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Article

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Posted Date: September 9th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10844125/v1>

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Additional Declarations: No competing interests reported.

PASS: Perturbation augmented space group structure sampling for transferable Fe-O machine learning interatomic potential

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Abstract:

Iron (Fe) oxidation is a fundamental phenomenon that is scientifically significant and technologically vital. Despite substantial experiment research effort, accurate atomistic modelling of Fe oxidation remains elusive. This requires a reliable interatomic potential, which necessitates an extensive and representative first-principles dataset for training. However, Fe-oxygen (O) system is known for its structural and magnetic complexity, rendering the generation of high-quality dataset challenging. In this work, we propose the Perturbation Augmented Space group structure Sampling (PASS) method to generate representative dataset consisting of small-cell structures with less than 10 atoms. Based on PASS, we present a systematic approach to developing a transferable machine learning interatomic potential (MLIP) for Fe-O system adopting the atomic cluster expansion (ACE) framework. We thoroughly validate the accuracy and capability of the ACE potential across both pure Fe and Fe-O systems through bulk, surface, and interface properties. We showcase the formation of FeO-like structure in large-scale Fe oxidation simulation using the ACE potential. This work demonstrates that the PASS method yields an accurate and transferable MLIP which is capable of capturing the reactive complexity of oxide growth while remaining computationally practical for extended systems.

Keywords:

Iron oxidation, Space groups, Machine learning interatomic potentials, Molecular dynamics

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Introduction

For decades, iron (Fe) oxidation has been a subject of substantial research effort due to its scientific significance and technological importance¹. Scientifically, studying it not only helps understand Earth's geochemical evolution² but also provides insights into biological mechanisms, for example ferritins detoxification by catalyzing the oxidation of Fe^{2+} ions³. Technologically, as energy production can be obtained through the heat of Fe powders oxidation, it potentially enables a safe, stable and high-density energy storage technology⁴. Moreover, it is usually linked with detrimental corrosion, whose prevention is key to achieve sustainability and durability of materials^{5,6}. Therefore, Fe oxidation has been extensively investigated by all kinds of experimental techniques, such as low-energy electron diffraction^{7,8}, X-ray scattering⁹, and *in situ* environmental scanning/transmission electron microscopy¹⁰. From an atomistic perspective, oxidation involves a series of critical atomic-scale events¹¹, including atomic adsorption, diffusion, and surface reconstruction. The combination of those crucial events poses a challenge to experimental studies, that is how to achieve three-dimensional atomic resolution for structural and chemical information *in situ*¹². On the other hand, this challenge can be better tackled by atomistic modelling, especially molecular dynamics (MD) simulation, where structural and chemical information at the atomistic level, and thermodynamics and kinetics information can be obtained simultaneously¹³.

Nevertheless, accurately modelling Fe oxidation is a challenging task due to the complexity of Fe-oxygen (O) system. First of all, multiple Fe oxides can exist under different conditions^{14,15}, with wüstite (FeO), hematite (Fe_2O_3), and magnetite (Fe_3O_4) being the most stable ones at different O concentrations. Furthermore, various crystal structures and different stoichiometries add up to the structural complexity. For instance, Fe_2O_3 has a corundum structure, while FeO has a rock-salt structure with non-stoichiometric characteristics because of its high vacancy defect concentration¹⁶. In addition to the structural variety, Fe oxides have distinctive magnetic orderings. FeO and Fe_2O_3 exhibit antiferromagnetic arrangement of magnetic moments^{17,18}, while Fe_3O_4 is ferrimagnetically ordered¹⁹. Consequently, due to the concurrent occurrence of multiple kinetic events of oxidation in combination with oxides' structural and magnetic ordering complexity, a reliable, robust and transferable interatomic potential is imperative, i.e., the one which is capable not only of capturing the elementary reaction steps during initial oxidation but also of distinguishing between the

nucleation, growth and phase transformations among the various iron oxide phases during growth of the oxide layer.

Notably, reactive force field (ReaxFF), due to the explicit usage of bond order in its functional form, is effective in describing the bond breaking and forming processes. This makes it quite suitable for the oxidation process simulation²⁰. Several ReaxFFs had been developed for the Fe-O system^{21,22} and applied to study the oxidation process^{9,23}. However, after comparing six ReaxFFs on the prediction of liquid Fe oxide properties, Thijs et al. found significant differences of properties obtained by them²⁴. We previously benchmarked three ReaxFFs on their performance for O adsorption on Fe surfaces, which is the first yet quite important step in oxidation, but found that they had unsatisfactory descriptive capability, as the accuracy of the adsorption energy with regard to first-principles calculation is insufficient²⁵. Therefore, a more accurate and broadly transferrable Fe-O interatomic potential is needed.

For the past two decades, owing to the capability to learn from large data and the achieved near-quantum accuracy, machine learning interatomic potential (MLIP) has attracted lots of attention^{26,27}. Compared to empirical interatomic potentials, MLIPs do not have a pre-defined functional form. Instead, they use atomic descriptors (also called structural fingerprints) to encode the local atomic environments (LAEs). A number of atomic descriptors have emerged to capture the essential characteristics of LAEs, including atom-centered symmetry functions²⁸, smooth overlap of atomic positions (SOAP)²⁹, moment tensor³⁰, and atomic cluster expansion (ACE)³¹. Despite the different varieties, the general development workflow is the same. After high-fidelity first-principles dataset is obtained, the LAEs are first encoded to be descriptors which are subsequently used as input to ML algorithm, while the configurations' corresponding energies, forces, and stresses act as output to be reproduced. In this way, an MLIP is trained to learn the mapping from LAEs to potential energy surfaces (PES). In other words, MLIP training is essentially a regression process, establishing the critical link between LAEs and PES.

For complex reactive systems, the limiting factor for getting an accurate and broadly transferrable MLIP is no longer only the regression process, but the systematic generation of representative training dataset, which should cover a large and relevant configurational space. Conventionally,

researchers manually generate structures based on domain expertise, aiming at configurations that are expected to be sampled during MD simulations. For example, to train an MLIP for fracture simulation, Zhang et al. included highly strained configurations that may appear at crack tip according to anisotropic classical linear elastic theory³². Moreover, active learning is often utilized to generate structures in unexplored regions of the configurational space to enhance MLIP's extrapolative capability^{33–35}. Recently, random structure searching (RSS) has proven to be an efficiently automated approach for constructing training datasets by iteratively exploring the configurational space of materials^{36–38}. To summarize, existing strategies either require prior knowledge about the material, depend on iterative active learning exploration procedures, or fail to systematically cover diverse LAEs in a controlled manner. Since crucial LAEs in oxidation encompass not only various stable oxides, but also strained, defective, interfacial, and non-equilibrium configurations, existing strategies are inadequate for the Fe-O system. It is unfeasible to manually enumerate all the necessary configurations based on domain expertise. In addition, as iterative exploration cycles are required, active learning is not efficient, whereas it is challenging for RSS to accurately sample complex dynamical processes³⁸. Notably, Poul et al. proposed the Automated Small SYmmetric Structure Training (ASSYST) strategy for constructing systematic training dataset, based on extensively exploring all possible space groups of crystal structures^{39,40}. Its effectiveness was demonstrated by various tests on out-of-distribution structures (i.e., not explicitly considered in the training dataset). The strategy was first applied to elemental magnesium³⁹ and further extended to multicomponent alloys⁴⁰.

In this work, we propose the Perturbation Augmented Space group structure Sampling (PASS) method, a symmetry-informed, perturbation-augmented, descriptor-based one-shot sampling strategy for building compact and diverse MLIP training dataset. Then, following the PASS workflow, we generate extensive and representative Fe-O dataset, composed of structures of less than 10 atoms. Next, based on the ACE framework, we develop an MLIP and subsequently validate it on various properties across pure Fe and Fe oxides to demonstrate its accuracy and transferability. Finally, we apply the ACE MLIP to study large-scale Fe oxidation, showcasing the formation of FeO-like oxide. By applying the sampling of small-cell structure LAE to the simulation of large-scale oxidation for the first time, this work demonstrates that PASS is systematic, effective, and capable of enabling accurate and transferable MLIPs for chemically complex reactive processes.

Results

The PASS workflow

A central bottleneck in MLIP development for complex reactive materials is representative dataset construction, which we try to solve by introducing PASS. PASS not only avoids iterative active learning exploration but also allows an ACE potential trained on small-cell structures to transfer to: (1) large structures, such as surfaces and interfaces; (2) application-relevant events, for example atomic diffusion and defect migration; and (3) complex reaction processes, for instance large-scale Fe oxidation. The essential ideas behind PASS are first generating a comprehensive configurational space and then selecting the most representative structures while simultaneously capturing both equilibrium and non-equilibrium configurations. Specifically, two consecutive steps are performed, namely dataset generation and descriptor-based selection, as shown in Fig. 1(a) and (b), respectively.

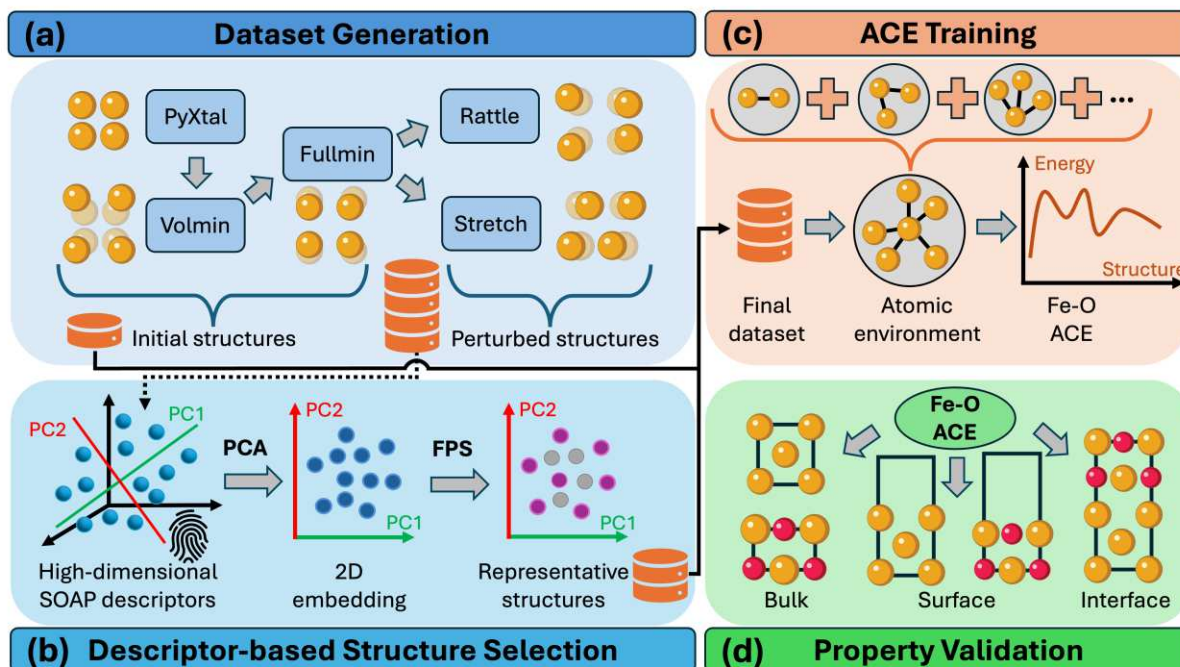


Fig. 1. Overview of the PASS workflow for developing a transferable ACE potential for Fe-O system. (a) Dataset generation. Space group structures are first generated using PyXtal and then

optimized through stepwise volume and full structural relaxation to obtain initial equilibrium configurations. Perturbed structures are subsequently generated from the relaxed structures through systematic rattle and stretch operations, introducing non-equilibrium LAEs. **(b)** Descriptor-based structure selection. The generated perturbed structures are encoded using high-dimensional SOAP descriptors, projected into a 2D embedding space by principal component analysis (PCA), and selected by farthest point sampling (FPS) to retain the most representative structures while reducing redundancy. **(c)** ACE training. The DFT-labelled final dataset is used to train an Fe-O ACE potential. **(d)** Property validation. The trained ACE potential is further systematically validated on bulk, surface, and interface properties across Fe and Fe-O systems to assess its accuracy and transferability.

Two parts of dataset, namely initial and perturbed structures, are constructed in the dataset generation step. The initial structures are obtained by stepwise relaxation of space group structures, following the protocols proposed by Poul et al.^{39,40}, and the perturbed structures are constructed by applying perturbations (i.e., rattle and stretch) to the relaxed initial structures. As shown in Fig. 1(a), PyXtal generates structures according to user-specified space groups with the maximum number of atoms and atomic compositions provided as input parameters. In this work, we set 10 to be maximum number of atoms per structure for both Fe and Fe-O systems. Subsequently, the volumes of PyXtal structures are relaxed, leading to Volmin structures. Afterwards, Volmin structures are fully relaxed to form Fullmin structures. Note that for the purpose of obtaining equilibrium configurations in a less computational demanding way, the stepwise relaxation processes are performed at a lower density-functional theory (DFT) accuracy in terms of both energy and force convergence criteria and k -point density. Finally, all the structures (i.e., PyXtal, Volmin, and Fullmin) are collected, forming the initial set of structures for the final high-fidelity DFT labelling.

Next, to generate perturbed structures, two separate actions are taken on Fullmin structures, i.e., rattle and stretch. As proposed originally⁴⁰, the rattle is applied by changing atomic positions by normally distributed noise with a standard deviation of σ_{rattle} and then repeated n_{rattle} times. A uniformly random strain matrix is coupled with random displacements in this action. The stretch is implemented n_{stretch} times by changing cells using diagonal and off-diagonal entries. Note that

two strain modes are randomly selected i.e., 70% hydrostatic (diagonal) and 30% shear (off-diagonal), with strain magnitudes ϵ_{hydro} and ϵ_{shear} , respectively.

The first crucial element in the PASS method is to extensively sample the configurational space in a controlled way. Specifically, we apply a grid of perturbation parameters (i.e., σ_{rattle} , ϵ_{hydro} , and ϵ_{shear}) to significantly increase the number of perturbed structures. The values of those parameters for both Fe and Fe-O systems are presented in Supplementary Table 1. To summarize, the space group structures are generated first, providing compact and diverse crystalline prototypes. Then, extensive perturbations are applied, aiming at generating non-equilibrium LAEs. In this way, a comprehensive configurational space is generated.

The second crucial element in PASS method lies in the descriptor-based selection or sampling process, as shown in Fig. 1(b). After filtering out structures with unphysically short interatomic distances, high-dimensional SOAP descriptors are utilized to encode the perturbed structures' LAEs. Consequently, the structural characteristics can be systematically quantified, enabling a convenient comparison between LAE differences. Next, principal component analysis (PCA) is adopted to reduce the high-dimensional descriptor space to a 2D embedding space. Finally, farthest point sampling (FPS) method is used to select the most representative structures and thus avoid redundancy. 10,000 structures are chosen for pure Fe and Fe-O systems, respectively. Combined with the initial structures (i.e., PyXtal, Volmin, and Fullmin), a structure pool is now established and will eventually be labelled with high-fidelity DFT to form the final training dataset. The composition of the final training dataset is shown in Table 1. Note that PASS method is only applied to obtain Fe and Fe-O structures following the procedures described above. For the O part, we directly adopt structures from existing datasets, including OQMD^{41,42} and OMat24⁴³.

Table 1. Composition of the final training dataset.

System	Subset	Number of structures
Fe	Initial	3,063
	Perturbed	10,000
Fe-O	Initial	3,802

	Perturbed	10,000
	OQMD	33
O	OMat24	1,193
	Total	28,091

Generation of extensive and representative dataset

The purpose of PASS is not simply to enlarge the training dataset, but to construct a compact and representative one that spans a broad range of physically relevant LAEs. The initial space group structures provide chemically and crystallographically diverse equilibrium configurations, while the systematic and extensive rattle and stretch perturbations introduce non-equilibrium LAEs potentially associated with defective, strained, and transition state configurations. Then, descriptor-based selection removes redundancy by selecting structures that are maximally separated in the reduced SOAP descriptor embedding space. Therefore, the final dataset is designed to balance diversity and efficiency such that it retains representative LAEs without relying on manually designed oxidation pathways or iterative active learning exploration cycles.

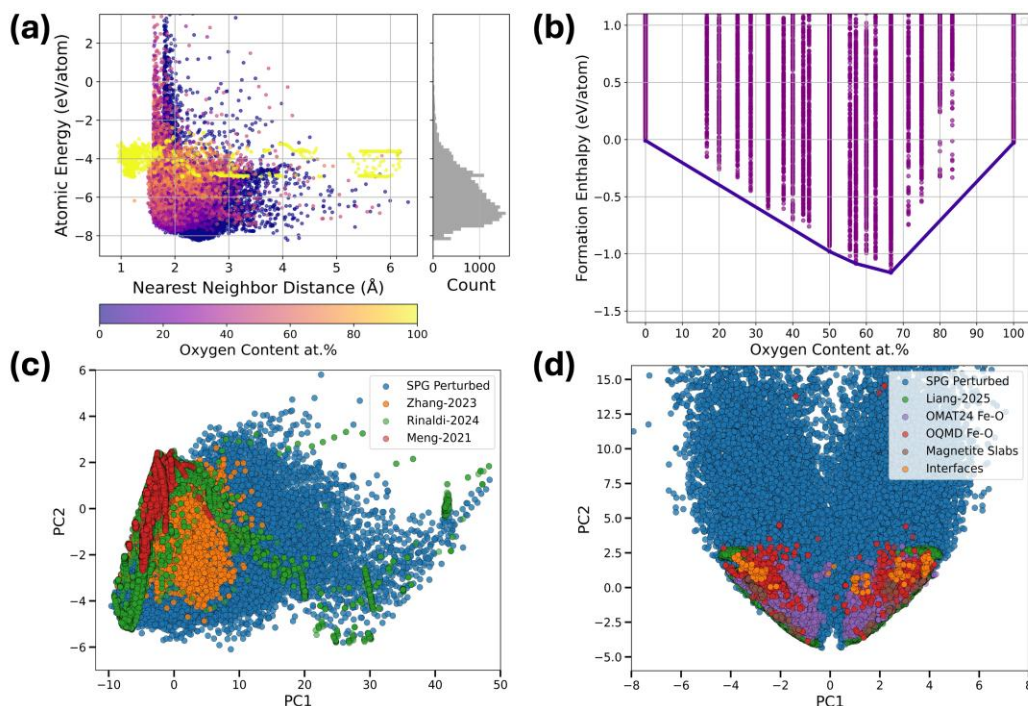


Fig. 2. Diversity and representativeness of final dataset for Fe-O system. (a) Distribution of atomic energy as a function of nearest neighbor distance, with data points colored by O content and accompanying histogram showing the structure count, illustrating the energetic and geometric diversity of the generated configurations. (b) Formation enthalpy of the final dataset as a function of O atomic percentage, showing broad coverage of the Fe-O compositional space, including pure Fe, Fe-O, and pure O structures. (c) PCA projection of SOAP descriptors for pure Fe, compared with existing Fe datasets including Meng-2021⁴⁴, Rinaldi-2024⁴⁵, and Zhang-2023³². Each point represents one structure-level SOAP average. The small-cell PASS dataset covers the LAE space sampled by these application-specific (e.g., deformation and fracture) datasets. (d) PCA projection of SOAP descriptors for Fe-O, compared with existing Fe-O datasets (i.e., Liang-2025¹⁶, OMAT24 Fe-O⁴³, and OQMD Fe-O^{41,42}) and representative structures (i.e., Fe oxide slabs⁴⁶ and interfaces⁴⁷). Each point represents the LAE of an individual atom. The broad coverage indicates that the small-cell PASS dataset contains diverse LAEs relevant to bulk oxides, surfaces, defects, and interfaces.

Figure 2 illustrates the diversity and representativeness of the final dataset for the Fe-O system generated following the PASS method. As shown in Fig. 2(a), the distribution of the atomic energy with respect to nearest neighbor distance is displayed, along with O content and structure count. Due to the filtering process, the minimum atomic distances in Fe and Fe-O systems are 1.8 and 1.6 Å, respectively. This ensures that all configurations are physical, i.e., not overly distorted. In addition, the atomic energy can be observed to distribute in a wide range, indicating that a broad region of the energy landscape is covered, which is formed by including both equilibrium and non-equilibrium configurations. Furthermore, data points with different O content are widely scattered, meaning that diverse Fe-Fe, Fe-O, and O-O coordination environments are included, indicative of quite distinctive configurations being generated. Then, the formation enthalpy of all structures as a function of the atomic percentage O content is shown in Fig. 2(b). A large compositional space is covered by the final dataset, including pure Fe, Fe-O systems, and O structures.

To demonstrate that the small-cell PASS dataset is representative of larger and more complex structures in application-relevant events such as fracture and oxidation processes, it is vital to compare the LAEs with those of existing datasets regarding various applications. Atomic descriptors enable both phase classification and detection of point defects and interfaces⁴⁸. To this

end, the SOAP descriptor is used to represent the LAEs of both Fe and Fe-O systems, followed by PCA performed for dimension reduction to ensure a clearer visual comparison. Figure 2(c) and (d) display the LAE comparison between PASS dataset and chosen ones for Fe and Fe-O systems, respectively. Note that for pure Fe system each point stands for the LAE of the whole structure, while for Fe-O system each point is the LAE of individual atom.

For the Fe system, three existing datasets are chosen for comparison, i.e., Meng-2021⁴⁴, Rinaldi-2024⁴⁵, and Zhang-2023³². Meng et al. developed a neural network interatomic potential for the Fe-H system⁴⁴, from whose training dataset we extracted the configurations containing only Fe and mark them as Meng-2021. A large variety of configurations is included in Meng-2021, consisting of self-interstitial atoms (SIA), vacancies, surfaces, and dislocations. To comprehensively sample both atomic positions and magnetic moments, Rinaldi et al. generated extensive Fe configurations associated with various properties (e.g., elastic constants, phonon, and transformation path)⁴⁵, which we mark as Rinaldi-2024. Based on anisotropic classical linear elastic theory, Zhang et al. generated structures representative of the large deformations at crack tip³², here marked as Zhang-2023. As can be seen in Fig. 2(c), Rinaldi-2024 has more structural diversity than Meng-2021, while Zhang-2023 occupies a large configurational space uncovered by the others, especially corresponding to the highly strained crack-tip configurations. Compared to the three datasets, the LAEs in our dataset (marked as SPG Perturbed) could represent those complex configurations (e.g., vacancies and dislocations) in various applications (e.g., fracture and tensile stretch). Furthermore, LAEs in SPG Perturbed dataset are even more widespread and diverse, which may be related to more complex structures such as transition states. The comparison not only demonstrates small-cell PASS dataset's outstanding representativeness but also shows its superior structural complexity.

For the Fe-O system (see Fig. 2(d)), three other important datasets along with several representative structures are included for comparison. Liang et al. employed deep learning methods to train an Fe-O interatomic potential, with training dataset focusing on the defective FeO structures as well as various FeO surfaces¹⁶, referred to as Liang-2025. In addition, Fe-O structures are extracted from both OQMD^{41,42} and OMat24⁴³ datasets. OQMD contains equilibrium or near-equilibrium commonly occurring Fe-O crystal structures, while OMat24 consists of diverse non-

equilibrium atomic configurations. Including those two datasets enables a more general LAE comparison beyond that of defective FeO dataset of Liang et al. Moreover, since the interfacial transformations among Fe, FeO and Fe₃O₄ are essential to the Fe oxidation process⁴⁹, Fe₃O₄ slabs⁴⁶ and complex interfaces⁴⁷ between Fe and Fe₃O₄ are also included. As can be seen in Fig. 2(d), OMAT24 Fe-O covers more space than OQMD Fe-O, indicating its inclusion of non-equilibrium configurations. Fe₃O₄ slabs and complex interfaces are observed to occupy distinct regions of the configurational space due to their different LAEs, demonstrating the ability of atomic descriptors in identifying diverse LAEs. As clearly shown in Fig. 2(d), the Fe-O system's LAEs in SPG Perturbed dataset not just cover the configurational space of all other datasets but also extend beyond it, owing to the extensive perturbations. This clearly demonstrates the representativeness and diversity of the final dataset.

Systematic validation of the ACE MLIP for pure Fe

As shown in Fig. 1(c), the ACE framework is adopted for MLIP training. It should be noted that we do not explicitly include magnetic degrees of freedom in the training process. To simplify, we use ferromagnetic (FM) ordering for Fe element in all DFT calculations for labelling the final dataset. The parameterized ACE potential yields the mean absolute training errors of 31.89 meV/atom and 120.52 meV/Å for energy and force, respectively. As schematically illustrated in Fig. 1(d), to verify the accuracy and demonstrate the transferability of the ACE potential, a series of validation tests are subsequently performed in a progressive manner, starting from thermodynamics to kinetics and from pure Fe to Fe-O system, covering structural, mechanical, and chemical properties.

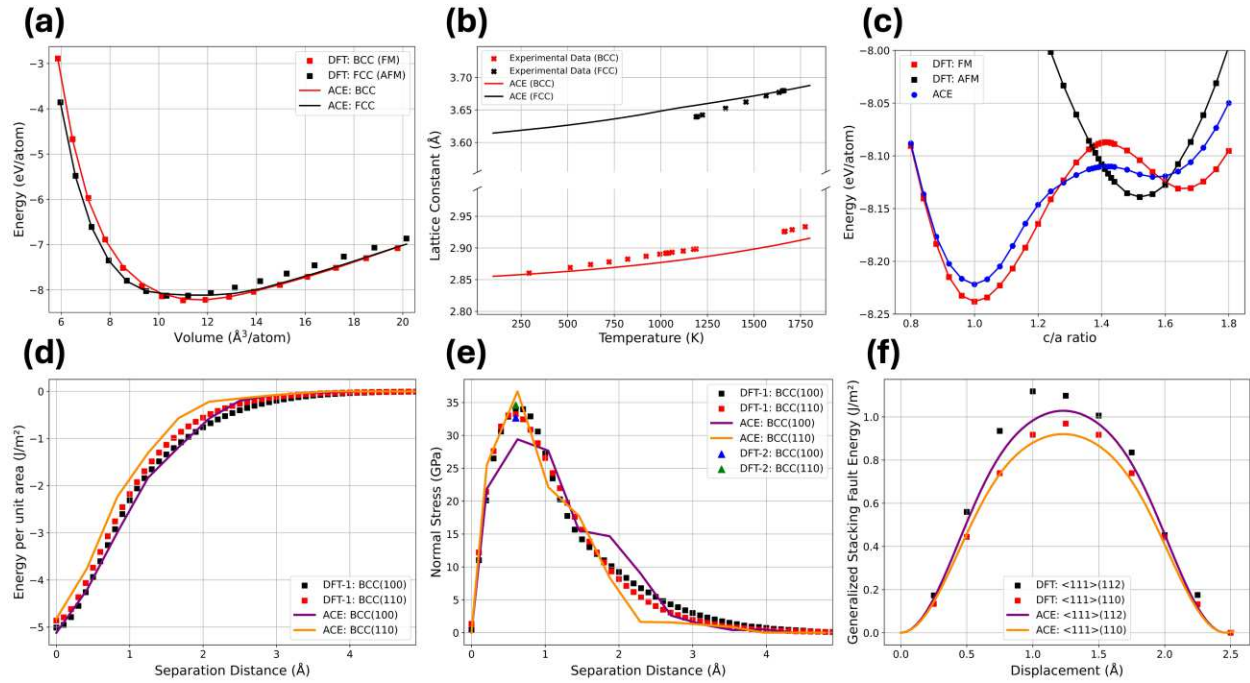


Fig. 3. Validation of the ACE potential for structural and mechanical properties of pure Fe.

(a) Equation of state curves for body-centered cubic (BCC) and face-centered cubic (FCC) Fe predicted by the ACE potential and compared with DFT reference data. Ferromagnetic (FM) and antiferromagnetic (AFM) orderings are used in the corresponding DFT calculations for BCC and FCC Fe, respectively. (b) Temperature-dependent equilibrium lattice parameters of BCC and FCC Fe predicted by the ACE potential and compared with experimental data, showing the ability of the ACE potential to reproduce lattice thermal expansion. The experimental data is taken from Ref. 50. (c) Bain path energy profiles as a function of the c/a ratio. The ACE potential prediction is compared with DFT calculations using both FM and AFM settings, assessing whether a geometry-based ACE potential captures the structural energetics associated with the BCC-FCC transformation pathway. (d) Rigid body separation energy curves for BCC Fe (100) and (110) planes predicted by the ACE potential. The results are compared with DFT reference data taken from Ref. 51. (e) Traction-separation curves obtained from the derivative of the energy-separation curves, providing a measure of the normal stress during cleavage. The results are compared with DFT reference data taken from Ref. 51 (DFT-1) and Ref. 32 (DFT-2). (f) Generalized stacking fault energy profiles for BCC Fe on the (110) and (112) planes along the $\langle 111 \rangle$ slip direction predicted by the ACE potential and compared with DFT reference data, validating the accurate description of shear deformation. The DFT reference data is taken from Ref. 52.

We start the validation by comparing pure Fe structural properties. Figure 3(a) shows the comparison of the equation of states for both body-centered cubic (BCC) and face-centered cubic (FCC) Fe phases obtained by DFT and the ACE potential. Note that FM and antiferromagnetic (AFM) orderings are considered in DFT calculations for BCC and FCC Fe phases, respectively. A good agreement can be found for both the Fe phases, except for the large volumes of FCC Fe where a slight deviation is observed. Then, the equilibrium lattice parameters at finite temperature obtained by ACE potential are shown in Fig. 3(b), in comparison with experimental data⁵⁰. The ACE potential can well capture the influence of temperature and accurately describe the lattice thermal expansion of both the phases.

The Bain path model is widely used to study the martensitic transformation in steel⁵³, in which BCC Fe changes into FCC Fe (or vice versa) via a continuous tetragonal distortion (i.e., changing the c/a ratio). The comparison between atomic energy with respect to the varied c/a ratio predicted by the ACE potential and calculated by DFT is shown in Fig. 3(c). Note that both FM and AFM orderings are applied to the same structures in DFT calculations. AFM ordering is thermodynamically favored for the c/a ratio ranging from approximately 1.4 to 1.6, which corresponds to FCC-like phase, while FM ordering is favored outside this range. Although the ACE potential does not explicitly consider magnetic degrees of freedom, the Bain path test provides an important assessment of whether a geometry-based MLIP trained under a fixed magnetic setting can still reproduce the structural energetics associated with phase transformation. The comparison with FM and AFM DFT reference curves shows that the ACE potential accurately describes the BCC region and captures the qualitative change in the energy landscape near the FCC-like region, illustrating that the structural component of the phase transformation is captured.

Next, we validate the ACE potential by testing its predictions of mechanical properties. For BCC Fe, brittle fracture is the dominant failure mechanism, which happens in the form of cleavage³². As cleavage occurs on the plane with maximum normal stress, it is essential to evaluate the normal stress. To this end, the rigid body separation is performed for BCC Fe (100) and (110) planes, and the resulting energy-separation curves are shown in Fig. 3(d). In addition, DFT reference data taken from Ref. 51 is added to enable a clear comparison. The universal binding energy relation

of BCC(100) plane aligns well with DFT results, while for BCC(110) plane slight deviation from DFT calculations is observed, which is also found in Ref. 32. Additionally, BCC(100) and BCC(110) surface energies are calculated from Fig. 3(d) and obtained to be 2.60 and 2.42 J/m², respectively, matching well with DFT obtained values of 2.543⁵⁴ and 2.495⁵⁴ J/m². Then, as shown in Fig. 3(e), the traction-separation (T-S) curves are obtained by taking the derivative of the energy-separation curves⁵². The general trends match with DFT reference data⁵¹ (i.e., DFT-1). In addition, the maximum normal stresses for BCC(100) and BCC(110) planes are found to be close to the DFT results of 32.68³² and 34.62³² GPa (DFT-2, marked by blue and green triangles, respectively). Although local minima are present, the T-S curves are quite smooth compared to those of benchmarked MLIPs in Ref. ⁵². Moreover, the generalized stacking fault (GSF) energy is crucial for understanding nanoscale plasticity, ideal shear strength, and how crystalline materials deform^{55,56}. Thus, it is beneficial to add GSF profiles in the validation. Figure 3(f) shows the GSF energy of BCC(110) and BCC(112) planes slipping along <111> direction as predicted by the ACE potential, in comparison with DFT reference data⁵². The ACE potential can distinguish the shear deformations on the two planes, obtaining unstable (i.e., maximum) stacking fault energies close to the DFT results.

Table 2. Validation of the ACE potential for point defects and surface formation energetics in pure Fe, in comparison with DFT and two MLIPs for pure Fe (i.e., Gaussian approximation potential (GAP)⁵⁴ and moment tensor potential (MTP)⁵⁷).

Property	ACE	DFT	GAP ⁵⁴	MTP ⁵⁷
Vacancy formation energy (eV)				
mono-vacancy	1.89	2.22 ⁵⁴ , 2.184 ⁵⁷	2.26	2.161
di-vacancy 1NN	3.80	4.24 ⁵⁴ , 4.231 ⁵⁷	4.41	4.124
di-vacancy 2NN	3.68	4.20 ⁵⁴ , 4.161 ⁵⁷	4.30	4.063
di-vacancy 3NN	3.83	4.45 ⁵⁴ , 4.396 ⁵⁷	4.55	4.308
di-vacancy 4NN	3.73	—	4.48	—
di-vacancy 5NN	3.78	—	4.47	—
SIA formation energy (eV)				
T site	4.30	4.79 ⁵⁴ , 4.548 ⁵⁷	4.75	4.87

O site	4.94	5.58 ⁵⁴ , 5.333 ⁵⁷	5.53	5.267
<100>	4.79	5.48 ⁵⁴ , 5.206 ⁵⁷	5.47	5.115
<110>	4.04	4.37 ⁵⁴ , 4.094 ⁵⁷	4.21	4.282
<111>	4.47	5.13 ⁵⁴ , 4.833 ⁵⁷	4.90	4.919
Surface energy (J/m ²)				
BCC(100)	2.60	2.543 ⁵⁴ , 2.525 ⁵⁷	2.547	2.543
BCC(110)	2.42	2.495 ⁵⁴ , 2.524 ⁵⁷	2.499	2.543
BCC(111)	2.92	2.752 ⁵⁴ , 2.714 ⁵⁷	2.756	2.723
BCC(211)	2.74	2.629 ⁵⁴	2.612	—

“NN” represents nearest neighbor, “2NN” refers to the second nearest neighbor, and beyond. “T” and “O” stand for tetrahedral and octahedral, respectively. The notation “< >” specifies the exact geometric orientation and configuration of the SIA defect.

Next, we validate the ACE potential’s capability of describing various defects. The vacancy, SIA and surface formation energies are calculated, with the corresponding results being presented in Table 2. To ensure a better comparison, two MLIPs specially trained for pure Fe, namely GAP⁵⁴ and MTP⁵⁷, are selected along with corresponding DFT data from the literature. The ACE potential can well predict the energetics of various defects, showing matching qualitative trends with DFT and GAP⁵⁴ and MTP⁵⁷ findings. Remarkably, none of the relevant configurations is explicitly included in the training dataset, thereby demonstrating the superior transferability of the ACE potential developed in this work.

Systematic validation from thermodynamics to kinetics for Fe-O

Since the accurate description of Fe-O system is significantly crucial in oxidation simulation, it is of vital significance to evaluate whether the ACE potential can capture the essential characteristics, such as structural properties of various oxides. In addition, as the ACE potential is trained on small-cell structures, the transferability to larger systems also needs to be validated. Therefore, we next focus on validating the ACE potential’s capability of capturing the thermodynamics and kinetic properties of Fe-O system, as well as its transferability to complex structures and critical events.

Firstly, the ACE potential is used to predict the structural properties of common Fe oxides, namely FeO, Fe₂O₃, and Fe₃O₄. Bienvenu et al. adopted ACE framework to train an MLIP on various phases present in the experimental Fe-O phase diagram, with magnetism explicitly considered in an Ising-like manner⁵⁸. We add this MLIP into comparison and hereafter refer to it as ACE-Bienvenu to distinguish with our ACE potential. As shown in Table 3, our ACE potential can describe those typical Fe oxides' structural properties as accurate as DFT (+*U*) results, with performance as good as ACE-Bienvenu. It is noteworthy mentioning that neither the structures nor the magnetism of the studied oxides (i.e. FeO, Fe₂O₃, and Fe₃O₄) are explicitly represented in the training dataset of our ACE potential, again demonstrating the effectiveness of the PASS method. Additionally, the formation enthalpies exhibit the same qualitative trend as the DFT (+*U*) results, indicative of our ACE potential capturing the correct thermodynamics.

Table 3. Lattice constants (a for cubic lattice, a and c for hexagonal lattice), bulk modulus B, and formation enthalpy ΔH_f of Fe and representative Fe oxides predicted by our ACE potential, DFT, and other MLIP (marked as ACE-Bienvenu)⁵⁸. DFT reference data is taken from Ref. ⁵⁸. The values in the parentheses are the results of DFT calculations with *U* correction. Lattice constants, bulk modulus, and formation enthalpy are in the units of Å, GPa, and eV/atom, respectively.

System	Property	ACE	DFT (+ <i>U</i>) ⁵⁸	ACE-Bienvenu ⁵⁸
BCC Fe	a	2.846	2.83 (2.95)	2.84
	B	171	188 (123)	165
FeO	a	4.296	4.26 (4.31)	4.29
	B	164	195 (164)	181
	ΔH_f	-1.57	-0.91 (-1.43)	-0.95
Fe ₂ O ₃	a	4.995	5.02 (5.07)	4.98
	c	13.513	13.90 (13.90)	14.06
	B	168	172 (191)	156
	ΔH_f	-2.00	-1.30 (-1.81)	-1.30
Fe ₃ O ₄	a	8.259	8.40 (8.47)	8.40
	B	156	172 (191)	165

$$\Delta H_f$$

$$-1.93$$

$$-1.29 (-1.75)$$

$$-1.29$$

Next, to validate the transferability to larger and complex structures, it is necessary to evaluate the ACE potential's performance on relevant configurations. To this end, the geometry optimizations of the studied Fe oxides in both bulk and surface forms are conducted by DFT (without U correction). Note that their magnetic moments are set according to the respective ground state magnetism. Since the interfacial configurations are valuable in oxidation simulation and FeO is formed initially at high-temperature oxidation⁴⁹, two interface structures between Fe and FeO (i.e., Fe(100)||FeO(100) and Fe(110)||FeO(111)) are additionally generated, calculated, and then added into the comparison. All the relaxation trajectories are extracted, and the corresponding energies are predicted by the ACE potential. Figure 4(a) displays the atomic energies predicted by the ACE potential alongside DFT reference values, confirming that the ACE potential captures well the energetics of diverse configurations.

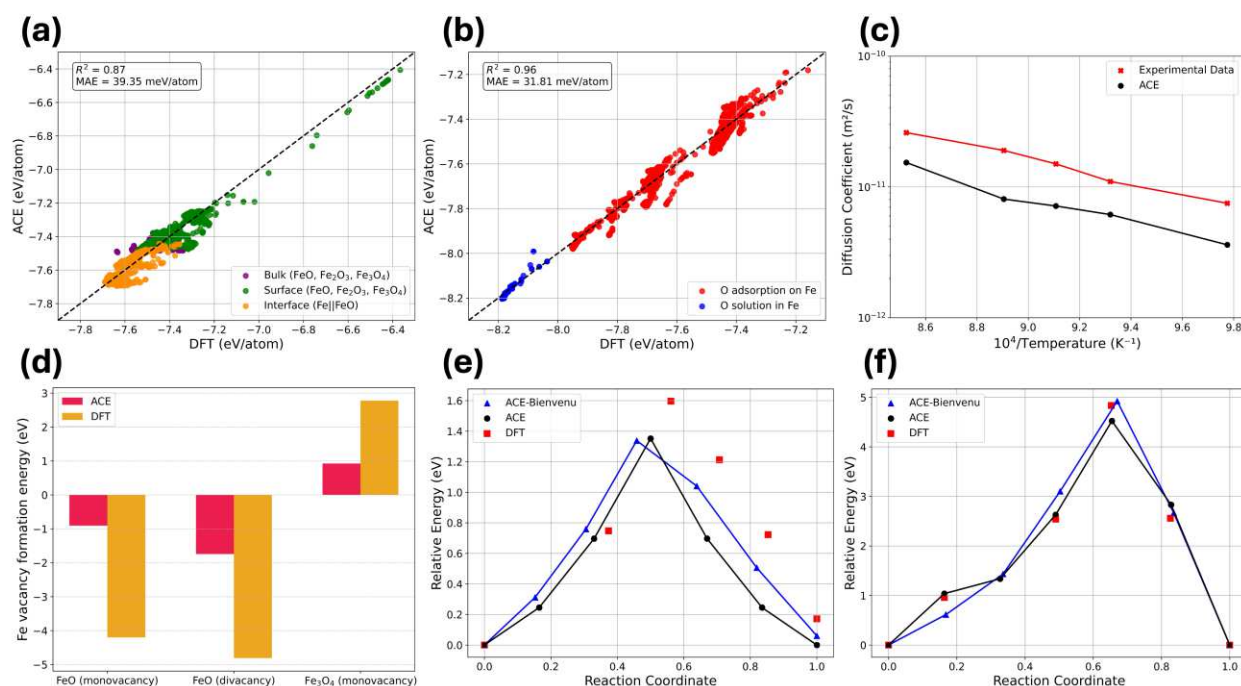


Fig. 4. Validation of the ACE potential for thermodynamics and kinetic properties of Fe-O system. (a) Comparison of atomic energies between DFT calculations and ACE potential predictions for relaxation trajectories of Fe oxide bulks, surfaces, and Fe/FeO interface structures, assessing the transferability to larger and more complex configurations. (b) Comparison of atomic

energies between DFT calculations and ACE potential predictions for oxidation-relevant configurations, including O adsorption on BCC Fe surfaces and O dissolution in BCC Fe. (c) Temperature-dependent diffusion coefficients of O in BCC Fe predicted by our ACE potential and compared with experimental data taken from Ref. ⁵⁹. (d) Fe vacancy formation energies in FeO and Fe₃O₄ predicted by the ACE potential and compared with DFT reference data. (e) Fe vacancy migration barriers in FeO obtained from climbing image nudged elastic band (CINEB) calculations by DFT, our ACE potential, and ACE-Bienvenu. (f) Fe vacancy migration barriers in Fe₃O₄ obtained from CINEB calculations by DFT, our ACE potential, and ACE-Bienvenu. The comparison evaluates the ability of the ACE potential to capture kinetic barriers of vacancy diffusion in Fe oxides.

In addition to the description of oxides, it is also essential for the ACE potential to accurately describe the application-relevant critical events. The oxidation process begins with O adsorption on the Fe surface, followed by O dissolution into the bulk and subsequent diffusion. It is beneficial to incorporate these relevant configurations into the comparison. Therefore, the DFT results for O adsorption on various BCC Fe surfaces at different coverages from our previous study are used as critical configurations²⁵. Then, we perform DFT calculations of O dissolution at both octahedral and tetrahedral sites, together with the energy barrier along the diffusion path between those sites. As can be seen from Fig. 4(b), though no related configurations are included in the training dataset, the prediction by the ACE potential matches well with the energies obtained by DFT, thereby indicating the superior transferability of our ACE potential. Furthermore, as shown in Fig. 4(c), the diffusivity of O in the BCC Fe bulk is simulated and the resulting diffusion coefficients are compared with experimental study⁵⁹, where a good agreement and consistent trend can be observed.

Finally, to further validate our ACE potential's ability to describe kinetic behaviors, we evaluate the vacancy diffusion barriers in FeO and Fe₃O₄ oxides. First, as shown in Fig. 4(d), the Fe vacancy formation energies are obtained for both FeO (mono- and di-vacancy) and Fe₃O₄ (mono-vacancy) by our ACE potential and DFT. Although the ACE potential underestimates the absolute formation energies, it qualitatively captures the thermodynamic properties of the system, as indicated by the consistent trend with regard to DFT. It should be noted that the ground state magnetic orderings of both oxides are explicitly treated in the DFT calculations. Then, the Fe vacancy diffusion barriers

for both FeO (Fig. 4(e)) and Fe₃O₄ (Fig. 4(f)) are obtained by both our ACE potential and DFT using climbing image nudged elastic band (CINEB) method. The 2NN diffusion path and octahedral Fe vacancy moving in (001) plane are considered for FeO and Fe₃O₄, respectively. The ACE-Bienvenu, developed by explicitly considering the most relevant defects in oxides, is therefore worth comparing to. It can be seen from Fig. 4(e) and (f) that our ACE potential performs similarly as the ACE-Bienvenu and shows a comparable trend with respect to DFT.

Application to large-scale oxidation simulation

By comparing the small-cell PASS dataset with the existing ones, it can be deduced that our final dataset is both extensive and representative. After a systematic validation, our ACE potential is demonstrated to be accurate and transferable, capable of capturing both thermodynamics and kinetic properties. Consequently, it is essential to assess the ability of the ACE potential to capture complex reaction processes. Therefore, the ACE potential is further applied to study large-scale BCC Fe surface oxidation.

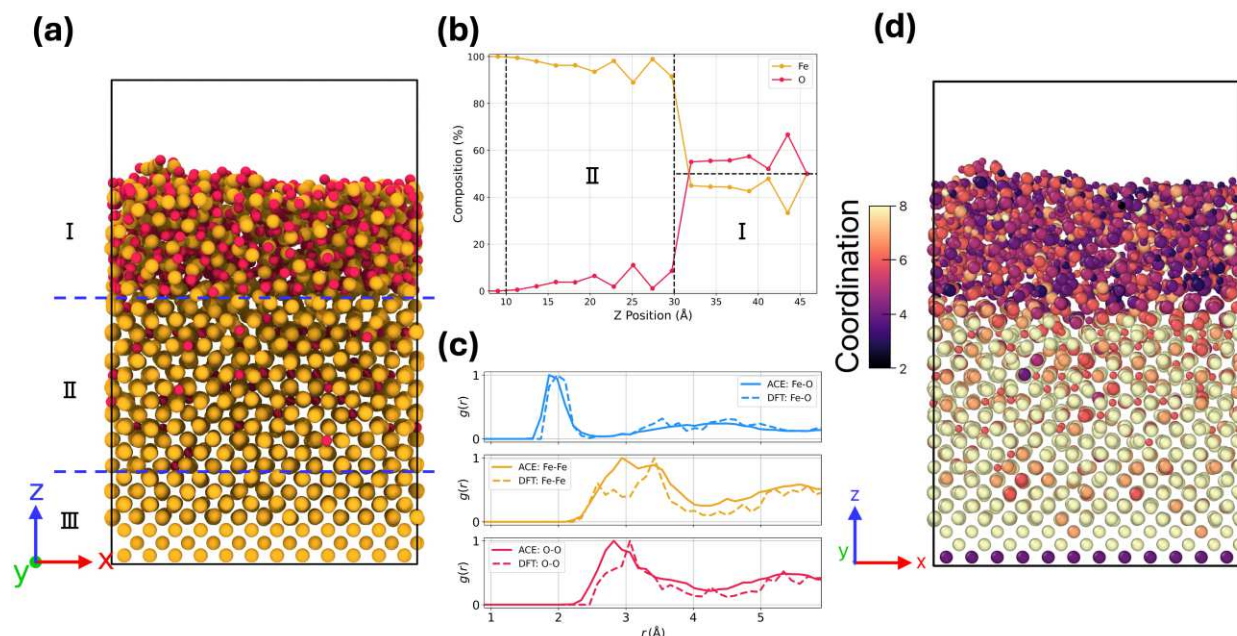


Fig. 5. Large-scale BCC Fe surface oxidation simulation using the ACE potential. (a) Final configuration after 1 ns high-temperature oxidation of the BCC Fe (100) surface. Three regions

are identified along the Z direction: an oxide layer near the surface (region I), an intermediate region containing O atoms dissolution in Fe (region II), and an underlying BCC Fe bulk region (region III). **(b)** Layer-resolved Fe and O atomic composition profiles along the Z direction. The horizontal dashed line indicates atomic composition of 50%, while the vertical dashed lines mark the approximate boundaries between three regions. The near-equal Fe and O contents in region I suggest the formation of an FeO-like oxide layer. **(c)** Normalized radial distribution functions (RDF) of the extracted oxide layer (region I) compared with the RDF of DFT-relaxed FeO, including Fe-O, Fe-Fe, and O-O pair correlations. The agreement in peak positions indicates that the short-range order of the oxide layer is FeO-like. **(d)** First-shell coordination number analysis of the final configuration. The coordination number distribution distinguishes the BCC Fe bulk, O dissolution in Fe, and FeO-like oxide layer, further supporting the structural characterization of the formed oxide.

The simulation process is described in detail in Methods section. Figure 5 displays the final configurations of the oxidation process and illustrates the analysis of the formed oxide layer. Firstly, the final configuration in the oxidation process is shown in Fig. 5(a), where three different regions can be clearly visualized, separated by two blue dashed lines. The formation of an oxide layer can be clearly seen in region I, O dissolution in BCC Fe is visible in region II, while the pure Fe bulk remains intact in region III. The concurrent appearance of these three regions demonstrates that the ACE potential can simultaneously capture the formation of oxides and oxide/Fe interfaces, O diffusion into the Fe bulk, and high-temperature Fe dynamics, highlighting its strong transferability.

Since FeO forms at 873 K, we analyze the oxide layer composition to verify the ACE potential's capability to capture this phase. The final configuration is scanned along the Z direction and the composition at each Z value is calculated as the atomic ratio of Fe and O elements. The compositions in regions I and II are displayed in Fig. 5(b), where the vertical dashed line between regions I and II indicates the onset of the oxide layer (the region to the right of the vertical line corresponds to the oxide) and the horizontal dashed line in region I indicates the 50% atomic ratio. With Z values increasing, O concentration starts to increase due to the inward diffusion of O atoms to region II, but at a relatively low level. Then, it suddenly increases to around 50% at Z larger than 30 Å, indicating the formation of the oxide layer. Notably, the Fe and O concentrations are

nearly equal across region I with both close to 50%, indicating the formation of a stable oxide, likely FeO.

Next, to further probe the structure of the oxide layer, region I is extracted and the corresponding radial distribution function (RDF) curve is obtained. For comparison, the FeO structure is geometrically optimized by DFT, and the corresponding RDF is obtained as well. The comparison between the two RDF curves is shown in Fig. 5(c). Note that the curves are normalized to ensure a better visualization of the comparison. The main Fe-O, Fe-Fe, and O-O peak positions of the formed oxide layer are consistent with those of the FeO DFT reference. The agreement of the first Fe-O peak indicates the formation of Fe-O nearest neighbor bonds, while the corresponding Fe-Fe and O-O correlations suggest that the cation and anion sublattices in the oxide layer resemble those of FeO. Compared with the DFT-relaxed FeO structure, the RDF peaks of the simulated oxide layer are broader, which is expected for a finite-temperature oxidation product containing structural disorder, surface effects, and possible point defects. Since the RDF curves are normalized for comparison, the analysis focuses mainly on peak positions rather than peak intensities. Together with the near-equal Fe and O composition, the RDF results indicate that the dominant local structure of the oxide layer is FeO-like rather than a perfect crystalline FeO phase.

Finally, to quantify the local atomic structure, the first-shell coordination numbers are calculated and displayed in Fig. 5(d). A clear difference in coordination number can be seen between Fe bulk (region III and II) and the oxide layer (region I). Region III mainly contains Fe atoms with coordination number close to 8, indicative of the ideal BCC lattice. In region II, the dissolution of O atoms reduces the coordination number of Fe atoms to 6 or 7, while an O coordination number of 6 indicates that O atoms occupy octahedral sites, in agreement with the DFT result. In region I, the majority of Fe atom has coordination number of 5 or 6, matching with that of defective FeO with one O vacancy or perfect FeO.

To briefly summarize, the large-scale oxidation simulation demonstrates the practical transferability of the ACE potential from training dataset of small-cell structures to an extended, chemically evolving Fe-O system. The formation of an O-rich oxide layer, together with the inward diffusion of O atoms, indicates that our ACE potential captures the early-stage coupling between

surface adsorption, diffusion, and oxide growth. The layer-resolved composition profile shows that the oxide layer region approaches an Fe to O atomic ratio close to that of FeO, while the RDF of the extracted oxide layer reproduces the main Fe-O, Fe-Fe, and O-O features of DFT-relaxed FeO structure. These results suggest that the short-range ordering in the oxide layer is predominantly FeO-like under the simulated high-temperature conditions.

Discussion

We propose the PASS method for building representative MLIP dataset of small-cell structures in a single step. The extensive validation tests and large-scale oxidation simulation demonstrate the effectiveness of PASS method. To the best of our knowledge, this work provides the first demonstration of a space group based small-cell structure sampling and training strategy for a transferable MLIP applied to large-scale and chemically complex Fe surface oxidation.

PASS generates training dataset comprising of small-cell structures in the one-shot way. This avoids the heavy computational cost of extending dataset using iterative active learning explorations. Additionally, training MLIP on the small-cell structures is advantageous, as it reduces the computational cost for the DFT calculations, thus allowing higher-fidelity DFT labelling. The most essential point is that MLIP learns the critical link from LAEs to PES, so small-cell structures' diversity can transfer to large and complex systems if the relevant LAEs are covered. The effectiveness of PASS can be attributed to the fact that it generates a broad range of LAEs, and the perturbation samples non-equilibrium configurations relevant to complex structures (e.g., defects and interfaces) and critical processes (e.g., adsorption and diffusion). Nevertheless, the active learning strategy may still be useful for targeted refinement, especially for rare oxidation events or highly defective interfaces, where uncertainty quantification plays a vital role⁶⁰. In addition, due to the size of small-cell structures, long-range interactions are inevitably neglected.

Compared to the ASSYST strategy proposed by Poul et al.⁴⁰, PASS takes advantage of the expressive ability of atomic descriptors to represent the LAEs. This makes it convenient to compare structural differences and further select the most representative structures. It is demonstrated by Qi et al. that featurization of the configuration space could be used to help develop

reliable MLIPs⁶¹. It is also worth mentioning that in addition to RSS, Subramanyam and Perez also make use of random initial configurations, maximizing their information entropy to diversify the dataset for MLIP training⁶². In comparison, PASS not only makes sure that the MLIP is symmetry-informed by taking space group structures instead of random structures, but also ensures that the broad range of LAEs are generated in a controlled manner by applying a mesh of perturbations.

It is worthwhile noting that the current ACE MLIP does not explicitly consider magnetism and thus is not a spin-aware interatomic potential. Instead, it should be interpreted as a structurally transferable and computationally practical interatomic potential trained on a highly systematic, oxidation-agnostic, small-cell dataset under a fixed magnetic setting. Consequently, its applicability is limited in regimes where magnetism strongly influences energetics and kinetics. For example, the FM to paramagnetic phase transition in BCC Fe depend on both spin and lattice degrees of freedom. In addition, the ACE MLIP also cannot simulate high-temperature spin fluctuations and magnetic disorder above the Curie or Néel temperatures. Its transferability comes from the extensive structural sampling and systematic validation, but future work could incorporate magnetic descriptors with explicit spin degrees of freedom, spin-labelled datasets, or separate magnetic treatment of oxidation states.

Methods

Dataset generation and selection

The pyiron integrated development environment (IDE) is adopted as the dataset generation platform^{63,64}. Firstly, the initial space group structures are generated by the PyXtal package⁶⁵. After the stepwise relaxation is complete, the rattle and stretch perturbations are applied to Fullmin structures using the ASSYST⁴⁰ tool implemented in pyiron IDE. To encode the LAEs, the SOAP descriptor^{29,66} is adopted, as implemented in the DScibe package^{67,68}. The parameters $r_{\text{cut}} = 7$, $n_{\text{max}} = 12$, $l_{\text{max}} = 4$, and $\sigma = 0.3$ are used for constructing the SOAP descriptor.

DFT calculations

Collinear spin-polarized DFT calculations are performed using VASP^{69,70} at $T = 0$ K^{71,72}. The interactions between the valence electrons and the ionic core are described using the projected

augmented wave (PAW) method⁷³. The generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form is adopted for exchange-correlation energy⁷⁴. The Brillouin zone is sampled by the Γ -centered k -point mesh, with a consistent k -point spacing of $0.2 \text{ \AA}^{-1}$. The Gaussian method is used to treat fractional occupancies with the Fermi surface smearing width of 0.05 eV . A cutoff energy of 520 eV is chosen for plane-wave basis set. The convergence criteria of the energy for the electronic self-consistency loop and the force for the ionic relaxation loop are set to 10^{-6} eV and $0.01 \text{ eV/\AA}$, respectively. The diffusion barriers are obtained by performing CINEB calculations⁷⁵, where the intermediate images are linked by a spring constant of $5 \text{ meV/\AA}^2$.

MLIP training and validation

The ACE MLIP is trained by employing the PACEMAKER package^{76–78}. The Finnis-Sinclair-type non-linear embedding function is adopted for both Fe and O elements. The simplified spherical Bessel functions are used as the radial basis functions. We use 800 B-basis functions per element, leading to 4,448 parameters. A global cutoff of $6 \text{ \AA}$ is used for neighbor list construction. The force-to-energy weight ratio in the loss function is set to 10^{-2} . Both L1- and L2-regularization coefficients are set to 10^{-8} . The parameters are optimized by the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm for 4,000 steps. Most validation tests are conducted in a workflow based on Atomic Simulation Environment (ASE) package⁷⁹. We use the FIRE algorithm⁸⁰ with a force convergence criterion of $5 \times 10^{-2} \text{ eV/\AA}$ in all calculations where structural optimization is needed.

MD simulations

All MD simulations are performed using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)⁸¹. For the diffusivity of O atoms in Fe bulk, a $10 \times 10 \times 10$ BCC supercell containing 2,000 Fe atoms is created, with 20 O atoms randomly inserted. Periodic boundary conditions are applied in all three directions. The system is relaxed at each temperature for 10 ps, followed by another 500 ps of production run. Isothermal-Isobaric (NPT) ensemble and canonical ensemble (NVT) ensemble with a timestep of 0.5 fs are adopted in relaxation and production run, respectively. The diffusion coefficients are obtained by fitting the mean square displacement of O atoms to the Einstein relation. For the Fe surface oxidation simulation, BCC(100) surface is selected and a $12 \times 12 \times 24$ supercell is created, amounting to 3,456 Fe atoms. Then, 400 O_2

molecules are randomly distributed on top of the surface. During the oxidation simulation, periodic boundary conditions are adopted in both X and Y directions, while fixed boundary condition is applied along the Z direction, with both the top and bottom simulation box being set to be reflective walls. The atoms in three bottom layers of Fe slab are fixed so as to mimic the surface condition. Before the oxidation, the O₂ molecules and Fe slab are relaxed at 300 K in the NVT ensemble for 100 ps, respectively, so as for O₂ molecules randomly distributed over the surface and the initial configuration to be reasonable. In the oxidation process, the timestep is set to 1 fs and the temperature of the entire system is regulated at a constant 873 K by Nosé-Hoover heat bath method^{82,83} for 1 ns. Open Visualization Tool (OVITO)⁸⁴ is utilized for all the visualizations.

Data availability

Data will be made available upon reasonable request.

Code availability

The files for the ACE MLIP will be publicly available once the manuscript is accepted.

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Acknowledgements

This research was carried out under project number T23003 in the framework of the Research Program of the Materials innovation institute (M2i) (www.m2i.nl) supported by the Dutch government. This work was supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO; the Netherlands Organization for Scientific Research), Domain Science, for

access to supercomputing facilities. We also acknowledge the use of the DelftBlue supercomputer provided by the Delft High Performance Computing Center (DHPC; <https://www.tudelft.nl/dhpc>). We thank Dr. Wanda Melfo Prada and Dr. Marga Zuiderwijk from Tata Steel Nederland Technology B.V. for fruitful discussions and insightful suggestions.

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Z.W.: Conceptualization, Methodology, Software, Data curation, Formal analysis, Writing – original draft, Writing – review & editing. F.S.: Conceptualization, Formal analysis, Writing – review & editing. P.D.: Funding acquisition, Resources, Project administration, Supervision, Writing – review & editing.

Competing interests

The authors declare no competing interests.

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