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Polarization of ferroelastic domain boundaries in strontium titanate

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Abstract

The polarity of ferroelectric antiphase boundaries (APB) in SrTiO_3 (STO) has been studied in depth over the past years. While previous works have analyzed the macroscopic polarization emerging in ferroelastic twin boundaries (TB) in bulk STO using first principle methods, they were challenged by the limited system sizes accessible to the methods used. Long range inhomogenous strain makes it impossible to use standard ab initio methods as the computational cost increases drastically with the system size required to account for long range effects. In this thesis the temperature and pressure dependence of the individual polarization components were investigated using machine learned interatomic potentials to overcome this limiting factor.

Training a neural network potential (NNP) to reasonable accuracy generally requires a large set of ab initio data. By finetuning pretrained **MACE** foundation models, this limitation was overcome, allowing the development of a reasonably accurate NNP using only a handful of ab initio configurations. Furthermore, a custom post processing tool was developed to extract the order parameter (OP) and polarization profiles from molecular dynamics trajectories.

The resulting OP profiles agree with the ones reported in the literature confirming the correct atomistic structure for ferroelastic TBs. The polarization extracted from relaxed supercells show the expected behavior across all pressures. While the OP and polarization in head-tail TBs averaged over molecular dynamics trajectories show the expected profiles, the OP and polarization in head-head MD trajectories deviated heavily from the anticipated profiles.

Kurzfassung

Die Polarität ferroelektrischer Antiphasengrenzen (APB) in SrTiO_3 (STO) wurde in den letzten Jahren eingehend untersucht. Während frühere Arbeiten unter Verwendung von First-Principles-Methoden die makroskopische Polarisierung analysierten, die in ferroelastischen twin boundaries (TB) in STO auftritt, waren sie durch die begrenzten Systemgrößen, die mit den verwendeten Methoden zugänglich waren, eingeschränkt. Aufgrund der weitreichenden inhomogenen Deformation ist es unmöglich Standard-Ab-initio-Methoden zu verwenden, da der Rechenaufwand mit der Systemgröße, die zur Berücksichtigung der weitreichenden Effekte erforderlich ist, drastisch ansteigt. In dieser Arbeit wurde die Temperatur- und Druckabhängigkeit der einzelnen Polarisationskomponenten unter Verwendung maschinell gelernter interatomarer Potenziale untersucht, um diesen limitierenden Faktor zu überwinden.

Das Training eines neuronalen Netzwerkpotenzials (NNP) mit ausreichender Genauigkeit erfordert in der Regel eine große Anzahl an ab-initio Daten. Durch das finetuning vortrainierter **MACE** foundation Modelle konnte diese Einschränkung überwunden werden, sodass die Entwicklung eines angemessen genauen NNPs unter Verwendung nur einer Handvoll ab-initio Konfigurationen möglich war. Darüber hinaus wurde ein Analysetool entwickelt, um den Ordnungsparameter (OP) und die Polarisationsprofile aus Molekulardynamik Trajektorien zu extrahieren.

Die resultierenden OP Profile stimmen mit denen in der Literatur überein und bestätigen die korrekte Kristallstruktur für ferroelastische TBs. Die aus relaxierten Superzellen extrahierte Polarisierung zeigt das erwartete Verhalten für alle simulierten Drücke hinweg. Während die OP und Polarisierung in head-tail TBs, gemittelt über MD Trajektorien, die erwarteten Profile aufweisen, weichen die OP und Polarisierung in head-head MD Trajektorien stark von den antizipierten Profilen ab.

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1. Introduction

Domain walls (DW) in ferroic materials show unusual physical properties [1] which led to a recent boost in research on so called "domain wall engineering", where DWs are deliberately engineered into nanoelectronic devices as functional nanoscale elements [2]. Examples for DW properties in perovskites range from conducting DWs in BaTiO₃ [3] to DWs carrying an emergent polarization in otherwise nonpolar perovskites such as SrTiO₃ [4] or CaTiO₃ [5]. While the bulk domains remain nonpolar, hard antiphase boundaries (APB) [6, 7] and twin boundaries (TB) [6, 8], which are explained in more detail in Section 1.3, host an emergent polarization. For APBs in SrTiO₃ it has been observed that the polarization in these ferroelectric domain walls is reversible under the influence of an external electric field [9], which in principle allows them to be utilized as nanoscale platforms for binary bit encoding, possibly paving the way toward a new generation of low power non-volatile memory and data-storage technologies [10, 11].

While the ferroelectric behavior of APBs has been investigated extensively [6, 7, 9], ferroelastic twin boundaries remain less well understood. This thesis addresses this problem by analyzing the atomistic structure and polarization of ferroelastic twin DWs in SrTiO₃.

1.1. Lattice dynamics

The collective motion of atoms in a crystal can be purely described by the theory of harmonic lattice vibrations as long as the displacements

$$\mathbf{u}_{\kappa l}^{\pm}(\mathbf{q}, j) = \frac{1}{\sqrt{Nm_{\kappa}}} \mathbf{e}_{\kappa}(\mathbf{q}, j) e^{i(\mathbf{q}\mathbf{r}_l \pm \omega_{\mathbf{q}, j}t)} \quad (1.1)$$

relative to the equilibrium structure are small enough for the harmonic approximation to be applicable. The displacements are described in form of plane waves, where the superscript $\pm$ distinguishes two similar waves propagating in opposite directions. The indices $\kappa = 1, \dots, N$ and $l = 1, \dots, N_z$ denote the κ^{th} atom in the l^{th} primitive unit cell (UC) respectively, while the mass of each atom is given by m_{κ} . For each wave vector $\mathbf{q}$ there are $3N$ (one longitudinal and two transverse) vibrational modes enumerated by j , which differ by their polarization vector $\mathbf{e}_{\kappa}(\mathbf{q}, j)$ as well as their frequency $\omega_{\mathbf{q}, j}$. If the wave vectors are limited to the first Brillouin zone, the lattice vibrations can be represented as superpositions of $3NN_z$ normal modes, one for each systematic degree of freedom,

$$\mathbf{u}_{\kappa, l} = \sum_{\mathbf{q}} \sum_j A_{\mathbf{q}, j} \mathbf{u}_{\kappa l}^{+}(\mathbf{q}, j) + A'_{\mathbf{q}, j} \mathbf{u}_{\kappa l}^{-}(\mathbf{q}, j), \quad (1.2)$$

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where the relation $A'_{\mathbf{q},j} = A_{-\mathbf{q},j}^*$ holds. Factorizing out $e^{i\mathbf{q}\mathbf{r}_l}$ and writing the displacements as $3N$ -dimensional vectors in terms of normal coordinates $Q_{\mathbf{q},j} = A_{\mathbf{q},j}e^{-i\omega_{\mathbf{q},j}t} + A'_{\mathbf{q},j}e^{i\omega_{\mathbf{q},j}t}$ results in

$$\mathbf{u}_l = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} \sum_j Q_{\mathbf{q},j} \mathbf{M} \mathbf{e}(\mathbf{q}, j) e^{i\mathbf{q}\mathbf{r}_l}. \quad (1.3)$$

Here $\mathbf{M}$ is a diagonal matrix containing the masses of all atoms. The normal coordinates encode the amplitude of a specific mode and its weight. Using Equation [1.3](#) the Hamiltonian of the system can be written in terms of uncoupled harmonic oscillators.

$$H = \frac{N_z}{2N} \sum_{\mathbf{q}} \sum_j \left(\frac{dQ_{\mathbf{q},j}}{dt} \right)^2 + \omega_{\mathbf{q},j}^2 Q_{\mathbf{q},j}^2 \quad (1.4)$$

The normal mode's polarizations and frequencies are given by the eigenvectors and the root of the eigenvalues $\omega_{\mathbf{q},j}^2$ of the dynamic matrix

$$\mathbf{D}_{\kappa\kappa'}(\mathbf{q}) = \frac{1}{\sqrt{m_{\kappa}m_{\kappa'}}} \mathbf{F}_{\kappa\kappa'}(\mathbf{q}), \quad (1.5)$$

respectively. The Fourier-transformed force constant matrix $\mathbf{F}_{\kappa\kappa'}(\mathbf{q})$ is given by

$$\mathbf{F}_{\kappa\kappa'}(\mathbf{q}) = \sum_{l'} \mathbf{V}(\kappa l, \kappa' l') e^{i\mathbf{q}(\mathbf{r}_{l'} - \mathbf{r}_l)} \quad (1.6)$$

with the force constant matrix elements

$$V_{\alpha\beta}(\kappa l, \kappa' l') = \left. \frac{\partial^2 V}{\partial u_{\kappa l}^{\alpha} \partial u_{\kappa' l'}^{\beta}} \right|_o \quad (1.7)$$

defined as the second derivative of the potential energy with respect to the displacements of atoms α and β from the equilibrium positions.

In the quantum mechanical extension these harmonic oscillators can be viewed as quasiparticles, so called phonons, which correspond to the quantum of vibrational energy ($\hbar\omega_{\mathbf{q},j}$) needed to increase the vibrational energy to the next energy level. The allowed energy levels of a mode $(\mathbf{q}, j)$ in the quantum mechanical description are thus given by

$$E_{\mathbf{q},j}^{(n)} = \left(n + \frac{1}{2} \right) \hbar\omega_{\mathbf{q},j}. \quad (1.8)$$

The frequency of the normal modes are dependent on the wave vector. This behavior is shown in the STO phonon dispersion relations in Figure [1.1](#). There are always three phonon branches with $\omega_{\mathbf{q}} \rightarrow 0$ as $\Gamma \rightarrow 0$ which exhibit a linear dispersion relation in the vicinity of the Γ -point. These phonon branches are called "acoustic" branches. The remaining $3N - 3$ branches are called "optical" branches and have a finite frequency at the Γ -point. Furthermore the eigenvalues for some branches are degenerate. This can be seen as an overlap or crossing of phonon branches due to the dispersion relation being a projection of the $\mathbf{q} - \omega$ space along specific high symmetry points in the Brillouin zone [\[12, 13\]](#).

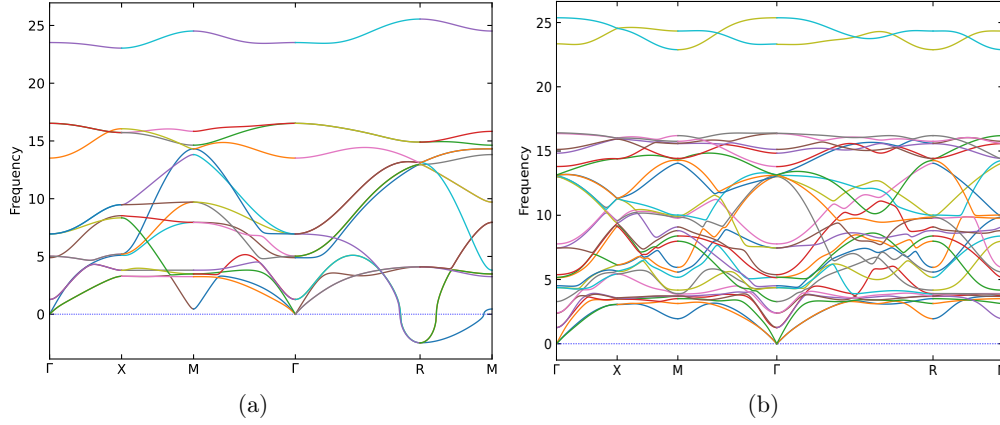


Figure 1.1.: Phonon dispersion relation for the (a) high symmetry cubic and (b) lower symmetry tetragonal phase calculated at 40kbar to suppress the ferroelectric mode at the Γ -point (see Section 2.2.1).

1.2. Phase transitions in SrTiO₃

Not all phonon branches in the calculated dispersion relation are stable. Some modes show imaginary frequencies where the dynamic matrix has negative eigenvalues resulting in imaginary frequencies which are conventionally drawn along the negative axis. They occur if the dispersion relation is calculated in an unstable crystal state.

These modes correspond to dynamical instabilities in the crystal [14]. The appearance of imaginary phonon frequencies leads to a structural reorganization of the crystal lattice. In cubic STO at a lattice constant of $a = 3.85857\text{\AA}$ (relaxed with 12x12x12 k-points mesh and PBEsol) the instabilities occur at the Γ and R point in the Brillouin zone. Due to the presence of Equation 1.7 in the dynamical matrix, the eigenvalues are proportional to the curvature of the potential energy surface of the current configuration. Negative eigenvalues correspond to a negative curvature indicating a local maximum of the energy.

When cooling the system from the high temperature regime $T > 105\text{K}$ the triply degenerate R-modes soften towards 0 and freeze in (condense) at a finite value at $T = 105\text{K}$ inducing a structural phase transition from the high symmetry cubic ($\text{Pm}\bar{3}\text{m}$) to the lower symmetric tetragonal (I4/mcm) phase as depicted in Figure 1.1

Breaking of the symmetry changes the Brillouin zone and the cubic R-mode gets folded into a tetragonal Γ -mode. There this triply degenerate modes split into an A_{1g} -mode driving the octahedra rotations along the c-direction and a doubly degenerate E_g -mode corresponding to the tilts of the oxygen octahedra along the a_1 - and a_2 -directions. The difference between the high temperature cubic and low temperature tetragonal unit cell in STO can be seen in Figure 1.2. Crossing below the critical temperature forces the system into one of the minima thus lowering the energy further. The order parameter describing the phase transition driven by the R-modes is the three dimensional pseudo vector $\phi = (\phi_1, \phi_2, \phi_3)$ denoting the tilt angles of the oxygen octahedra along the $[100]$, $[010]$ and $[001]$ directions respectively. Given that the R-point lies at the zone

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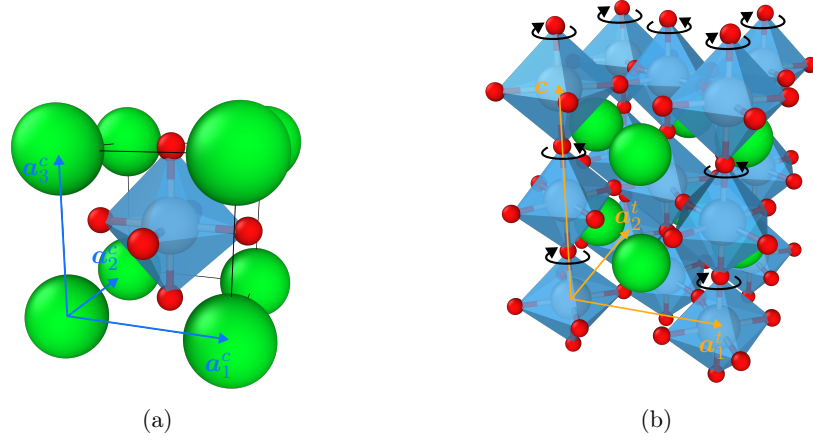


Figure 1.2.: Unit cells for the (a) high symmetry cubic and (b) lower symmetry tetragonal phase.

boundary of the Brillouin zone, rotations of two neighboring octahedra alternate and cancel out any local dipole moment created by the displacement of the atoms, hence, the phase transition is called antiferrodistortive. A schematic representation of the effective potential for an antiferrodistortive mode in the cubic reference frame is visualized in Figure 1.3 with Q being the displacement amplitude and $V(Q)$ the potential energy for that displacement. For high temperatures the phonon mode is finite, thus the potential exhibits

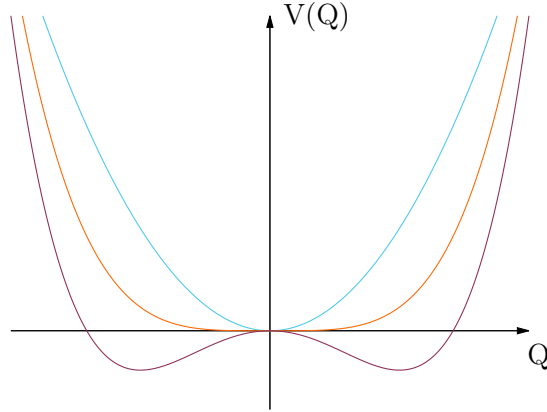


Figure 1.3.: Single particle potential energy for the R-mode instability. The structural phase transition corresponds to the quadratic potential (blue) at $T > T_c$ transforming first into a flat bottomed quartic potential (orange) at $T = T_c$ and finally changing to an even double well potential (purple) for $T < T_c$.

a quadratic form. At the critical temperature, the mode becomes zero and as a result the potential flattens to then transition into a double well potential as the mode becomes

1.3. Domain formation and domain walls in SrTiO_3

imaginary in the lower temperature regime pointing to a negative curvature. The two wells correspond either to a right or left rotation. When disregarding thermal fluctuations the atoms are sitting at their respective high symmetry positions corresponding to the top of the barrier. This conformation is highly unstable and the atoms fall into one well, collectively leading to a right or left rotation of the oxygen octahedra [15, 16].

The second imaginary mode in STO belongs to a polar optical phonon at the Γ -point split into an A_{2u} mode along the c -direction and a doubly degenerate E_u mode along the a_1 - and a_2 -direction. Yet the instability of this mode is an artefact from using the Born-Oppenheimer (BO) approximation in density functional theory (see section 2.2). In STO, density functional theory (DFT) calculations predict a ferroelectric (FE) phase transition below 40K [17] creating a dipole moment due to the displacement of the Ti ions relative to the O ions within the UC, leading to a macroscopic spontaneous polarization which is switchable under application of an external electric field. In reality, however, STO remains paraelectric, albeit on the verge of being ferroelectric. The condensation of the FE-mode is only suppressed by anharmonic nuclear quantum fluctuations (NQF) which are not accounted for in DFT [18]. In the harmonic approximation the potential corresponding to the FE instability presumably takes the shape of a shallow double well, making it possible to overcome the barrier by quantum tunneling resulting in a net zero polarization on average. Including anharmonic effects and temperature in the calculation of the phonon dispersion, the Γ -mode is stable in both the cubic and tetragonal phase matching with experimental observations and the corresponding potential takes a quadratic form. The stabilization of the FE mode is very sensitive to disturbances such as uniaxial strain [19] or switching to a different oxygen isotope [20] resulting in a material remaining on the verge of becoming ferroelectric. Consequently, STO is a quantum paraelectric/incipient ferroelectric [15, 21].

1.3. Domain formation and domain walls in SrTiO_3

As the soft mode condenses, the symmetry breaks locally and a potential energy minimum is chosen stochastically leading to the formation of multiple uncorrelated domains in the crystal. For the antiferrodistortive phase transition this choice corresponds to an initial right or left rotation of the oxygen octahedra. The alternating tilt pattern propagates throughout the lattice creating domains with opposite rotations or orientation.

When neighboring domains meet, the tilt pattern is forced to change from one conformation to the one of the other domain at the boundary. This change requires a reorientation of the atoms in proximity of the domain boundary which can spread over a few lattice constants. If the rotation axis of two domain pairs (DP) align and only differ in their translational state an antiphase boundary (APB) forms between the DP. APBs can be classified into two groups, easy and hard APBs, which are depicted in Figure 1.4 (a). Easy APBs do not force the TiO_6 octahedra to distort in order to match the rotation pattern in the neighboring UC. These DBs are atomistically sharp and perpendicular to the tetragonal axis. Hard APBs, however, lie parallel to the tetragonal axis and require the oxygen octahedra to distort, otherwise the oxygen positions would not match in

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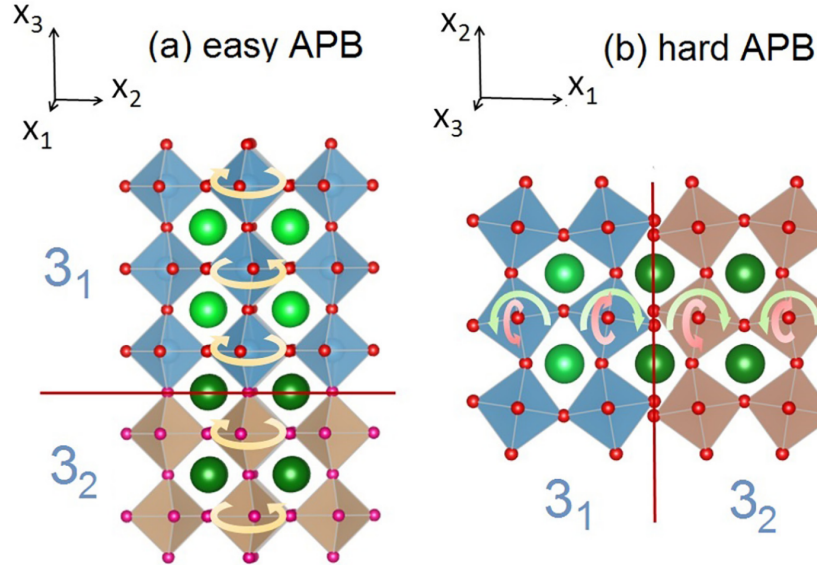


Figure 1.4.: Easy (a) and hard (b) antiphase boundaries. [9]

the next UC. To avoid the energetically costly distortions of the TiO_6 octahedra these types of APBs extend spatially to allow for a fluid transition between the rotation states of the domain pairs. On the other hand, domains with different orientations lead to the formation of head-tail (HT), or easy, twinned domain boundaries (TB), whereas domains that differ both in orientation and transition form head-head (HH), or hard, twin boundaries. Figure 1.5 shows the structural differences between head-head and head-tail twinned domain boundaries [6].

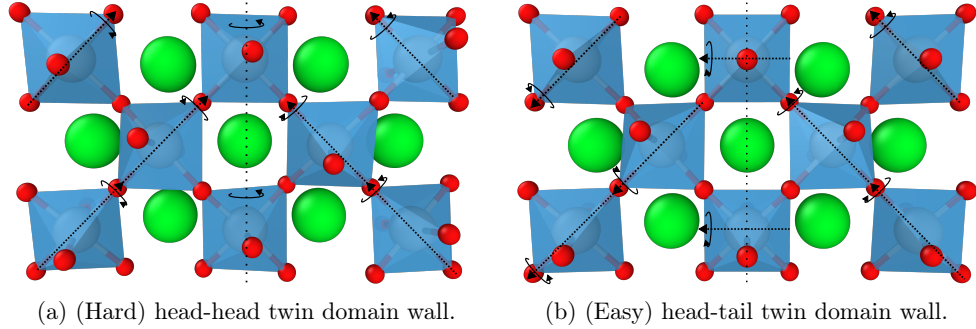


Figure 1.5.: Schematic of a head-head (left) and head-tail (right) twin domain boundary. The arrows indicate the displacement of the center oxygen atom and the dashed line represents the center of the twin boundary.

As discussed in Section 1.2 STO sits on the brink of a ferroelectric instability. Small disturbances in the lattice can lead to a ferroelectric state. Easy APBs do not exhibit any distortions or secondary tilts (Neel component in the OP) of the TiO_6 octahedra and

1.3. Domain formation and domain walls in SrTiO_3

thus remain nonpolar, but hard APBs do. The interplay of the Ising component of the OP vanishing within the DW center, the strain induced by the secondary TiO_6 tilts gives way for the ferroelectric mode to take over and a spontaneous polarization confined to the boundary emerges [7]. Twin walls in STO, on the other hand, show ferroelastic behavior. The two domains differ in their strain state resulting in a large strain gradient within the DW. As Schiaffino and Stengel [8] have demonstrated that the polarization in twinned domain boundaries results from a combination of flexoelectric (coupling between the shear strain gradient and polarization) and rotopolar (coupling between the polarization and the gradient of the TiO_6 amplitudes) couplings as well as a trilinear term considering the antiferroelectric Ti displacement inducing a macroscopic polarization that is local to the twin boundary.

2. Methods

Extracting the polarization behavior in twinned bulk STO is not straightforward and demands a multi-step protocol. First, symmetry adapted twin-wall supercells are constructed. These are used in an active learning loop combining accurate ab-initio calculations and the "query by committee" approach to train a MACE neural network potential (NNP) which will be used to run molecular dynamics (MD) simulations. Furthermore, the spatially resolved polarization and structural order parameter profiles across the supercell are calculated.

2.1. Supercell construction

Careful construction of symmetry-adapted twin-wall supercells is crucial to provide an optimized initial cell that minimizes the amount of structural relaxation steps (see Section 2.2.1). These relaxed structures are further used to bootstrap the active learning loop and as initial configurations in MD simulations.

First a bulk STO lattice is created with the relaxed lattice constant at 50 kbar ($a = 3.85857\text{\AA}$) by translating copies of the unit cell consisting of one Sr, one Ti and three O atoms along the lattice vectors of a tetragonal Bravais lattice. Then the lattice is rotated by $\alpha = \pi/4$ and shifted so that the diagonal and the z-axis are aligned. Everything on the lefthand side of the diagonal separation line along $\mathbf{d} = \hat{\mathbf{a}}_1 + \hat{\mathbf{a}}_3$, starting from the bottom left Sr atom, is removed. This modified bulk lattice is further mirrored along the z-axis and duplicated atoms are removed. Furthermore the lower part of the lattice is cut and shifted to create a tetragonal supercell obeying periodic boundary conditions (PBC) along all three axis resulting in a cell with one domain wall in the center and at the boundary of the elongated axis.

To initialize the OP profile, the rotation angles of the O octahedra are separated into two components, ϕ_3 and ϕ_1 , and follow the profile illustrated in Figure 2.1 for HT-type DWs. For HH-type DWs the profiles of the components ϕ_3 and ϕ_1 are switched. The amplitudes for rotations around the local z-axis of the unit cell are given by

$$\phi_3(x) = \begin{cases} \alpha \tanh\left(\frac{x}{\xi}\right) & \text{if } x \leq \frac{a'_1}{4} \wedge x \geq -\frac{a'_1}{4} \\ \alpha \tanh\left(\frac{x + \frac{a'_1}{2}}{\xi}\right) & \text{if } x < -\frac{a'_1}{4} \\ \alpha \tanh\left(\frac{x - \frac{a'_1}{2}}{\xi}\right) & \text{if } x > \frac{a'_1}{4} \end{cases} \quad (2.1)$$

2. Methods

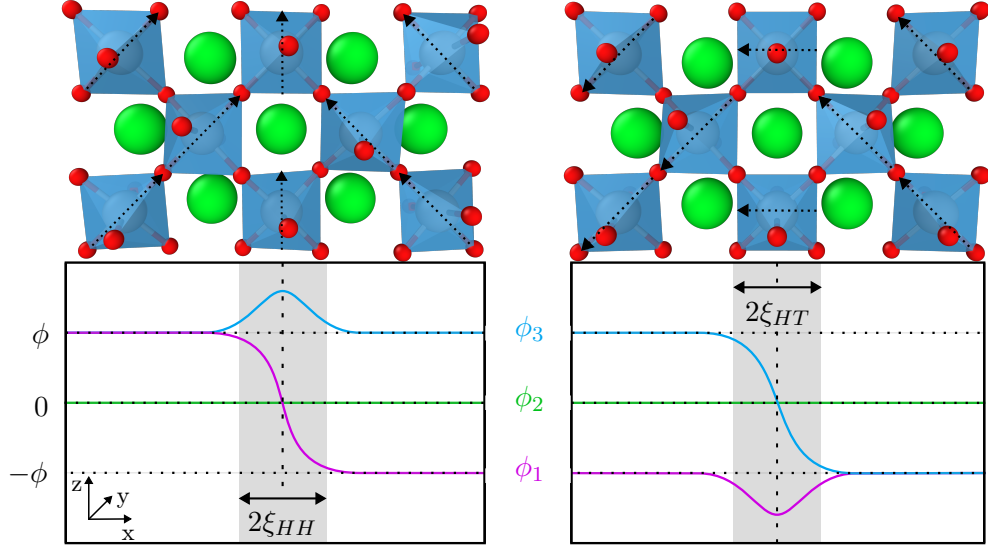


Figure 2.1.: Head-head (left) and tail-tail (right) twin domain wall in SrTiO_3 . The black arrows in the unit cells represent the local z -axis with the oxygen octahedra rotate around. In the bulk sections those correspond to the tetragonal c -axis which then rotates through the domain wall to match the orientation of the other domain. Below is a schematic representation of the OP profile. The OP components ϕ_1, ϕ_2 and ϕ_3 are the rotation angles around the cartesian basis vectors $\hat{e}_x, \hat{e}_y, \hat{e}_z$ respectively.

and for rotations around the local x -axis the positional angles are defined as

$$\phi_1(x) = \begin{cases} 3\sqrt{2} + a \exp\left(-\frac{1}{2} \left(\frac{x}{\xi}\right)^2\right) & \text{if } x \leq \frac{a'_1}{4} \wedge x \geq \frac{a'_1}{4} \\ 3\sqrt{2} + a \exp\left(-\frac{1}{2} \left(\frac{x + \frac{a'_1}{4}}{\xi}\right)^2\right) & \text{if } x < -\frac{a'_1}{4} \\ 3\sqrt{2} + a \exp\left(-\frac{1}{2} \left(\frac{x - \frac{a'_1}{4}}{\xi}\right)^2\right) & \text{if } x > \frac{a'_1}{4} \end{cases}. \quad (2.2)$$

Here, $\xi = 7.5\text{nm}$ represents half of the DW thickness as predicted in [8], a'_1 is the length of the supercell along the x -axis. The parameters are chosen so that the O octahedra rotations follow the expected OP profile respecting PBCs and the two DWs in the supercell. The new point $\mathbf{x}'$ after rotating $\mathbf{x}$ is given by Rodrigues' rotation formula

$$\mathbf{x}' = \cos(\psi)\mathbf{x} + (1 - \cos(\psi))(\hat{\mathbf{k}} \cdot \mathbf{x})\hat{\mathbf{k}} + \sin(\psi)(\hat{\mathbf{k}} \times \mathbf{x}), \quad (2.3)$$

where $\hat{\mathbf{k}}$ is the unit vector describing the rotation axis. Each UC is shifted so that the Ti atom lies in the origin. Then the rotations of the O atoms is carried out. As rotations are not commutative, calculating the new position of the O atom is twofold. First the O

atom is rotated around the local x-axis and then the local z-axis. Next the new position is again calculated but in the opposite order. To obtain the final position, the two positions are averaged. Furthermore, the sign of the angle is alternated in every unit cell to model the antiferrodistortive pattern of the rotations.

For the training of the system a small supercell consisting of 480 atoms was used with dimensions $32.6905\text{\AA} \times 15.3900\text{\AA} \times 10.9347\text{\AA}$. For the production runs a $276.125\text{\AA} \times 15.62\text{\AA} \times 11.045\text{\AA}$ supercell consisting of 4000 atoms was needed to ensure a strain free bulk region between the two DWs.

2.2. Density functional theory

The quality of a machine learned NNP is fundamentally limited by the amount and quality of the data it has been trained on. In order to achieve the highest accuracy possible, ab-initio calculations are of utmost importance. One of the most commonly used ab-initio methods is density functional theory (DFT).

DFT allows to calculate ground state properties of condensed matter systems, however, treating the entire system of electrons and nuclei quantum mechanically is impossible from a computational perspective. This limitation requires to work within the Born-Oppenheimer approximation. Still treating solely the electrons quantum mechanically requires more computational resources than we can currently afford, thus, calling for further simplifications of the treatment [22]. It is possible to show [23] that there is a functional $G[n(\mathbf{r})] = T_s[n(\mathbf{r})] + E_{XC}[n(\mathbf{r})]$, consisting of a kinetic energy T_s for a non interacting system and the exchange-correlation energy E_{XC} for an interacting system, for which the energy functional

$$E_v[n(\mathbf{r})] = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + G[n(\mathbf{r})] \quad (2.4)$$

has the ground state energy for the potential $v(\mathbf{r})$ as its minimum value. This makes it possible to calculate the energy as a functional of the electron density $n(\mathbf{r})$ and rendering the calculation of the N-electron wavefunction obsolete. Based on this, Kohn and Sham [24] proposed to replace the 3N dimensional many body problem with a set of N three dimensional, independent, self consistent single particle equations, known as the Kohn-Sham equations. These equations are given by

$$\left\{ -\frac{1}{2}\nabla^2 + [\phi(\mathbf{r}) + \mu_{XC}(n(\mathbf{r}))] \right\} \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (2.5)$$

with the exchange-correlation contribution to the chemical potential

$$\mu_{XC}(n(\mathbf{r})) = \frac{d(n\epsilon_{XC}(n(\mathbf{r})))}{dn}, \quad (2.6)$$

where $\epsilon_{XC}(n(\mathbf{r}))$ is the exchange-correlation energy for one electron in a uniform N-electron gas with the density

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2. \quad (2.7)$$

2. Methods

One further approximation used in DFT is the estimation of the exchange-correlation potential as the exact functional will always remain fundamentally unknown. The simplest form is the local density approximation (LDA), which was introduced by Kohn and Sham [24] and assumes that $E_{XC}[n(\mathbf{r})]$ can be written in the specific form

$$E_{XC}[n(\mathbf{r})] = \int n(\mathbf{r})\epsilon_{XC}(n(\mathbf{r}))d\mathbf{r}, \quad (2.8)$$

where $\epsilon_{XC}(n(\mathbf{r}))$ is the exchange-correlation energy of a homogeneous electron gas at density n . In other words, one approximates the exchange-correlation energy by locally assuming a homogeneous electron gas and thus disregarding any gradient and other possibly nonlocal corrections.

In the pursuit of higher accuracy better approximations for the exchange-correlation energy functional are needed. LDA potentials were extended to the generalized gradient approximation (GGA) pseudo-potentials [25] by introducing a local density gradient term in the exchange-correlation energy functional which eliminates the overestimation of dissociation energies [26] when using the LDA potential for DFT calculations.

In this work the potential used for carrying out the energy and force evaluations of the configurations is PBEsol [27], which is a modified version of the PBE-GGA potential. Standard PBE is prone to underestimate equilibrium lattice constants, an error which PBEsol aims to correct. Even small deviations can strongly affect properties, such as phonon frequencies and crucial to this work, ferroelectricity, as well as others strongly.

Besides just evaluating the energy and atomic forces of a configuration, DFT can further be used to determine the ground state configuration by executing a structural relaxation algorithm such as the ones described in [28].

2.2.1. Electronic minimization and structural relaxation of the supercell

Both for single point energy minimization and structural relaxation calculations, the Vienna ab-initio simulation package (VASP) [28] is used. To ensure that the per atom forces in the initial configurations for the MD run are reasonable, a structural relaxation is performed. The protocol is as follows: First the configuration generated as described in [2.1] was relaxed with a conjugate gradient (CG) algorithm for updating the atom positions after each electronic minimization routine. The electronic self consistency cycle was done with the "all bands simultaneous update" algorithm to optimize the atomic orbitals. Once the total energy of the system started to plateau, the CG algorithm was abandoned in favor of the RMM-DIIS-scheme to get closer to the system's ground state. The structural optimization was performed at a hydrostatic pressure of 50kbar to ensure the suppression of the bulk ferroelectric soft mode, which would otherwise expose the bulk ferroelectricity of the Born-Oppenheimer approximation [7].

The INCAR and KPOINTS files used for the structural relaxation as well as the energy and force evaluation can be found in the appendix [A.2].

2.3. MACE potentials

DFT provides a first-principle approach to investigating the physical phenomena in materials with substantial accuracy. Even with all the approximations made, this level of precision, however, bears a significant computational cost. To extend beyond the computational limits of DFT, machine learning can be leveraged to predict the forces and energies of a given configuration. For this reason an on-the-fly machine learned force field utilizing kernel based regression, which is coupled with a Bayesian error estimation to be used in an active learning loop (see Section 2.5), was implemented in VASP [29]. These force fields allow for efficient training during an ab-initio molecular dynamics simulation but sacrifice some accuracy. With the emergence of message passing neural networks (MPNNs) [30] and the recent release of MACE potentials [31, 32] near DFT-like accuracy can be achieved [33].

MACE is a representative of equivariant MPNNs. In general, MPNNs are graph neural networks [34]. This entails that the atomic environment is internally modeled by a labeled graph and mapped to a target space. The resulting space can be either a graph- or a vector space. The nodes on this graph correspond to atoms in the system and share edges with each other if the corresponding atoms are within a specified cutoff radius r_{cut} . Furthermore each node is represented by a state

$$\sigma_i^{(t)} = \left(\mathbf{r}_i, z_i, \mathbf{h}_i^{(t)} \right), \quad (2.9)$$

carrying information about the atom, such as the position $\mathbf{r}_i \in \mathbb{R}^3$, the chemical element z_i and the learnable features $\mathbf{h}_i^{(t)}$. The label t indicates the message passing layer in which the node is embedded. One forward propagation consists of multiple message construction, update and readout steps.

MACE exploits higher order messages by using the atomic cluster expansion (ACE) formalism [35, 36] and applying a hierarchical body order expansion. This allows to have accurate models whilst only using two message passing layers. The architecture is described in [32] in detail. Each message passing layer t of a MACE model begins with a multi-layer perceptron (MLP), learning a radial basis $R_{kl_1l_2l_3}^{(t)}$. This is done by first expanding interatomic distances r_{ji} with Bessel functions and applying a smooth cutoff at r_{cut} then feeding this through the MLP. The interatomic unit vector $\hat{\mathbf{r}}_{ji}$ is then encoded by evaluating spherical harmonics $Y_{l_1}^{m_1}$ and further projected onto the learned radial basis. Furthermore, the previous node features are included via a learnable weights as well, forming permutation invariant 2-body features (reference atom and one neighbor). Formally this can be written as

$$A_{i,kl_3m_3}^{(t)} = \sum_{l_1m_1,l_2m_2} C_{l_1m_1,l_2m_2}^{l_3m_3} \sum_{j \in N(i)} R_{kl_1l_2l_3}(r_{ji}) Y_{l_1}^{m_1}(\hat{\mathbf{r}}_{ji}) \sum_{\tilde{k}} W_{k\tilde{k}l_2}^{(t)} h_{j,\tilde{k}l_2m_2}^{(t)}. \quad (2.10)$$

The standard Clebsch-Gordan coefficients $C_{l_1m_1,l_2m_2}^{l_3m_3}$ ensure the correct equivariance of the $A_{i,kl_3m_3}^{(t)}$ -features. From these $A_i^{(t)}$ -features higher order messages are constructed by

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multiplying the 2-body features with each other:

$$\mathbf{B}_{i,\eta\nu LM}^{(t)} = \sum_{\mathbf{lm}} C_{\eta\nu, \mathbf{lm}}^{LM} \prod_{\xi=1}^{\nu} \sum_{\tilde{k}} w_{k\tilde{k}l\xi}^{(t)} A_{i,\tilde{k}l\xi m\xi}^{(t)} \quad (2.11)$$

with $\mathbf{lm} = \{l_1 m_1, \dots, l_\nu m_\nu\}$ and the generalized Clebsch-Gordan coefficients $C_{\eta\nu, \mathbf{lm}}^{LM}$. The index ν enumerates all possible couplings of $l_1, \dots, l_\nu$ that correspond to the equivariance specified by the parameter L . The correlation order ν gives the maximum number of consecutive multiplications and amounts to one less than the body order of the final message

$$m_{i,kLM}^{(t)} = \sum_{\dot{\nu}} \sum_{\eta\dot{\nu}} W_{z_i k L, \eta\dot{\nu}}^{(t)} \mathbf{B}_{i,\eta\dot{\nu} k LM}^{(t)}, \quad (2.12)$$

where the higher order features are weighted with a learnable weight matrix $W_{z_i k L, \eta\dot{\nu}}^{(t)}$. For the next message passing layer the node features are calculated using a learnable update function U_t^{kL}

$$\begin{aligned} h_{i,kLM}^{(t+1)} &= U_t^{kL} \left(\sigma_i^{(t)}, \mathbf{m}_i^{(t)} \right) \\ &= \sum_{\tilde{k}} W_{kL, \tilde{k}}^{(t)} m_{i,\tilde{k}LM} + \sum_{\tilde{k}} W_{z_i, kL, \tilde{k}}^{(t)} h_{i,\tilde{k}LM}^{(t)}. \end{aligned} \quad (2.13)$$

After each message passing layer the invariant part of the node features, which the site energy in each layer is calculated from, is then read out using readout functions. These energy contributions are then summed up to form the system energy

$$E_i = E_i^{(0)} + \dots + E_i^{(T)}. \quad (2.14)$$

Between layers, the site energies are calculated by using learnable weights $W_{readout}^{(t)}$ and linear readout functions. In the final layer T , however, the energy is read out using a one-layer MLP.

$$E_i^{(t)} = \begin{cases} \sum_{\tilde{k}} W_{readout}^{(t)} h_{i,\tilde{k}00}^{(t)} & \text{if } t < T \\ \text{MLP}_{\tilde{k}} \left(\left\{ h_{i,\tilde{k}00}^{(t)} \right\}_{\tilde{k}} \right) & \text{if } t = T \end{cases} \quad (2.15)$$

In order to utilize the full power of MACE models the Mace-MPA-0 foundation model [37] was used. This model showed better performance for higher pressure regimes, which is crucial for the simulations in this thesis. The refining parameters for the model are attached in the appendix A.3.

2.4. Molecular dynamics simulations

Simulating the dynamics of atomistic structures also requires accurate energies and forces. Before the adoption of NNPs, the energies and forces were derived from empirical interatomic potentials or with DFT (ab-initio molecular dynamics). However, empirical

potentials lack the sufficient accuracy whereas DFT calculations are too expensive to evaluate for generating statistically relevant trajectories from molecular dynamics (MD) simulations. By employing NNPs, their benefits can be leveraged to speed up the computationally most expensive part of MD simulations while still maintaining highly accurate forces.

In molecular dynamics the equations of motion (EOM) are integrated. Most commonly, the velocity Verlet algorithm [38]

$$\begin{aligned} \mathbf{r}(t + \Delta t) &= \mathbf{r}(t) + \mathbf{v}(t)\Delta t + \frac{\mathbf{F}(t)}{2m}\Delta t^2 + O(\Delta t^4) \\ \mathbf{v}(t + \Delta t) &= \mathbf{v}(t) + \frac{\mathbf{F}(t) + \mathbf{F}(t + \Delta t)}{2m}\Delta t + O(\Delta t^3) \end{aligned} \quad (2.16)$$

is used, ensuring time reversible and phase space volume conserving trajectories. Calculating the observable averages from a sufficiently long trajectory purely obtained from Eq. 2.16 corresponds to the ensemble averages from the microcanonical ensemble. In order to simulate other ensembles additional modifications to the integrator are necessary, such as thermostats, barostats or a combination of them.

For the production run the supercell box and the atomic positions were first structurally relaxed by minimizing the interatomic forces and while accounting for an external pressure. With these initial configurations all trajectories were obtained with MD simulations conducted in the Isothermal-Isobaric (NpT) ensemble with LAMMPS [39] as the MD engine. In the NpT ensemble, the particle number remains fixed and, while in equilibrium, the pressure as well as the temperature fluctuate around their respective equilibrium values. This requires to use both thermostats and barostats. To ensure proper mapping between LAMMPS dump files and VASP POSCAR files, the numeric atom types have been associated with an atom type label. This framework is explained in [40].

There are various different approaches to controlling the temperature in MD simulations, ranging from simple stochastic schemes, like the Andersen thermostat [41] to more complex methods, such as the Nosé-Hoover (NH) thermostats [42] which instead change the ensemble being sampled. Only weakly anharmonic or stiff systems don't produce ergodic dynamics using the NH thermostats. To bypass this flaw, NH thermostats can be chained together to form NH chains [43] (NHCs) resulting in ergodic dynamics. In LAMMPS the EOMs derived by Shinoda et. al. [44] are integrated. These incorporate a NHC coupled to the particle degrees of freedom acting as a thermostat by changing their velocity based on the thermostating mechanism. The barostat is implemented in the EOM by coupling a NHC to the degrees of freedom of the cell matrix, effectively scaling the cell, hence, simulating an external hydrostatic pressure. The integrator used to propagate the system forward in time is derived by Tuckerman et. al. [45].

2.5. Query by committee

A good first measure for the performance of a machine learned model is to evaluate it on unseen data. The predictions on the test set are then compared with the labels in the

2. Methods

test set. The downside of this is that it does not give any intuition about the behavior of the model when it encounters data which is not covered by the distribution spanned by the training set. In the context of MD simulations this means that a good score on the test set does not guarantee good phase space coverage. To overcome this limitation a "query by committee" approach in conjunction with active learning [46] can be adopted.

This requires training multiple models with different random seeds on the same training set, running a MD simulation and evaluating trajectory with all models. Using this data a committee disagreement measure across the models for a given trajectory can be calculated. Given that the models were trained with the same dataset, they will predict the same energies and forces (up to an error) for configurations within the domain of the training set. If they encounter configurations that differ strongly from the familiar ones, the models are forced to extrapolate. As they are all trained with a different seed, they will predict different energies and forces. This disagreement is then calculated and configurations which the model struggles to predict correctly are identified and added to the training set. These configurations are used to refine the committee, effectively increasing the stability of the final model.

By unifying all of the methods discussed, a protocol to train the MACE potential can be derived. The protocol is illustrated in Figure 2.2. The committee is composed of five MACE foundation models (Mace-MPA-0), which are initially refined with different random seeds (62, 389, 725, 6, 69) on 10 bulk configurations of the high temperature cubic and 40 configurations of the low temperature tetragonal phase randomly picked from the dataset of the force field from previous work [7]. To provide the models with some information about STO twin walls, the initial training set was expanded with additional 10 configurations obtained from the structural relaxation trajectory of the starting structure for the MD simulations in the active learning loop. These configurations were removed for the subsequent generations as to not blur the information from the configurations with the highest disagreement. In each iteration of the committee, one model is used to run an MD simulation in the NpT ensemble. The settings for the thermostat and barostat depend on the committee generation. After the trajectory of the current MD run has been obtained, the energies and forces are predicted on each frame. First, the root mean squared force deviation (RMSFD) was chosen as the committee disagreement measure. This is calculated by first obtaining the average force on each atom per frame across all models

$$\langle \mathbf{F}_i \rangle^{(t)} = \frac{1}{M} \sum_{m=1}^M \mathbf{F}_{i,m}^{(t)}, \quad (2.17)$$

where $i = 1, \dots, N$ represents the atoms in the frame, M is the number of models building the committee and $t = 0, \dots, T$ corresponds to the number of frames in the trajectory. This is further used to calculate the force variance of each atom from the committee mean

$$\left[\sigma_i^{(t)} \right]^2 = \frac{1}{M} \sum_{m=1}^M \left(\mathbf{F}_{i,m}^{(t)} - \langle \mathbf{F}_i \rangle^{(t)} \right)^2. \quad (2.18)$$

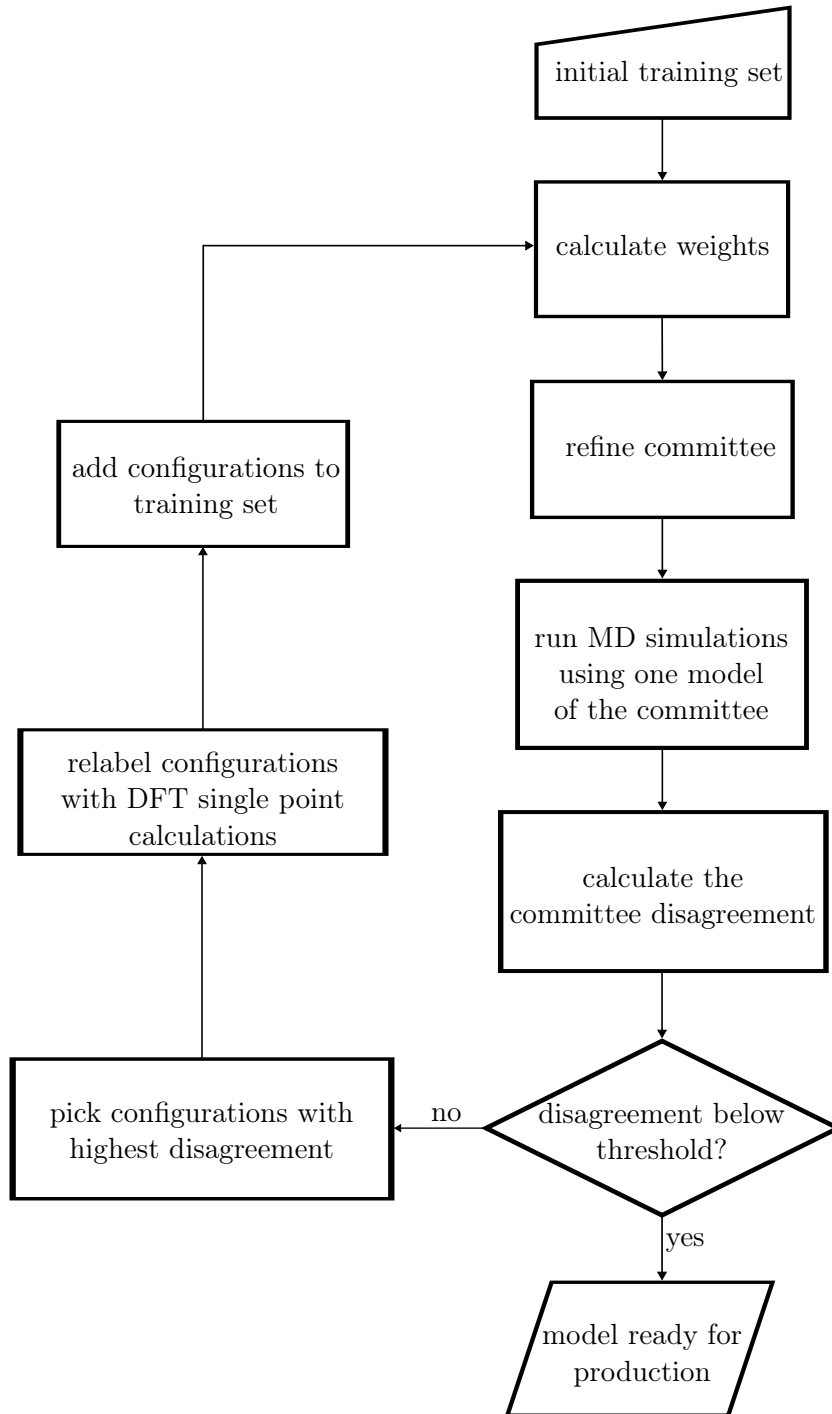


Figure 2.2.: Flowchart picturing the workflow of training a machine learned interatomic potential utilizing the "query by committee" approach in an active learning loop.

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Lastly, the RMSFD is obtained by taking the square root and summing over the variance

$$\text{RMSFD}^{(t)} = \sqrt{\frac{1}{N} \sum_{i=1}^N [\sigma_i^{(t)}]^2}. \quad (2.19)$$

This measure, however, is dependent on temperature. It is acceptable to use for constant temperature simulations, but when simulating temperature ramps, the RMSFD shows a drift following the temperature trend. This behavior makes it impossible to use a constant threshold to select the configurations, thus requiring a rescaling with the average magnitude of the mean net force across the committee. The disagreement measure then becomes the relative RMSFD

$$\text{RRMSFD}^{(t)} = \frac{\text{RMSFD}}{\frac{1}{N} \sum_{i=1}^N ||\langle \mathbf{F}_i \rangle^{(t)}||}. \quad (2.20)$$

In each generation the selected configurations are relabeled with an electronic minimization using DFT in order to get accurate energies and forces. The frames are picked by selecting all frames from the trajectory that result in the highest 10% of the RRMSFD and selecting the configurations corresponding to the 12 highest peaks, which are between 100fs apart. This strategy systematically adds the most informative configurations to the training set. Then the five models are refined on this growing training set. In each iteration the base foundational model is used instead of the refined one from the previous generation. Using the entire dataset and starting each generation from the same base model mitigates catastrophic forgetting, where previously learned information would be lost as it is lacking the training set. The weights for the classes (cubic bulk, tetragonal bulk, twinned DWs) are recalculated using the inverse class frequency method before refining the committee

$$w_i = \frac{\text{total number of configurations}}{\text{number of classes} \cdot \text{number of configurations in class } i}. \quad (2.21)$$

During the active learning all temperatures and pressures that will be used in the production runs should be covered. When the RRMSFD does not change substantially between generations, the active learning loop is terminated. With this approach, there is high confidence that the final model has good phase space coverage and can evaluate the configurations it could encounter during production MD runs accurately. For the case of twinned SrTiO₃ this means covering temperature ranges from 20K – 100K and pressure ranges from 20kbar – 120kbar. The temperature and pressure protocols for each generation are listed in Table [2.1](#). In the initial generation the 10 configurations with the highest committee disagreement were added to the training set. Another 2 configurations were added to the validation set. Then, in the first generation, 20 configurations (5 per pressure value) were picked for the training set and 4 (1 per pressure value) for the validation set. In the second generation 30 configurations (6 per pressure) were selected for the training set and 5 (1 per pressure value) structures for the validation set. Additionally, a total of 18 configurations were obtained for three different temperature and pressure combinations of HH-type twin-walls in the third generation. Over the course

Gen	Structure	T-ramp (K)	p (kbar)	T-p pairs (K, kbar)
0	480 atoms, HT	–	–	(90, 50)
1	480 atoms, HT	50–100	20, 80, 100, 120	–
2	480 atoms, HT	20–40	20, 40, 80, 100, 120	–
3	480 atoms, HH	–	–	(20, 20) (30, 50) (90, 80)

Table 2.1.: Initial Structure and parameters used to run the NpT simulation in each generation of the active learning loop. T-ramp indicates the initial and final temperature for each constant pressure p. T-p pairs correspond to discrete temperature and pressure pairs.

of all generations the model’s accuracy improves. Figure 2.3 shows the accuracy, measured by the root mean squared error (RMSE) of the forces on the testset, for each committee generation. The testset used was created by combining the configurations of twinned STO obtained during the test phase of the active learning protocol and consists of 42 frames, which were relabeled with DFT. Initially the model was retrained from the base foundation model in each generation for 20 epochs to minimize the chance of overfitting due to a very small dataset. The production model, however, was trained through 800 epochs without any signs of overfitting. Indeed it resulted in a fairly accurate NNP.

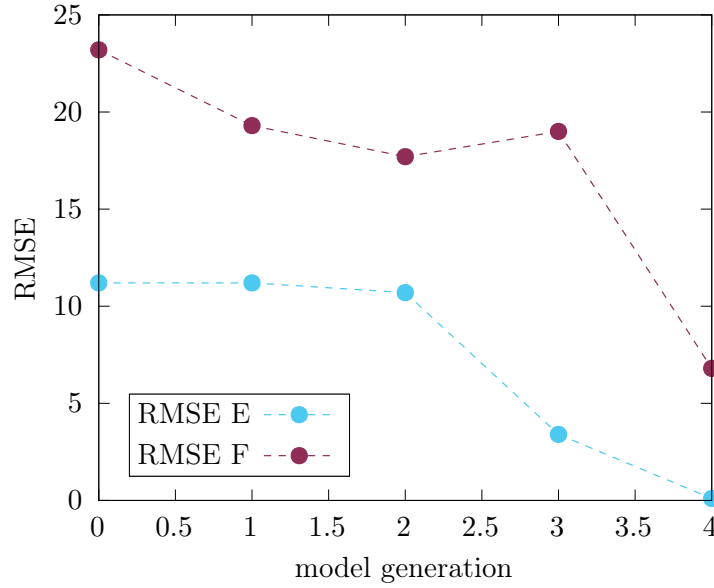


Figure 2.3.: Epochwise RMSE E and RMSE F for the MACE model trained. The fourth epoch marks the one used in the production runs.

2.6. Polarization analysis and post-processing

After obtaining the trajectories from the production MD simulations the profiles of the spontaneous polarization within the domain wall and of the primary OP across the domains have to be extracted. For each frame, first, a nearest-neighbor (NN) list is calculated for each Ti atom in the frame, then the eight closest Sr atoms are selected an enumerated deterministically according to their relative position w.r.t the center of mass (COM). These atoms form the pseudo cubic unit cells (PUC) in the strained supercell. In order to obtain the lattice constant of the non-distorted unit cell (UC) for this level of theory the primitive cubic UC was relaxed for each pressure simulated in the MD. These values are displayed in Table 2.2.

pressure (kbar)	cubic lattice constant (Å)
20	3.87711
40	3.86443
60	3.85193
80	3.84056
100	3.82897
120	3.81706

Table 2.2.: Cubic lattice constant at different pressures relaxed with PBEsol.

Next, the UC needs to be fitted into the PUC. This is done by a gradient descent algorithm. The loss function which is being minimized is the total squared distance of the Sr corners depending on the quaternion which rotates the UC into the same orientation as the PUC and is given by

$$\mathcal{L}(\hat{q}) = \sum_{i=1}^8 \|\mathbf{r}'_i\|^2 + \|\mathbf{r}_i\|^2 - 2(\mathbf{r}_i^T \mathbf{R}(\hat{q}) \mathbf{r}_i), \quad (2.22)$$

where $\mathbf{r}_i$ and $\mathbf{r}'_i$ correspond to the i^{th} atom sitting at the vertex of the UC and the PUC respectively. The update protocol of the quaternion is given by

$$\hat{q}^{(k+1)} = \hat{q}^{(k)} - [\eta g^{(k)} + \lambda \hat{q}^{(k)}] \quad (2.23)$$

Here $k = 1, \dots, N$ denotes the current iteration of the gradient descent algorithm, $g^{(k)}$ corresponds to the gradient of the loss function with the quaternion of iteration k and λ a Lagrange multiplier respecting the constraint of updating the unit quaternion on the unit sphere S^3 . The parameter η is a hyperparameter scaling the maximum step length in each iteration. The full derivation of the gradient descent algorithm can be found in the appendix A.1.

After performing this gradient descent a unit quaternion, which rotates the reference frame of the PUC into the global reference frame of the supercell, is obtained. The displacement vectors between the atoms in UC and PUC are calculated in the reference

frame of the PUC and can be expressed as a 15-dimensional vector

$$\mathbf{u}_{x,y,z}^c = \begin{pmatrix} \mathbf{u}_{\text{Sr}} \\ \mathbf{u}_{\text{Ti}} \\ \mathbf{u}_{O_y} \\ \mathbf{u}_{O_z} \\ \mathbf{u}_{O_x} \end{pmatrix}, \quad (2.24)$$

where x, y, z are the PUC indices along $\hat{\mathbf{e}}_x, \hat{\mathbf{e}}_y$ and $\hat{\mathbf{e}}_z$. With this the polarization and OP local to each PUC are obtained. In order to calculate the OP profile given by the pseudo vector $\boldsymbol{\phi} = (\phi_1, \phi_2, \phi_3)$, the mass weighed displacement vectors

$$\mathbf{u}_i^c = \sqrt{\frac{1}{\sum_j m_j}} \begin{pmatrix} \sqrt{m_{\text{Sr}}} \mathbf{u}_{\text{Sr}} \\ \sqrt{m_{\text{Ti}}} \mathbf{u}_{\text{Ti}} \\ \sqrt{m_{O_y}} \mathbf{u}_{O_y} \\ \sqrt{m_{O_z}} \mathbf{u}_{O_z} \\ \sqrt{m_{O_x}} \mathbf{u}_{O_x} \end{pmatrix} \quad (2.25)$$

are projected on to the phonon polarization vectors. These correspond to the displacements of the O in the octahedra when rotating it around the unit vectors $\hat{\mathbf{e}}'_x, \hat{\mathbf{e}}'_y, \hat{\mathbf{e}}'_z$ of the local basis respectively. The displacement patterns induced by the R_{25} mode are depicted in Figure 2.4. and the resulting phonon polarization vectors are given by

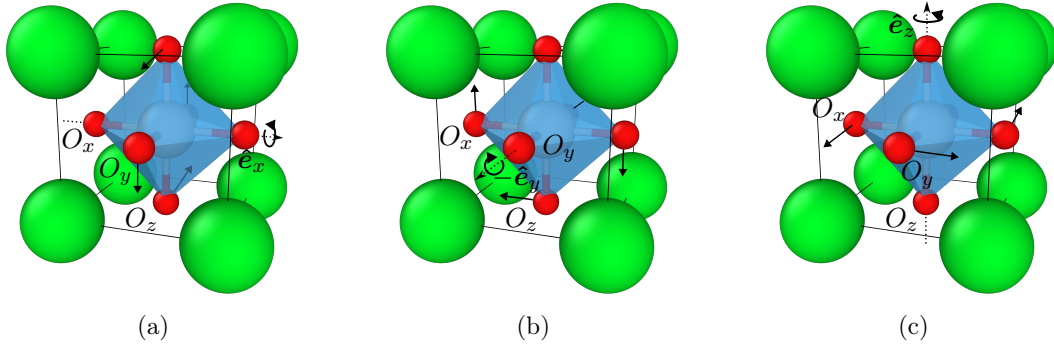


Figure 2.4.: Oxygen displacements when rotating the octahedron around the local basis vectors a) $\hat{\mathbf{e}}'_x$, b) $\hat{\mathbf{e}}'_y$, c) $\hat{\mathbf{e}}'_z$.

$$\Phi_1 = \begin{pmatrix} \vec{0} \\ \vec{0} \\ -\hat{\mathbf{e}}'_y \\ \hat{\mathbf{e}}'_z \\ \vec{0} \end{pmatrix} \quad \Phi_2 = \begin{pmatrix} \vec{0} \\ \vec{0} \\ \vec{0} \\ -\hat{\mathbf{e}}'_x \\ \hat{\mathbf{e}}'_z \end{pmatrix} \quad \Phi_3 = \begin{pmatrix} \vec{0} \\ \vec{0} \\ -\hat{\mathbf{e}}'_x \\ \vec{0} \\ -\hat{\mathbf{e}}'_y \end{pmatrix}. \quad (2.26)$$

This local OP however changes sign for each subsequent PUC. To flatten the OP in the domains and to visualize how it changes at the boundary, it has to be multiplied with

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by factors $-1^{(x+y+z)}$. One computationally expensive way to obtain these factors are is to sort the array of PUCs w.r.t to their position along the cartesian axis. A better alternative however is to traverse the already calculated nearest Ti neighbor list as a graph with a two coloring breadth first search (BFS) algorithm. This sets an initial "color" (± 1) and propagates the alternating behavior throughout the crystal.

To extract the spontaneous polarization the displacement vectors have to be multiplied with the Born effective charge (BEC) tensor Z_{κ}^* . In this work the BEC tensor of the cubic reference was used and was obtained by density functional perturbation theory (DFPT). The BEC tensor is defined as

$$Z_{\kappa,\alpha\beta}^* = \frac{\Omega}{e} \frac{\partial P_{\alpha}}{\partial u_{\kappa\beta}}, \quad (2.27)$$

where κ denotes the ions in the unit cell, Ω is the cell volume of the reference cell, e the elementary charge and u_{κ} are the displacements of the ions. From this follows

$$dP_{\alpha} = \frac{e}{\Omega} Z_{\kappa,\alpha\beta}^* du_{\kappa\beta}, \quad (2.28)$$

which was used to calculate the polarization vectors. The BEC tensors are given by

$$\begin{aligned} Z_{Sr}^* &= \begin{pmatrix} 2.54 & 0 & 0 \\ 0 & 2.54 & 0 \\ 0 & 0 & 2.54 \end{pmatrix}, \quad Z_{Ti}^* = \begin{pmatrix} 7.12 & 0 & 0 \\ 0 & 7.12 & 0 \\ 0 & 0 & 7.12 \end{pmatrix}, \\ Z_{O_x}^* &= \begin{pmatrix} -5.66 & 0 & 0 \\ 0 & -2 & 0 \\ 0 & 0 & -2 \end{pmatrix}, \quad Z_{O_y}^* = \begin{pmatrix} -2 & 0 & 0 \\ 0 & -5.66 & 0 \\ 0 & 0 & -2 \end{pmatrix}, \\ Z_{O_z}^* &= \begin{pmatrix} -2 & 0 & 0 \\ 0 & -2 & 0 \\ 0 & 0 & -5.66 \end{pmatrix} \end{aligned} \quad (2.29)$$

Then the local polarization vectors are rotated back into the global reference frame. Finally the local OP and polarization vectors in each PUC are averaged over the y-z cross section to obtain the profiles for each frame w.r.t. x . The full code used for extracting the polarization and primary OP profile from the trajectory is available on github (<https://github.com/jpils/STOTools.git>, commit fd22243).

For the MD trajectories the per-frame-profiles are further processed by first fitting the ϕ_3 profile, Extracting the domain wall center and centering each frame w.r.t. the DW center and then block averaging over the OP and polarization.

3. Results and Discussion

The main results of this thesis are the profiles of the order parameter $\phi(x)$ and the polarization $\mathbf{P}(x)$ components across twin domain boundaries in SrTiO₃. First the simulations were relaxed for pressures of 20, 40, 60, 80, 100 and 120 kbar. Then MD simulations were conducted for these pressures at 20 K and 35 K. During the MD runs the structures were first equilibrated over 100 ps and the frames used for the analysis were sampled every 10 ps over the duration of 50 ps.

In the first section of this chapter the results for the relaxed structures are discussed. The following section repeats the analysis using NpT ensemble MD simulations at two temperatures close to the ferroelectric phase transition of the two DW types. For all figures shown the DW is centered at 0 along the x axis, which lies normal to the DW plane.

3.1. OP and polarization of SrTiO₃ twin boundaries in structurally relaxed supercells

The OP profiles extracted from the relaxed structures in Figures 3.1 (b) and 3.2 (b) match for both, HH and HT type DWs, with the ones reported in the literature [8]. Comparing the OP profiles of the HT and HH boundary it is clearly visible that the ϕ_3 component in the HT- (ϕ_3^{HT}) and the ϕ_1 component in the HH wall (ϕ_1^{HH}) change sign when transitioning through the boundary. The OP components were rescaled with the bulk value $\bar{\phi}$ of the ϕ_3^{HT} component and the ϕ_1^{HH} component, respectively for better comparison across the different pressures. This swapping behavior of the ϕ_3^{HT} and ϕ_1^{HH} profiles when changing the DW type further confirms the correctness of the configurations. For all simulated pressures the ϕ_2 component in the HT as well as the HH structures remained 0.

The domain wall widths, 2ξ , plotted in Figures 3.1 (a) and 3.2 (a) were extracted from a tanh fit of the ϕ_3^{HT} and ϕ_1^{HH} profiles respectively. For both HT and HH configurations the DW widths exhibit an inverse proportional trend w.r.t. an external pressure. The domain walls in the HT structure remained larger throughout the simulated pressure range.

In Figures 3.1 (c, d) and 3.2 (c, d) the polarization components P_1 and P_3 are depicted. The graph of the P_2 component was omitted as it was zero for all simulations conducted. While the P_3 component shows a symmetric trend parallel to the DW plane, the P_1 component exhibits an antisymmetric profile for all pressures. Additionally the P_1 profiles are slightly asymmetric. This effect is more pronounced in the HH boundaries. One possibility for this behavior could be due to the supercell simply being too narrow to

3. Results and Discussion

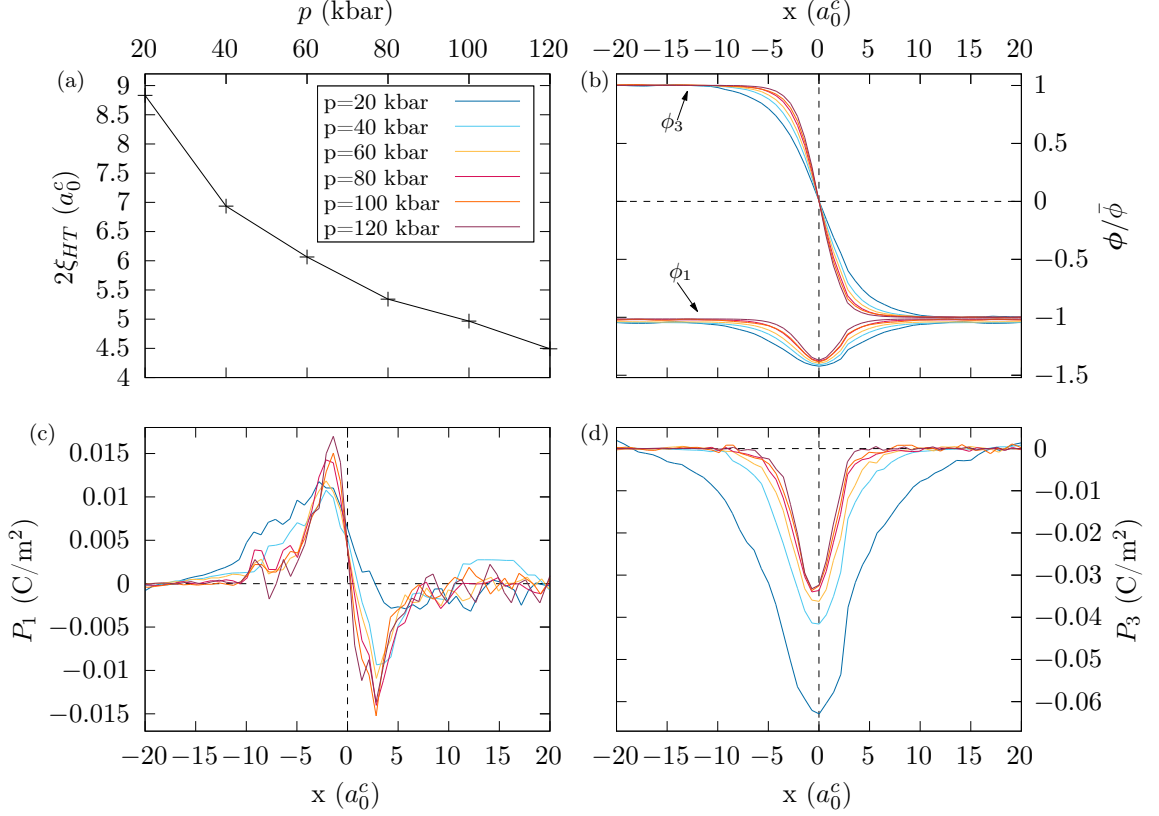


Figure 3.1.: Pressure dependence of the HT-DW width ξ measured in cubic lattice constants $\text{\AA}$ (a). Pressure dependence of the order parameter profiles ϕ_1 and ϕ_3 in cubic lattice constants and rescaled with the bulk value $\bar{\phi}$ (b). Polarization profiles of the P_1 (c) and P_3 (d) component for the pressures 20, 40, 60, 80, 100 and 120 kbar. The ϕ_2 OP and P_2 polarization component remained 0 for all pressures simulated.

accommodate two twin boundaries which could lead to interactions with each other. The structures were relaxed to a maximum force component $F_{max} < 2 \text{ meV/\AA}$, which is already within the magnitude of current models' force error of roughly $5 \text{ meV/\AA}$. Surprisingly, the profiles show strong fluctuations in the P_1 component. Comparing the P_1 and P_3 components for both domain boundary types qualitatively one can see that the P_1 component is notably smaller in magnitude. Furthermore the polarization components do not swap their profiles when changing from a HT configuration to a system with a HH domain wall unlike the OP. The P_3 component shows, similarly to the DW width, a nonlinear, decreasing trend for increasing pressures. While the P_1 component in the HH configuration remains roughly constant, the P_1 component of the HT boundary increases slightly. Quantitatively, the amplitudes of the polarization components of the HT and HH DWs differ only by small factor, which is shown in Figure 3.3. The exception is

3.1. OP and polarization of SrTiO₃ twin boundaries in structurally relaxed supercells

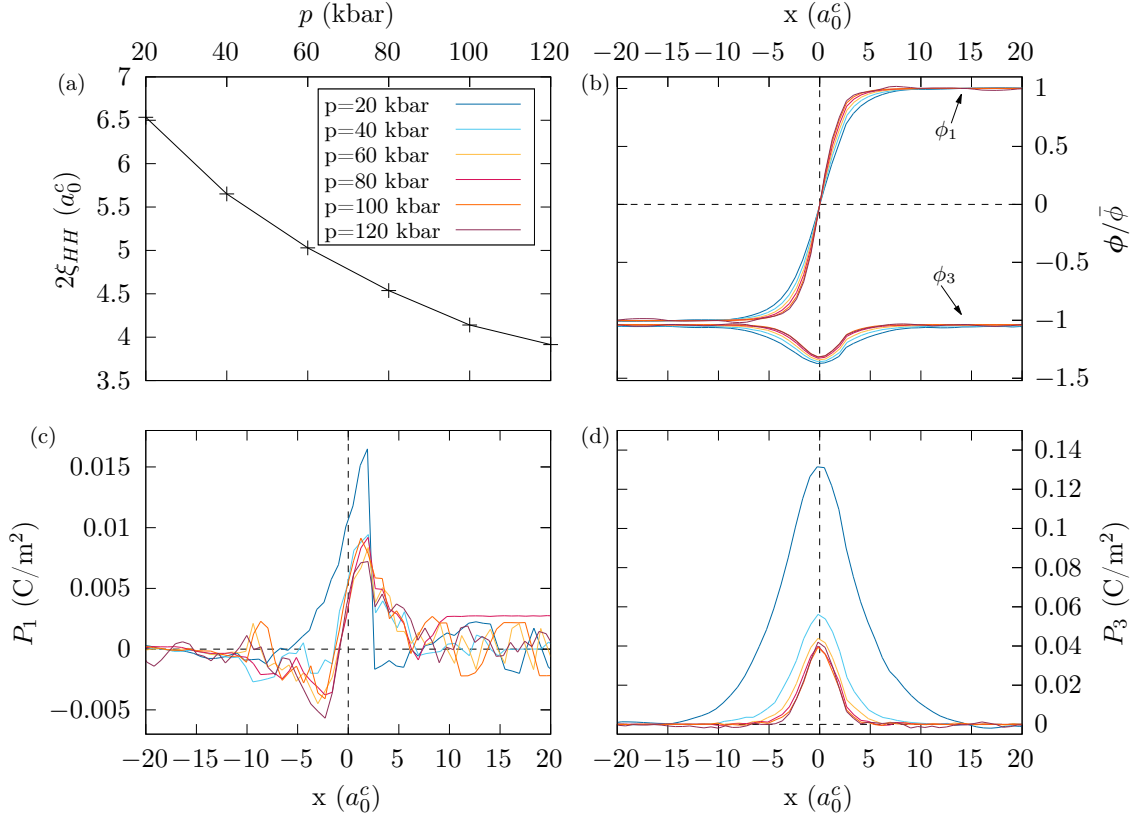


Figure 3.2.: Pressure dependence of the HH-DW width ξ measured in cubic lattice constants Å (a). Pressure dependence of the order parameter profiles ϕ_1 and ϕ_3 in cubic lattice constants and rescaled with the bulk value $\bar{\phi}$ (b). Polarization profiles of the P_1 (c) and P_3 (d) component for the pressures 20, 40, 60, 80, 100 and 120 kbar. The ϕ_2 OP and P_2 polarization component remained 0 for all pressures simulated.

the P_3 profile at an external pressure of 20 kbar in a HH domain boundary, being more than double the magnitude of its HT counterpart. Eventhough these relaxed structures are effectively at zero temperature and thus well below the critical temperature for the ferroelectric phase transition, its effect cannot be extracted by comparing the polarization profiles between relaxed HT and HH structures alone. Further information has to be gathered by including the results from structures obtained by MD in proximity of the critical temperature.

3. Results and Discussion

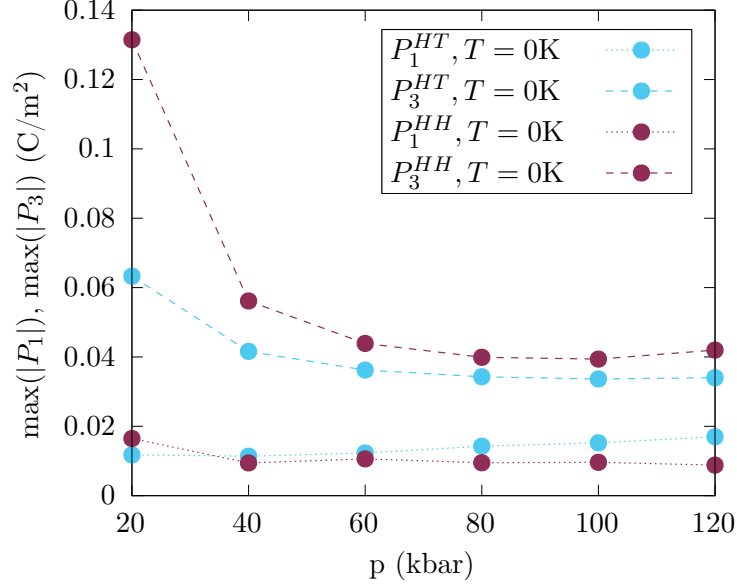


Figure 3.3.: Comparison of the polarization amplitudes for the ϕ_1 and ϕ_3 profiles in the HT and HH configurations.

3.2. OP and polarization of SrTiO₃ twin boundaries in the NpT ensemble

Analyzing the MD trajectories required more care than the simple relaxed structures. Introducing temperature to the simulations thermal fluctuations naturally arised. To combat this the OP and polarization vectors had to be calculated as ensemble averages. This was implemented as a sliding window tracking the DW across frames and averaging over the data in the window to account for the DW drift as the bondary region is not static. Surprisingly the DW showed itself to be highly mobile. Measuring its diffusion constant would, however, be unconvulsive as the effect could be amplified by a current limitation in the analyzation tool. As of now, it is only able to accurately handle static domain boundaries as tracking and adapting to the drifting DW is not yet implemented and thus could lead to artifacts, such as artificially introduced subdomains and not handling the symmetry of each domain correctly. Therefore, the profiles shown in Figure 3.4 and 3.5 should be treated with caution, eventhough they show encouraging results. These figures correspond to the data obtained from MD trajectories in the NpT ensemble at temperatures of 20 K and 35 K respectively over the same pressure range as for the relaxed configurations. The averaging protocol smoothed out the very strong fluctuations, which, on top of thermal noise, are most likely caused by using the cubic unit cell instead of the tetragonal as the reference, which is reported in [7] and are present in the results of the relaxed structures as well. For the profiles extracted from the trajectory at 20 K one can see that the polarization profiles for both, P_1 and P_3 decreased by almost half. Note

3.2. OP and polarization of SrTiO₃ twin boundaries in the NpT ensemble

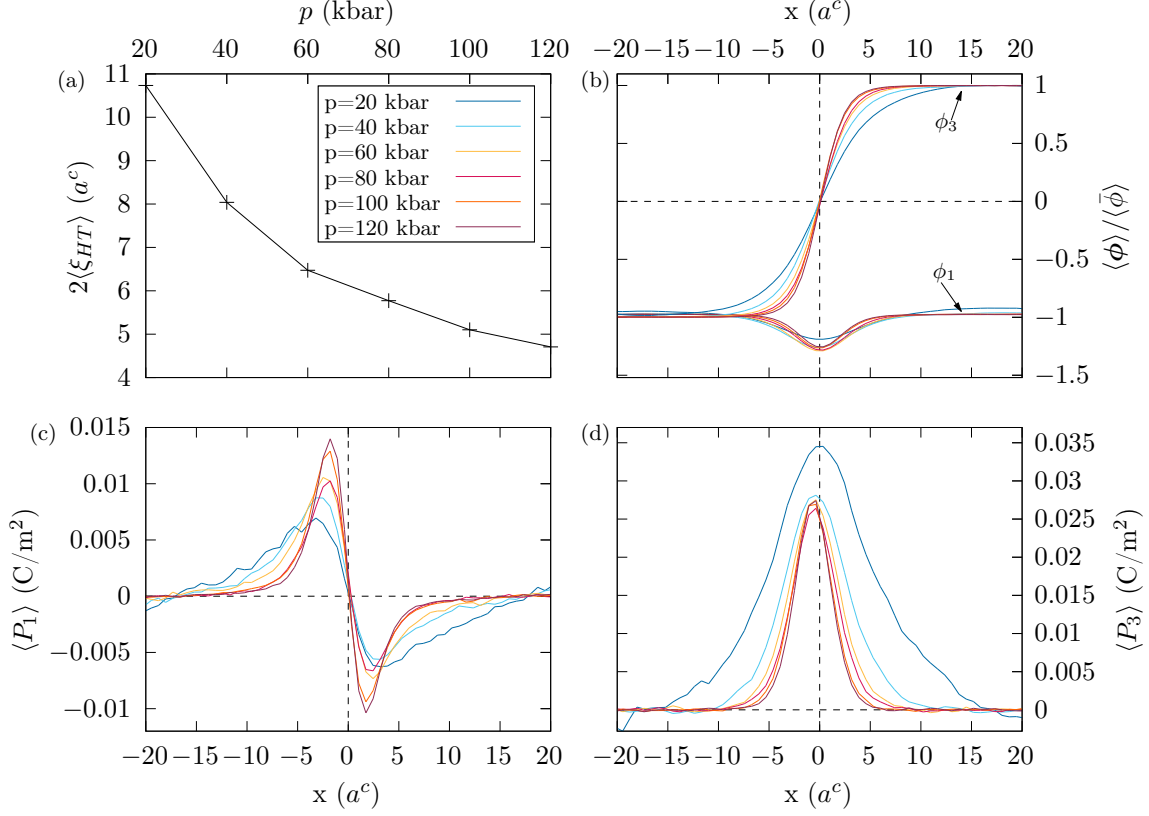


Figure 3.4.: Pressure dependence of the average HT-DW width ξ measured in cubic lattice constants $\text{\AA}$ (a). Pressure dependence of the averaged order parameter profiles $\langle\phi_1\rangle$ and $\langle\phi_3\rangle$ in cubic lattice constants and rescaled with the bulk value $\bar{\phi}$ (b). Polarization profiles of the $\langle P_1\rangle$ (c) and $\langle P_3\rangle$ (d) component for the pressures 20, 40, 60, 80, 100 and 120 kbar at a temperature of 20 K. The $\langle\phi_2\rangle$ OP and $\langle P_2\rangle$ polarization component remained 0 for all pressures simulated.

that, just as for the figures of the relaxed configurations, the ϕ_2 and P_2 components are not displayed as it remained zero up to thermal fluctuations. Considering the mobility of the boundary and the thermal noise precise domain wall widths are difficult to define as they appear smeared out, thus appearing larger than they might actually be. The ensemble averages of the domain wall widths are displayed in Figures 3.4 (a) and 3.5 (a). As expected, the averaged DWs are larger than in the relaxed structures and also follow the same trend of decreasing in width the higher the external pressure becomes. Similarly to the relaxed structures the polarization average $\langle P_1\rangle$ exhibits an inverse proportionality with the external pressure, while the amplitude remains slightly smaller. Interestingly, the amplitude of this polarization component is nearly half of what it would be in a relaxed system, shrinking further as the pressure increases. For both, relaxed structures and the averaged trajectories the polarization leaks out of the DW before converging to 0, which is

3. Results and Discussion

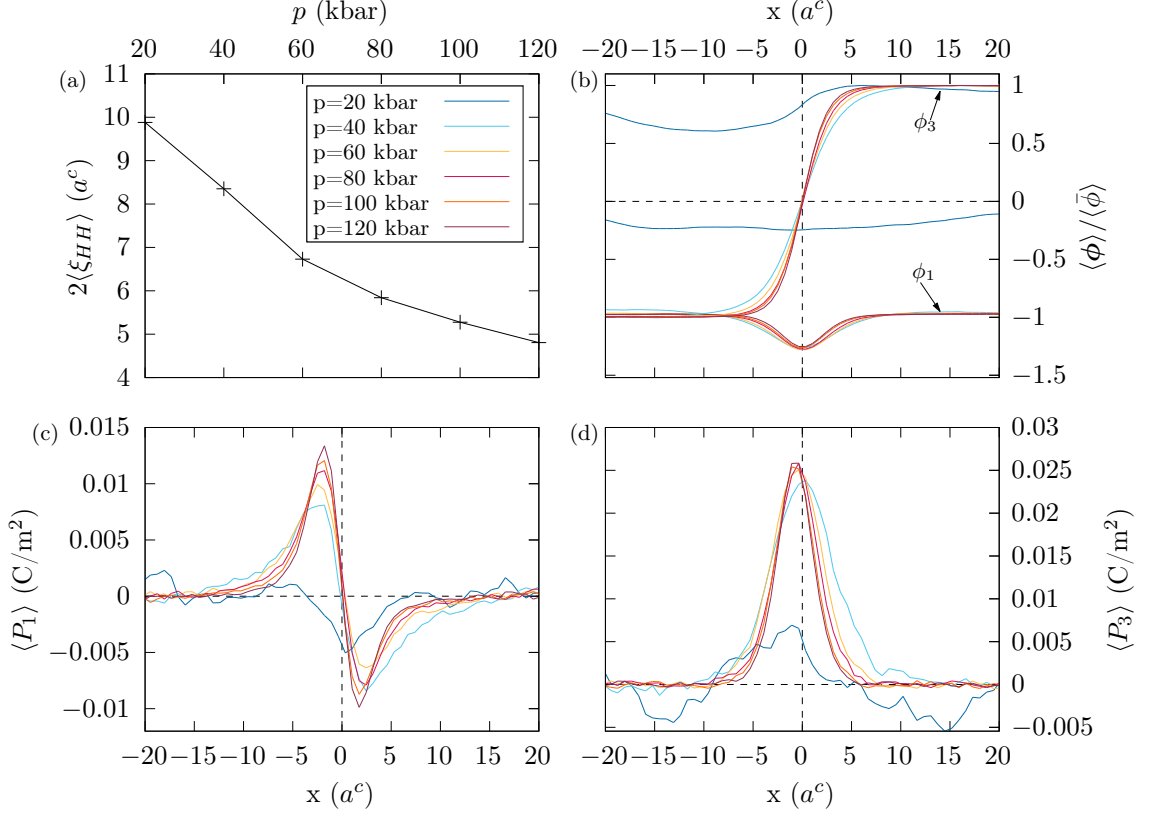


Figure 3.5.: Pressure dependence of the average HT-DW width ξ measured in cubic lattice constants Å (a). Pressure dependence of the averaged order parameter profiles $\langle\phi_1\rangle$ and $\langle\phi_3\rangle$ in cubic lattice constants and rescaled with the bulk value $\bar{\phi}$ (b). Polarization profiles of the $\langle P_1\rangle$ (c) and $\langle P_3\rangle$ (d) component for the pressures 20, 40, 60, 80, 100 and 120 kbar at a temperature of 35 K. The $\langle\phi_2\rangle$ OP and $\langle P_2\rangle$ polarization component remained 0 for all pressures simulated.

most noticeable in the P_1 components. This could lead to unintentional interactions of the two domain walls and needs to be investigated further with a larger supercell. The single limiting factor of the supercell dimensions is the memory available on the GPUs used for the simulation. With the architecture of the **MACE** model and the supercell containing 4000 atoms it was not possible to increase its size any further. Heating the system up to 35 K leads to the polarization to reduce in amplitude slightly, while the effect of the external pressures remains similar to the profiles simulated at 20 K. Note the averaged OP and polarization profiles for the system at 20 kbar behaving drastically different than for the other simulations.

Pointing out the issue of the profiles deviating from the expected values so much is not straight forward due to the amount of variables at play. The reason could be either the analyzation tool not being able to properly function due to serious domain wall

3.2. OP and polarization of SrTiO₃ twin boundaries in the NpT ensemble

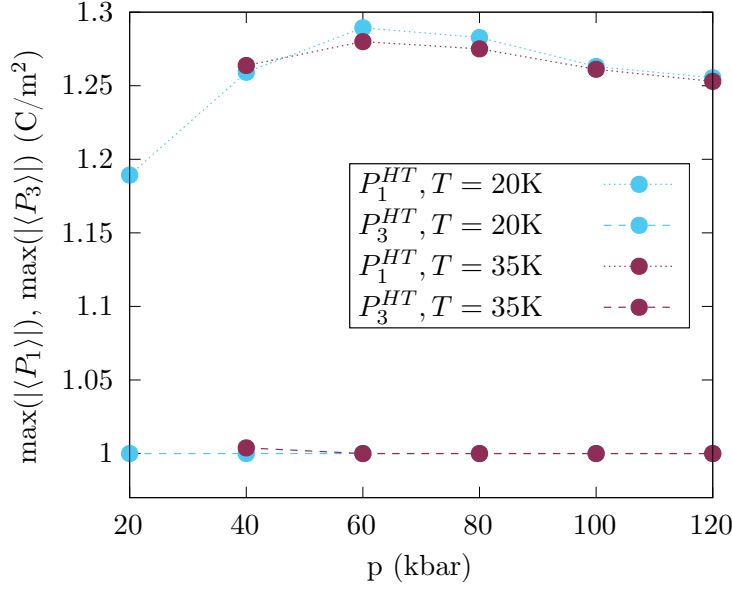


Figure 3.6.: Comparison of averaged polarization profiles for the HT configurations simulated at temperatures of 20 K and 35 K.

drift, the supercell to be not wide enough to accommodate both DWs or an issue in the MD simulation itself, although a ferroelectric phase is to be ruled out given the OP being so different than what the literature and previous simulations suggest. Figure 3.6 shows the difference and change between the $\langle P_1 \rangle$ and $\langle P_3 \rangle$ polarization components across the pressure range simulated at temperatures 20 K and 35 K. Over the pressure range simulated, the average polarization amplitudes of the P_1 and P_3 component remain roughly constant for both pressures. The result of the simulation conducted at a pressure of 20 kbar and a temperature of 35 K are not shown, as the OP suggests that the structure deviates strongly from the expected HT configuration.

Even though MD simulations for configurations containing HH type DWs were conducted, they resulted mostly in unphysical domain wall and polarization profiles and are therefore omitted from this thesis. This could be hinting towards artifacts introduced by the constraints in the analyzation tool. Why it only showed in HH type configurations, however, remains unclear.

4. Conclusion

In this thesis the order parameter and polarization profiles for HT and HH type domain boundaries in twinned SrTiO_3 were investigated. For relaxed structures the profiles were obtained for both types of domain walls, while for MD simulations only the HT configurations succeeded. It was shown that the DW width decrease with larger external pressures applied. Furthermore, it was shown that for the relaxed structures the polarization amplitude in the HH boundary remained larger throughout the simulated pressure range than in the HT domain walls.

Given only HT configurations produced usable results the behavior of the polarization profiles above and below the ferroelectric transition of the DW cannot be concluded and remains to be researched in future work. Furthermore, the OP and polarization profiles should be validated against the Landau-Ginzburg-Devonshire phenomenology to further extend the research conducted in [9]. Emphasis should be put on these results being just an approximation due to using DFT level of theory. One way to overcome this would be to include nuclear quantum fluctuations into the simulations by using path integral molecular dynamics. Additionally, the analyzation tool should be further developed to allow the tracking of the domain boundaries across trajectories, ideally without requiring prior knowledge of the location of the DW center.

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A. Appendix

A.1. Gradient descent using unit quaternions

The loss function is defined as the total squared distance of the Sr atoms of the pristine unit cell with position $\mathbf{r}_i$ and the distorted pseudo unit cell with positions $\mathbf{r}'_i$ and $i = 1, 2, \dots, 8$. It is given as

$$\mathcal{L}(\hat{q}) = \sum_{i=1}^8 \left\| \mathbf{r}'_i - \mathbf{R}(\hat{q})\mathbf{r}_i \right\|^2, \quad (\text{A.1})$$

with $\hat{q} = (q_0; q_1, q_2, q_3) = (q_0, \mathbf{q})$, $\|\hat{q}\| = 1$ being a unit quaternion. The matrix $\mathbf{R}(\hat{q})$ describes a generic rotation, first around the z axis in the initial frame, then around the x axis in the one time rotated frame and then a rotation around the z axis in the twice rotated frame (x convention), similar to Euler angles but written in the frame of unit quaternions. The rotation matrix is given by

$$\mathbf{R}(\hat{q}) = 2 \begin{pmatrix} q_0^2 + q_1^2 - \frac{1}{2} & q_1q_2 - q_0q_3 & q_1q_3 + q_0q_2 \\ q_1q_2 + q_0q_3 & q_0^2 + q_2^2 - \frac{1}{2} & q_2q_3 - q_0q_1 \\ q_1q_3 - q_0q_2 & q_2q_3 + q_0q_1 & q_0^2 + q_3^2 - \frac{1}{2} \end{pmatrix} \quad (\text{A.2})$$

The loss function can be simplified to

$$\begin{aligned} \mathcal{L}(\hat{q}) &= \sum_{i=1}^8 (\mathbf{r}'_i - \mathbf{R}(\hat{q})\mathbf{r}_i)^T (\mathbf{r}'_i - \mathbf{R}(\hat{q})\mathbf{r}_i) \\ &= \sum_{i=1}^8 \left\| \mathbf{r}'_i \right\|^2 - \mathbf{r}'_i{}^T (\mathbf{R}(\hat{q})\mathbf{r}_i) - (\mathbf{R}(\hat{q})\mathbf{r}_i)^T \mathbf{r}'_i + (\mathbf{R}(\hat{q})\mathbf{r}_i)^T (\mathbf{R}(\hat{q})\mathbf{r}_i) \\ &= \sum_{i=1}^8 \left\| \mathbf{r}'_i \right\|^2 - \mathbf{r}'_i{}^T \mathbf{R}(\hat{q})\mathbf{r}_i - \mathbf{r}_i^T \mathbf{R}^T(\hat{q})\mathbf{r}'_i + \mathbf{r}_i^T \mathbf{R}^T(\hat{q})\mathbf{R}(\hat{q})\mathbf{r}_i \\ &= \sum_{i=1}^8 \left\| \mathbf{r}'_i \right\|^2 - \mathbf{r}'_i{}^T \mathbf{R}(\hat{q})\mathbf{r}_i - \mathbf{r}_i^T \mathbf{R}^T(\hat{q})\mathbf{r}'_i + \mathbf{r}_i^T \mathbf{r}_i \\ &= \sum_{i=1}^8 \left\| \mathbf{r}'_i \right\|^2 - \mathbf{r}'_i{}^T \mathbf{R}(\hat{q})\mathbf{r}_i - \mathbf{r}_i^T \mathbf{R}(\hat{q})\mathbf{r}_i + \left\| \mathbf{r}_i \right\|^2 \\ &= \sum_{i=1}^8 \left\| \mathbf{r}'_i \right\|^2 + \left\| \mathbf{r}_i \right\|^2 - 2(\mathbf{r}'_i{}^T \mathbf{R}(\hat{q})\mathbf{r}_i) \end{aligned} \quad (\text{A.3})$$

A. Appendix

The gradient $\nabla = (\partial_{q_0}, \partial_{q_1}, \partial_{q_2}, \partial_{q_3})^T [\mathcal{L}(\hat{q})]$ of the loss function is calculated as follows:

$$\nabla \mathcal{L}(\hat{q}) = \sum_{i=1}^8 \nabla [\|\mathbf{r}'_i\|^2 + \|\mathbf{r}_i\|^2 - 2(\mathbf{r}'_i{}^T \mathbf{R}(\hat{q}) \mathbf{r}_i)] \quad (\text{A.4})$$

Taking the gradient of the summand

$$\begin{aligned} \nabla [\|\mathbf{r}'_i\|^2 + \|\mathbf{r}_i\|^2 - 2(\mathbf{r}'_i{}^T \mathbf{R}(\hat{q}) \mathbf{r}_i)] &= 0 - 2\nabla [\mathbf{r}'_i{}^T \mathbf{R}(\hat{q}) \mathbf{r}_i] \\ &= -2\mathbf{r}'_i{}^T \nabla [\mathbf{R}(\hat{q})] \mathbf{r}_i \end{aligned} \quad (\text{A.5})$$

Hence the gradient of the loss function is

$$\nabla \mathcal{L}(\hat{q}) = -2 \sum_{i=1}^8 \mathbf{r}'_i{}^T \nabla [\mathbf{R}(\hat{q})] \mathbf{r}_i \quad (\text{A.6})$$

with the gradient entries

$$\frac{\partial}{\partial q_0} \mathbf{R}(\hat{q}) = 2 \begin{pmatrix} 2q_0 & -q_3 & q_2 \\ q_3 & 2q_0 & -q_1 \\ -q_2 & q_1 & 2q_0 \end{pmatrix} \quad (\text{A.7})$$

$$\frac{\partial}{\partial q_1} \mathbf{R}(\hat{q}) = 2 \begin{pmatrix} 2q_1 & q_2 & q_3 \\ q_2 & 0 & -q_0 \\ q_3 & q_0 & 0 \end{pmatrix} \quad (\text{A.8})$$

$$\frac{\partial}{\partial q_2} \mathbf{R}(\hat{q}) = 2 \begin{pmatrix} 0 & q_1 & q_0 \\ q_1 & 2q_2 & q_3 \\ -q_0 & q_3 & 0 \end{pmatrix} \quad (\text{A.9})$$

$$\frac{\partial}{\partial q_3} \mathbf{R}(\hat{q}) = 2 \begin{pmatrix} 0 & -q_0 & q_1 \\ q_0 & 0 & q_2 \\ q_1 & q_2 & 2q_3 \end{pmatrix} \quad (\text{A.10})$$

Given this, the coefficient-wise update rule of the quaternion in each iteration is

$$\begin{aligned} q_\alpha^{(k+1)} &= q_\alpha^{(k)} + 2\eta \sum_{i=1}^8 \mathbf{r}'_i{}^T \frac{\partial}{\partial q_\alpha} \mathbf{R}(\hat{q}) \mathbf{r}_i \\ \hat{q}^{(k+1)} &= \frac{q^{(k+1)}}{\|q^{(k+1)}\|}, \end{aligned} \quad (\text{A.11})$$

where $\alpha = 0, \dots, 3$ enumerates the quaternion entries and η is a hyperparameter scaling the step size. This rule can be rewritten using the gradient tensor $\mathbf{G}_{\alpha\beta\gamma} \in \mathbb{R}^{4 \times 3 \times 3}$ containing the gradients of $R(\mathbf{q})$.

$$q_\alpha^{(k+1)} = q_\alpha^{(k)} + 2\eta \sum_{i=1}^8 \mathbf{r}'_{i,\beta} \mathbf{G}_{\alpha\beta\gamma} \mathbf{r}_{i,\gamma}. \quad (\text{A.12})$$

A.1. Gradient descent using unit quaternions

This approach, however, is only valid for infinitesimal η . If the step size is finite it leads to over-/undershooting. For small angles this deviation becomes more severe. Instead the update step should be constrained to S^3 and follow a geodesic on the unit sphere. In order to do this we calculate the gradient with Lagrange multiplier. In general the constrained Lagrange function is given by

$$\mathcal{L}(\hat{q}, \lambda) = \mathcal{L}(\hat{q}) + \sum_{\alpha} \lambda_{\alpha} \sigma_{\alpha}(\hat{q}) \quad (\text{A.13})$$

with the Lagrange multiplier λ_{α} and the constraint functions $\sigma_{\alpha}(\hat{q})$. The only constraint here is that we strictly work with unit quaternions, hence, $\|\hat{q}\| \stackrel{!}{=} 1$. There are two conditions for the constraint function:

1. The quaternion lies initially on the unit sphere $\rightarrow \sigma(\hat{q}) = 0$
2. The quaternion has to move along the unit sphere $\rightarrow \nabla[\sigma(\hat{q})] \stackrel{!}{=} 0$

With this, the constraint function is

$$\begin{aligned} \sigma(\hat{q}) &= \frac{1}{2}(\|\hat{q}\|^2 - 1) \\ \nabla[\sigma(\hat{q})] &= \nabla[\sigma(\hat{q})] = \hat{q} \end{aligned} \quad (\text{A.14})$$

The full gradient of the constrained Lagrange function can be written as

$$\begin{aligned} \nabla \mathcal{L}(\hat{q}, \lambda) &= \nabla \mathcal{L}(\hat{q}) + \lambda \nabla \sigma(\hat{q}) \\ &= -2 \sum_{i=1}^8 \mathbf{r}'_{i,\beta} \mathbf{G}_{\alpha\beta\gamma} \mathbf{r}_{i,\gamma} + \lambda q_{\alpha} \end{aligned} \quad (\text{A.15})$$

Using this, the coefficient-wise update rule respecting the constraint is then

$$q_{\alpha}^{(k+1)} = q_{\alpha}^{(k)} + 2\eta \sum_{i=1}^8 \mathbf{r}'_{i,\beta} \mathbf{G}_{\alpha\beta\gamma} \mathbf{r}_{i,\gamma} - \lambda q_{\alpha}^{(k)} . \quad (\text{A.16})$$

This can be further simplified by introducing the gradient of the unconstrained loss function $g_{\alpha}(\hat{q}) := -2 \sum_{i=1}^8 \mathbf{r}'_{i,\beta} \mathbf{G}_{\alpha\beta\gamma} \mathbf{r}_{i,\gamma}$ and the update rule becomes

$$\hat{q}^{(k+1)} = \hat{q}^{(k)} - (\eta g(\hat{q}^{(k)}) + \lambda \hat{q}^{(k)}) . \quad (\text{A.17})$$

It remains to find a λ in each update step that ensures that the gradient term also lies on S^3 . In order to do this the right hand side of the update rule has to be of unit length

$$\left\| \hat{q}^{(k)} - (\eta g(\hat{q}^{(k)}) + \lambda \hat{q}^{(k)}) \right\|^2 \stackrel{!}{=} 1 . \quad (\text{A.18})$$

A. Appendix

For simplicity the iteration index is ignored in the nex steps.

$$\begin{aligned}
& \|\hat{q} - (\eta g(\hat{q}) + \lambda \hat{q})\|^2 = \\
& = (\hat{q} - (\eta g(\hat{q}) + \lambda \hat{q}))^* \cdot (\hat{q} - (\eta g(\hat{q}) + \lambda \hat{q})) \\
& = \hat{q}^* \hat{q} - \hat{q}^* (\eta g(\hat{q}) + \lambda \hat{q}) - (\eta g(\hat{q}) + \lambda \hat{q})^* \hat{q} \\
& \quad + (\eta g(\hat{q}) + \lambda \hat{q})^* (\eta g(\hat{q}) + \lambda \hat{q}) \\
& = 1 - \hat{q}^* \eta g(\hat{q}) - 2\lambda - \eta [g(\hat{q})]^* \hat{q} + \eta^2 [g(\hat{q})]^* g(\hat{q}) + \lambda \eta [g(\hat{q})]^* \hat{q} \\
& \quad + \lambda \eta \hat{q}^* g(\hat{q}) + \lambda^2 \\
& = \lambda^2 + \lambda (\eta [g(\hat{q})]^* \hat{q} + \eta \hat{q}^* g(\hat{q}) - 2) + 1 - \hat{q}^* \eta g(\hat{q}) - \eta [g(\hat{q})]^* \hat{q} \\
& \quad + \eta^2 [g(\hat{q})]^* g(\hat{q}) \\
& = \lambda^2 + \lambda (\eta \hat{q}^* g(\hat{q}) + \eta \hat{q}^* g(\hat{q}) - 2) + 1 - \eta \hat{q}^* g(\hat{q}) - \eta \hat{q}^* g(\hat{q}) \\
& \quad + \eta^2 \|g(\hat{q})\|^2
\end{aligned} \tag{A.19}$$

Setting $a := \hat{q}^* g(\hat{q})$ and $b := \|g(\hat{q})\|^2$ this reduces to

$$\begin{aligned}
\|\hat{q} - (\eta g(\hat{q}) + \lambda \hat{q})\|^2 &= \lambda^2 + \lambda(2\eta a - 2) + 1 + (\eta^2 b - 2\eta a) = 1 \\
\lambda^2 + \lambda(2\eta a - 2) + (\eta^2 b - 2\eta a) &= 0
\end{aligned} \tag{A.20}$$

Solving for λ :

$$\begin{aligned}
\lambda_{1,2}(\hat{q}^{(k)}, \eta) &= -(\eta a - 1) \pm \sqrt{(\eta a - 1)^2 + 2\eta a - \eta^2 b} \\
&= 1 - \eta a \pm \sqrt{\eta^2(a^2 - b) + 1}
\end{aligned} \tag{A.21}$$

There are two possible branches that satisfy the condition in Eq. [A.18](#). Comparing with Eq. [A.17](#) it is apparent that for $\eta \rightarrow 0$ the quaternion $\hat{q}^{(k+1)}$ will remain the same as the quaternion in the previous iteration, hence the branch that satisfies $\eta g(\hat{q}^{(k)}) + \lambda \hat{q}^{(k)} = 0$ should be chosen. For this condition to hold when $\eta \rightarrow 0$, the second term has to vanish as well which is true if $\lambda \rightarrow 0$. Checking the behavior for the first branch as $\eta \rightarrow 0$

$$\lim_{\eta \rightarrow 0} \lambda_1(\hat{q}^{(k)}, \eta) = \lim_{\eta \rightarrow 0} 1 - \eta a + \sqrt{\eta^2(a^2 - b) + 1} = 2 \tag{A.22}$$

and for the second branch

$$\lim_{\eta \rightarrow 0} \lambda_2(\hat{q}^{(k)}, \eta) = \lim_{\eta \rightarrow 0} 1 - \eta a - \sqrt{\eta^2(a^2 - b) + 1} = 0 \tag{A.23}$$

shows that λ_2 satisfies the condition.

With this, the steps for the quaternion update in each iteration are

1. Evaluate $g(\hat{q}^{(k)})$
2. Calculate $\lambda_2(\hat{q}^{(k)}, \eta)$
3. Update the quaternion with $\hat{q}^{(k+1)} = \hat{q}^{(k)} - (\eta g(\hat{q}^{(k)}) + \lambda \hat{q}^{(k)})$

A.2. VASP input files

The INCAR file used for the structural relaxations is shown below. Initially the calculation was done with the CG (IBRION=2) algorithm, then a second pass was done with the RMM-DIIS (IBRION=1) scheme.

```
IBRION = 2
ISIF = 3
ISMEAR = 0
SIGMA = 0.05
GGA = PS
ENCUT = 700
EDIFF = 0.1E-05
EDIFFG = -0.001
LREAL = Auto
ALGO = All
PREC = Accurate
AMIN = 0.01
PSTRESS = XXX # eg. 80
```

For the single point calculations the following INCAR file was used.

```
IBRION = -1
NSW = 0
ISMEAR = 0
SIGMA = 0.05
GGA = PS
ENCUT = 700
EDIFF = 0.1E-05
EDIFFG = -0.001
LREAL = Auto
ALGO = All
PREC = Accurate
AMIN = 0.01
```


A. Appendix

A.3. MACE configuration files

The model parameters used for refining the MACE foundational model are listed below. The weights for each configuration type (cubic, tetragonal, twinned) were updated for each model generation and can be found in Table [A.1](#).

```
# model weights
config_type_weights:
  cubic: X.XX
  tetragonal: X.XX
  twinned: X.XX
energy_key: "REF_energy"
forces_key: "REF_forces"
stress_key: "REF_stress"
energy_weight: 1.0
forces_weight: 50.0
stress_weight: 0.5

# training protocol
multiheads_finetuning: False
r_max: 5
lr: 1.0e-4
default_dtype: float64
batch_size: 4
valid_batch_size: 4
max_num_epochs: 25
patience: 5
ema: True
swa: True
start_swa: 20
swa_lr: 1.0e-5
E0s: "foundation"
```

Gen	cubic	tetragonal	twinned
0	1.67	0.42	3.33
1	2	0.4	2
2	2.67	0.53	0.89
3	3.5	0.88	0.64
4	2.67	0.67	0.89

Table A.1.: Configuration type weights for each generation.