Te_1 with different batch sizes: a) batch size of 1, b) batch size of 32, c) batch size of 128.

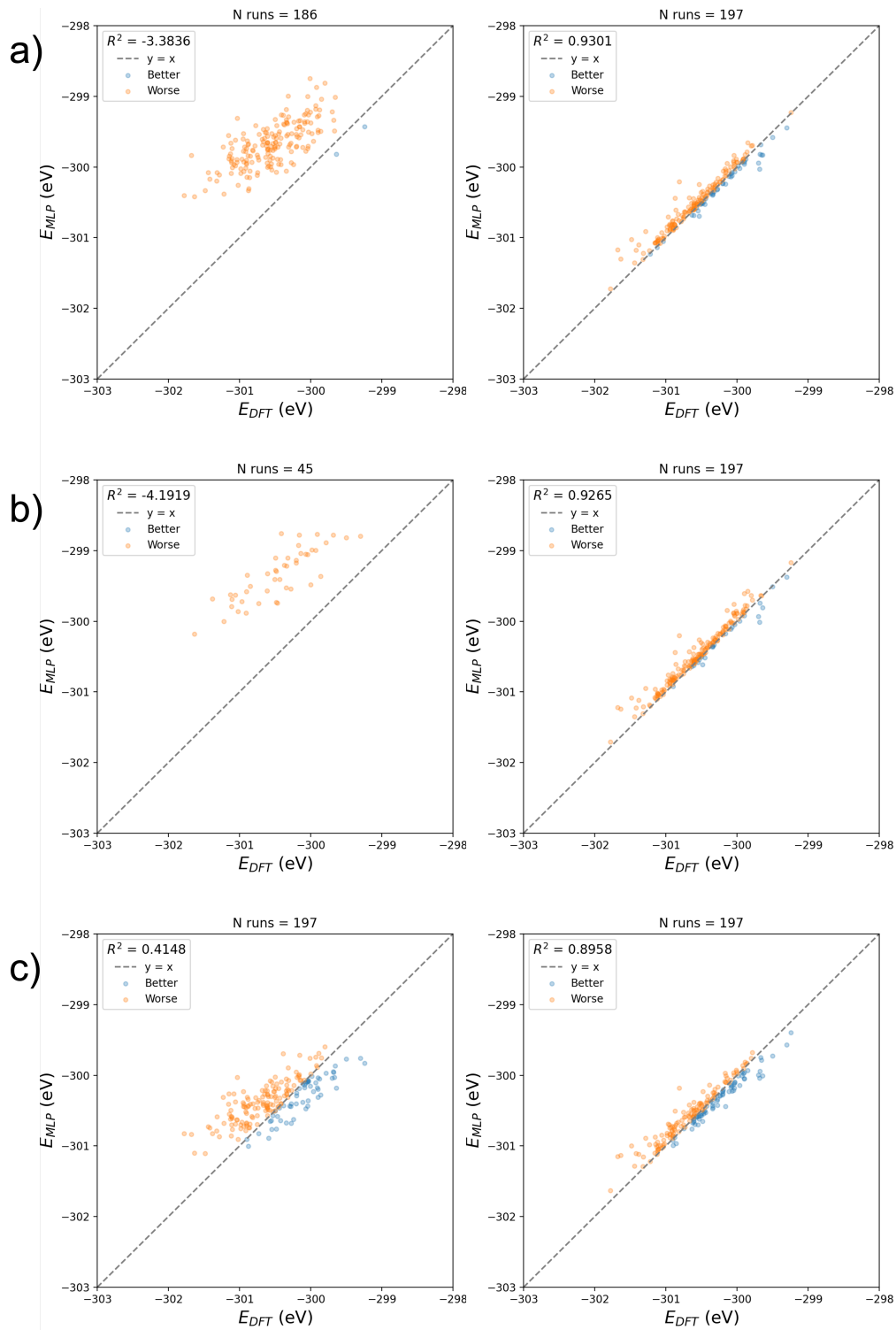
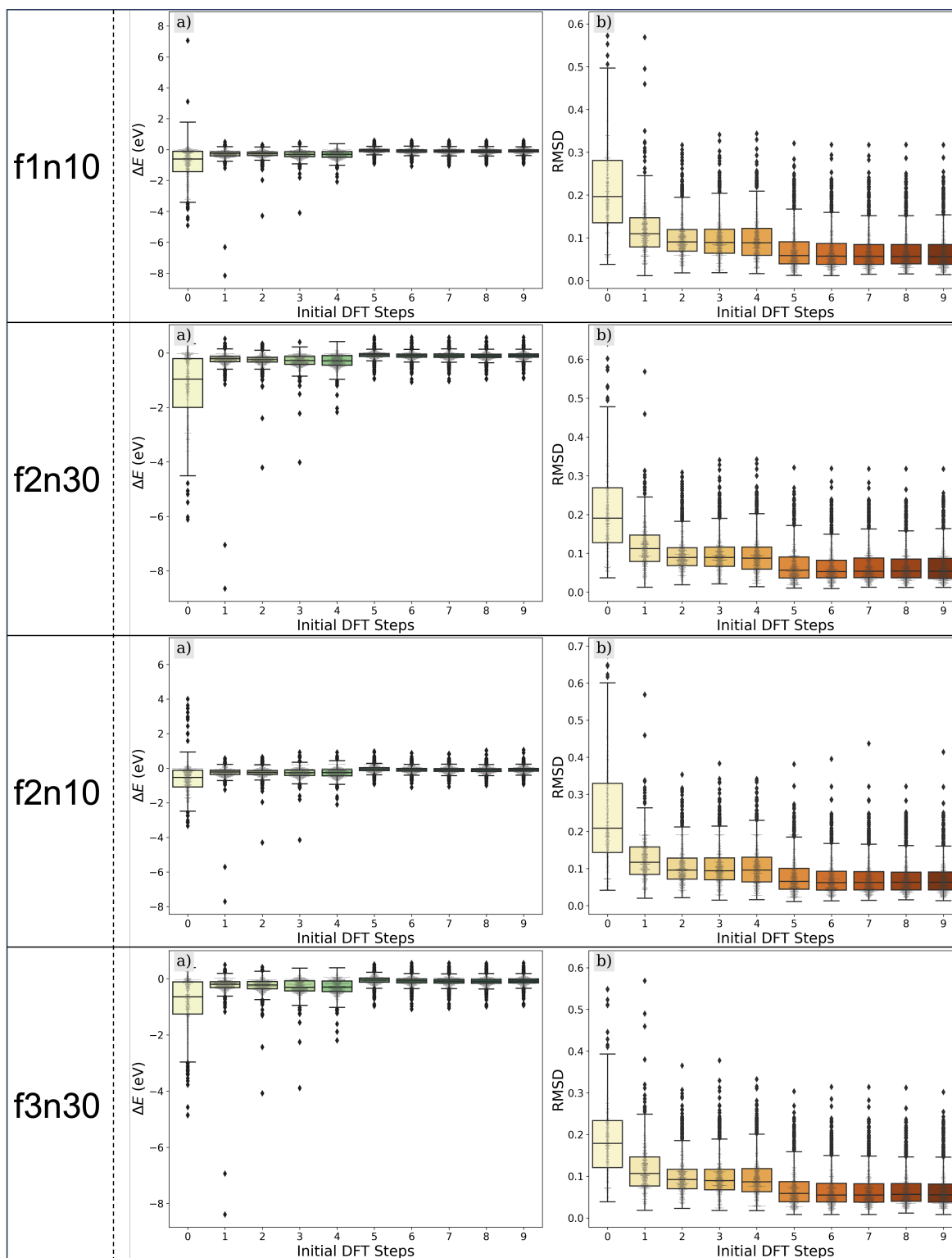


Figure C.4: Parity plot of the total energy for MLP trained on VS₁Te₁ with different batch sizes: a) batch size of 1, b) batch size of 32, c) batch size of 128, for initial DFT steps 0 (left) and 5 (right).

C.2.2 Improved accuracy for all MLPs



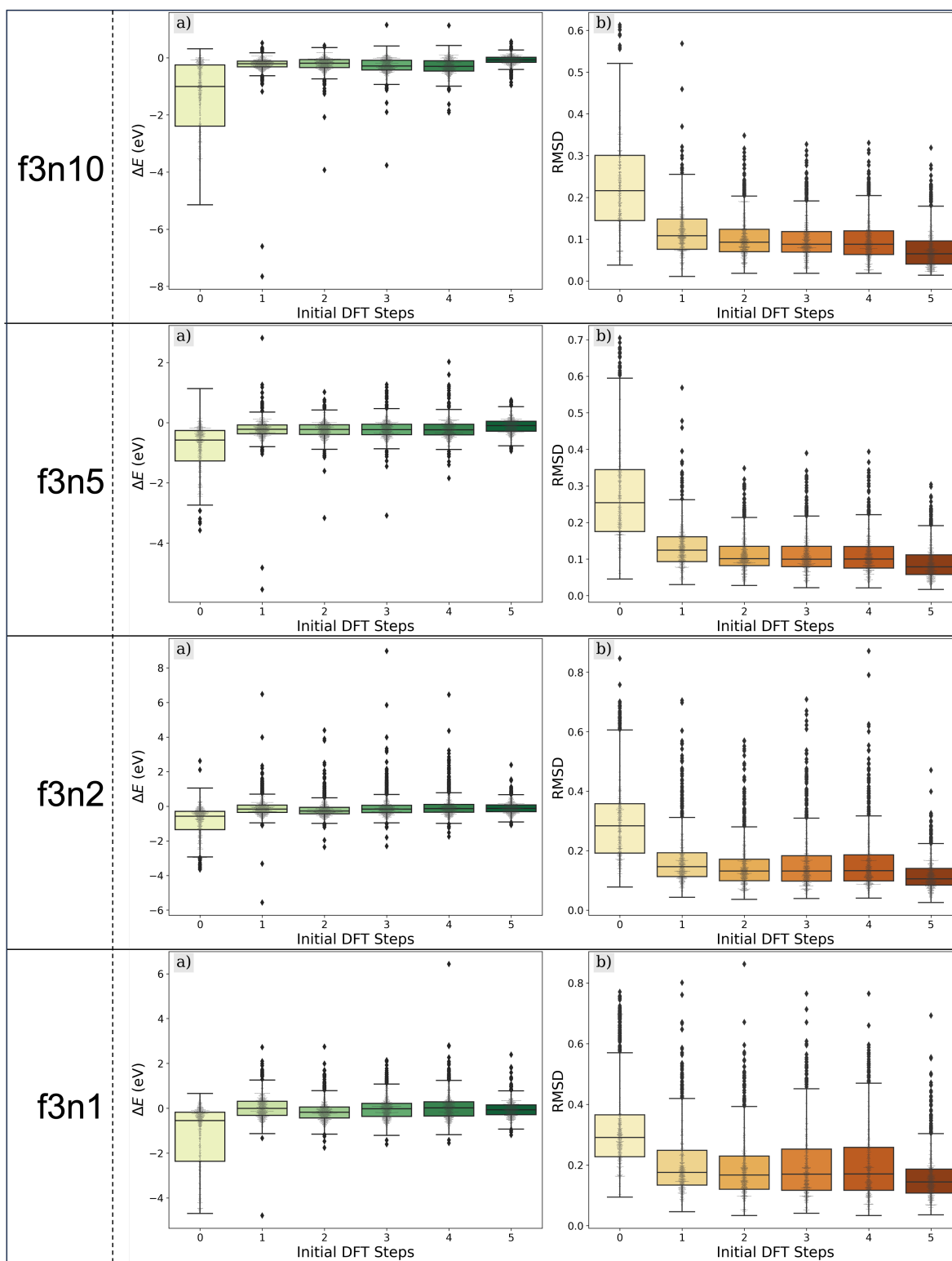


Figure C.5: Distribution ΔE (a) and RMSD (b) between MLP and DFT optimized structures with incorporation of N initial DFT steps.

C.3 MLP trained on VS_1Te_1

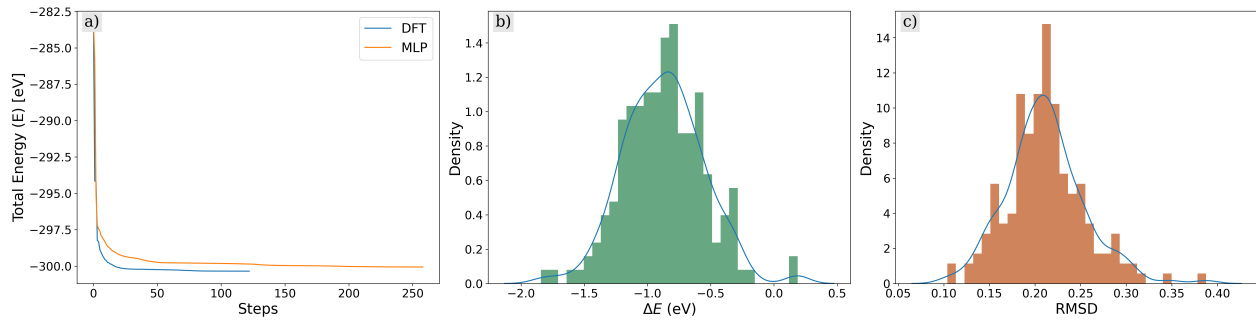


Figure C.6: Evaluation of the MLP model trained on VS_1Te_1 . a) An example energy minimization trajectory. b) Histogram of ΔE after relaxation, where ΔE equals to total energy differences between DFT and MLP optimized structures. c) Histogram of RMSD between MLP and DFT optimized structures.