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Emergent Ferroelectric Phases in Moiré Complex Oxides

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Abstract

Strontium titanate (SrTiO_3) is an incipient ferroelectric perovskite whose structural and polar properties are highly sensitive to lattice distortions and reduced dimensionality. In twisted bilayered SrTiO_3 the moiré geometry introduces spatially varying local atomic environments, providing an additional degree of freedom to modify the structural behaviour and polarization through the twist angle. This thesis investigates how these properties evolve with twist angle using a combination of first-principles calculations and machine-learning-based atomistic simulations.

Density functional theory (DFT) calculations were used to generate the reference dataset for both bulk and layered SrTiO_3 systems. The datasets were used to train separate Allegro/NequIP-based machine-learning interatomic potentials which were subsequently employed with LAMMPS to relax bulk and twisted bilayered structures. This approach enabled the investigation of large moiré supercells which would be computationally demanding to treat directly with DFT.

The relaxed bulk SrTiO_3 system was analyzed over a range of lattice parameters to identify characteristic structural regions, including $I4/mcm$ -, $I4cm$ -, $Ima2$ -, and $R3c$ -like configurations, which were used as references for interpreting the local structural environments of the twisted bilayers.

The relaxed twisted bilayered structures develop strongly nonuniform polarization patterns that vary with twist angle. The out-of-plane polarization (P_z) exhibits spatially distributed regions of positive and negative polarization across the moiré supercell. The relative in-plane and out-of-plane polarization contributions evolve approximately symmetrically around 45.041° . At small twist angles, the in-plane polarization forms vortex-like textures, whereas at intermediate angles, strong out-of-plane polarization components emerge. Local structural analysis reveals a corresponding evolution of the identifiable bulk-reference-like environments, from $Ima2$ -like character at 10.389° , through $I4cm$ -like character near 45.041° , to stronger $I4/mcm$ -like character at 83.267° , although mixed and low-symmetry environments remain dominant throughout.

Overall, these results establish a connection between twist angle, local structural reconstruction and spatial organization of the polarization field, highlighting moiré engineering as a route for generating complex polar states in twisted SrTiO_3 bilayers.

Santrauka

Stroncio titanatas (SrTiO_3) yra besiformuojantis feroelektrinis perovskitas, kurio struktūrinės ir polinės savybės yra labai jautrios kristalinės gardelės iškraipymams ir sumažintam matmenų skaičiui. Susuktuose dvisluoksniuose SrTiO_3 dariniuose moirė geometrija sukuria erdviškai kintančią lokalią atominę aplinką, todėl posūkio kampas tampa papildomu parametru, leidžiančiu keisti struktūrines savybes ir poliarizaciją. Šiame magistro darbe, derinant pirmųjų principų skaičiavimus ir mašininį mokymusi pagrįstus atomistinius modeliavimus, tiriama, kaip šios savybės kinta priklausomai nuo posūkio kampo.

Tankio funkcionalo teorijos (DFT) skaičiavimai buvo naudojami etaloniniams tūrinių ir sluoksniuotų SrTiO_3 sistemų duomenų rinkiniams sudaryti. Remiantis šiais duomenų rinkiniais, buvo apmokyti atskiri Allegro/NequIP mašininio mokymusi pagrįsti tarpatominės sąveikos potencialai, kurie vėliau kartu su LAMMPS buvo naudojami tūrinėms ir susuktoms dvisluoksnėms struktūroms relaksuoti. Šis metodas leido tirti dideles moirė supergardelės, kurių tiesioginiai DFT skaičiavimai pareikalautų itin didelių skaičiavimo išteklių.

Relaksuota tūrinė SrTiO_3 sistema buvo analizuojama plačiame gardelės parametrų intervale, siekiant nustatyti būdingas struktūrines sritis, apimančias į $14/\text{mcm}$, 14cm , $1\text{ma}2$ ir $\text{R}3\text{c}$ panašias konfigūracijas. Šios konfigūracijos buvo naudojamos kaip etalonai susuktų dvisluoksnių struktūrų lokalioms struktūrinėms aplinkoms interpretuoti.

Relaksuotose susuktose dvisluoksnėse struktūrose susidaro labai netolygūs poliarizacijos raštai, kurie kinta priklausomai nuo posūkio kampo. Statmenoji poliarizacijos komponentė (P_z) moirė supergardelėje sudaro erdviškai pasiskirsčiusias teigiamos ir neigiamos poliarizacijos sritis. Santykiniai lygiagretieji ir statmenieji poliarizacijos indėliai kinta apytikriai simetriškai $45,041^\circ$ kampo atžvilgiu. Esant mažiems posūkio kampams, lygiagrečioji poliarizacija sudaro į sukurius panašias tekstūras, o esant tarpiniams kampams išryškėja stiprios statmenosios poliarizacijos komponentės. Lokali struktūrinė analizė parodė atitinkamą identifikuojamų, į tūrines etalonines struktūras panašių aplinkų kitimą: nuo į $1\text{ma}2$ panašaus pobūdžio esant $10,389^\circ$ kampui, per į 14cm panašų pobūdį ties $45,041^\circ$ kampu, iki ryškesnio į $14/\text{mcm}$ panašaus pobūdžio esant $83,267^\circ$ kampui. Vis dėlto visuose nagrinėtuose kampuose vyrauja mišrios ir žemos simetrijos aplinkos.

Apibendrinant galima teigti, kad gauti rezultatai atskleidžia ryšį tarp posūkio kampo, lokalios struktūrinės rekonstrukcijos ir poliarizacijos lauko erdvinės organizacijos. Jie taip pat parodo, kad moirė inžinerija gali būti perspektyvus būdas sudėtingoms polinėms būsenoms susuktuose SrTiO_3 dvisluoksniuose dariniuose formuoti.

Preface

This thesis was completed in the Correlated Quantum Materials Group at Aalto University as part of the Erasmus Mundus Joint Master's Programme in Intelligent Photonics for Security, Reliability, Sustainability, and Safety (iPSRS). Working on this project has been a rewarding and transformative experience, allowing me to deepen my knowledge of computational materials physics and explore the fascinating properties of moiré complex oxides.

First and foremost, I would like to express my deepest gratitude to Allah Almighty for His countless blessings, guidance, and strength throughout this journey. His grace gave me the patience and courage to overcome challenges and complete this thesis.

I would like to express my sincere gratitude to my supervisor, Dr. Adolfo Otero Fumega, for his invaluable guidance, patience, encouragement, and continuous support throughout this research. His scientific insight and thoughtful feedback helped me overcome many challenges and greatly contributed to my development as a researcher. I am also grateful to the members of the Correlated Quantum Materials Group for providing a welcoming and intellectually stimulating research environment.

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Contents

Abstract	iii
Santrauka	v
Preface	vii
List of Figures	x
List of Tables	xi
List of Abbreviations	xiii
1 Introduction	1
1.1 Overview of Complex Oxides	1
1.2 Moiré Patterns in Complex Oxides	2
1.3 Ferroelectricity in Perovskite Oxides	3
1.4 Chirality and Polar Topology in Moiré Oxides	5
1.5 Motivation	7
2 Background	9
2.1 Structural and Ferroic Properties of Bulk SrTiO ₃	9
2.1.1 Bulk Crystal Structure and Antiferrodistortive Transition	9
2.1.2 Surface, Interface, and Defect-Induced Polar Response	9
2.1.3 Oxygen Vacancies and Structural Stability	9
2.1.4 Chemical Modification and Processing Effects	10
2.2 Reduced-Dimensional SrTiO ₃ and Emergent Polar Behaviour	10
2.3 Layered and Twisted Bilayer SrTiO ₃ Structures	11
3 Methodology	13
3.1 DFT Calculations	13
3.2 Dataset Generation and Filtering	15
3.3 Machine-Learning Interatomic Potential Training	17
3.4 Structure Relaxation and LAMMPS Simulations	18
3.4.1 Mathematical Characterization of Polarization, Bound Charge, Polar Vortices, and Skyrmion-like Textures	19
3.5 Phase and Structural Analysis	21
4 Results and Discussion	23
4.1 Results for Bulk SrTiO ₃	23

4.1.1	DFT Convergence Test Results	23
4.1.2	Dataset Generation and Filtering	24
4.1.3	Machine-Learning Interatomic Potential Training Evaluation . .	27
4.1.4	Bulk Phase Analysis as a Function of Lattice Strain	28
4.2	Results for Twisted SrTiO ₃ Bilayers	32
4.2.1	Dataset Generation and Filtering	32
4.2.2	Machine-Learning Interatomic Potential Training	34
4.2.3	Ferroelectric-Phase Analysis as a Function of Twist Angle	35
4.2.4	In-plane Polarization Textures	41
4.2.5	Local Structural Character of the Emergent Polar States	41
5	Conclusion	45
5.1	Limitations and Future Work	46
	Bibliography	47
A	Supplementary Results	53
A.1	Calculated Twisted-Bilayer Configurations	53
A.2	Additional Layer-Resolved Polarization Maps	53
	Personal Statement of Non-Plagiarism	57
	Supervisor Approval	59

List of Figures

1	Cubic SrTiO ₃ perovskite structure	1
2	Moiré-pattern formation in twisted lattices	2
3	Conventional ferroelectric polarization	4
4	Polar-vortex and polar-skyrmion textures	6
5	Computational workflow	13
6	Perturbed bulk SrTiO ₃ structure	16
7	Layered SrTiO ₃ structure	17
8	Energy-convergence analysis	23
9	Force- and pressure-convergence analysis	24
10	DFT calculation wall times	24
11	Effect of filtering on the training dataset	25
12	Energy and force distributions of the original training dataset	26
13	Energy and force distributions of the validation dataset	26
14	Energy and force distributions of the filtered training dataset	27
15	Bulk-MLIP validation errors	28
16	Bulk SrTiO ₃ structural phase diagram	29
17	Bulk SrTiO ₃ relative-energy landscape	29
18	Representative <i>I4/mcm</i> and <i>Ima2</i> structures	30
19	Representative <i>I4cm</i> and <i>R3c</i> structures	31
20	Layered training-dataset filtering	33
21	Layered validation-dataset filtering	34
22	Layered-MLIP validation errors	34
23	Layer-resolved P_z distribution at 45.041°	36
24	Polarization fractions versus twist angle	36
25	Out-of-plane polarization and relaxed structures	38
26	Polarization–structure overlay at 83.267°	39
27	Local structures at polarization extrema	40
28	In-plane polarization textures	42
29	Layer-resolved polarization at $\theta = 25.989^\circ$	54
30	Layer-resolved polarization at $\theta = 60.513^\circ$	55
31	Layer-resolved polarization at $\theta = 72.055^\circ$	56

List of Tables

1	Summary of the original and filtered SrTiO_3 datasets used for MLIP training and validation.	25
2	Initial, minimum, and final validation errors of the trained MLIP model.	27
3	Ti–O bond distances in representative bulk phases	32
4	Summary of the original and filtered layered SrTiO_3 datasets used for MLIP training and validation.	32
5	Initial, minimum, and final validation errors of the trained layered SrTiO_3 MLIP model.	35
6	Polarization and Ti–Ti separation at selected twist angles	40
7	Fractions of local bulk-reference-like structural environments identified in the top and bottom layers for the three representative twist angles. The classifications indicate similarity to characteristic bulk SrTiO_3 distortion patterns rather than exact local crystallographic phases. Values are given as percentages of Ti sites.	43
8	Commensurate twisted-bilayer SrTiO_3 configurations considered in this work.	53

List of Abbreviations

AFD	Antiferrodistortive
DFT	Density Functional Theory
FE	Ferroelectric
GGA	Generalized Gradient Approximation
LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator
MAE	Mean Absolute Error
MLIP	Machine-Learning Interatomic Potential
PBE	Perdew–Burke–Ernzerhof
PBC	Periodic Boundary Conditions
QE	Quantum ESPRESSO
STO	Strontium titanate, SrTiO_3

1

Introduction

1.1 Overview of Complex Oxides

Oxide groups consisting of two or more different cations are called complex or mixed oxides. Complex oxides are an important class of inorganic materials because they offer a combination of structural versatility, chemical robustness, and diverse functional properties. Within this broad family, there are several important structural groups, such as perovskites, pyrochlores, tetragonal tungsten bronzes, and Bi (bismuth)-containing layered perovskite-like oxides [1]. Since complex perovskite oxides are made from oxygen-octahedral units, even a subtle change in their composition, symmetry, or local distortion can strongly influence their electrical, magnetic, and dielectric behaviour. Among them, perovskite oxides are especially important, as they have a flexible structure and can accommodate a large variety of cations, distortions, and defect chemistries.

The general formula for perovskite compounds is ABO_3 , or more broadly ABX_3 , where A and B are cations of differing sizes that occupy an octahedral site, and X is an anion, most commonly oxygen in oxide perovskites [2]. Structurally, perovskite oxides have a three-dimensional structure with B cations surrounded by regular octahedra of oxygen, while A cations have larger spaces between the octahedra, each surrounded by 12 oxygen atoms [3]. This unique structural arrangement allows a diversity of elemental substitutions, defects, and distortions, which explains why the perovskite family has wide chemical and physical diversity. The three-dimensional structure of a perovskite oxide is shown in Fig. 1.

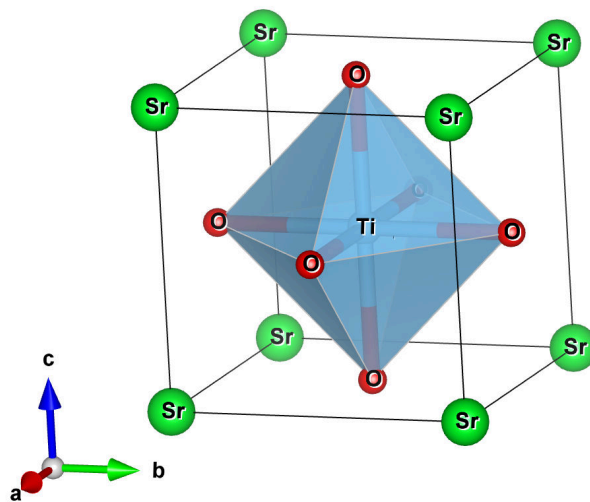


Figure 1: Cubic SrTiO₃ perovskite oxide structure

The scientific importance of complex oxides comes from the interaction between charge, spin, and lattice degrees of freedom, because these interactions are closely related, even a minute structural variation can cause drastic change in its electronic and

physical properties. Complex oxides can have a variety of ordered phases including ferroelectric, antiferroelectric, dielectric, superconducting, ferromagnetic, antiferromagnetic, ferrimagnetic, and multiferroic states. These states are all closely related to how flexible the structure is. This combination of structural tunability and competing ground states makes complex oxides a good platform for building and designing different materials with targeted functionalities.

In addition to their scientific importance, complex oxides are also very attractive from a technological point of view. They combine multifunctionality and chemical stability, which leads to intensive investigations into their use in electronics, sensors, magnetic devices, catalysis, thermoelectric systems, and solid oxide fuel cells. They exhibit electrical conductivity, ionic conductivity, mixed ionic–electronic conductivity, catalytic activity, and high thermal and chemical stability under demanding conditions, making them suitable for energy technologies.

Within this family of perovskite oxides, SrTiO_3 is a widely studied model perovskite oxide due to its structural simplicity and well-established role in perovskite oxide physics. It is a very suitable system for studying how structural modifications alter the properties and functionalities of other complex oxide systems [4].

1.2 Moiré Patterns in Complex Oxides

A moiré pattern is formed when two periodic lattices are superimposed and rotated with a small twist angle or a slight lattice mismatch. The overlapping lattices form a new interference pattern with a much larger length scale than the original lattice periodicity, as shown in Fig. 2.

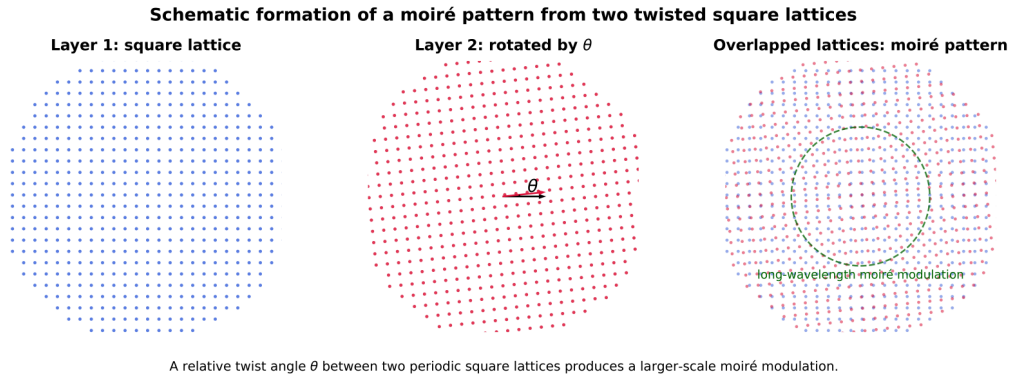


Figure 2: Schematic illustration of moiré-pattern formation when two periodic lattices are stacked with a relative twist angle θ .

Twisted SrTiO_3 bilayers contain alternating AA- and AB-stacking regions. AA stacking corresponds to Sr–Sr and TiO–TiO alignment between the layers, whereas AB stacking corresponds to Sr–TiO and TiO–Sr alignment. Their periodic arrangement forms the moiré superlattice [5]. In layered materials, this periodic structure results in a moiré superlattice. These patterns can either arise from the stacking of two layers of the same material, called **homo-moiré patterns** or from the stacking of two different materials, called **hetero-moiré patterns**. For homogeneous materials, the moiré superlattice relies heavily on the twist angle, while for heterostructures it is not only affected by the twist angle but also by the lattice mismatch [6]. This stacking not only changes the geometry of the structure but can also significantly modify the electronic and optical properties of

the materials by generating minibands, new Dirac points, and flat bands, especially at small twist angles. These flat bands can also enhance interactions and lead to correlated quantum behaviour [7]. This pattern locally modifies the materials and provides access to phenomena such as electronic band structures, unconventional superconductivity, correlated insulating states, moiré excitons, moiré phonons, and topologically nontrivial states. Through moiré engineering, we are able to control materials geometry and tune material properties without introducing any chemical modification or defects into the materials. This is a more controllable and cleaner method of tuning material properties [6].

The strongest experimental evidence for the power of moiré engineering has so far come from van der Waals materials, particularly in twisted bilayer graphene and transition-metal dichalcogenide heterostructures. In twisted bilayer graphene, even a small change in its twist angle can have a significant effect on its properties. The intrinsic band structure of graphene is not flat at low energies; in 2011, Bistritzer and Macdonald developed a low-energy continuum Hamiltonian model to investigate moiré bands in bilayer graphene. They found that the Fermi energy at the Dirac point is influenced by the twist angle. When the twist angle is close to 1.05° , the Fermi velocity is close to zero and it causes the moiré bands to flatten. This angle is called the magic angle. At this point the electrons significantly slow down and become localized in the moiré superlattice. This leads to enhanced electron-electron interactions and stronger correlation [6].

While most of the initial work on moiré superlattices has focused on van der Waals materials, this idea is important beyond the van der Waals systems because a moiré structure demonstrates a general idea that one can modulate material properties by controlling the relative alignment between the layers. This makes moiré superlattices promising platforms for designing materials with desired electronic, optical, and transport properties. In the case of complex oxides, recent advances in the synthesis of perovskites now allow monolayers to be achieved similar to van der Waals materials. This enables new opportunities to create artificial moiré structures based on the complex-oxides family. Moiré engineering provides a promising method for manipulating and exploring the materials' transport properties by controlling the stacking and twisting of the oxide layers. SrTiO_3 is a well-known complex perovskite oxide, exhibiting a variety of properties, including a high dielectric constant, superconductivity, and a flexible electronic structure. The properties of this material can be further fine-tuned by stacking the SrTiO_3 layers to form moiré superlattices. Its properties can be further tuned by controlling the alignment of the layers. This study mainly focuses on investigating the behaviour of these layers, specifically examining the effects of the twist angle on structural relaxation, polarization, chirality, and emergent ferroelectric phases at different locations.

1.3 Ferroelectricity in Perovskite Oxides

Ferroelectric materials are characterized by the presence of spontaneous electric polarization, which can be reversed by the application of an external electric field. This phenomenon arises from the absence of inversion symmetry in the crystal structure, which creates an emergent electric dipole moment. From a crystallographic perspective, ferroelectricity emerges when a polar material undergoes a phase transition from the higher-symmetry parent phase to a lower-symmetry polar phase, resulting in multiple equivalent polarization states [8]. The origin of ferroelectricity in perovskite oxides

has been extensively studied for many decades due to its importance in both fundamental physics and technological applications. Early theories explained the ferroelectric behaviour in terms of ionic size effects and electrostatic interactions within the crystal lattice, modern first-principles calculations have shown that the phenomenon is strongly connected to the electronic structure of the material. The ideal cubic perovskite phase is centrosymmetric, with the B-site cation located at the center of an oxygen octahedron. In this configuration, the crystal possesses no net dipole moment. As illustrated in Fig. 3, a ferroelectric state emerges when the B-site ion is displaced from its centrosymmetric position, generating a permanent electric polarization.

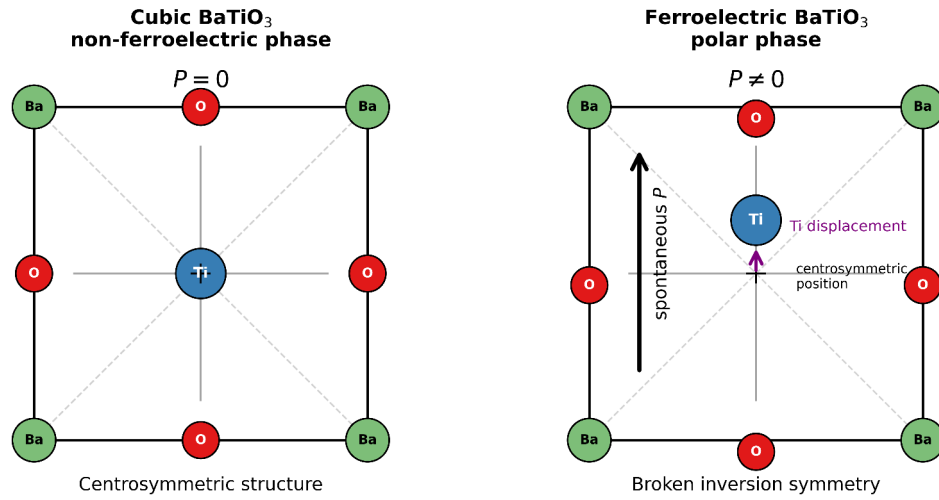


Figure 3: Schematic comparison between a cubic non-ferroelectric perovskite and a ferroelectric perovskite.

In compounds such as BaTiO₃ and PbTiO₃, this polarization is associated with the displacement of Ti ions relative to the surrounding oxygen framework. The energetic preference for the distorted phase originates from the covalent character of Ti–O bonding. Therefore, in Ti-based perovskite oxides ferroelectricity is mainly associated with strong hybridization between Ti 3d and O 2p electronic states. This orbital interaction stabilizes the distorted structure by lowering its energy and supports the displacement of a Ti ion from the center of an oxygen octahedron, leading to the non-centrosymmetric ferroelectric phase [9]. Consequently, ferroelectricity is now understood as a strong interaction between electronic bonding and crystal structure rather than a purely ionic effect.

In addition to conventional ferroelectricity, oxide systems can also exhibit improper ferroelectric phases, where polarization is not the primary driving source behind the phase transition; instead, spontaneous polarization emerges through the coupling between nonpolar lattice distortions. A notable example was demonstrated in oxide superlattices, where interactions between oxygen-octahedral rotation modes were shown to induce ferroelectricity [10]. This mechanism highlighted the importance of structural coupling, lattice distortions, and interface effects in determining the ferroic behaviour and stimulated extensive research on hybrid improper ferroelectricity in layered perovskites and oxide heterostructures. Among the perovskite oxides, SrTiO₃ is particularly important because it lies near a ferroelectric phase transition while remaining para-

electric in its bulk form under ambient conditions. The structure of SrTiO_3 is sensitive to external perturbations such as chemical substitution, strain, dimensional confinement, defects, or electric fields. This behaviour has led to its classification as a quantum paraelectric or incipient ferroelectric material [11]. The exceptional sensitivity of SrTiO_3 makes it an ideal model system for studying emergent polar phases in engineered oxides.

1.4 Chirality and Polar Topology in Moiré Oxides

The twist angle between two crystalline layers introduces chirality into the resulting moiré superlattice by breaking mirror symmetry and generating a structure with well-defined handedness. This adds a new degree of freedom. Depending on the direction of rotation, the sign of the twist angle determines whether the system has left handed or right handed configuration. The two structures are mirror images of each other but they cannot be superimposed such structures are termed as chiral because they lack mirror symmetry.

In moiré materials, chirality can influence a variety of physical properties by modifying local symmetry and atomic arrangements throughout the superlattice [12]. In moiré oxide systems, twisting generates spatially varying strain fields throughout the superlattice. The resulting strain gradients can couple to polarization through the flexoelectric effect (generation of electric polarization due to a strain gradient), resulting in the formation of local dipoles even in materials that are not ferroelectric in their bulk form. Consequently, twisting provides a mechanism for generating polar order via structural reconstruction even in materials that do not exhibit conventional ferroelectric behaviour.

Unlike conventional ferroelectrics, where polarization often remains uniform within each domain, the induced polarization within the moiré superlattice is typically nonuniform and forms complex spatial patterns known as polarization textures. A polarization texture describes the local arrangement or orientation of electric dipoles throughout a material. A moiré system has a continuously varying local stacking arrangement and therefore host highly nonuniform dipole configurations [12, 13]. These polarization textures can adopt a variety of topological forms, including vortices, antivortices, skyrmions, and related structures.

Among the most important polarization textures are polar vortices and polar skyrmions. Figure 4 provides a schematic illustration of polar vortex and skyrmion polarization textures. Polar vortices are defined by the continuous rotation of polarization vectors around the central core, producing a circulating dipole pattern. The clockwise and counterclockwise rotation of these dipoles give the vortex a local handedness, which directly links the polar textures to chirality. Vortex structures have been observed in oxide heterostructures and more recently in twisted oxide membranes, where they emerge naturally from moiré-induced strain and structural reconstruction [12].

An even more complex topological structure is polar skyrmion. In a polar skyrmion, the polarization vector rotates from the center towards the boundary. Skyrmions have nontrivial topological character, which makes them remarkably stable, and they have attracted considerable interest as potential information carriers for future nanoelectronic devices. Polar skyrmions, antiskyrmions, and related topological polarization states have been reported in a variety of oxide systems through both experimental and theoretical studies [13]. These discoveries highlight the growing importance of topological

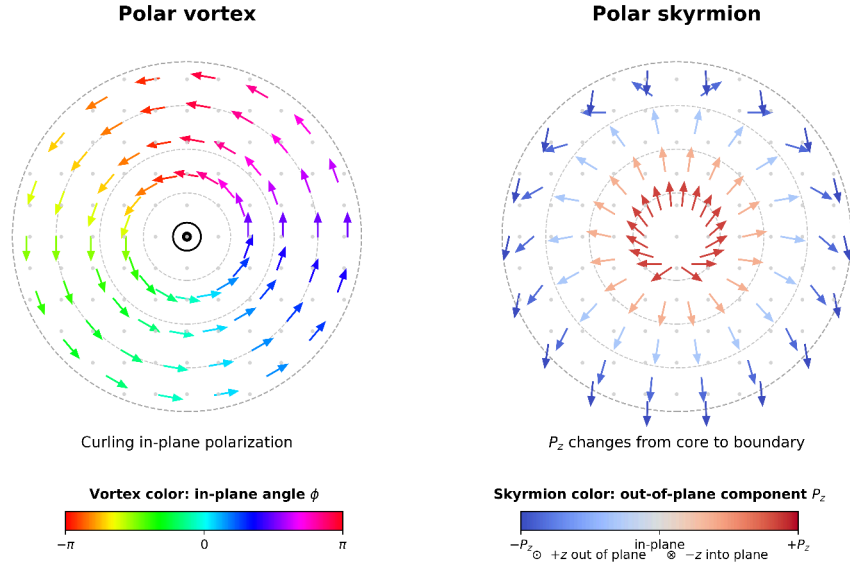


Figure 4: Schematic illustration of polar vortex and polar skyrmion polarization textures. In the polar vortex, the arrows represent a curling in-plane polarization field, and the color indicates the in-plane polarization angle ϕ . In the polar skyrmion, the arrows represent the local polarization direction, while the color indicates the out-of-plane polarization component P_z , changing from positive near the core to negative near the boundary through intermediate in-plane components.

ferroic states in modern condensed matter physics.

1.5 Motivation

The discovery of moiré-induced ferroelectricity in complex oxide systems has opened a new way to create polar and topological phases through structural control. Unlike conventional methods based on changing the chemical composition or applying an external electric field, moiré engineering allows the twist angle between two layers to play the role to serve as a tuning parameter. Twisting the layers alters the local stacking configuration and consequently modifies the material's properties. This makes twisted oxide bilayers an attractive platform for studying emergent polar and topological phases.

In this thesis, we focus on the structure of SrTiO_3 . It is particularly suitable for this study because it is an incipient ferroelectric material and is very sensitive to structural perturbations. Recent experimental studies on twisted SrTiO_3 membranes have demonstrated that even though bulk SrTiO_3 is not ferroelectric, twisting the bilayer structure is capable of inducing strain gradients, local dipoles, vortex-antivortex textures, and chiral polar structures through flexoelectric coupling [12]. Although previous studies have demonstrated that twisted SrTiO_3 can host strain-induced local dipoles and vortex-antivortex polar textures. However, a systematic understanding of how different moiré configurations lead to different electric phases is yet to be understood at the atomistic level. This thesis is motivated by the need to clarify in particular the connection between twist angle, structural relaxation, polarization, and chirality.

A brief overview of the methodology used in this work includes DFT-based calculations of SrTiO_3 structures to generate reference atomic configurations. Then, the DFT datasets were filtered and prepared for training machine-learning interatomic potentials based on Allegro/NequIP. The trained model was evaluated using the MAEs of the predicted energies and forces. Next, we constructed the layered and twisted SrTiO_3 moiré structures at different twist angles. LAMMPS was used to relax bulk, layered, and twisted SrTiO_3 structures. We analyzed the angle-dependent structural behaviour of the twisted SrTiO_3 bilayer and investigated the emergence of moiré ferroelectric phases.

This thesis comprises five chapters. Chapter 1 introduces complex perovskite compounds, moiré engineering, and the properties of materials that can be enhanced through the twisting of bilayer structures such as ferroelectricity, polarization textures, and chirality. This chapter also briefly explains the methodology used to carry out this work. In the following chapters, chapter 2 provides a detailed overview of the state of the art concerning the SrTiO_3 structure and its properties. Chapter 3 explains in detail the computational framework and the steps followed in this thesis, starting from DFT calculations to the final phase analysis of the resulting structures. Chapter 4 presents the results obtained using the machine-learning interatomic potential model and explains the phases of the twisted SrTiO_3 structures in detail. Finally, chapter 5 concludes this thesis, demonstrates the field-relevant significance of this work, and highlights future research directions.

2

Background

2.1 Structural and Ferroic Properties of Bulk SrTiO₃

2.1.1 Bulk Crystal Structure and Antiferrodistortive Transition

Although SrTiO₃ adopts a simple cubic perovskite structure under ambient conditions, it is highly sensitive to external perturbations and exhibits strong structural and dielectric responses. The high-temperature phase of SrTiO₃ has an ideal cubic perovskite structure with Sr at the A-site, Ti at the B-site, and oxygen atoms forming TiO₆ octahedra, as shown in Fig. 1. In the high-temperature paraelectric phase, SrTiO₃ crystallizes in the cubic perovskite structure with space group $Pm\bar{3}m$. The ideal cubic structure of SrTiO₃ contains a Ti atom positioned at the center of the oxygen octahedron, so the cubic phase is centrosymmetric and does not possess spontaneous polarization [14]. Therefore, polarity in SrTiO₃ can be understood in terms of two key structural distortions: the displacement of Ti from the centre of the oxygen octahedron and the rotation of the oxygen octahedra [15]. Previous studies have shown that the polar response of SrTiO₃ is closely related to the local Ti-O environment. A displacement of Ti away from the octahedral center breaks the symmetry and can generate a local dipole. Since Ti-O bonding involves both ionic displacement and electronic hybridization between the Ti 3d and O 2p states, structural changes in the octahedron can also modify the electronic charge distribution. This explains why small Ti-O distortions can have a significant effect on the polarization behaviour of SrTiO₃ [14, 15, 16, 17]. Upon cooling, SrTiO₃ undergoes a cubic-to-tetragonal structural transition near 105 K. This transition occurs in the SrTiO₃ structure because its TiO₆ octahedra slightly rotate around the *c*-axis. Adjacent octahedra rotate in opposite directions, producing an antiferrodistortive structure rather than a ferroelectric one. The resulting tetragonal distortion is very small, but it is significant because it reflects the instability of the cubic lattice toward rotational distortion [18, 14].

2.1.2 Surface, Interface, and Defect-Induced Polar Response

This sensitivity of the SrTiO₃ structure becomes clear when the surface, interfaces, and defects are considered. Near the surface, the behaviour of cubic-to-tetragonal transition deviates from the bulk SrTiO₃ structure because of local strain and boundary constraints. At interfaces, SrTiO₃ can develop polarization through cation-oxygen displacements and interface-induced dipoles. Similarly, the defects such as dislocation-induced strain gradients can produce local flexoelectric polarization. The effect of oxygen vacancies on the structural stability of SrTiO₃ has been investigated in both cubic and antiferrodistortive phases. These examples show that SrTiO₃ can become locally polar when its symmetry is broken by local structural conditions [19, 20, 21].

2.1.3 Oxygen Vacancies and Structural Stability

The effect of oxygen vacancies on the structural stability of SrTiO₃ has been investigated in both cubic and antiferrodistortive phases. Studies have shown that oxygen vacancies lower the relative stability of the antiferrodistortive phase with respect to the cubic phase, indicating that defect concentration can directly affect the phase behaviour of

SrTiO₃ [22]. Similarly, the study of oxygen-deficient SrTiO_{3-δ}, where δ represents the concentration of missing oxygen atoms or oxygen vacancies, found that these defects are energetically more stable at surfaces, interfaces, and phase boundaries than inside the ideal crystal. The study also showed that oxygen vacancies can introduce donor-like states within the bandgap, although the films generally remain wide-bandgap insulators [23]. These findings indicate that oxygen vacancies should not be treated only as isolated point defects only, because their effect depends strongly on local structure, spatial distribution, and boundary conditions.

2.1.4 Chemical Modification and Processing Effects

The same sensitivity is observed when SrTiO₃ is chemically modified, for example, through doping. Impurity substitution can induce ferroelectricity in SrTiO₃ based systems by introducing local off-centre displacements or elastic strain. In Ce-doped SrTiO₃, ferroelectric-like hysteresis has been observed, in contrast to the lossy paraelectric response of undoped SrTiO₃ [24]. In ceramic-SrTiO₃-based systems, the functional response is also strongly influenced by phase composition, annealing temperature, crystallinity, and structural ordering [25]. Donor doping and reductive processing can also modify the defect structure of SrTiO₃. Mixed donor doping in SrTiO₃ ceramics increases A-site deficiency and oxygen-vacancy-related defect states. This indicates that the functional response of SrTiO₃ can be tuned through non-stoichiometry, defect formation, and processing-induced local disorder [26]. Together, these studies show that local chemistry, defects, and processing history can strongly modify the ferroic response of SrTiO₃.

2.2 Reduced-Dimensional SrTiO₃ and Emergent Polar Behaviour

Another key feature of SrTiO₃ is its quantum paraelectric, or incipient ferroelectric, character. Although SrTiO₃ is close to a ferroelectric instability, pure bulk SrTiO₃ does not develop long-range ferroelectric order upon cooling. Instead, its dielectric response increases at low temperatures, whereas the formation of a stable ferroelectric phase is suppressed by quantum fluctuations [27, 28, 29]. Microscopically, this can be related to the zero-point motion (the small motion or vibration that atoms still have even at 0 K) of Ti ions, which is larger than the Ti off-center displacement needed to stabilize the ferroelectric state. Therefore, SrTiO₃ remains paraelectric even though it is very close to a polar instability [14, 29]. However, in reduced-dimensional systems, surfaces, interfaces, strain, defect redistribution, and electrical boundary conditions become more important than in the bulk [30, 31]. Therefore, reduced-dimensional SrTiO₃ provides an important platform for understanding how polar behaviour can emerge from a material that is centrosymmetric and paraelectric in its ideal bulk form. Ferroelectric size effects are not controlled by the size alone, they are also strongly influenced by boundary conditions such as competition between polarization, depolarization fields, screening, defects, and domain formation. In ultrathin ferroelectric systems, the stability of the polar state can be reduced by depolarization fields caused by imperfect screening. Additionally, extrinsic factors such as oxygen vacancies, dead layers, and interface quality can strongly change the measured response [30].

Strain is one of the main mechanisms for modifying the polar instability of SrTiO₃. Thickness and strain act together in ultrathin SrTiO₃ films, where thinner strained films show ferroelectric-like behaviour at room temperature. Biaxial strain can shift SrTiO₃ away from its quantum paraelectric ground state and toward ferroelectric phases [31, 32]. Reduced dimensionality can also stabilize local polar nanoregions. Strain-free ultra-

thin SrTiO_3 films can exhibit room-temperature ferroelectricity when polar nanoregions associated with local Sr deficiency become stabilized and aligned at nanometer thicknesses [33]. In nanosized SrTiO_3 , particle-size effects suppress the dielectric response, while intrinsic tensile strain can drive Ti off-centering and form ultrafine 90° ferroelectric nanodomains [34, 35]. Reduced dimensionality does not automatically lead to ferroelectricity in SrTiO_3 ; some thin film remain paraelectric. This behaviour shows that crystallinity, microstructure, strain state, and interface quality also play important roles [36]. Therefore, reduced-dimensional system can be considered a locally sensitive systems, where strain, defects, interfaces, and boundary conditions can create responses that do not appear in the bulk SrTiO_3 system. This idea is directly relevant to moiré SrTiO_3 , where spatial variations in stacking and strain may create local conditions for stabilizing nonuniform polar states.

2.3 Layered and Twisted Bilayer SrTiO_3 Structures

The reduced-dimensional sensitivity of SrTiO_3 provides an important basis for understanding its structural and polar response in layered and twisted bilayer structures. When two SrTiO_3 layers are stacked, the interface creates local atomic environments that are absent in the bulk crystal. When the two layers are rotated relative to each other, the local atomic arrangement at the interface changes periodically, producing a moiré superlattice. Therefore, twisted SrTiO_3 layers are considered an interface-coupled system in which local atomic registry, strain, and the interlayer interaction vary spatially.

The early experimental demonstration of moiré-pattern formation in twisted SrTiO_3 was reported by Shen et al. They demonstrated that twisted SrTiO_3 nanomembranes can produce observable moiré patterns, confirming that oxide moiré structures are possible beyond van der Waals materials [37]. More recent studies have also shown that these moiré structures can produce real interfacial reconstruction. Twisted SrTiO_3 bilayers develop opposite shear strain patterns in the upper and lower layers near the interface, showing that the moiré pattern is accompanied by atomic-scale strain modulation [5].

A key mechanism for polar behaviour in twisted SrTiO_3 is flexoelectricity. This is important for SrTiO_3 . Since ideal bulk SrTiO_3 is centrosymmetric and paraelectric, the appearance of polar behaviour in twisted SrTiO_3 requires a mechanism that can break local inversion symmetry. Flexoelectricity provides such a mechanism, because it allows strain gradients to induce polarization even in centrosymmetric crystals. Several studies support the flexoelectric behaviour of SrTiO_3 . Large strain gradients near nanorack tips have been shown to induce reversible flexoelectric polarization in SrTiO_3 [38]. Dislocation engineering has also been shown to enhance the flexoelectric response of single-crystal SrTiO_3 [39]. In addition, wrinkle-induced strain gradients have been used to create ordered polar patterns in nonpolar SrTiO_3 nanofilms [40]. These results show that SrTiO_3 can develop polar responses when its local strain field becomes nonuniform.

This idea has now been extended directly to twisted SrTiO_3 structures. The strongest experimental evidence for emergent polar topology in twisted SrTiO_3 comes from the observation of polar vortex arrays in twisted bilayers of paraelectric SrTiO_3 [41]. Multislice electron ptychography allowed the upper and lower layers to be reconstructed separately, making it possible to observe polar displacement patterns through the thickness of the bilayer. The important result is that polar vortices appear only in the twisted bilayer region and not in the individual-layer regions. This indicates that the vortex

state is generated by interlayer coupling and moiré-related structural effects. Another study provided a more direct link between the polar vortex pattern and flexoelectricity, demonstrating that in twisted SrTiO_3 membranes the moiré structure produces a spatially nonuniform shear-strain field. The strain gradients associated with this modulation induce polar vortices and antivortices through the flexoelectric effect [12]. Another particularly significant phenomenon is the reversal of vortex handedness with the twist direction; this is important because it confirms that the polar texture is governed by the chirality of the twisted bilayer. Similar behaviour has also been observed in clean twisted SrTiO_3 moiré superlattices, where interfacial strain gradients generate alternating clockwise and counterclockwise polar vortices [5]. Theoretical studies further support this mechanism. Elastic-theory and phase-field simulations show that twisted stacking produces a periodic displacement field and strain gradient pattern. Through flexoelectric coupling, these strain gradients induce rotating polarization textures, leading to moiré polar vortices. The stability of these vortices results from a balance between lattice deformation energy, flexoelectric coupling, and the energy cost of spatially varying polarization [42]. This agrees with the broader framework of polar topological phases in oxide nanostructures, where vortices and skyrmions come from competing electrostatic, elastic, and gradient energies under nanoscale boundary conditions [43].

In addition to polar vortices, twisted SrTiO_3 has also been predicted to host more complex polar and electronic states. First-principles calculations have shown that twisting two centrosymmetric SrTiO_3 monolayers can create ferroelectricity and an ultrahigh-density polar skyrmion lattice. The emergent polarization originates from strong interlayer coupling, local charge redistribution, and twist-induced ionic displacements that break local centrosymmetry [13]. Related theoretical work further predicts vortex-antivortex polar textures, charge modulation, flat bands, and possible hole-doping-induced d^0 magnetism in twisted SrTiO_3 bilayers [41]. Overall, these studies show that twisted bilayer SrTiO_3 is a highly tunable moiré system. Local stacking, strain gradients, interfacial reconstruction, and atomic registry can generate polar vortices, polar skyrmions, charge modulation, and flat electronic bands. This directly supports the central idea of this thesis: moiré-induced structural modulation can activate emergent ferroelectric and topological polar phases in SrTiO_3 , even though bulk SrTiO_3 is centrosymmetric and paraelectric.

Methodology

3.1 DFT Calculations

The first computational method used in this thesis was density functional theory (DFT). The purpose of using DFT is to perform highly accurate calculations on SrTiO_3 that enable us to create a reliable dataset to later train a machine-learning interatomic potential that can be used to obtain relaxations of the atomic positions in the moiré structures. Figure 5 illustrates the computational workflow followed in this work.

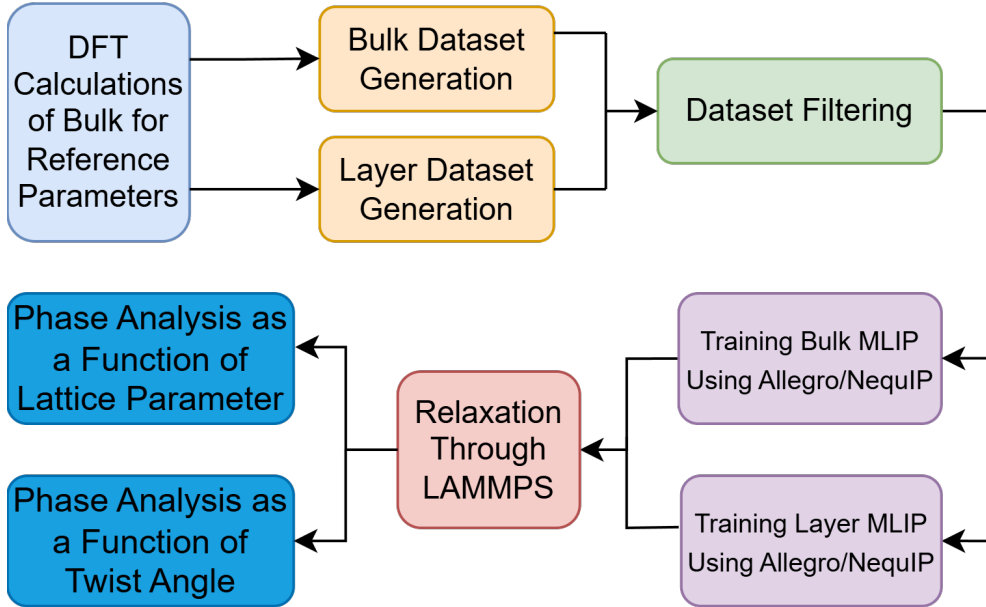


Figure 5: Computational workflow used for the investigation of the phases of twisted SrTiO_3 moiré structures.

While DFT is an accurate level of theory, it is computationally limited to the analysis of structures that have a smaller number of atoms. Since moiré structures contain a huge number of atoms, our goal is to derive an interatomic potential to tackle the problem.

DFT is a widely used method in computational materials science studies, since it allows us to calculate the material properties from the electronic ground state. In DFT, the many-body problem is solved by taking the electron density instead of solving the full many-body electron wave function directly. This makes the calculations feasible for crystalline solids and complex materials [44, 45]. Electronic structure methods are commonly used to predict equilibrium structures, atomic forces, stresses, phonons, and other material properties from a first-principles description of electrons and nuclei [46].

The theoretical basis of DFT is connected to the Hohenberg–Kohn theorem and the Kohn–Sham formulation. In the Hohenberg–Kohn framework, the ground-state electron density contains all the information needed to determine the ground-state properties of the system. All the ground-state properties can be expressed as a functional

of the ground-state electron density. However, this theoretical result alone is not sufficient for practical calculations. The Kohn-Sham makes DFT computationally practical by replacing the many-electron problem with an auxiliary noninteracting system. The effect of electron exchange and correlation is then included through an exchange–correlation functional. This formulation is widely used in modern electronic-structure calculations of atoms, molecules, solids, and condensed–matter systems [45]. In this work, the DFT calculations were performed within the Born–Oppenheimer approximation. In this approximation, the motion of electrons and nuclei is separated because nuclei are much heavier and move more slowly. Therefore, for each fixed atomic configuration, the electronic ground state is solved first, and the total energy is treated as a function of the atomic positions. The atomic forces are then obtained from the first derivative of the total energy with respect to the atomic coordinates. The determination of these forces is essential for structure relaxation, dataset generation and molecular dynamics simulations.

As the exact exchange–correlation energy is not known, practical DFT calculations require an approximation for the exchange–correlation functional. Therefore, the DFT calculations require approximations such as the local density approximation (LDA), generalized gradient approximation (GGA), meta-GGA functionals, or hybrid functionals. Schleder et al. emphasize that, although DFT is formally exact, practical DFT calculations require approximations related to the treatment of core–valence electrons, exchange–correlation functionals, and basis representation [47]. Therefore, in this thesis, we will use the GGA approximation in the PBE scheme, which has been previously reported to provide good structural description of SrTiO_3 [48].

The DFT calculations in this thesis were performed using Quantum ESPRESSO. It is open-source software developed for first-principles calculations of condensed-matter systems. The package is based on density functional theory and uses a plane-waves basis set together with pseudopotentials to describe the electronic ground states, making it suitable for periodic crystalline structures such as SrTiO_3 . The code supports a wide range of ab initio calculations, including total-energy calculations, structural relaxation, phonon calculations, elastic-property evaluation, and molecular dynamics [49]. In this work, the Plane-Wave Self-Consistent field code, Plane-Wave Self-Consistent Field (PWscf), was used as the main computational engine. PWscf solves the Kohn–Sham equations within the plane-wave pseudopotential framework and provides access to key quantities such as ground-state energies, Kohn–Sham orbitals, atomic forces, and stresses. These capabilities were essential for optimizing the SrTiO_3 structures and evaluating their structural stability [50]. For each SrTiO_3 -based configuration, the Quantum ESPRESSO input files contained information about atomic species, atomic positions, simulation cell, kinetic energy cutoff, and k -point mesh. The next step is to use these input files to obtain the output files for DFT reference data calculations.

In our work, before generating the final set of DFT reference calculations, we performed convergence tests to determine a reliable set of computational parameters. The convergence behaviour was examined using plane-wave cutoff energy (E_{cut}) and Brillouin-zone sampling (K -mesh). The plane wave cutoff energy determines the maximum kinetic energy of the plane waves included in the basis set. This plane-wave cutoff energy controls the completeness of plane wave basis set, whereas the k -point mesh controls the sampling of the Brillouin zone. These parameters determine the accuracy. If they are too small, the calculated energy, forces, and pressure or stress may not be accu-

rate. If they are too large, the calculations become unnecessarily expensive. Therefore, we needed to perform the convergence tests to find a balance between accuracy and computational cost. The convergence tests were systematically performed by changing the cut-off energy and k -point mesh and comparing the resulting energy, forces, and pressure. The total energy differences with respect to the reference energy, which corresponds to the highest cut-off energy and densest k -point mesh, were used to evaluate the energy convergence. Similarly, forces difference was also evaluated to check the forces stability. Pressure or stress convergence was also considered because stress is directly related to the mechanical response and lattice stability.

After selecting the converged DFT parameters, we performed calculations for our SrTiO_3 configurations. These calculations included bulk SrTiO_3 structures and distorted structures in which lattice parameters and atomic positions were perturbed. These distorted configurations helped us understand how energy, forces, and stress change when the atoms move away from their equilibrium position. This is important because real atomic systems are not limited to a single ideal structure. Their properties depend on how the potential energy surfaces respond to atomic displacements, lattice perturbation, stress, and forces. These distortions are directly related to the concepts of lattice dynamics because the lattice perturbation affect the atomic vibrations. These changes influence the phonon behaviour and modify the total energy of the system. The forces are obtained from the first derivative of the energy, this means that this distortion also affects the forces in the system. Even though this subsection focuses only on the DFT-calculations only, accurate DFT-calculated forces are very important because they explain how atoms respond to structural perturbations.

The final outputs from the DFT calculations were atomic forces, energy, pressure, stresses, atomic coordinates, and cell parameters. These quantities collectively describe the SrTiO_3 structure from a first-principles point of view. The DFT stage is very important. It provides the physical and numerical foundation for the later computational steps. It helps us to identify reliable computational parameters for larger SrTiO_3 structures through convergence testing of energy, forces, and pressures for a smaller system.

3.2 Dataset Generation and Filtering

After we selected the converged DFT parameters, the next step is to generate the reference dataset for the SrTiO_3 structure. A series of configurations were obtained by applying controlled perturbation to the in-plane lattice parameter a , the out-of-plane lattice parameter c , and the atomic positions as shown in Fig. 6.

The aim of this step was to create a diverse set of atomic configurations that included both equilibrium and non-equilibrium structures. This is important for representing real atomic systems because real systems are not limited only to ideal structures, especially when thermal vibrations, strains, or structural distortions are present. Therefore, we included distorted configurations to understand the phonon behaviour and how the system responds to lattice perturbations. The initial dataset was generated from the bulk SrTiO_3 structure, which provides the fundamental perovskite reference structure. We started from the relaxed geometry and applied controlled lattice and atomic perturbation to the system. Atomic displacements helped us to sample local deviations from the equilibrium positions, while lattice perturbations represented different strain states and helped build the dataset. These distortions are important for describing lat-

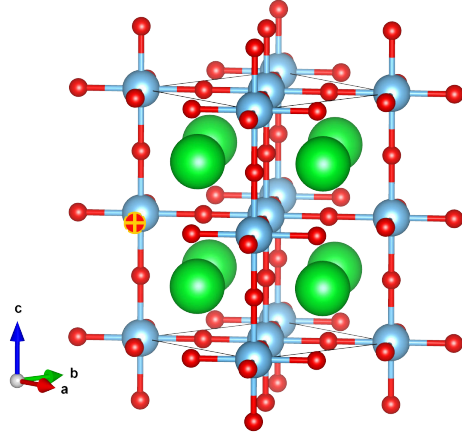


Figure 6: Bulk structure to which lattice and atomic perturbations were applied.

tice dynamics and how thermal properties of the system change when lattice and atomic perturbations were introduced.

After we generated the configurations, DFT calculations were performed to obtain the corresponding total energies, atomic forces, and stress values. These quantities describe how the system responds to the applied structural distortions. However, not all configurations are physically meaningful. Some randomized configurations may contain atoms too close to each other, highly distorted cells, very large forces, or unrealistic stress values. Therefore, we filtered out unrealistic and nonphysical configurations from our dataset. The filtering was done on the basis of energies, forces, and pressure criteria. The structures with extremely high energies were removed because they may represent severe atomic overlap or excessive distortions. Pressure or stress-based filtering was also performed by removing configurations with unrealistic lattice distortions. This filtering step helped improve the dataset by keeping only physically meaningful SrTiO_3 configurations.

In addition to the bulk SrTiO_3 distorted structures, the layered and twisted bilayered structures were also considered. At DFT level we did not perform calculations directly on twisted bilayers, instead, we used the layered structure shown in Fig. 7.

We performed calculations on layered structures in which stacking configuration was randomly modified. In this way, we locally modelled different stacking regions that appear in the large twisted systems. The layered systems are more important because they introduce interface effects and local environments that do not exist in a simple bulk structure. Twisted structures are also very important for moiré systems because the relative rotation between the two layers can produce local long-ranged moiré-type structural modulations. The layered and twisted bilayer structures are more complex and larger than the bulk SrTiO_3 system and are therefore important for explaining the structural complexity of layered oxide systems.

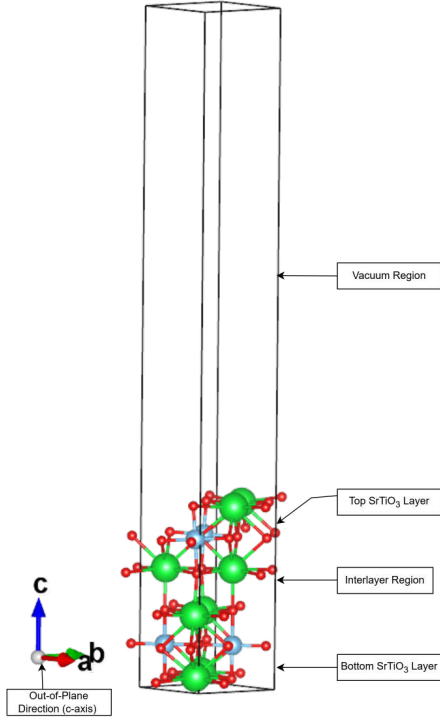


Figure 7: Layered system having stacking of two layers of SrTiO_3

3.3 Machine-Learning Interatomic Potential Training

After dataset generation and filtering, the remaining physically meaningful SrTiO_3 -based configurations were stored in extended XYZ (.extxyz) format. We used this file format because it can save not only the atomic species and atomic coordinates, but also additional information required for machine-learning interatomic potential training. These additional quantities include DFT-calculated total energies, interatomic forces, stress, and simulation cell parameters. Hence, each configuration in the final dataset contains both the atomic structure and the corresponding first-principle reference quantities.

The machine-learning interatomic potential was trained on the final dataset to reproduce the DFT reference data. The motivation for using a machine-learning interatomic potential was that DFT calculations are accurate, but they are computationally expensive for larger systems and longer simulation times. This limitation becomes particularly important because twisted bilayer SrTiO_3 structures requires larger supercells. A machine-learning interatomic potential provides a practical solution by learning the relationship between atomic configurations and DFT-calculated quantities such as total energy and atomic forces. Schleder et al. described this workflow as a progression from DFT-based calculation towards modern machine-learning methods that can extract patterns from simulation data and accelerate materials modeling [47].

In this thesis, the dataset consists of filtered SrTiO_3 structures stored in .extxyz format. We split the data into training and validation subsets with 80% in training subset and 20% in validation subset. The training set was used to optimize the parameters of the machine-learning model, while the validation set was used to monitor model performance on structures that were not directly used for fitting. This separation is

very important. It helps us to check whether the model is learning the relationships between the structure and their DFT properties or only memorizing the training configurations. The standard machine-learning workflow in materials science includes data collection, preprocessing, splitting into training, validation, and test sets, model training, and model evaluation [47].

The machine-learning interatomic potential model was trained using an allegro/NequIP-type equivariant neural network model. These models are designed for atomistic systems and use the local atomic environment to predict the total energy and forces of a structure. Atomic systems are governed by geometric symmetries such as translation, rotation, and inversion, and equivariant neural networks are designed to respect these transformations [51]. This is important because the model must provide both accurate energies and physically consistent forces for later atomic relaxation and molecular dynamics. Since phonon behaviour is strongly connected to lattice vibrations, an accurate description of forces is very important for later thermal transport studies. Allegro/NequIP are based on equivariant representations, meaning they respect the symmetry of the system. Scalar quantities such as total energy remain unchanged under translation and rotation, while the force vectors transform consistently when the system is rotated or translated. This symmetry-aware design is important because the predicted physical properties should not be affected by arbitrary orientations of the structure in space. Allegro was introduced as a strictly local equivariant neural network potential capable of predicting accurate atomic energies and forces while maintaining scalability to simulation of larger systems [51].

The trained Allegro model was tested using a validation dataset that was not directly used during fitting. The validation errors in forces and energies were monitored to check whether the model could reproduce the DFT reference quantities correctly. The energy and force errors decreased gradually and reached stable low values, meaning the model learned the force response of the structure. Similarly, the energy error decreased sharply in the early stages of training and remained within a low range afterward. A small variation in the energy error at later epochs (complete passes through the training dataset) is expected because the model is simultaneously learning the energy and force information. The mean absolute error used to measure the differences between the DFT reference values and values predicted by machine-learning interatomic potential. The energy MAE was evaluated in eV/atom, while the force MAE was measured in eV/Å. These metrics are commonly used to assess the performance of the MLIP [51].

3.4 Structure Relaxation and LAMMPS Simulations

After training and validating the MLIP model, LAMMPS was used for structural relaxations and molecular dynamics simulations. LAMMPS stands for Large-scale Atomic/Molecular Massively Parallel Simulator. It is a classical molecular dynamics code used for modelling interacting particles in solids, liquids, and gaseous systems. LAMMPS can model many different kinds of polymeric, biological, solid-state (metals, ceramics, oxides), granular, coarse-grained, or macroscopic systems using different interatomic potentials and boundary conditions. It can also handle two-dimensional and three-dimensional systems ranging from only a few particles up to billions of particles [52]. Molecular dynamics simulations track the motion of atoms and molecules by calculating the forces acting on the atoms and integrating the equations of motion over time. Gowthaman

explained molecular dynamics as a computational method for investigating the movement, deformation, interaction, and structural behaviour of atoms and molecules. The same review explained that LAMMPS is used to simulate and analyse the atomic and molecular movement and it is widely used in materials science, chemistry, polymers, semiconductors, and related fields [53].

In the present work, LAMMPS was used after DFT and MLIP modelling. The DFT calculations provided the accurate reference data on energies, forces, pressures or stress acting on the system. After the DFT calculations, these reference data were used to train an Allegro/NequIP machine-learning interatomic potential. After training, the MLIP provided the predicted energies and atomic forces. The system was then allowed to relax to the ground state using LAMMPS with the trained MLIP and applying molecular dynamics simulations to update the atomic positions. This workflow allows larger SrTiO_3 -based structures to be treated at a much lower computational cost than direct DFT. LAMMPS is suitable for this stage because it integrates Newton's equation of motion for large-scale interacting particles and uses neighbor lists to track the nearby particles, improving the computational efficiency for short-range interactions. LAMMPS also supports computing using spatial decomposition with MPI parallelization, in which the simulation domain is divided into subdomains assigned to different processors.

For the relaxation stage, LAMMPS was used to minimize the energy of the SrTiO_3 structure using the trained interatomic potential. During the relaxation process, the atoms were allowed to move to more stable configurations by reducing the total energy and atomic forces. This step is important because the starting bulk or twisted bilayer structures may not initially be in mechanical equilibrium. The relaxation process helps to obtain stable or metastable configurations prior to further analysis.

For the bulk phase analysis, a series of initial SrTiO_3 configurations were generated from the reference $\sqrt{2} \times \sqrt{2} \times \sqrt{2}$ cubic structure by systematically varying the lattice parameters a and c , while keeping $a = b$. For each selected pair of a and c , the structure was adapted to the new cell parameters by scaling the atomic positions accordingly. A small random perturbation was then applied to the atomic positions to allow possible symmetry-breaking distortions during relaxation. Each generated configuration was written in both VASP and LAMMPS data formats, and a corresponding LAMMPS input file was automatically created. In each LAMMPS input file, the trained Allegro interatomic potential was specified using the `pair_style allegro` and `pair_coeff` commands. The model file `allegro_bulk_SrTiO3.NequIP.pt2` was used as the potential for interaction among Sr, Ti, and O atoms during relaxation. The structures were then minimized in LAMMPS, and the final relaxed configurations and energies were extracted for phase identification and further structural analysis.

Thus, LAMMPS provides the simulation framework required to apply the trained MLIP to SrTiO_3 -based structures. By using the potential energy surface learned from DFT data, LAMMPS enables efficient structural relaxation and finite-temperature atomistic simulations of larger systems.

3.4.1 Mathematical Characterization of Polarization, Bound Charge, Polar Vortices, and Skyrmion-like Textures

To investigate the emergence of polar topological textures in twisted SrTiO_3 bilayers, the first step is to describe the local polarization field. The polarization is treated as a vector quantity. The local polarization vector at position $\mathbf{r}$ is written as

$$\mathbf{P}(\mathbf{r}) = (P_x, P_y, P_z), \quad (3.1)$$

where P_x , P_y , and P_z are the Cartesian components of the polarization. In an atomistic description, the local polarization can be evaluated from the displacement of ions relative to a nonpolar reference structure using a Born-effective-charge-based expression,

$$\mathbf{p}_i = \frac{e}{\Omega_i} \sum_j w_j Z_j^* \Delta \mathbf{u}_j. \quad (3.2)$$

Here, $\mathbf{p}_i$ is the local polarization of unit cell i , e is the elementary charge, Ω_i is the local unit-cell volume, w_j is the weighting factor assigned to atom j , Z_j^* is the isotropic Born effective charge assigned to atom j , and $\Delta \mathbf{u}_j$ is its displacement from the reference paraelectric configuration. This formulation relates local polar order to the separation between positive and negative charge centers caused by twist-induced ionic displacements. In SrTiO_3 , such local polar distortions are associated with relative displacements between Ti, Sr, and O sublattices, which can break local centrosymmetry in the moiré supercell [13].

After obtaining the polarization field, the electrical bound charge associated with the polarization field can be calculated using divergence of polarization.

$$\rho_b = -\nabla \cdot \mathbf{P}. \quad (3.3)$$

For a three-dimensional polarization field this can be written as,

$$\nabla \cdot \mathbf{P} = \frac{\partial P_x}{\partial x} + \frac{\partial P_y}{\partial y} + \frac{\partial P_z}{\partial z}. \quad (3.4)$$

For an in-plane polarization field,

$$\nabla_{\parallel} \cdot \mathbf{P}_{\parallel} = \frac{\partial P_x}{\partial x} + \frac{\partial P_y}{\partial y}. \quad (3.5)$$

The divergence describes the behaviour of polarization field, it describes whether the polarization field behaves as a source or a sink. If the divergence is positive, the polarization vectors spread outward, it corresponds to source-like polar configuration, whereas negative divergence corresponds to an inward or sink-like configuration. Therefore, divergence is useful for identifying the charge related polar features or convergent and divergent polar textures and for connecting the polarization field to the spatial distribution of bound charge.

Polar vortices were identified using the curl of the polarization field. For an in-plane polarization field,

$$\mathbf{P}_{\parallel} = (P_x, P_y), \quad (3.6)$$

the out-of-plane vorticity is,

$$\omega_z^P = (\nabla \times \mathbf{P})_z = \frac{\partial P_y}{\partial x} - \frac{\partial P_x}{\partial y}. \quad (3.7)$$

This equation measures the local rotation of the polarization vectors. A non-zero value of ω_z^P indicates local rotation of the polarization field. A positive or negative

value of ω_z^P distinguishes opposite circulation directions, corresponding to clockwise and counterclockwise polar vortices.

The same idea can also be applied to the lattice displacement field, if the in-plane displacement is,

$$\mathbf{u} = (u, v), \quad (3.8)$$

then, the displacement vorticity is,

$$\omega_z^u = (\nabla \times \mathbf{u})_z = \frac{\partial v}{\partial x} - \frac{\partial u}{\partial y}. \quad (3.9)$$

Comparison between ω_z^u and ω_z^P shows that whether the rotation of atomic lattice is coupled with the rotation of polarization field in the moiré supercell. This is important because moiré polar vortices in twisted SrTiO₃ have been related to periodic displacement vorticity and flexoelectrically induced polarization produced by twist-generated strain gradients [42].

To identify skyrmion-like textures, the polarization vector must first be normalized:

$$\hat{\mathbf{P}}(\mathbf{r}) = \frac{\mathbf{P}(\mathbf{r})}{|\mathbf{P}(\mathbf{r})|}. \quad (3.10)$$

The skyrmion topological charge, or skyrmion number, was then calculated as

$$N_{\text{sk}} = \frac{1}{4\pi} \iint \hat{\mathbf{P}} \cdot \left(\frac{\partial \hat{\mathbf{P}}}{\partial x} \times \frac{\partial \hat{\mathbf{P}}}{\partial y} \right) dx dy. \quad (3.11)$$

The corresponding local topological charge density is

$$q(x, y) = \frac{1}{4\pi} \hat{\mathbf{P}} \cdot \left(\frac{\partial \hat{\mathbf{P}}}{\partial x} \times \frac{\partial \hat{\mathbf{P}}}{\partial y} \right), \quad (3.12)$$

so that

$$N_{\text{sk}} = \iint q(x, y) dx dy. \quad (3.13)$$

The skyrmion number tells whether the polarization texture is topologically nontrivial. A value close to +1 or -1 indicates a skyrmion-like texture, while a value close to zero usually indicates a trivial texture or cancellation of opposite topological contributions.

Therefore, divergence, curl, and skyrmion number describe different aspects of the polar texture. Divergence is related to bound charge, curl identifies vortex rotation, and the skyrmion number confirms whether the full polarization texture has skyrmion-like topology.

3.5 Phase and Structural Analysis

After the structural relaxation of bulk, layered, and twisted SrTiO₃ configurations, an analysis of the phase and structure was performed to identify how the local geometry changes under different structural conditions. The purpose of this analysis was to compare the relaxed atomic configurations and investigate whether after the relaxation, the system remains close to the reference centrosymmetric configuration or develops local distortions associated with polar or ferroelectric-like behaviour. For the bulk structure, the phase character was examined from the relaxed lattice parameters, tetragonal

distortion, and Ti displacement relative to the center of the surrounding oxygen octahedron. For the layered and twisted structures, the same local structural descriptors were evaluated along selected paths across the moiré cell. These paths passed through different local stacking regions and allowed the variation of structural phase character to be followed as a function of position and twist angle.

In summary, this chapter presented the computational workflow used in this thesis. First, we discussed the convergence of the DFT parameters to confirm the reliability of the reference calculations. The resulting SrTiO_3 datasets were then summarized and the trained machine-learning interatomic potentials were validated in terms of energy and force errors. Based on this validation, the relaxed bulk, layered, and twisted SrTiO_3 structures were studied. The twist-angle-dependent phase behaviour was explored by means of structural descriptors, local polarization fields, divergence, curl, and skyrmion-like topological charge. Based on this implementation, the next chapter provides a detailed analysis of the results.

Results and Discussion

4.1 Results for Bulk SrTiO_3

4.1.1 DFT Convergence Test Results

The convergence test results helped us determine the reliable parameters of plane-wave energy cutoff and k -point mesh.

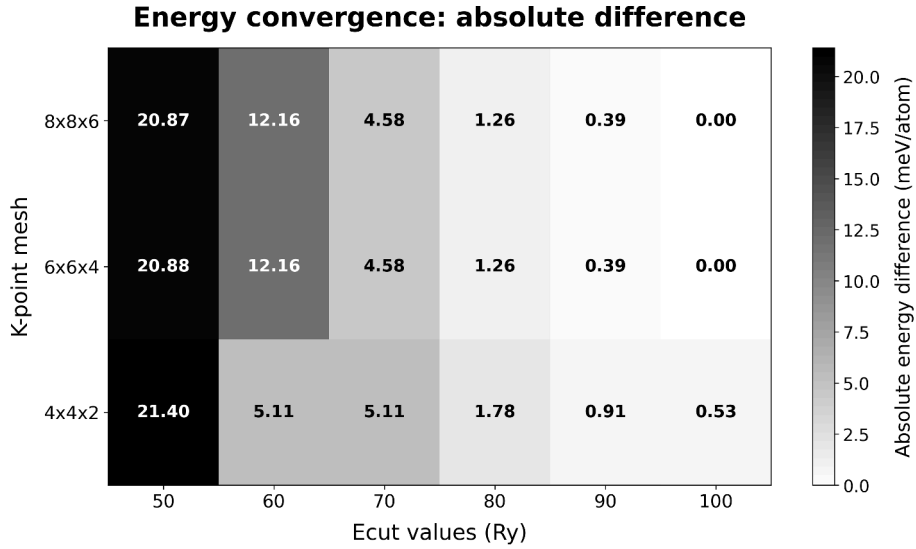


Figure 8: Convergence analysis of energy with respect to cutoff energy and k -point mesh.

The convergence of the total energy was analyzed as a function of plane-wave cutoff energy and the k -point mesh. The highest cutoff energy 100 Ry and the densest k -point mesh of $8 \times 8 \times 6$ were taken as the reference. As expected, the difference in energy with respect to the reference energy decreases when either the cutoff energy or the k -point mesh density increases. The largest deviation is seen at the lowest cutoff energy and coarsest k -point mesh, especially at 50 Ry, while this difference becomes smaller as the cutoff energy values increases. The comparison between different k -point meshes shows that the $6 \times 6 \times 4$ and $8 \times 8 \times 6$ meshes give nearly identical convergence behaviour. This indicates that increasing the k -point mesh beyond $6 \times 6 \times 4$ does not significantly change the total energy. Therefore, the $6 \times 6 \times 4$ k -point mesh provides a good balance between numerical accuracy and computational cost. Based on this convergence test, a cutoff energy of 100 Ry together with the $6 \times 6 \times 4$ k -point mesh was considered suitable for the DFT reference calculations.

Forces and pressure parameters were also checked. The observed convergence confirmed that this combination of cutoff energy and k -point mesh is also suitable for structural relaxation and the evaluation of mechanical stress in the system.

At the same time, the selected parameter combination was considerably less computationally expensive than the reference calculation¹⁰. As shown in the following time grid, the computational time was reduced from 32.22 min to 9.86 min compared with the reference case.

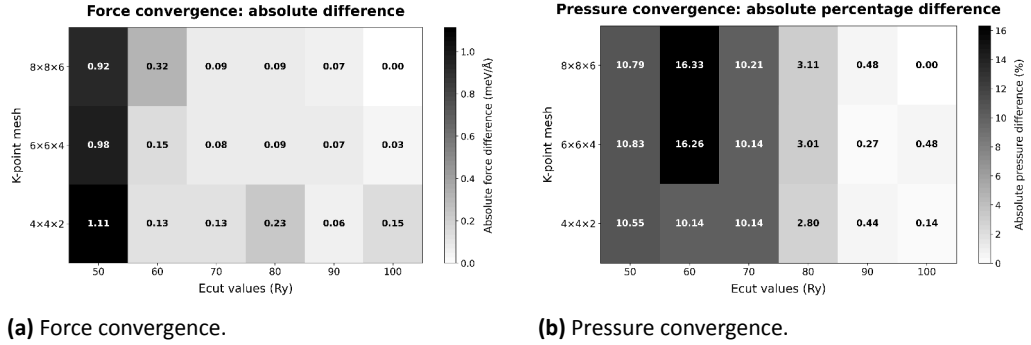


Figure 9: Convergence analysis of force and pressure with respect to cutoff energy and k -point mesh.

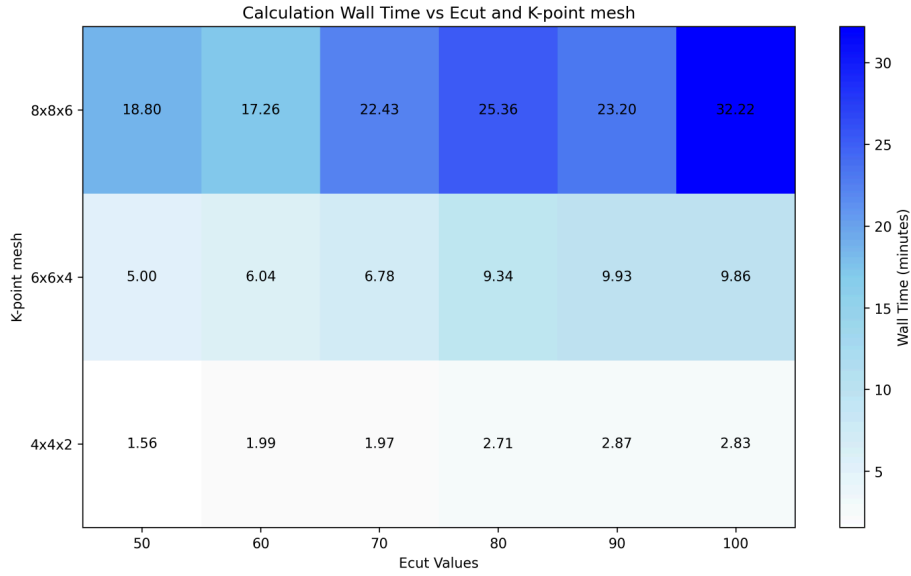


Figure 10: Wall time grid obtained for different combinations of cutoff energy and k -point mesh.

This reduction is important because the DFT reference dataset requires calculations for a large number of SrTiO_3 configurations. Consequently, even a moderate decrease in the computational cost of each calculation can substantially reduce the total time required for dataset generation. The small deviations in energy, forces, and pressure relative to the reference values indicate that this improvement in computational efficiency was achieved without a significant loss of numerical accuracy. Therefore, the selected combination of cutoff energy and k -point mesh was considered suitable for the subsequent DFT reference calculations.

4.1.2 Dataset Generation and Filtering

After selecting the DFT reference parameters, these parameters were used to generate dataset required for training a machine-learning interatomic potential for bulk SrTiO_3 . The generated configurations contained the corresponding DFT reference quantities, including total energies, atomic forces, stresses, atomic positions, and cell parameters. These quantities were used as target data for training the model. The final dataset was divided into train and validation subsets. In this work, 80% of the dataset was used for

training, while the remaining 20% was used for validation. The training subsets were used to optimize the parameters of the machine-learning model, whereas the validation subset was used to evaluate the model on configurations that were not directly used during training. This is important because, for the validation of the trained model, we need some data that had not been used during model training. The initial training dataset contained 13,422 configurations, while the initial validation dataset contained 3,355 configurations. This corresponds approximately to an 80:20 split of the original dataset. The generated configurations included both near-equilibrium and distorted structures, allowing the dataset to sample different regions of the potential-energy surface.

Dataset	Configurations	Max ΔE (meV/atom)	Max $ F $ (eV/Å)	Mean $ F $ (eV/Å)
Original training	13422	59.36	2.52	0.040
Original validation	3355	55.03	2.34	0.043
Filtered training	1760	19.73	0.295	0.032
Filtered validation	710	22.19	0.500	0.056

Table 1: Summary of the original and filtered SrTiO₃ datasets used for MLIP training and validation.

Before training the machine-learning interatomic potential, the dataset was filtered to remove nonphysical or highly distorted configurations.

Figure 11 shows the energy and force distributions of the original dataset and the corresponding distributions after filtering. In the original training dataset, the maximum relative energy reached approximately 59.36 meV/atom, while the maximum force magnitude reached 2.52 eV/Å. After filtering, the strongly distorted and high-force configurations were removed. The maximum relative energy in the training dataset was reduced to 19.73 meV/atom, and the maximum force magnitude was reduced to 0.295 eV/Å.

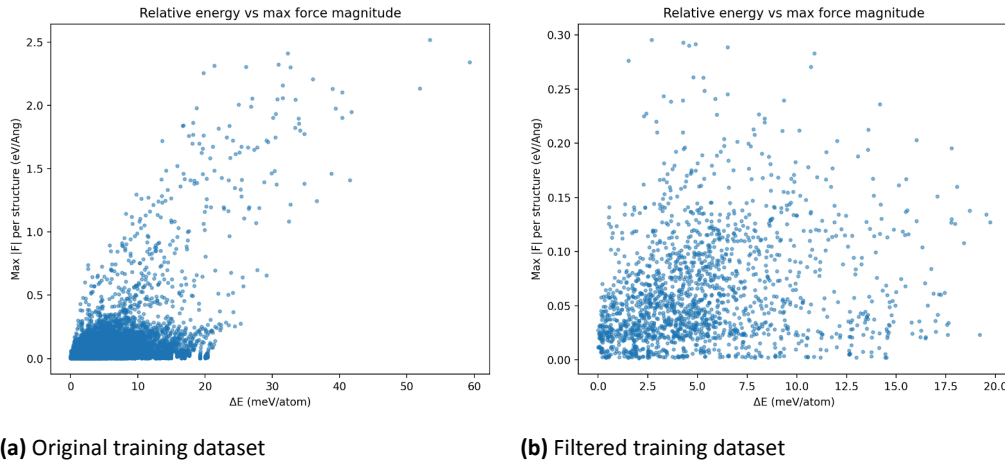


Figure 11: Comparison of the relative energy and maximum atomic force in the original and filtered training datasets. The original dataset contains high-energy and high-force configurations associated with strongly distorted atomic environments. After filtering, the configurations are concentrated in the low-energy and low-force region, confirming the removal of nonphysical outliers from the training dataset.

A similar trend was observed for the validation dataset as shown in Fig.13. The original validation dataset had a maximum relative energy of 55.03 meV/atom and a

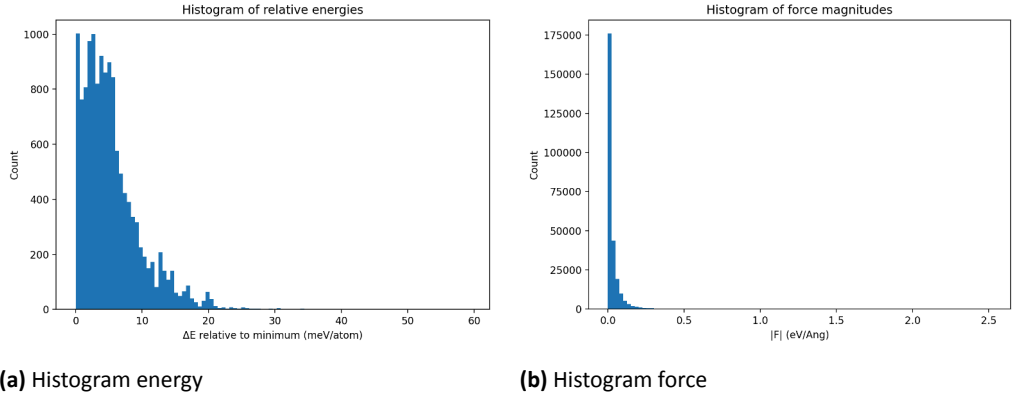


Figure 12: Relative-energy and force-magnitude distributions of the original training dataset. Most configurations are concentrated at relatively low energies and forces, while the extended high-energy and high-force tails indicate the presence of strongly distorted configurations that require filtering before MLIP training.

maximum force magnitude of $2.34 \text{ eV/\AA}$. After filtering, these values were reduced to 22.19 meV/atom and $0.500 \text{ eV/\AA}$, respectively. The final filtered dataset contained 1,760 training configurations and 710 validation configurations. These filtered configurations were then used to train and evaluate the machine-learning interatomic potential.

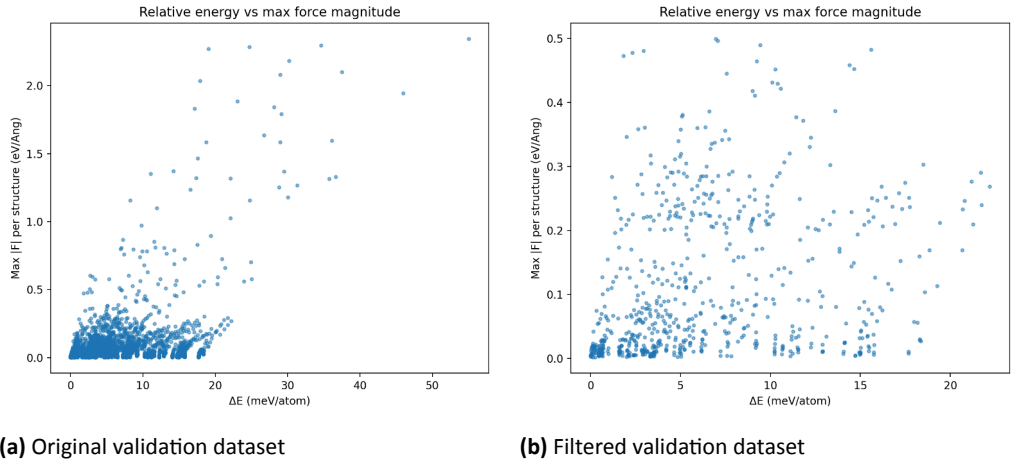


Figure 13: Relative-energy and force-magnitude distributions of the original and filtered validation datasets. The reduction of the high-energy and high-force tails confirms that strongly distorted configurations were removed while configurations representative of the physically relevant energy landscape were retained for model validation.

The scatter plots of relative energy versus maximum force further support the effect of filtering. In the original dataset, some configurations showed both high relative energy and high force values. This indicates strongly distorted atomic environments, in which some atoms might have been placed too close to each other, resulting in such high forces. After filtering, the dataset became more concentrated in the low-energy and low-force region. This indicates that the final dataset mainly contains physically meaningful configurations that can be used for building a reliable machine-learning interatomic potential. The histograms strongly support the filtering of both the training and validation datasets as shown in Figs. 12 and 14. The relative energy distribution

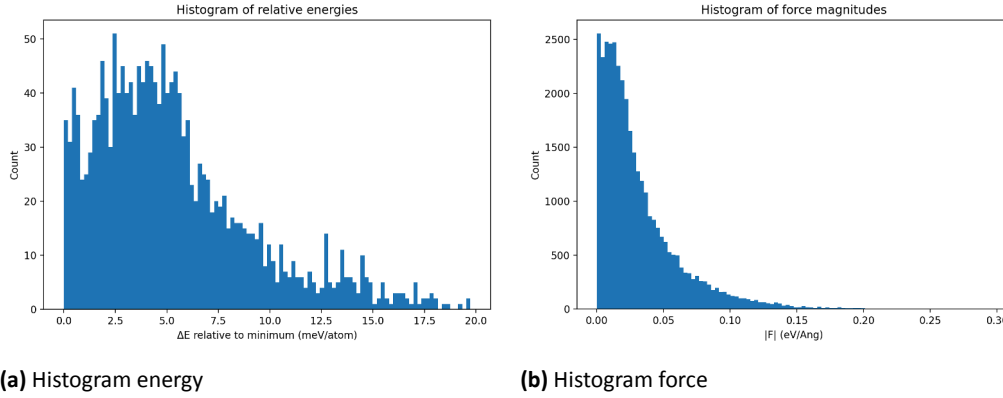


Figure 14: Relative-energy and force-magnitude distributions of the filtered training dataset. Compared with the original dataset, the distributions are restricted to lower-energy and lower-force ranges, demonstrating that highly distorted configurations were removed while physically meaningful configurations were retained for MLIP training.

histograms show that most of the configurations are located close to the minimum-energy structure and only a smaller number of configurations extend towards higher relative energies. Similarly, the force magnitude histograms show that most atomic forces are small. This indicates that the majority of the atomic structures in the dataset are not severely distorted. Therefore, the filtered dataset provides a physically cleaner and more stable set of configurations for training the machine-learning interatomic potential.

4.1.3 Machine-Learning Interatomic Potential Training Evaluation

After filtering the dataset, the remaining configurations were used to train a machine-learning interatomic potential. The performance of the trained model was evaluated using the validation dataset that was not used during training. Figure 15 shows the validation mean absolute error (MAE) of the predicted forces and energies as a function of the number of training epochs. Mathematically, the MAE is defined as

$$\text{MAE} = \frac{1}{N} \sum_{i=1}^N |y_i^{\text{DFT}} - y_i^{\text{MLIP}}| \quad (4.1)$$

Here, N is the number of data points, y_i^{DFT} is the DFT reference value, and y_i^{MLIP} is the value predicted by the trained model. In this work, MAE was used to evaluate both energy and force prediction errors.

Quantity	Initial value	Minimum value	Final value
Energy MAE (eV/atom)	0.00377	0.00104	0.00112
Force MAE (eV/Å)	0.01210	0.00651	0.00679

Table 2: Initial, minimum, and final validation errors of the trained MLIP model.

The energy validation MAE decreases sharply in the initial training epochs, and then remains in a low-error range with small fluctuations. The initial energy MAE is approximately 3.77×10^{-3} eV/atom, while the final value is approximately 1.12×10^{-3} eV/atom. After the initial decrease, the energy MAE remains within a low range with small fluctuations. These fluctuations are expected because the model is simultaneously optimizing both energy and atomic forces during training.

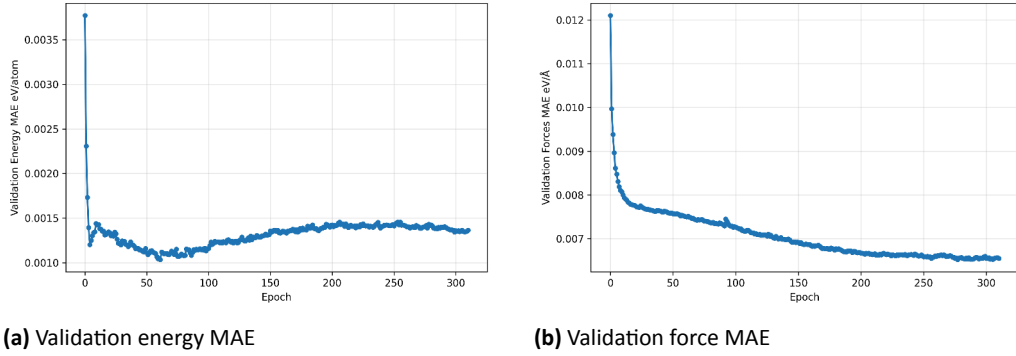


Figure 15: Validation mean absolute error as a function of training epoch for the trained machine-learning interatomic potential.

Similarly, the force validation MAE decreases rapidly during the early training epochs and then gradually approaches a stable value. The initial force MAE is approximately 1.21×10^{-2} eV/Å, while the final value is approximately 6.79×10^{-3} eV/Å. This decreasing trend indicates that the model is progressively learning and improving its predictions of atomic forces during training.

Overall, the validation curves show that the trained model reached a stable low-error regime. This indicates that the model has learned the relationship between the SrTiO₃ atomic configurations and the corresponding DFT reference energies and forces. Therefore, the trained model can be used for subsequent structural relaxation in LAMMPS of larger SrTiO₃ structures.

4.1.4 Bulk Phase Analysis as a Function of Lattice Strain

Following validation of the bulk machine-learning interatomic potential, the model was implemented in LAMMPS to relax the bulk SrTiO₃ configurations over the investigated range of in-plane and out-of-plane lattice parameters. The fully relaxed structures were subsequently used to construct the bulk-phase diagram and analyse the evolution of octahedral rotations and Ti off-centering as a function of lattice strain. The relaxed bulk structures were used to construct the phase diagram of SrTiO₃ in the a and c lattice-parameter space. The resulting phase diagram as shown in Fig. 16, indicates different regions. Each region of the diagram corresponds to a different relaxed structural phases. The aim of this analysis was to determine how changing the lattice parameters affects the relaxed structural phases, octahedral rotation pattern, and the emergence of ferroelectric-like distortions. For each point in a and c grid, the final relaxed configuration and the relaxed total energy were examined.

Figure 16 shows the bulk phase analysis of SrTiO₃ as a function of lattice parameters a and c . The structural phase diagram shows that different regions of the scanned parameter space relax into different structural phases, indicating that the final relaxed structure of SrTiO₃ is sensitive to lattice geometry. The phase diagram shows that octahedral rotations are an important structural response in bulk SrTiO₃. For example, the I4/mcm region is mainly associated with octahedral rotations, while phases such as I4cm, Ima2, and R3c include additional ferroelectric-like distortions along different directions. This shows that varying the lattice parameters not only changes the unit-cell shape but also changes the balance between rotational distortions and polar Ti displacements inside the TiO₆ octahedra.

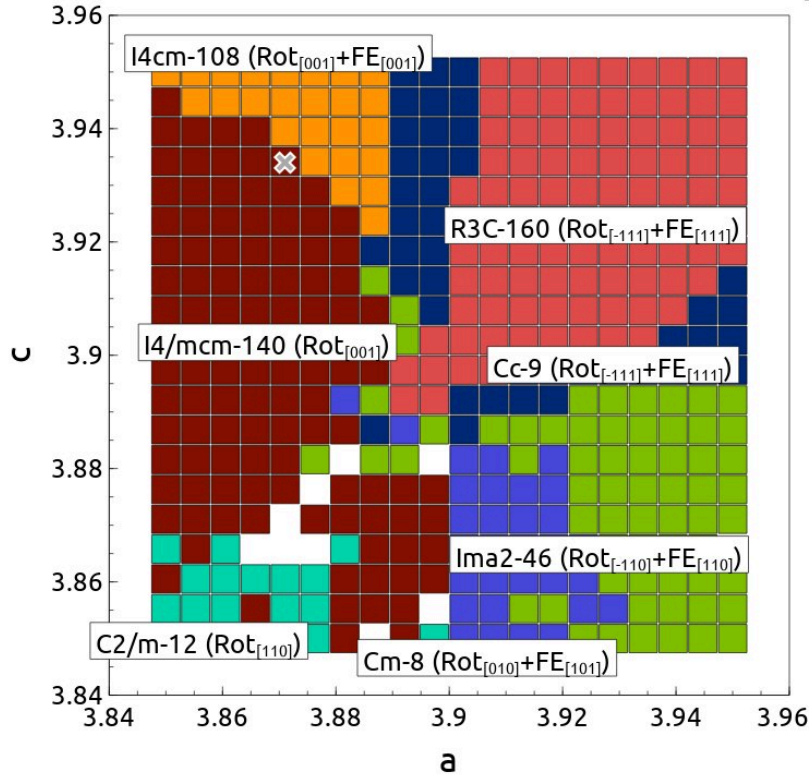


Figure 16: Structural phase diagram of bulk SrTiO_3 in the a - c lattice-parameter space, showing the relaxed phase regions with distinct octahedral rotation patterns and ferroelectric-like distortion directions.

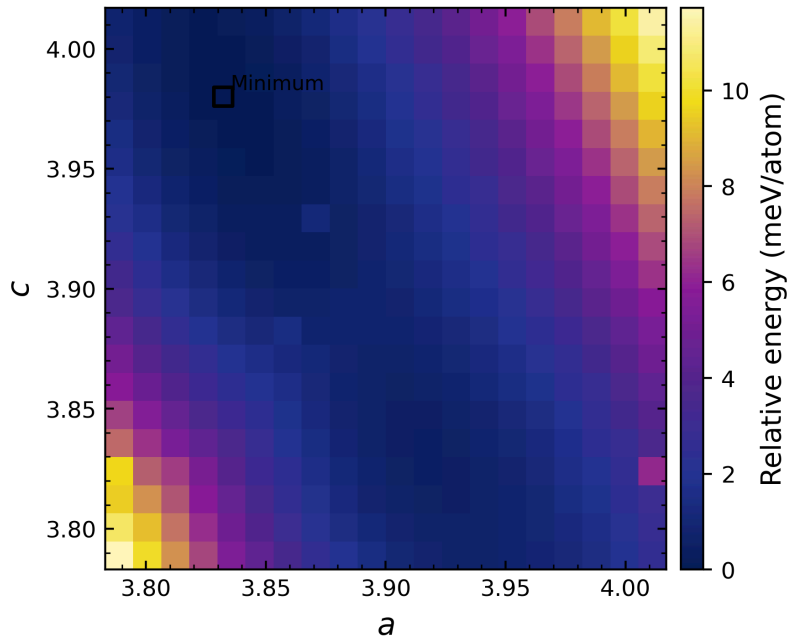


Figure 17: Relative-energy landscape of bulk SrTiO_3 as a function of the lattice parameters a and c . The minimum-energy pathway can be used to evaluate the effective Poisson response.

The relative-energy landscape in Fig. 17 shows how the energy of SrTiO_3 varies with the in-plane and out-of-plane lattice parameters, a and c . The relaxed total energies were first normalized per atom and then shifted with respect to the lowest-energy configuration in the scanned grid. The marked point represents the minimum-energy configuration within the sampled parameter space. The darker regions correspond to lower relative energies, while the brighter regions represent higher relative energies. The minimum-energy region therefore identifies the energetically preferred lattice configurations. By following the minimum-energy value of c as a function of a , the transverse lattice response to in-plane strain can be determined and used to estimate the effective Poisson's ratio. A comparison between the structural phase diagram and the relative-energy landscape shows that the energetically favourable region is close to phases dominated by octahedral rotations, while polar phases appear nearby in the same lattice-parameter space. This suggests that the relaxed bulk structures are influenced by the coupling between lattice deformation, octahedral rotations, and Ti off-centering.

Representative Structures from Selected Phases. Figures 18 and 19 show the representative relaxed structures selected from the main regions of the bulk phase diagram. These structures were used to examine the local structural distortions in more detail. For each phase, three different views are presented. These help illustrate the evolution of the TiO_6 octahedral environment from one phase to another.

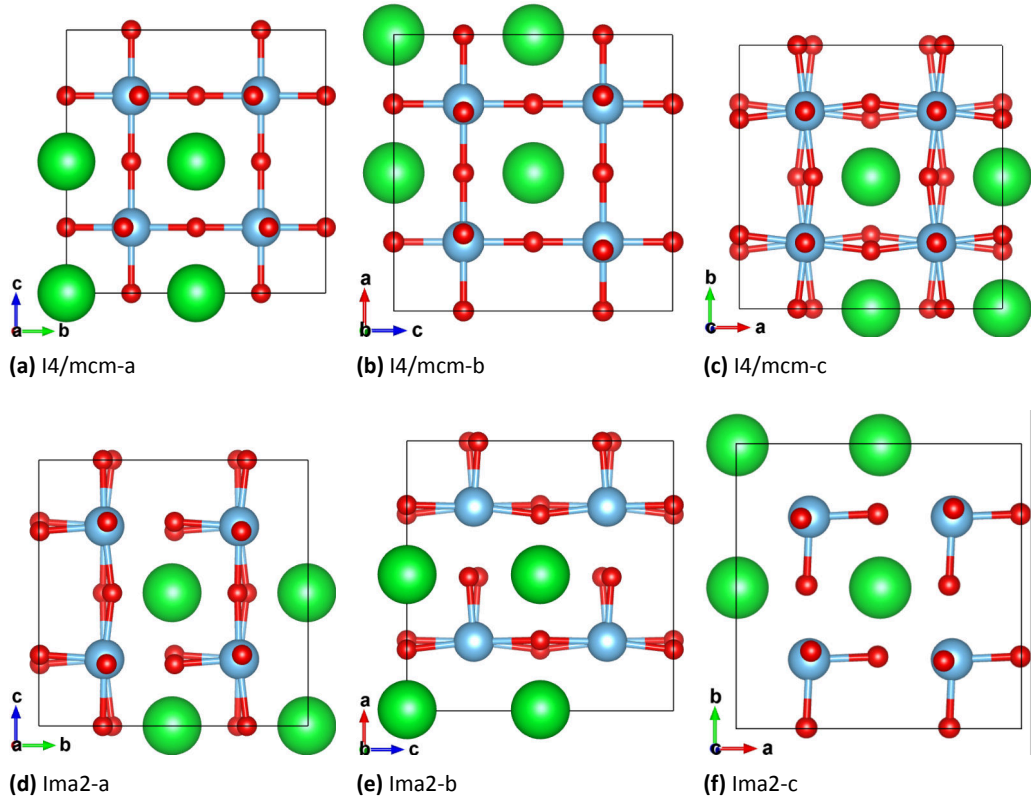


Figure 18: Representative relaxed structures selected from the $I4/mcm$ and $Ima2$ regions of the bulk phase diagram. The $I4/mcm$ structures mainly show octahedral rotations, while the $Ima2$ structures show in-plane polar distortion.

Figure 18 represents the $I4/mcm$ and $Ima2$ phases. It shows two different types of structural distortions. The $I4/mcm$ structure shows that the opposite Ti-O distances are

nearly symmetric in all three directions. This means there is no Ti off-centering in this case hence; there is no evidence of ferroelectricity. The main distortion in this phase is associated with the octahedral rotation only about z -direction, rather than a polar displacement. In contrast, the $I4cm$ phase shows Ti off-centering mainly along the x and y directions with a difference between opposite bond lengths of approximately 0.172 Å. This suggests that the Ti atom is displaced mainly within the xy plane. This phase also shows octahedral rotations about the $-x$ - and y -directions. Therefore, while $I4/mcm$ can be interpreted as a mainly rotational phase, $I4cm$ shows an in-plane ferroelectric-like polar distortion.

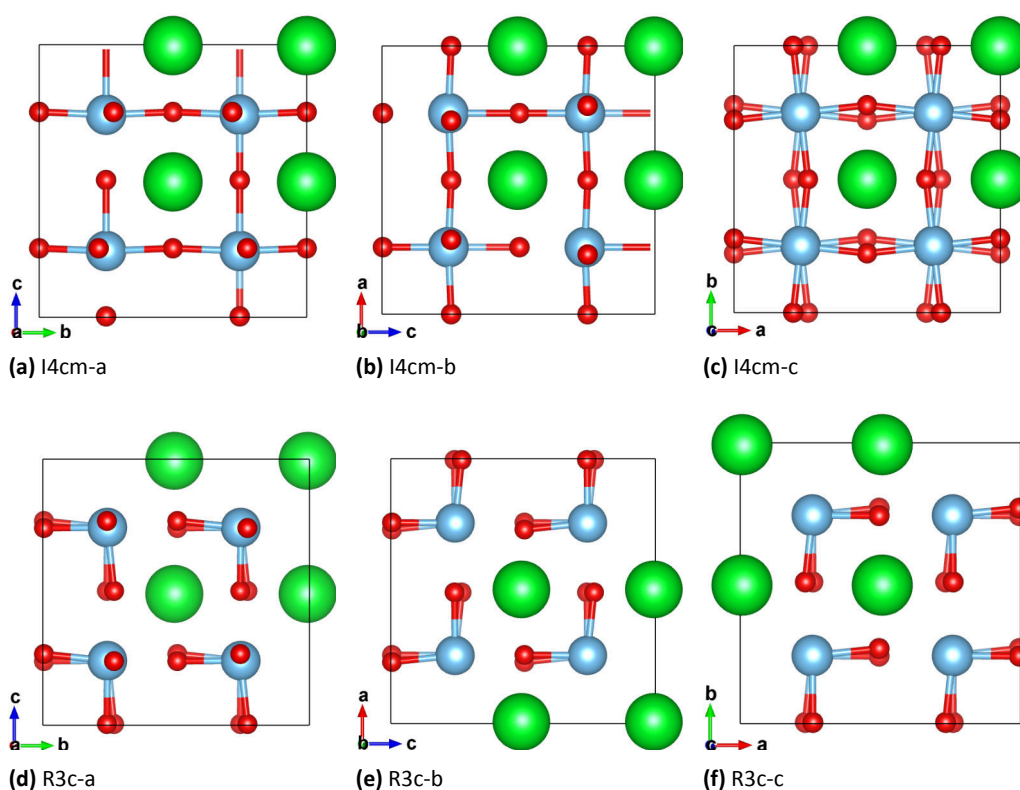


Figure 19: Representative relaxed structures selected from the $I4cm$ and $R3c$ regions of the bulk phase diagram. The $I4cm$ structures show out-of-plane Ti off-centering, while the $R3c$ structures show stronger polar distortion involving all crystallographic directions.

Figure 19 represents the structural distortions of $I4cm$ and $R3c$ phases in three different directions. Both the $I4cm$ and $R3c$ phases show clear Ti off-centering, but the direction and strength of the polar distortion are different. In $I4cm$ the Ti-O bond distances in the x - and y -directions remain nearly the same, whereas strong asymmetry appears along the z direction. The difference between opposite Ti-O bond lengths along z is approximately 0.16087 Å. This indicates that Ti is mainly displaced in out-of-plane direction corresponding to an out-of-plane ferroelectric-like distortion. This phase also has rotation about the z -direction. In the $R3c$ phase, large Ti-O bond asymmetry is observed in all three directions, with an opposite-bond difference of approximately 0.192 Å. This indicates a stronger three-dimensional Ti off-centering within the TiO_6 octahedron. Therefore, $R3c$ represents the strongest polar distortion among the selected phases. The values of corresponding Ti-O distance for each phase in different directions

are summarized in Table 3.

Table 3: Ti–O bond distances and corresponding structural interpretations for representative relaxed bulk SrTiO₃ phases.

Phase	<i>x</i> -direction Ti–O (Å)	<i>y</i> -direction Ti–O (Å)	<i>z</i> -direction Ti–O (Å)	Opposite-bond difference	Interpretation
I4/mcm	1.93829 1.93829	1.93829 1.93830	1.94869 1.94869	Very small	Nearly symmetric bonds; no clear Ti off-centering.
Ima2	1.88744 2.05933	1.88728 2.05943	1.94719 1.96214	Large in <i>x, y</i> : ~ 0.172 Å	In-plane Ti off-centering and polar distortion within the <i>xy</i> plane.
I4cm	1.94891 1.94893	1.94891 1.94893	1.89193 2.05280	Large along <i>z</i> : 0.16087 Å	Ti off-centering along <i>z</i> , indicating an out-of-plane polar distortion.
R3c	1.88869 2.08117	1.88869 2.08116	1.88869 2.08116	Large in <i>x, y, z</i> : ~ 0.192 Å	Strong three-dimensional Ti off-centering in all directions.

Overall, the Ti–O bond-distance analysis shows a progression from a mainly rotational I4/mcm phase to increasingly polar phases in Ima2, I4cm, and R3c. This confirms that Ti off-centering within the TiO₆ octahedra is a useful structural indicator of ferroelectric-like behaviour in the relaxed bulk SrTiO₃ phases.

4.2 Results for Twisted SrTiO₃ Bilayers

4.2.1 Dataset Generation and Filtering

After the bulk, the dataset generation and filtering procedure used for bulk SrTiO₃ was applied to the layered SrTiO₃ system. The layered dataset represents a more complex atomic environment than the bulk dataset because it contains surface effects, interlayer interactions, and different stacking configurations between the two SrTiO₃ layers. The purpose of this step was to prepare a reliable dataset for training a machine-learning interatomic potential that could describe layered and later twisted SrTiO₃ systems.

Dataset	Configurations	Max ΔE (meV/atom)	Mean ΔE (meV/atom)	Max $ F $ (eV/Å)	Mean $ F $ (eV/Å)
Original training	9954	240.86	40.45	3.14	0.094
Original validation	2489	210.41	53.26	3.20	0.101
Filtered training	7074	59.97	11.91	1.50	0.051
Filtered validation	1485	59.80	12.14	1.50	0.056

Table 4: Summary of the original and filtered layered SrTiO₃ datasets used for MLIP training and validation.

Before training the model for layers, the dataset was first filtered to remove highly distorted and nonphysical configurations. As summarized in Table 4, the filtering was done based on relative energy and force magnitude criteria. This step has reduced both the energy and force magnitude ranges in the training and validation datasets.

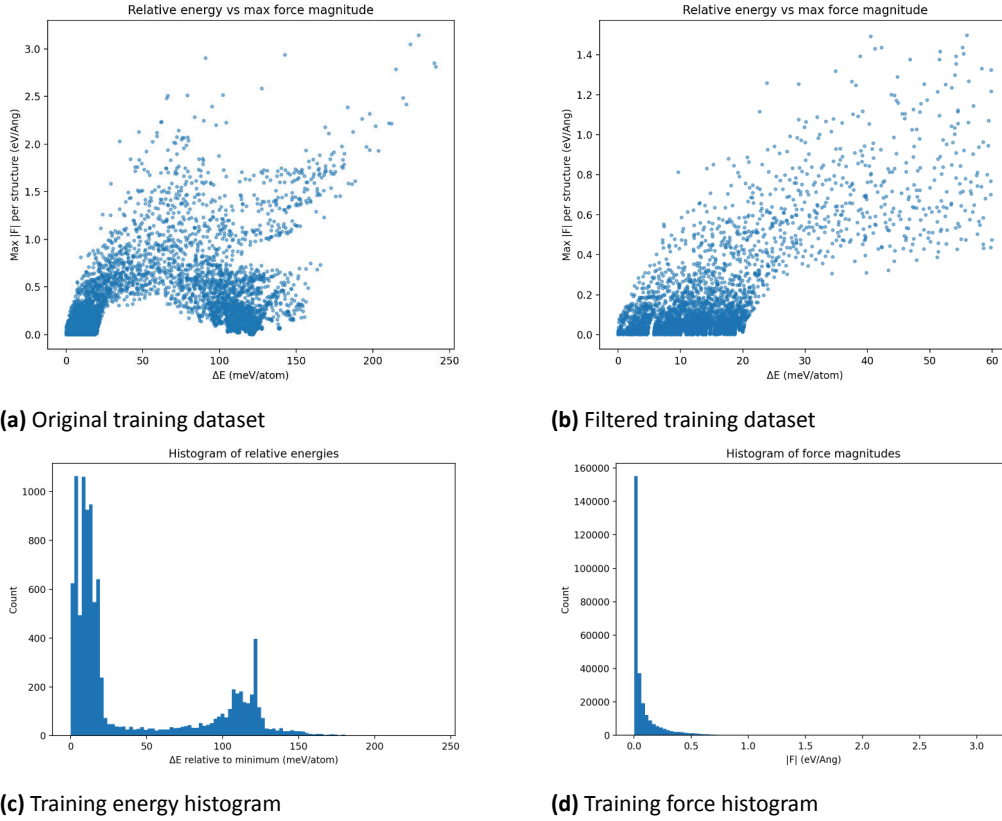


Figure 20: Training dataset generation and filtering analysis for layered SrTiO_3 .

The scatter plots of relative energy versus maximum force show the effect of this filtering step. In the original dataset, some configurations appeared in high-energy and high-force regions, suggesting strongly distorted atomic arrangements. After filtering, the remaining configurations were mainly located in the low-energy and low-force regions, indicating that the dataset now contains more physically reasonable structures. The histograms further support this observation. Overall, the filtering process improved the quality of the layered dataset while still preserving the structural diversity needed to describe layered systems. Although the layered dataset remains more complex than the bulk dataset, this is expected because layered structures contain surfaces, interfaces, and stacking-dependent distortions.

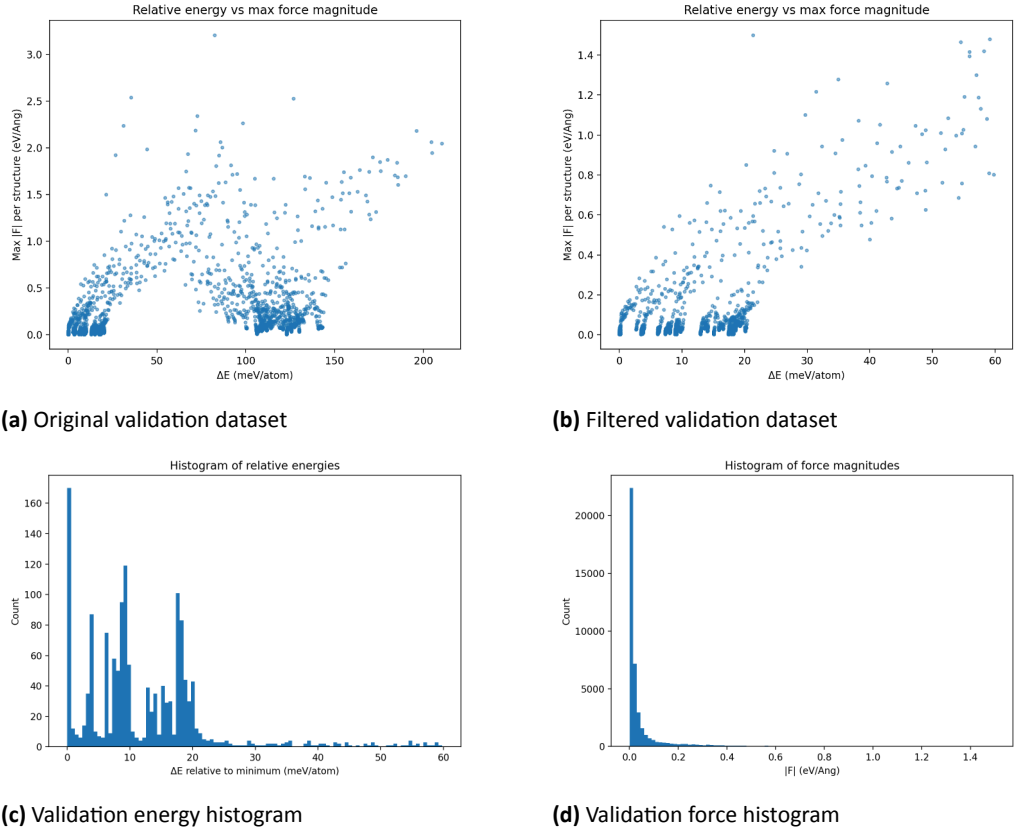


Figure 21: Validation dataset generation and filtering analysis for layered SrTiO_3 .

4.2.2 Machine-Learning Interatomic Potential Training

After filtering the layered SrTiO_3 dataset, the remaining configurations were used to train the machine-learning interatomic potential. The model performance was evaluated using the validation dataset, and the energy and force MAE were monitored as a function of training epoch, as shown in Figure 22.

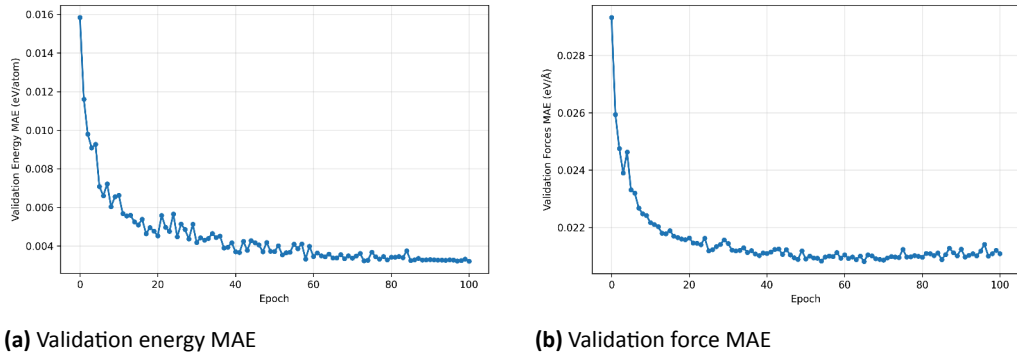


Figure 22: Validation mean absolute error as a function of training epoch for the trained machine-learning interatomic potential.

The validation energy MAE decreases rapidly during the early training epochs and then reaches a low-error region with small fluctuations. This indicates that the model learns the main energy response of the layered SrTiO_3 structures. The force MAE also

decreases at the beginning of training and then remains within a relatively stable range. Table 5 summarizes the results.

Quantity	Initial value	Minimum value	Final value
Energy MAE (eV/atom)	0.01580	0.00319	0.00455
Force MAE (eV/Å)	0.02930	0.02080	0.02330

Table 5: Initial, minimum, and final validation errors of the trained layered SrTiO₃ MLIP model.

Compared with the bulk model, the layered model shows larger validation errors. This is expected because the layered structures contain more complex atomic environments, including surfaces, interfaces, interlayer interactions, and stacking-dependent distortions. Overall, the validation curves show that the trained model captures the main energy and force trends of the layered SrTiO₃ system and can be used for subsequent structural relaxation.

4.2.3 Ferroelectric-Phase Analysis as a Function of Twist Angle

To investigate the effect of twist angle, the trained layered MLIP was used in LAMMPS to relax the large commensurate moiré supercells. During relaxation, the atoms were allowed to reconstruct in response to the spatially varying local stacking environments. The resulting structures therefore provide the basis for extracting the layer-resolved polarization fields and examining their evolution with twist angle.

Layer-resolved polarization distribution

Figure 23 illustrates the layer-resolved spatial distribution of the out-of-plane polarization component (P_z) for a representative twisted SrTiO₃ bilayer structure with a twist angle of 45.041°. The polarization maps are shown separately for the top and bottom layers after interpolating the discrete polarization vectors onto a regular grid. A 2×2 periodic tiling of the supercell is used to demonstrate the continuity of the polarization texture across the periodic boundaries.

The first observation is that the polarization is not spatially uniform across the moiré supercell. Instead, distinct regions of positive and negative P_z are observed. These regions repeat periodically across the tiled supercell, showing that the polarization texture follows the underlying moiré periodicity rather than appearing as isolated local features. The regions of positive and negative polarization are separated by areas where the out-of-plane polarization reaches zero. This results in a continuous modulation of the polarization throughout the supercell. The presence of localized polarization extrema suggests that throughout the moiré supercell the local atomic environment varies.

Comparing the two layers shows that both the top and bottom layers develop a spatially modulated polarization with the same overall moiré periodicity. However, the detailed distribution of positive and negative P_z is layer-dependent, regions exhibiting strong positive out-of-plane polarization in one layer correspond to regions of strong negative polarization in the other layer, while regions of weak polarization occur at similar locations in both layers. This complementary behaviour suggests that the two layers respond cooperatively to the same moiré potential but with opposite directions of the local out-of-plane polarization. The following section investigates how the polarization distribution evolves with the twist angle and subsequently examines the atomic stacking associated with the regions of strongest and weakest out-of-plane polarization.

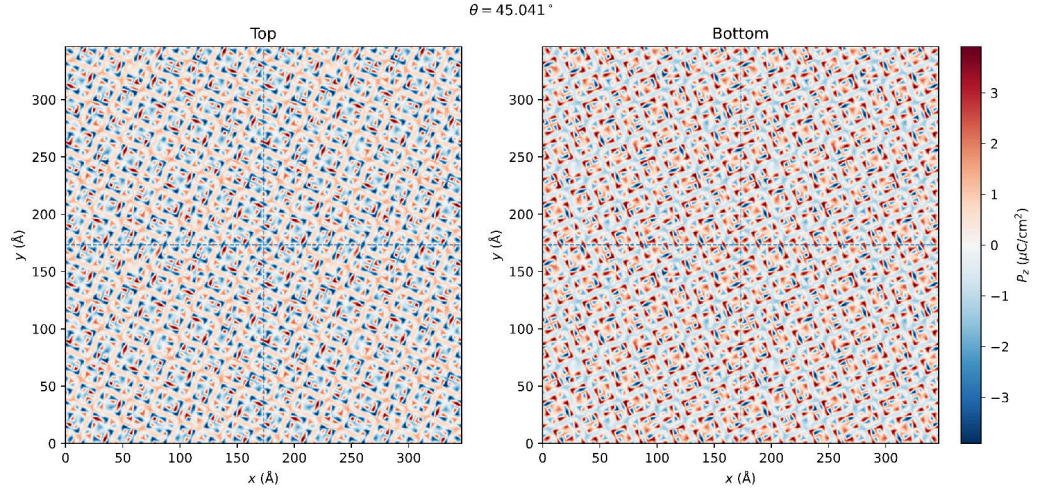


Figure 23: Out-of-plane polarization (P_z) distribution in the top and bottom layers of the relaxed twisted SrTiO_3 bilayer at a representative twist angle of 45.041° . The polarization field was interpolated onto a regular grid using periodic boundary conditions and displayed as a 2×2 tiled supercell to illustrate the continuity of the moiré polarization texture across the periodic boundaries. Positive and negative P_z values are represented by red and blue, respectively.

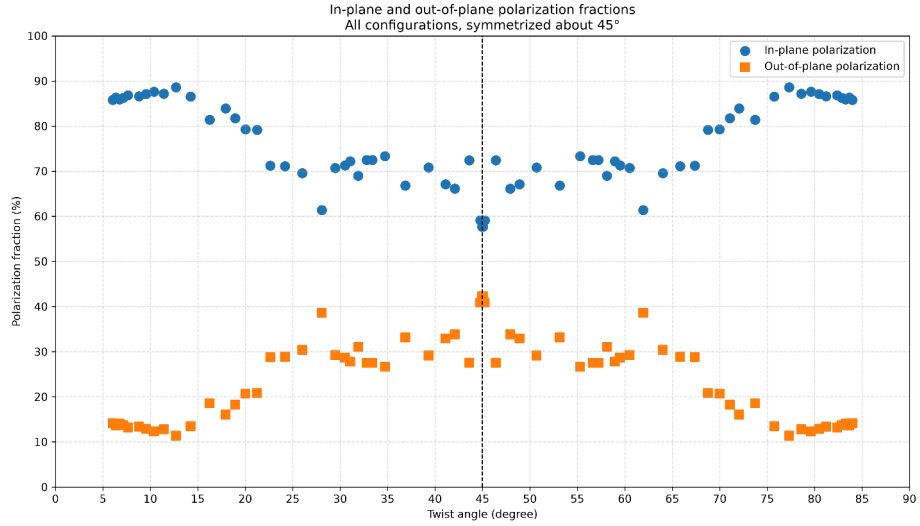


Figure 24: Fractional contributions of the in-plane and out-of-plane polarization components as a function of twist angle for all relaxed twisted SrTiO_3 bilayer configurations. The vertical dashed line indicates the symmetry point at 45.041° . The data exhibit an approximately symmetric evolution about 45.041° , highlighting the redistribution of the polarization between the in-plane and out-of-plane components with twist angle.

While the previous section demonstrated the local distribution of polarization in the representative moiré supercell, it is also important to examine how the in-plane and out-of-plane polarization components evolve with the twist angle. Figure 24 shows the fractional distribution of the in-plane and out-of-plane polarization components across a selected range of twist angle. The results reveal two distinct polarization regimes as a function of twist angle. In the range below approximately 20° and above approximately 70° , the polarization is strongly dominated by its in-plane component. The in-plane polarization contribution is relatively high, accounting for approximately 80-90% of the total polarization, whereas the out-of-plane polarization remains relatively small. As shown later by polarization maps, this dominant in-plane regime is associated with the formation of in-plane vortex like textures. At intermediate angles between approximately 20° and 70° the in-plane polarization decreases while the out-of-plane polarization increases. The largest redistribution occurs near the symmetry angle of 45.041° , where the in-plane polarization reaches its minimum and the out-of-plane polarization reaches its maximum. Although the polarization remained predominantly in-plane, the enhanced out-of-plane polarization at symmetry point indicates a quantitatively different polarization regimes from that observed at smaller and larger angles. Both polarization components evolve approximately symmetrically around 45.041° , with configurations at comparable angular distances from this point exhibiting similar fractional contributions. Figure 24 therefore provides the principal evidence for separating the investigated structures into an in-plane-dominated regime below approximately 20° and above approximately 70° , and an out-of-plane-enhanced regime at intermediate angles. The representative polarization maps and relaxed structures shown in Figure 25 are subsequently used to examine how these two global regimes are examined in the local polarization and atomic configurations.

Although this discussion only provides information about global measure of how the polarization components evolve with the twist angle, it does not reveal how the polarization is locally distributed within the moiré superlattice. The following section therefore examines the layer resolved polarization maps for representative twist angles to investigate the evolution of the local polarization textures and identify the regions exhibiting the strongest and weakest out-of-plane polarization.

Figure 25 compares the out-of-plane polarization for the three representative twist angles along with their representative relaxed atomic structures. The low- and high-angle structures at 10.389° and 83.267° exhibit more pronounced reconstruction and visibly enlarged AB-stacking regions (Sr–TiO and TiO–Sr registry), whereas the intermediate-angle structure at 45.041° shows weaker reconstruction. These representative configurations provide structural examples of the two polarization regimes identified from the full twist-angle dependence in Figure 24. The polarization texture changes noticeably with twist angle. A careful comparison between the two layers reveals that the spatial distribution of polarization is broadly similar, but with predominantly opposite signs at corresponding locations. In other words, regions with positive P_z in one layer generally correspond to regions with negative P_z in the other layer, indicating an approximately anti-aligned out-of-plane polarization response between the two layers. At $\theta = 10.389^\circ$, broad and well-defined regions of positive and negative P_z are repeated periodically across the moiré supercell. Near $\theta = 45.041^\circ$, the spatial modulation becomes smaller and more densely distributed, resulting in a more complex spatial polarization landscape over the enlarged twisted supercell. At $\theta = 83.267^\circ$, a more regular

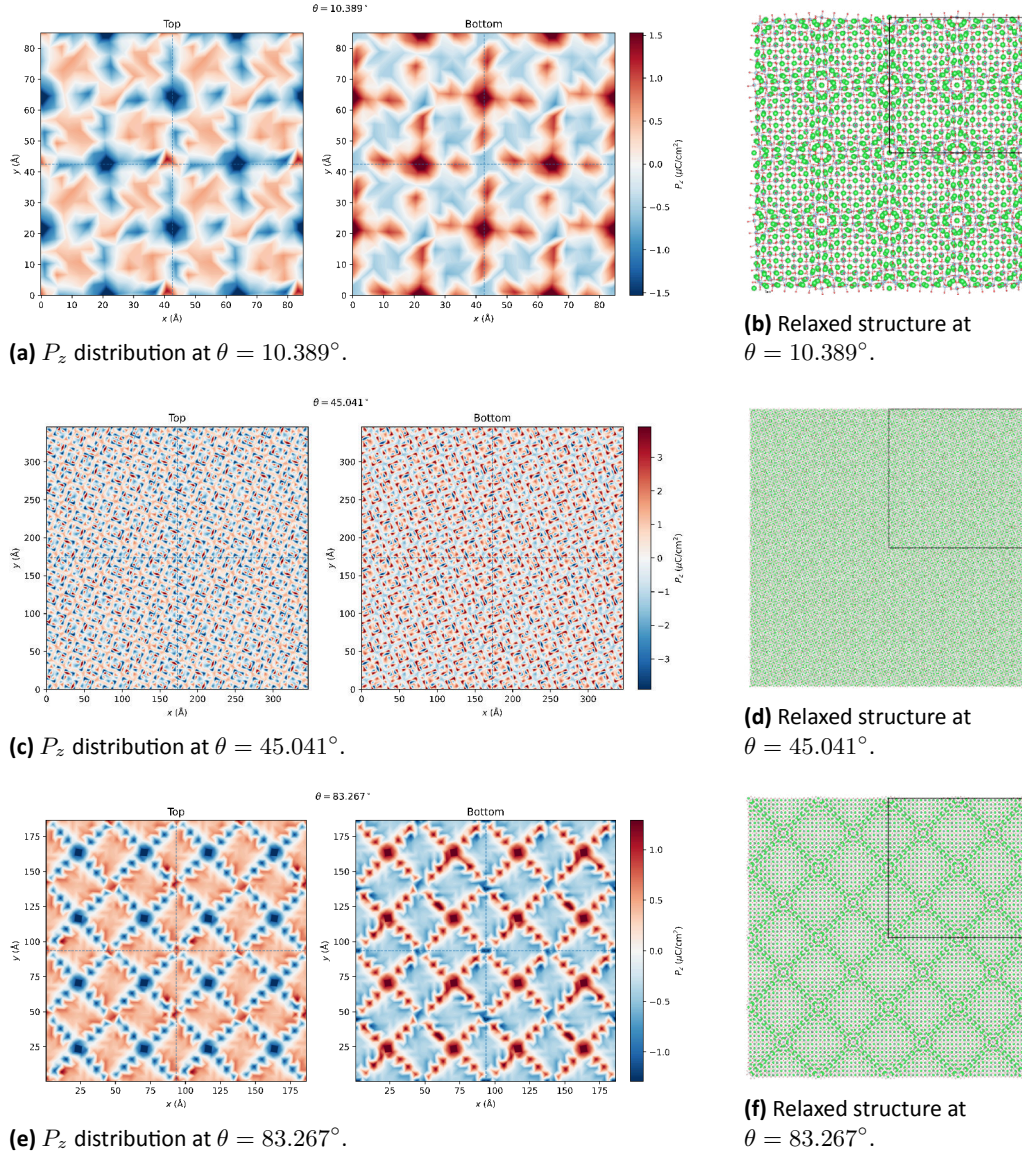


Figure 25: Representative out-of-plane polarization distributions and corresponding relaxed atomic structures of twisted SrTiO_3 bilayers at $\theta = 10.389^\circ$, 45.041° , and 83.267° . The left panels show the layer-resolved P_z distributions, while the right panels show the corresponding relaxed structures viewed along the out-of-plane direction. These representative configurations illustrate the evolution of the polarization texture across the investigated twist-angle range and provide the structural basis for examining the relation between local interlayer registry and the polarization extrema.

periodic texture reappears comprised of positive and negative polarization regions. The similarity between the low- and high-angle textures is consistent with the approximate symmetry of the polarization response around 45.041° .

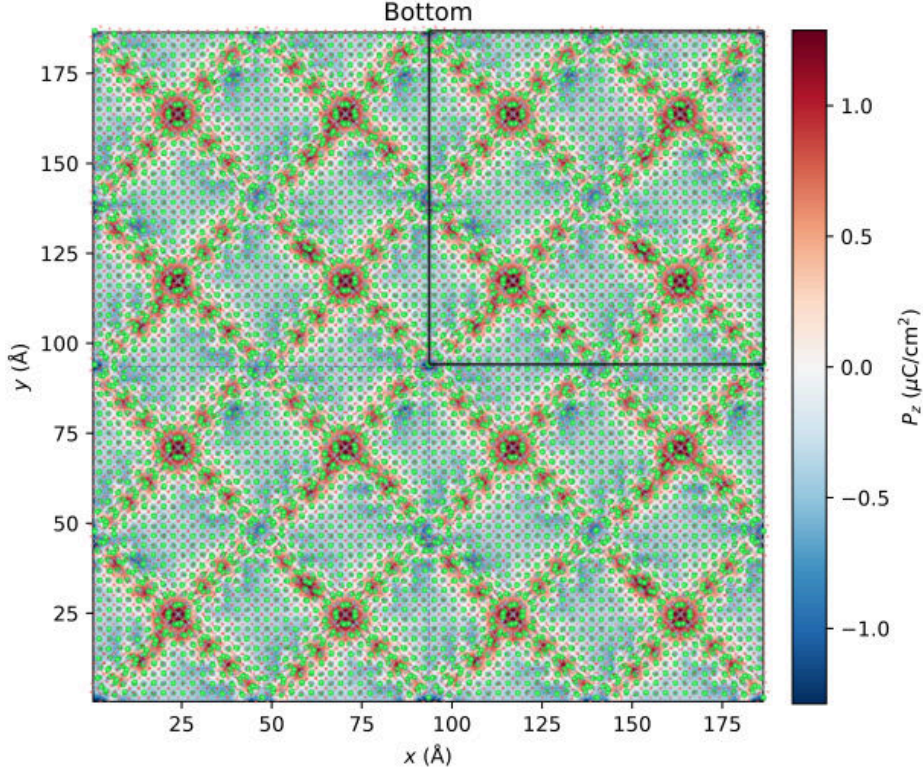


Figure 26: Out-of-plane polarization (P_z) distribution overlaid with the corresponding relaxed atomic structure of the bottom layer at $\theta = 83.267^\circ$. The atomic positions are superimposed on the polarization map to illustrate the spatial correspondence between the local polarization and atomic registry across the moiré supercell. The black square indicates the boundaries of the periodically repeated supercell.

To further investigate the structural origin of the spatial polarization variations, the relaxed atomic configurations were projected directly onto the corresponding P_z map, as shown in Fig. 26. The overlay shows that the polarization extrema are associated with specific locations within the periodically varying moiré registry rather than being randomly distributed across the supercell. Regions with large $|P_z|$ occur at particular local stacking environments, while weakly polarized regions are found at different registries. This correlation points to local interlayer stacking as an important factor governing the out-of-plane polarization texture.

To obtain further insights into the local structure associated with polarization extrema, Fig. 27 provides a closer view of the atomic environment of the surrounding representative positive and negative P_z extrema. The purple markers identify the selected polarization sites; they are not part of the atomic structure and are used only as visual guides. These enlarged views show that the polarization extrema are embedded within different local atomic registries generated by the relative rotation of the two SrTiO_3 layers.

To establish a quantitative connection between local atomic stacking and polarization magnitudes, the Ti sublattice alignment was subsequently analyzed at the max-

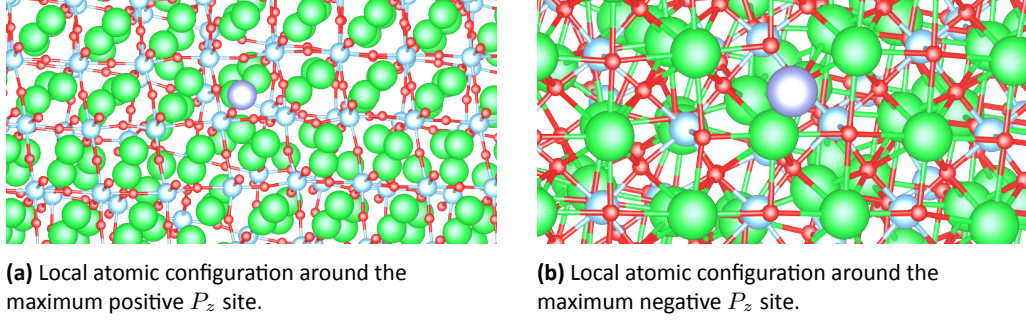


Figure 27: Representative local atomic configurations around the positive and negative out-of-plane polarization extrema. The purple spheres indicate the spatial positions of the selected polarization sites and are included only as visual markers, not as atomic species. The surrounding atomic environments are used to examine the local interlayer registry associated with the polarization extrema.

imum and minimum $|P_z|$ positions. Specifically, the lateral separation between the nearest Ti atoms belonging to the upper and lower layers was calculated. A small Ti–Ti separation represents close lateral alignment of the two Ti sites, whereas a larger separation indicates a more displaced local registry. The resulting comparison is presented in Table 6.

Table 6: Comparison of the out-of-plane polarization magnitude and local interlayer Ti–Ti lateral separation at the maximum- and minimum- $|P_z|$ sites for selected twist angles.

Twist angle (°)	Maximum $ P_z $ ($\mu\text{C}/\text{cm}^2$)	Ti–Ti at maximum (Å)	Minimum $ P_z $ ($\mu\text{C}/\text{cm}^2$)	Ti–Ti at minimum (Å)	Interpretation
10.389	2.176	0.019	1.0×10^{-5}	2.065	Near-complete lateral Ti alignment at maximum $ P_z $; shifted Ti registry at minimum $ P_z $.
25.989	7.342	0.396	3.0×10^{-4}	1.819	Closer Ti alignment at maximum $ P_z $ than at minimum $ P_z $.
45.041	5.729	0.462	7.0×10^{-4}	1.436	Closer Ti alignment at maximum $ P_z $; more displaced Ti registry at minimum $ P_z $.
53.130	5.306	0.193	0.00434	1.933	Close Ti alignment at maximum $ P_z $; shifted registry at minimum $ P_z $.
75.750	3.304	1.410	0.00745	2.118	Maximum $ P_z $ occurs at the less displaced Ti configuration.
83.267	2.771	0.086	9.3×10^{-4}	2.301	Near-complete lateral Ti alignment at maximum $ P_z $; shifted Ti registry at minimum $ P_z $.

The quantitative comparison reveals the consistent relationship between the local Ti registry and the magnitude of out-of-plane polarization. Across all the investigated configurations, the relationship can be summarized as

$$d_{\text{Ti-Ti}}^{xy}(\max |P_z|) < d_{\text{Ti-Ti}}^{xy}(\min |P_z|). \quad (4.2)$$

This indicates that the strongly polarized regions are generally associated with the closer lateral alignment of the Ti sublattice, whereas the weakly polarized regions occur at more laterally displaced configurations. However, when different angles were compared it is clear that the absolute value of polarization $|P_z|$ does not scale directly with Ti-Ti separation. This suggests that the local Ti registry is a useful descriptor for understanding the local polarization environment, but it is not the only factor determining polarization magnitude.

4.2.4 In-plane Polarization Textures

The out-of-plane polarization explained above describes the spatial distribution of the P_z component across the moiré supercell. In addition to the out-of-plane polarization, the relaxed twisted structures also exhibit the variation in the in-plane polarization components, P_x and P_y . Careful examination to the in-plane polarization reveals that its direction changes continuously across the moiré supercell and form localized rotational patterns.

Figure 28 shows the in-plane polarization texture of the top and bottom layers of the three representative twist angles. The arrows represent the local direction of the in-plane polarization vector, while the cyclic color scale represents its orientation angle. A comparison of top and bottom layers further reveals that, at corresponding spatial locations, the in-plane polarization vectors are predominantly oriented in opposite directions. Thus, although similar polarization textures occur in both layers, their local polarization orientations are approximately anti-aligned.

The in-plane polarization vectors show clear dependence on twist angle. The spatial organization of the polarization vectors changes substantially among the three configurations. At $\theta = 10.389^\circ$, the in-plane polarization field exhibits a dominant localized rotational pattern that is periodically repeated across the supercell. The polarization vectors progressively change their orientation around the central region, producing a spatially extended vortex-like texture rather than several isolated rotational centers. A substantially different polarization is observed for $\theta = 45.041^\circ$. Here the polarization vectors have rapid spatial variation in the polarization direction resulting in more complex and dense texture. Several localized rotational features can be observed, but they are smaller and less clearly separated than the dominant rotational structure found at $\theta = 10.389^\circ$. At $\theta = 83.267^\circ$, the in-plane polarization develops a more clearly organized rotational texture with both vortex-like and antivortex-like features appearing within each layer. These features form an organized and periodically repeated pattern across the moiré supercell.

4.2.5 Local Structural Character of the Emergent Polar States

To examine how the local structure changes with twist angle, the Ti-site environments were compared with the characteristic distortion patterns of several bulk SrTiO_3 phases. A dominant identifiable bulk-like contribution evolves from $Ima2$ -like character at $\theta = 10.389^\circ$ to $I4cm$ -like character near $\theta = 45.041^\circ$, and then to a stronger $I4/mcm$ -like contribution at $\theta = 83.267^\circ$. None of the structures are dominated by a single conventional bulk-like state, and the mixed/low-symmetry environments continue to make the largest contribution throughout. Table 7 summarizes the results.

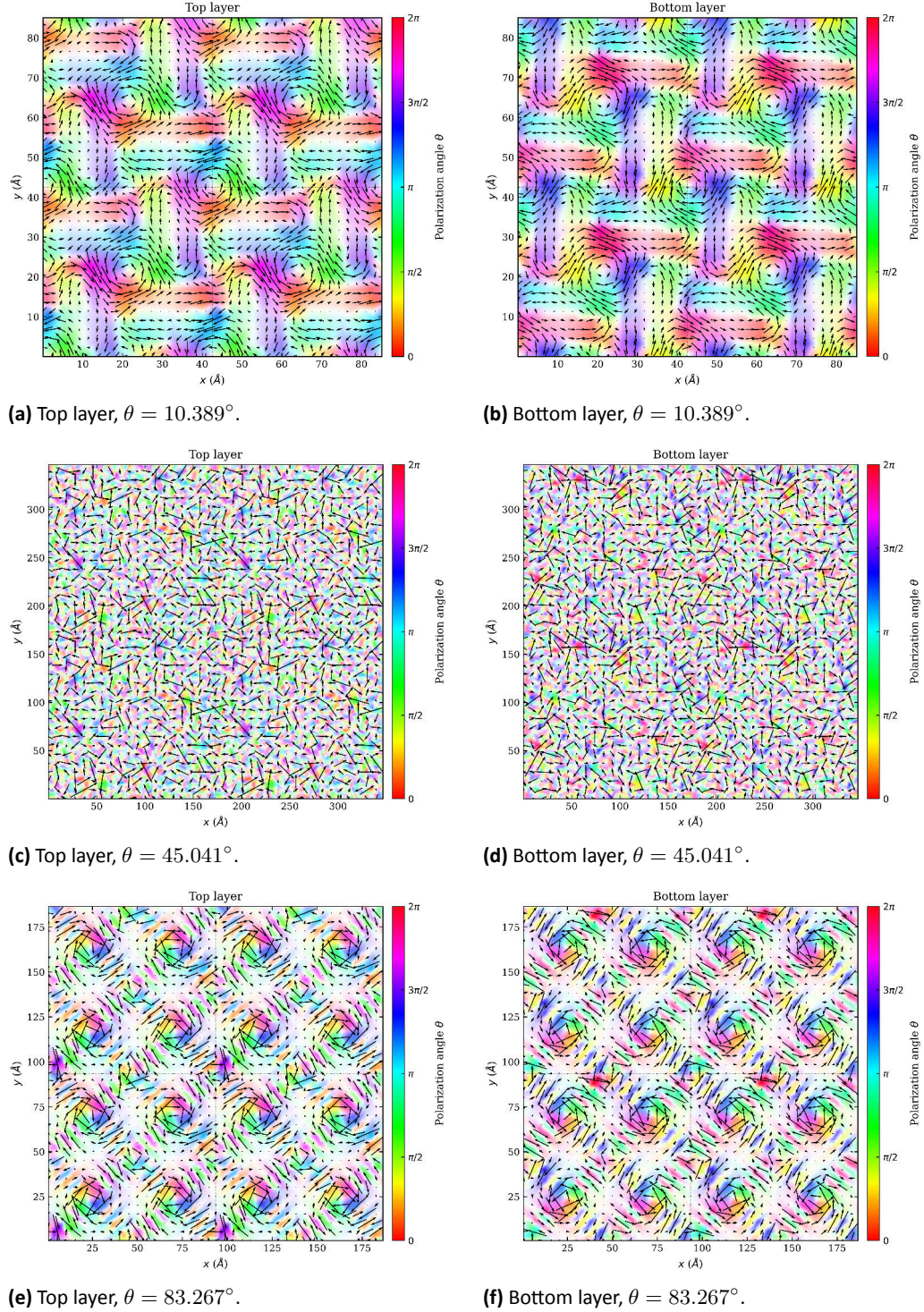


Figure 28: In-plane polarization textures of the top and bottom layers for representative twisted SrTiO_3 bilayers at twist angles of 10.389° , 45.041° , and 83.267° . The arrows represent the local direction of the in-plane polarization vector $\mathbf{P}_{\parallel} = (P_x, P_y)$, while the cyclic color map represents the corresponding polarization angle $\theta_P = \text{atan2}(P_y, P_x)$ from 0 to 2π . The displayed fields are repeated using a 2×2 tiling to make the periodic polarization textures more clearly visible.

θ ($^\circ$)	Layer	$I4/mcm$ (%)	$I4cm$ (%)	$Ima2$ (%)	$R3c$ (%)	Mixed/LS (%)
10.389	Top	6.56	0.82	13.11	0.82	78.69
	Bottom	7.38	0.00	14.75	0.00	77.87
45.041	Top	7.21	21.42	0.00	0.30	71.07
	Bottom	6.78	21.34	0.00	0.20	71.68
83.267	Top	34.31	0.17	0.00	0.00	65.52
	Bottom	34.48	0.00	0.00	0.00	65.52

Table 7: Fractions of local bulk-reference-like structural environments identified in the top and bottom layers for the three representative twist angles. The classifications indicate similarity to characteristic bulk SrTiO_3 distortion patterns rather than exact local crystallographic phases. Values are given as percentages of Ti sites.

The close similarity between top and bottom layer indicates that the overall structural response is similar for the two layers, despite their local polarization directions are mostly opposite. The angle-dependent redistribution of the bulk-reference-like environments thus reveals that in addition to the change of the polarization texture the local lattice distortions are affected by twisting.

The overall picture that emerges from this section is that the moiré geometry produces variation in both polarization field and local lattice structure of SrTiO_3 , and these features evolve together as the twist angle changes. The out-of-plane polarization changes significantly with angle, while the in-plane polarization evolves from broad rotational textures to more complex configurations. The appearance of out-of-plane polarization domains, rotational in-plane textures, and local environment with different structural characteristics demonstrates that twisting creates a highly non uniform polar state. At the same time, the local atomic environments do not correspond to a single bulk SrTiO_3 phase; instead, the twisted bilayers develop a heterogeneous state in which different polarization and structural features coexist within the same moiré supercell. This demonstrates that twisting provides an additional degree-of-freedom for generating and modifying complex polar states in SrTiO_3 twisted bilayers.

5

Conclusion

This thesis investigates the influence of twist angle on the structure and polar behaviour of the SrTiO_3 bilayers. Particular attention was given to how the local polar distortions and polarization textures that evolve as a function of twist angle. For computationally feasible analysis of large moiré structures, a multiscale workflow combining density functional theory, machine-learning interatomic potentials, and large-scale structural relaxation was employed.

The first step was to perform DFT calculations for bulk SrTiO_3 to generate reference energies and forces for training an Allegro/NequIP-based machine-learning interatomic potential. A separate DFT dataset was then generated for the layered SrTiO_3 system and used to train a second Allegro/NequIP-based machine-learning interatomic potential (MLIP) specifically for the layered SrTiO_3 system. These two trained potentials were then subsequently employed with LAMMPS to relax bulk, layered and twisted bilayered structures. This made it possible to access the moiré supercells that would be computationally demanding to treat directly using DFT and to analyze their local structure and polarization properties.

The bulk calculation provided a structural reference for interpreting the twisted systems. The relaxed bulk structure showed several characteristic distortion patterns, including $I4/mcm$ -, $I4cm$ -, $Ima2$ -, and $R3c$ -like configurations. These structural configurations emerge as a function of lattice strain, demonstrating that variations in the in-plane and out-of-plane lattice parameters modify the balance among octahedral rotations, Ti off-centering, and ferroelectric-like distortions in bulk SrTiO_3 .

The twisted SrTiO_3 bilayers exhibit a strong twist-angle dependence of their polarization response. The relaxed structures develop nonuniform out-of-plane polarization, with positive and negative regions distributed across the moiré supercell. The combined relaxation and polarization analyses reveal two distinct regimes. Below approximately 20° and above approximately 70° , the polarization is predominantly in-plane and forms vortex-like textures. The representative structures at 10.389° and 83.267° also exhibit pronounced structural reconstruction and enlarged AB-stacking regions. At intermediate twist angles, the out-of-plane polarization contribution becomes substantially stronger, while the representative structure at 45.041° shows weaker reconstruction. These regimes evolve approximately symmetrically around 45.041° , demonstrating that the twist angle controls both the local structural reconstruction and the orientation of the polarization.

The local structural analysis further demonstrates that the changes in the polarization field are accompanied by the redistribution of the underlying lattice distortions. Among the identifiable bulk reference like environment, the contribution changes from $Ima2$ -like at 10.389° to $I4cm$ -like near 45.041° , and to a stronger $I4/mcm$ -like contribution at 83.267° . However, mixed and low-symmetry environments remain dominant at all three representative angles. This suggests that the twisted bilayers cannot be described simply as local repetition of one conventional bulk SrTiO_3 phase. Instead, different structural environments coexist within the same moiré supercell and evolve with twist angle.

Overall, the results built a clear connection between twist angle, local structure reconstruction and resulting polarization textures in twisted SrTiO_3 bilayers. Twisting does not only simply modify the polarization magnitude, it also changes both the local structure environment and spatial organization of polarization. Thus the twisting acts as an additional degree of freedom that can generate complex and heterogeneous polar textures within moiré supercells.

5.1 Limitations and Future Work

The present study is limited to the finite set of commensurate twist angles considered in this work. This work only focuses on the structural and polarization properties of the twisted SrTiO_3 bilayers. Future work could extend the analysis to additional smaller twist angles and larger moiré supercells, as well as investigate the effects of temperature, strain, electric fields on the observed polar states. Furthermore, a more detailed and full three-dimensional topological analysis could also be done to investigate the possible emergence of the complex polar textures possessing skyrmion-like character. Experimental comparison would provide an important next step for validating the predicted twist-angle-dependent structural and polarization behaviour of SrTiO_3 bilayers.

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A

Supplementary Results

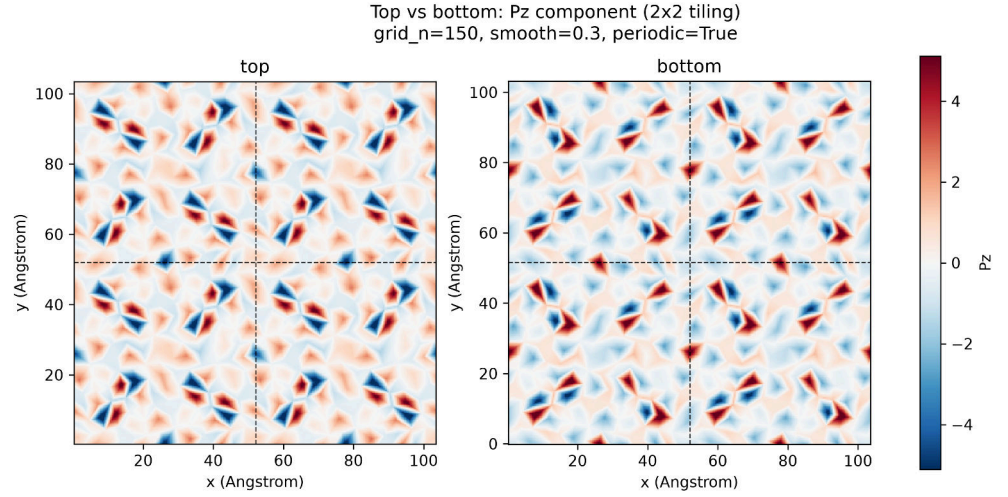
A.1 Calculated Twisted-Bilayer Configurations

$n_s = 5$		$n_s = 3$		$n_s = 1$	
(m_s, n_s)	$\theta (^\circ)$	(m_s, n_s)	$\theta (^\circ)$	(m_s, n_s)	$\theta (^\circ)$
(6, 5)	10.389	(6, 3)	36.870	(5, 1)	67.380
(7, 5)	18.925	(7, 3)	43.603	(6, 1)	71.075
(8, 5)	25.989	(8, 3)	48.888	(7, 1)	73.740
(9, 5)	31.891	(9, 3)	53.130	(8, 1)	75.750
(10, 5)	36.870	(10, 3)	56.602	(9, 1)	77.320
(11, 5)	41.112	(11, 3)	59.490	(10, 1)	78.579
(12, 5)	44.760	(12, 3)	61.928	(11, 1)	79.611
(13, 5)	47.925	(13, 3)	64.011	(12, 1)	80.473
(14, 5)	50.692	(14, 3)	65.810	(13, 1)	81.203
(15, 5)	53.130	(15, 3)	67.380	(14, 1)	81.829
(16, 5)	55.292	(16, 3)	68.761	(15, 1)	82.372
(17, 5)	57.221	(17, 3)	69.984	(16, 1)	82.847
(18, 5)	58.952	(18, 3)	71.075	(17, 1)	83.267
(19, 5)	60.513	(19, 3)	72.055	(18, 1)	83.640
				(19, 1)	83.974

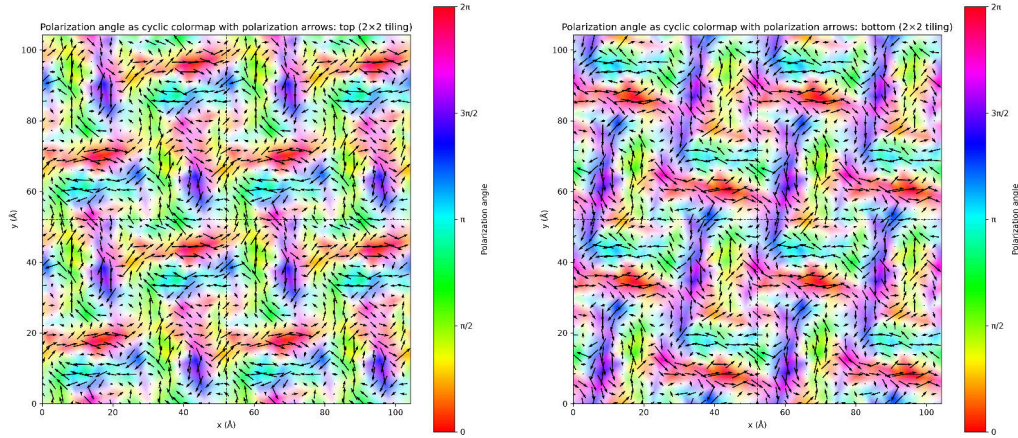
Table 8: Commensurate twisted-bilayer SrTiO_3 configurations considered in this work.

A.2 Additional Layer-Resolved Polarization Maps

Figures 29–31 present additional layer-resolved polarization maps for selected intermediate twist angles.



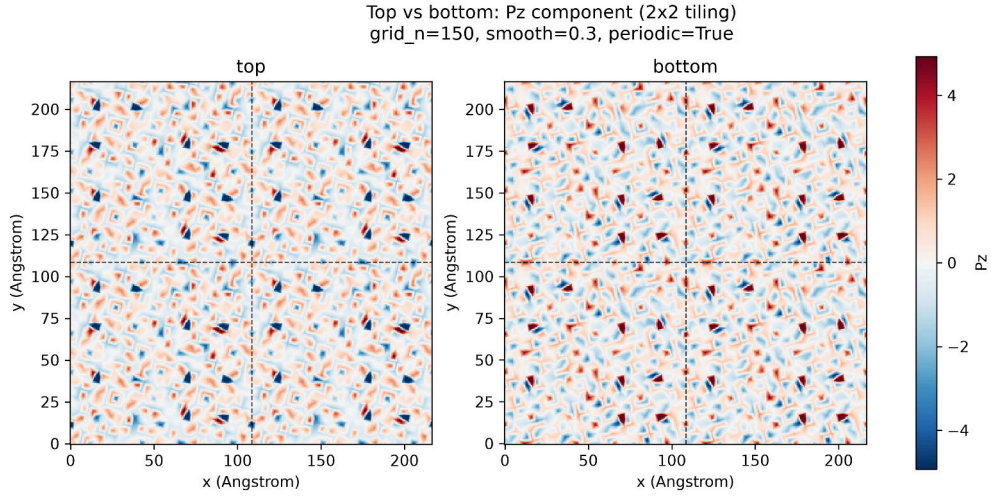
(a) Layer-resolved out-of-plane polarization component, P_z .



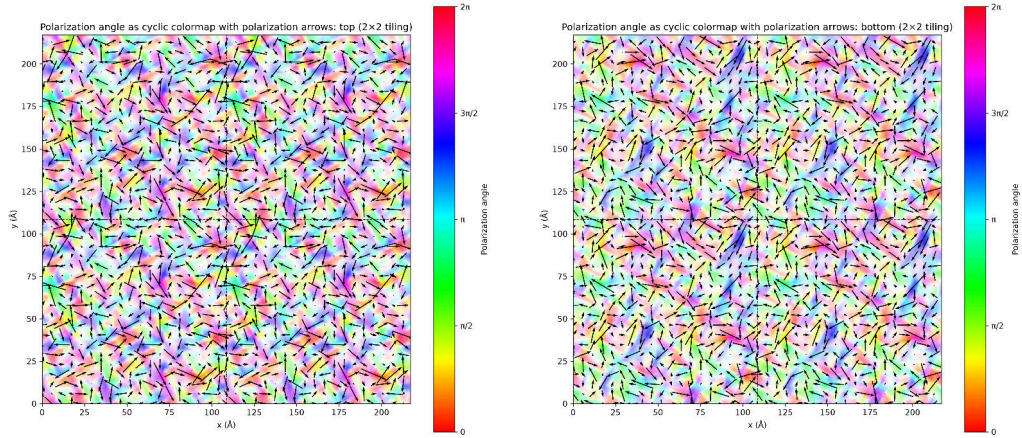
(b) In-plane polarization texture in the top layer.

(c) In-plane polarization texture in the bottom layer.

Figure 29: Layer-resolved polarization textures of the twisted SrTiO_3 bilayer at $\theta = 25.989^\circ$. Panel (a) shows the out-of-plane polarization component, P_z , in the top and bottom layers. Panels (b) and (c) show the in-plane polarization angles and polarization vectors in the top and bottom layers, respectively. A 2×2 periodic tiling is presented.



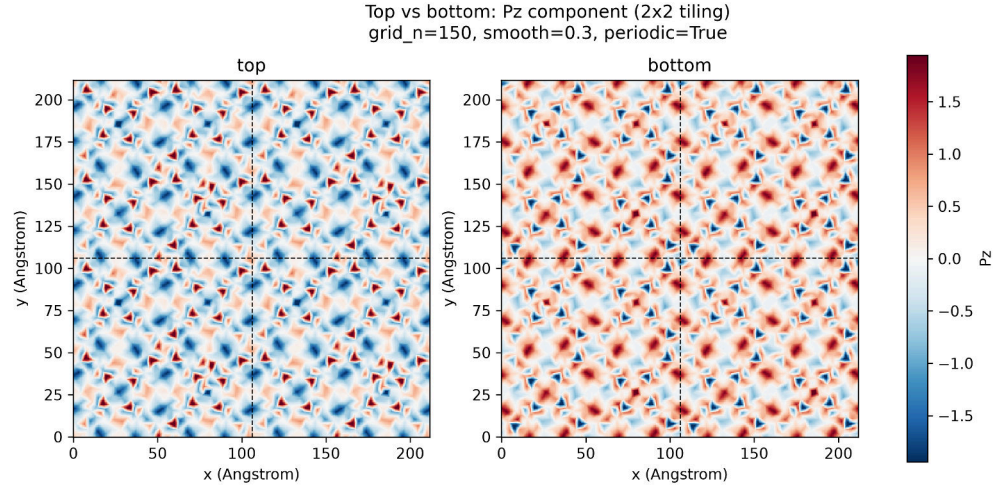
(a) Layer-resolved out-of-plane polarization component, P_z .



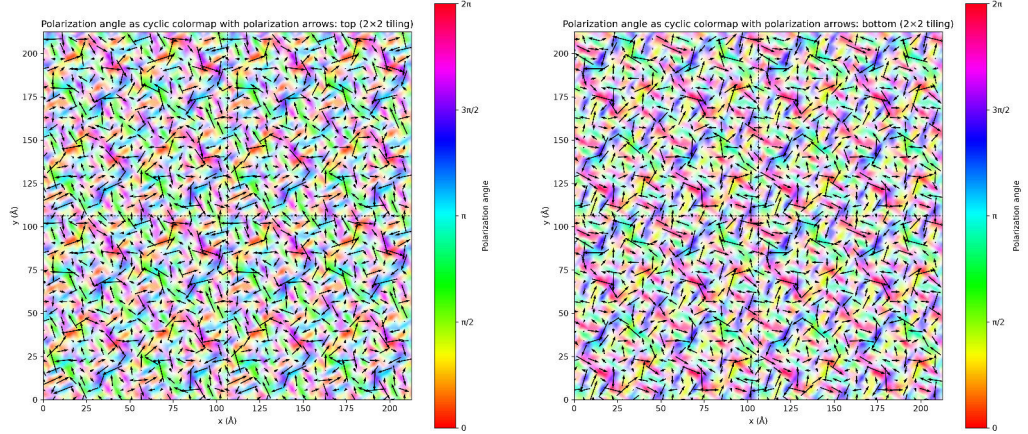
(b) In-plane polarization texture in the top layer.

(c) In-plane polarization texture in the bottom layer.

Figure 30: Layer-resolved polarization textures of the twisted SrTiO_3 bilayer at $\theta = 60.513^\circ$. Panel (a) shows the out-of-plane polarization component, P_z , in the top and bottom layers. Panels (b) and (c) show the in-plane polarization angles and polarization vectors in the top and bottom layers, respectively. A 2×2 periodic tiling is presented.



(a) Layer-resolved out-of-plane polarization component, P_z .



(b) In-plane polarization texture in the top layer.

(c) In-plane polarization texture in the bottom layer.

Figure 31: Layer-resolved polarization textures of the twisted SrTiO_3 bilayer at $\theta = 72.055^\circ$. Panel (a) shows the out-of-plane polarization component, P_z , in the top and bottom layers. Panels (b) and (c) show the in-plane polarization angles and polarization vectors in the top and bottom layers, respectively. A 2×2 periodic tiling is presented.

Personal Statement of Non-Plagiarism

I hereby declare that all information in this report has been obtained and presented in accordance with academic rules and ethical conduct and the work I am submitting in this report, except where I have indicated, is my own work.

Supervisor Approval

I, the undersigned, Dr. Adolfo Otero Fumega, supervisor of Maryam Ayaz, student of the iPSRS EMJMD, during her master thesis at Aalto University, certify that I approve the content of this master thesis report entitled *Emergent Ferroelectric Phases in Moiré Complex Oxides*

Date: _____

Signature of the supervisor: _____

Signature of the supervisor: _____