
UNIVERSITÉ DE LIÈGE

Structural Instabilities and Complex Polar Order

in

Perovskite Oxides

Insights and Control from
First- and Second-Principles

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by

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Structural Instabilities and Complex Polar Order in Perovskite Oxides Insights and Control from First- and Second-Principles

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Abstract

Oxide perovskites constitute one of the most versatile families of functional materials, exhibiting a broad spectrum of physical phenomena including ferroelectricity, antiferroelectricity, metal-insulator transitions, and the emergence of complex topological textures. Understanding these properties at the microscopic level remains challenging, as they emerge from the collective behavior of multiple coupled structural contributions that are computationally demanding to simulate at finite temperature and large scale. This thesis addresses these challenges through the systematic development, validation, and application of second-principles interatomic potentials for a series of representative perovskite oxides, and exploits these models to investigate the nature, stability, and dynamical control of topological polar textures in bulk crystals and heterostructures. A rich variety of such textures is identified and characterized, and their stability and tunability are systematically assessed. The dynamical manipulation of these textures is then addressed through two complementary strategies. Spatially modulated acoustic phonon excitations are shown to enable deterministic and reversible engineering of a broad family of polar topologies, while inhomogeneous, time-dependent electric fields allow precise control and displacement of individual topological objects, including the reversible switching between states of opposite topological charge in the same material. Together, these results establish a framework for the active *in situ* control of polar textures in bulk ferroelectrics. Finally, an initially non-polar perovskite is shown to harbor a hidden ferroelectric phase whose metastability is governed by a layer-by-layer nucleation mechanism, and an electric-field-driven first-order polarization switching process is identified as an alternative pathway to antiferroelectricity. The lattice dynamics of a correlated oxide across its metal-insulator transition are also examined, reproducing the triggered instability mechanism at the origin of the structural phase transition.

Résumé

Les oxydes pérovskites constituent l'une des familles de matériaux fonctionnels les plus remarquables, présentant une grande diversité de phénomènes physiques, notamment la ferroélectricité, l'antiferroélectricité, les transitions métal-isolant, et l'émergence de textures topologiques complexes. Ces propriétés émergent du comportement collectif de plusieurs degrés de liberté structuraux couplés, ce qui rend leur compréhension à l'échelle microscopique particulièrement ardue, d'autant que leur simulation à température finie et grande échelle est numériquement coûteuse. Cette thèse répond à ces défis par le développement systématique, la validation et l'application de potentiels interatomiques de seconds principes pour une sélection d'oxydes pérovskites soigneusement choisis, et exploite ces modèles pour étudier la nature, la stabilité et le contrôle dynamique de textures polaires topologiques dans des cristaux massifs et des hétérostructures. Ces textures se révèlent d'une grande diversité, et leur stabilité ainsi que les moyens de les contrôler sont systématiquement étudiés. La manipulation dynamique de ces textures est ensuite abordée selon deux stratégies complémentaires. D'une part, il est montré que des excitations de phonons acoustiques spatialement modulées permettent de construire de manière déterministe et réversible une large famille de topologies polaires. D'autre part, des champs électriques inhomogènes et dépendants du temps permettent le contrôle précis et le déplacement d'objets topologiques individuels, ainsi que la commutation réversible entre états de charge topologique opposée au sein d'un même matériau. Ces résultats ouvrent la voie à un contrôle actif *in situ* des textures polaires dans les ferroélectriques. Enfin, il est montré qu'un oxyde pérovskite initialement non polaire peut abriter une phase ferroélectrique cachée, dont la métastabilité est gouvernée par un mécanisme de nucléation couche par couche. Un processus de commutation de la polarisation du premier ordre, induit par champ électrique, est par ailleurs identifié comme voie alternative au comportement antiferroélectrique. La dynamique de réseau d'un oxyde corrélé au voisinage de sa transition métal-isolant est également étudiée, permettant de reproduire le mécanisme à l'origine de sa transition de phase structurale.

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Physical Review B 110 (5), 054109
4. E. Zatterin[†], P. Ondrejko[†], L. Bastogne[†], C. Lichtensteiger, L. Tovaglieri, DA. Chaney, A. Sasani, T. Schüllli, A. Bosak, S. Leake, P. Zubko, Ph. Ghosez, J. Hlinka, JM. Triscone, M. Hadjimichael
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Physical Review X 14 (4), 041052
5. L. Bastogne[†], F. Gómez-Ortiz[†], S. Anand, Ph. Ghosez
Dynamical manipulation of polar topologies from acoustic phonon excitations
Nano Letters 24 (43), 13783-13789

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7. F. Gómez-Ortiz[†], L. Bastogne[†], S. Anand, M. Yu, X. He, Ph. Ghosez
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8. S. Chege, L. Bastogne, F. Gómez-Ortiz, J. Sifuna, G. Amolo, Ph. Ghosez, J. Junquera
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Role of long-range dipolar interactions in the simulation of the properties of polar crystals using effective atomic potentials
Physical Review B 112 (10), 104324
10. L. Bastogne[†], Ph. Ghosez
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MULTIBINIT: toward automatized second-principles models – Lattice part

Condensed matter physics is unusual among physics disciplines in the breadth of approaches it welcomes. It can be studied at many levels of abstraction, from the mathematical elegance of symmetry and topology to the practical engineering of devices and materials. The field naturally draws on quantum mechanics, statistical physics, thermodynamics, special relativity and classical mechanics, and advances through the interplay of experiment, theory, and computation, each bringing its own indispensable perspective. It also bridges physics with chemistry, materials science, and even biology, offering a rare versatility in how one can contribute. Whether one is interested in abstract formalism or tangible applications, in microscopic mechanisms or macroscopic phenomena, condensed matter accommodates all.

This breadth of intellectual scope is matched by an equally remarkable spectrum of practical impact. The field has been recognized by a substantial fraction of Nobel Prizes in Physics, as illustrated in Figure 1.1, reflecting both its fundamental importance and its contribution to technological progress. Most of the technologies that define modern life are, at their core, condensed matter achievements. The transistor [3], the foundation of every computer and smartphone, emerged from the patient understanding of semiconductors [4]. The blue light-emitting diode, awarded the Nobel Prize in Physics in 2014 [5], transformed the way the world is illuminated and made energy-efficient lighting accessible to billions. Magnetic storage media [6], liquid crystal displays [7], photovoltaic cells [8], lithium-ion batteries [9], magnetic resonance imaging [10], and the superconducting qubits [11] at the heart of nascent quantum computers are all, fundamentally, products of condensed matter research. The path from the laboratory to society is often long and indirect, but it is real and consequential.

It would be misleading, however, to suggest that the appeal of condensed matter physics lies primarily in its applications. The deeper motivation, and the one that animates much of the work presented in this manuscript, is the pursuit of understanding. A small change in composition, temperature, or pressure can transform an insulator into a metal, a

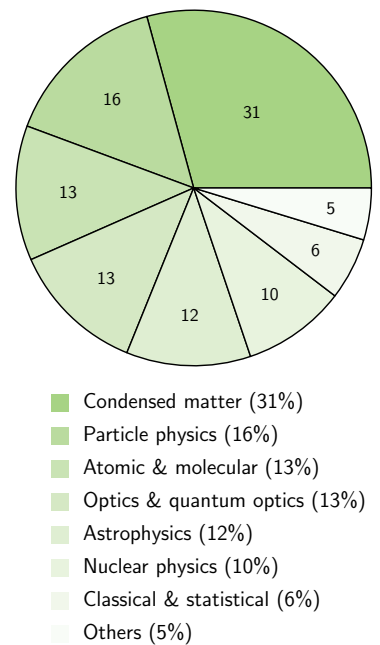


Figure 1.1: Distribution of Nobel Prizes in Physics by subfield (1901–2025). Condensed matter physics accounts for approximately one quarter of all awards. The classification is based on [1] for the period 1901–2000, extended to 2025 following [2].

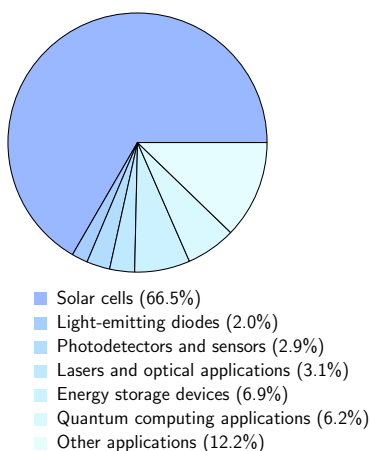


Figure 1.2: Global perovskite market revenue share by application (2024). The total market was valued at approximately USD 0.7 billion, with solar cells accounting for two-thirds of the revenue. Data adapted from [12].

paraelectric into a ferroelectric, or a trivial band structure into a topologically protected one. Each of these transitions is governed by a mechanism, often subtle and sometimes counterintuitive, and identifying these mechanisms is what drives the field forward. Applications follow, but they follow understanding.

Among the materials that have most consistently rewarded such investigation are the perovskite oxides. With the general formula ABO_3 , this family hosts an extraordinary range of physical phenomena such as ferroelectricity, antiferroelectricity, ferromagnetism, multiferroicity, superconductivity, colossal magnetoresistance, photovoltaic effect, and metal-insulator transitions. This richness arises from the delicate interplay between structural, electronic, and magnetic degrees of freedom that the perovskite structure accommodates. Small perturbations, epitaxial strain, chemical substitution, or applied electric or magnetic fields, can shift the balance between competing phases, making these materials both scientifically rich and potentially useful for applications in solar-cells, nanoelectronics, sensors, energy storage devices, and heating and cooling systems as alternatives to gas-based technologies.

Among the plethora of phenomena that perovskite oxides exhibit, this thesis focuses primarily on the structural properties of these materials: how atoms arrange themselves collectively, how they vibrate, and how these arrangements evolve with external stimuli. It is remarkable that, without any external instruction, vast numbers of atoms spontaneously organize into coherent patterns that extend across macroscopic distances. These collective arrangements give rise to the phenomena examined here: ferroelectricity, antiferroelectricity, and the spatially modulated polarization patterns that emerge in ferroelectric materials. Some of these patterns organize into arrangements that are inherently robust to perturbations, making them attractive for applications requiring stable nanoscale structures.

The theoretical and computational study of perovskite oxides has been particularly active over the past decades [13]. Density functional theory provides quantitative predictions of ground-state properties, but its computational cost restricts it to small systems at zero temperature. The phenomena addressed in this thesis, structural phase transitions, polar textures, and their dynamical manipulation, typically

involve hundreds or thousands of atoms over picosecond to nanosecond timescales. Bridging this gap requires effective models parametrized on first-principles data that can be deployed in large-scale molecular dynamics simulations. The second-principles approach and machine-learning interatomic potentials have emerged as the two main strategies for achieving this.

The present thesis is devoted to the construction, validation, and application of such models to a selection of perovskite oxides, with the aim of investigating their finite-temperature properties, the polar textures they host, the ways in which these textures can be manipulated through external stimuli, and the conditions under which ferroelectric and antiferroelectric instabilities compete and can be tuned.

The present manuscript is organized as follows. [Chapter 2](#) and [Chapter 3](#) provide some generic background on functional perovskite oxides, topological polar textures, and the computational methods employed throughout this work. [Chapter 4](#) is devoted to the construction and validation of interatomic potentials for the materials studied in this thesis. [Chapter 5](#) investigates the ferroic textures emerging in these materials, both in bulk and in superlattice geometries. [Chapter 6](#) addresses the dynamical manipulation of polar textures under external stimuli. [Chapter 7](#) focuses on the unconventional ferroelectric and antiferroelectric behavior of CaTiO_3 . Finally, [Chapter 8](#) investigates the finite-temperature lattice dynamics of YNiO_3 .

Background 2

Before turning to the original results of this thesis, it is necessary to set the stage with the theoretical concepts on which they rely. The perovskite oxides at the heart of this work display a rich variety of structural and polar behaviors, and making sense of these requires familiarity with a few key ideas that recur throughout the manuscript.

The discussion opens with the perovskite structure itself, the crystallographic framework from which all subsequent considerations stem. The distortions that lower its symmetry, together with the lattice vibrations that accompany them, are then examined, as they underlie the structural phase transitions encountered in later chapters. Attention next turns to ferroelectricity and antiferroelectricity, two phenomena central to this thesis, whose phenomenological description provides the vocabulary used to characterize polar order. The chapter closes with a discussion of topology in polar oxides, where notions of topological defects, solitons, and protection are introduced. These concepts will prove essential when polar textures of nontrivial topology are examined in subsequent chapters.

The aim here is not to provide an exhaustive review, but to equip the reader with the conceptual tools and physical intuition needed to engage with what follows.

2.1 The Perovskite structure

The compounds investigated in this work belong to the broad family of perovskite materials, a class of ternary crystals typically described by the chemical formula ABX_3 . In this notation, A and B denote cations of different ionic radii, and X is an anion, typically oxygen in oxide perovskites or a halogen in halide perovskites. In its aristotype cubic form (see Figure 2.1), the perovskite structure (space group $Pm\bar{3}m$) is defined by a primitive unit cell with lattice parameter a . The larger A cations occupy the cube corners, the smaller B cation resides at the body center, and the X anions are located at the face centers. The B cation is surrounded by six

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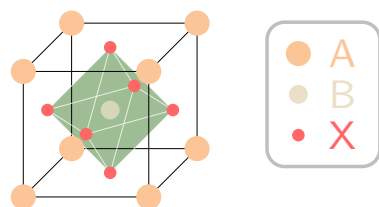


Figure 2.1: Illustration of the ideal $Pm\bar{3}m$ cubic unit cell ABX_3 perovskite structure.

X anions, forming BX_6 octahedra. Through periodic repetition, these octahedra connect via their corners, generating a three-dimensional network that constitutes the backbone of the structure. All members of this family adopt as slightly different structures which can all be viewed as distortions of this reference structure.

Aside from classical semiconductors such as silicon, perovskites constitute one of the most extensively studied classes of crystalline materials [14]. Their remarkable scientific relevance arises from the structural flexibility of the ABX_3 chemistry, which can accommodate a wide variety of metallic cations on both A and B sites. This chemical versatility gives rise to an exceptional diversity of physical properties, including ferroelectricity, magnetism, multiferroicity [15], superconductivity [16], metal–insulator transitions [17], complex topological textures [18] and remarkable optoelectronic properties exploited in photovoltaic applications [19]. As a result, the perovskite structure serves as an ideal platform for exploring how macroscopic functionalities emerge from microscopic interactions at the atomic scale.

2.1.1 Structural distortions

The crystallographic description of the perovskite structure was rationalized by Victor Goldschmidt in 1926 through his introduction of the tolerance factor concept, providing a geometric criterion for structural stability [20].

Although the perovskite family encompasses a vast number of compounds, the ideal cubic structure is rarely the ground state: most perovskites lower their symmetry through one or more structural distortions at low temperature, while preserving the fundamental framework of corner-sharing BX_6 octahedra. These deviations typically arise from size mismatches between the constituent ions.

Goldschmidt proposed a geometric interpretation of these distortions by modeling the ions as rigid spheres characterized by effective ionic radii. Within this picture, the stability of the cubic phase can be assessed by comparing two geometric constraints: the distance between ions in contact along the face diagonal of the cube and that along the edge defined by the octahedral network. For a perfectly cubic arrangement,

these distances satisfy a specific relation, which leads to the definition of the *Goldschmidt tolerance factor*

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}, \quad (2.1)$$

where r_A , r_B and r_X denote the ionic radii of the A, B, and X species, respectively. Values of t close to unity favor the cubic phase, whereas deviations from this condition typically lead to symmetry-lowering distortions of the perovskite structure, as illustrated in Figure 2.2 (a).

When $t < 1$, the A cation is undersized with respect to the cuboctahedral cavity formed by the surrounding BX_6 octahedra. In this situation, the A site is relatively spacious, while the octahedral network is geometrically overextended if kept perfectly cubic. The structure can lower its energy in two distinct, and not mutually exclusive ways. First, the corner-sharing octahedra may rotate cooperatively, thereby reducing the size of the A-site cavity without breaking the connectivity of the network. These rotations can occur around the Cartesian axes of the parent cubic structure. Adjacent octahedra along a given rotation axis may rotate in-phase or out-of-phase as illustrated in Figure 2.2 (b) and (c). Second, the A cation itself may displace within its cavity. Such off-centering motions can contribute to polar distortions if they break inversion symmetry as shown in Figure 2.2 (d) or to anti-polar distortions if the A cations of different site move in opposite directions. In practice, octahedral rotations are the most common response for $t < 1$, and multiple rotation axes may be involved simultaneously. The classification of these cooperative tilt patterns was introduced by Mike Glazer [21] through the notation $a^{\pm,0}, b^{\pm,0}, c^{\pm,0}$, where the letters indicate the rotation amplitudes around the x , y and z axes, and the superscript $+$, $-$ and 0 denote in-phase, anti-phase, or absent rotations, respectively. Among the 23 symmetry-distinct tilt systems identified, the $a^-a^-c^+$ pattern is the most frequently encountered, lowering the symmetry from cubic $Pm\bar{3}m$ to orthorhombic $Pbnm$ [22].

In perovskites with $t > 1$, the relative ionic sizes imply that the BX_6 octahedra provides excess space for the B cation, while the A cation more tightly fills its cuboctahedral cavity. In this situation, the structure cannot efficiently relax through octahedral tilting alone. Instead, it often lowers its energy through off-centering displacements of the B cations with

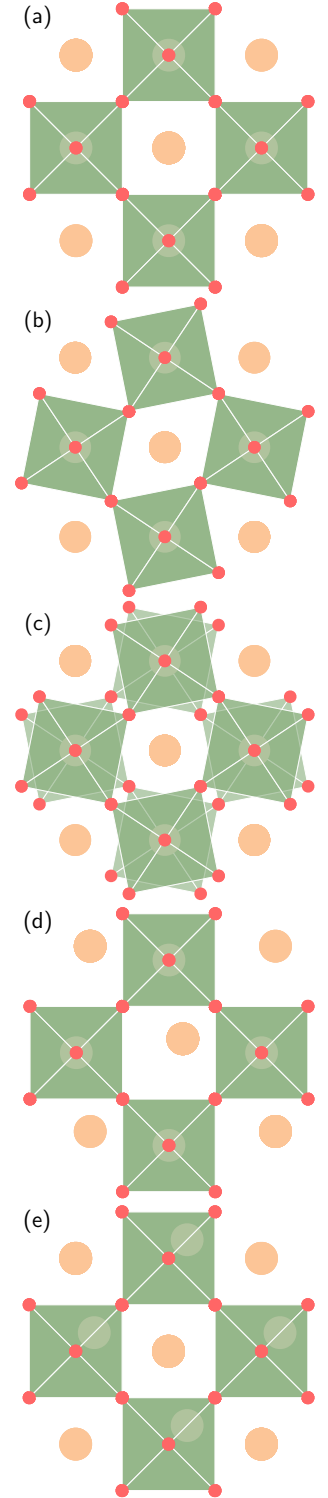
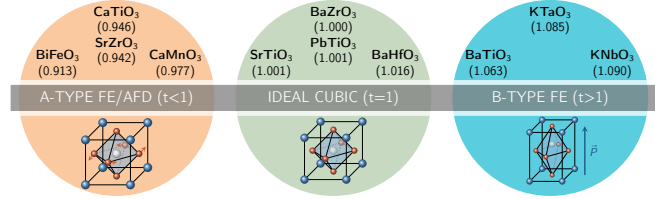


Figure 2.2: Illustration of the top view of (a) ideal cubic perovskite. (b) In-phase rotation. (c) Out-of phase rotation. (d) A-type polar distortion (e) B-type polar distortion.

Figure 2.3: Structural distortion associated with Goldschmidt tolerance factor for different perovskite oxides



respect to the surrounding anion network, as illustrated in Figure 2.2 (e). These polar distortions typically involve a displacement of the B cation within its octahedron along one or several Cartesian directions of the parent cubic structure. When this off-centering breaks inversion symmetry, it gives rise to a spontaneous polarization. In many oxide perovskites, this instability reflects not only geometric size effects captured by the tolerance factor, but also electronic mechanisms associated with B–X hybridization.

2.1.2 Phonons and structural instabilities

The structural distortions discussed above, such as octahedral rotations or polar displacements, can all be interpreted as collective atomic motions away from the high-symmetry positions of the ideal cubic structure. A natural framework for describing such collective atomic displacements in crystalline solids is provided by the phonon formalism. Within the harmonic approximation, a solid can be regarded as a collection of independent harmonic oscillators whose normal modes, referred to as phonons, define a complete orthogonal basis for the atomic displacements. Beyond providing a convenient basis for representing structural distortions, this formalism is also exploited as a powerful criterion for assessing the stability of a given reference structure.

Indeed, any arbitrary atomic distortion $\mathbf{u}$ can be expressed as a superposition of phonon eigendisplacements, which form a complete orthogonal basis for describing collective atomic displacements in a crystal (Figure 2.4),

$$u_{l\kappa\alpha} = \frac{1}{\sqrt{M_\kappa}} \sum_{j,\mathbf{q}} Q_{j\mathbf{q}} \gamma_{j\mathbf{q}}(\kappa\alpha) e^{i\mathbf{q}\cdot\mathbf{R}_l}, \quad (2.2)$$

where $u_{l\kappa\alpha}$ is the displacement of atom κ in the direction α in the cell l located at $\mathbf{R}_l$, $Q_{j\mathbf{q}}$ denotes the amplitude

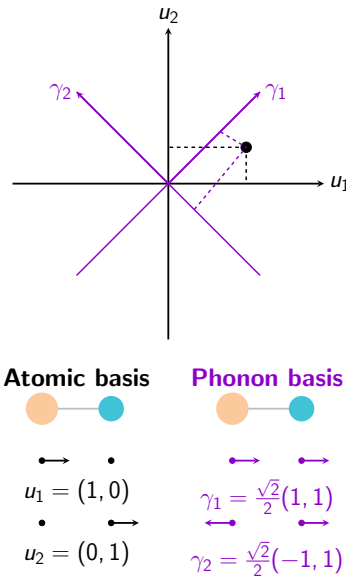


Figure 2.4: Schematic representation of the change of basis from the atomic displacement basis (u_1, u_2), where u_1 and u_2 denote the displacements of atoms 1 and 2 with respect to their reference positions, to the phonon basis (γ_1, γ_2), where γ_1 and γ_2 denote the relative motions of atoms 1 and 2 with respect to one another.

of the phonon mode and $\gamma_{j\mathbf{q}}$ its normalized eigenvector ($\langle \gamma_{j\mathbf{q}} | \gamma_{j\mathbf{q}} \rangle = 1$), obtained from the diagonalization of the dynamical matrix,

$$\sum_{\kappa'\beta} \tilde{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) \gamma_{j\mathbf{q}}(\kappa'\beta) = \omega_{j\mathbf{q}}^2 \gamma_{j\mathbf{q}}(\kappa\alpha), \quad (2.3)$$

where α and β label Cartesian directions, κ and κ' label atoms in the unit cell, $\mathbf{q}$ is the phonon wavevector and $\omega_{j\mathbf{q}}$ is the frequency associated to the phonon mode $\gamma_{j\mathbf{q}}$. The dynamical matrix $\tilde{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})$ is obtained from the Fourier transform of the interatomic force constants (IFC), normalized by the atomic masses,

$$\tilde{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) = \frac{\tilde{K}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})}{\sqrt{M_\kappa M_{\kappa'}}}, \quad (2.4)$$

where the IFC correspond to the second derivatives of the total energy with respect to atomic displacements,

$$K_{l\kappa\alpha,l'\kappa'\beta} = \frac{\partial^2 E}{\partial u_{l\kappa\alpha} \partial u_{l'\kappa'\beta}}. \quad (2.5)$$

Within the harmonic approximation, the energy associated with atomic displacements can be written as

$$E = \frac{1}{2} \sum_{l\kappa\alpha,l'\kappa'\beta} K_{l\kappa\alpha,l'\kappa'\beta} u_{l\kappa\alpha} u_{l'\kappa'\beta}. \quad (2.6)$$

The phonon frequencies $\omega_{j\mathbf{q}}^2$ are therefore directly related to the curvature of the energy surface along the corresponding phonon coordinate. This relation becomes particularly transparent when the energy is expressed in the phonon basis. By inserting Eq. (2.2) into Eq. (2.6), the energy can be written as

$$E = \frac{N}{2} \sum_{j,\mathbf{q}} \omega_{j\mathbf{q}}^2 |Q_{j\mathbf{q}}|^2, \quad (2.7)$$

where N denotes the number of unit cells in the crystal.

In this representation, the sign of $\omega_{j\mathbf{q}}^2$ directly reflects the dynamical stability of the structure with respect to a given distortion. A positive value corresponds to a local minimum of the energy surface along the associated coordinate, indicating that the reference structure is stable against this distortion. Conversely, a negative value, conventionally reported as an imaginary phonon frequency, signals a negative curvature of

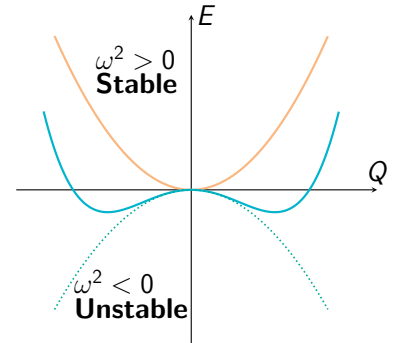


Figure 2.5: Illustration of different energy variation scenarios as a function of structural distortion Q . The orange curve displays a positive curvature of the energy landscape around the reference structure, corresponding to a real and positive vibrational frequency ω , indicative of a stable configuration. The blue curve, on the other hand, exhibits a negative curvature at the reference structure, giving rise to an imaginary frequency ω , which signals a structural instability. The dotted line represents the harmonic approximation associated with this latter case.

the energy surface, as illustrated in [Figure 2.5](#). In this case, the reference structure is unstable and will spontaneously distort along this mode in order to lower its energy.

Computing the phonon dispersion curves in the reference structure therefore allows identifying possible instabilities and anticipating the related distortions. In this respect, the phonon formalism provides a microscopic and quantitative counterpart to the empirical considerations introduced earlier through the Goldschmidt tolerance factor ([Section 2.1.1](#)). The distortions anticipated on geometric grounds, such as octahedra rotations and polar displacements, correspond to unstable modes at the center or the boundary of the Brillouin zone, and are thus captured by small supercells commensurate with these wavevectors. For most bulk perovskites, the ground-state structure is well reproduced by first-principles calculations on such small cells. Whereas the tolerance factor offers an intuitive geometric criterion for anticipating the propensity of a perovskite to distort, the analysis of the phonon dispersion curves reveals which specific atomic patterns are energetically favored, at which wavevectors, and with what relative strength. The geometric intuition is thus complemented by a rigorous and predictive tool grounded in the curvature of the energy landscape. Moreover, phonon dispersions can be obtained from first-principles using density functional perturbation theory ([Section 3.1.3](#)), providing direct access to these quantities without recourse to empirical parameters. However, when several distinct instabilities are simultaneously present in the phonon dispersion, anticipating the ground-state structure becomes considerably less straightforward. In such cases, the harmonic approximation alone is insufficient, as it provides no information on the relative energetics of the distorted phases or on how distinct unstable modes interact with one another. Resolving the ground state then requires going beyond the harmonic level, either by explicitly exploring the energy landscape through finite-distortion calculations, or by quantifying the anharmonic couplings between competing instabilities. This is precisely the regime encountered in many perovskite oxides, where octahedral rotation instabilities and polar instabilities coexist and compete, making the determination of the ground state a non-trivial problem that motivates the development of the methods discussed in the following sections.

This approach will be used extensively throughout this manuscript. Phonon dispersions of high-symmetry refer-

ence structures will serve as a systematic starting point for identifying structural instabilities, guiding the search for the ground state, and uncovering metastable phases that may compete energetically with it. They will also be employed to characterize the microscopic mechanisms underlying the structural phase transitions of the perovskites investigated in this work, to rationalize the emergence of polar and antipolar orders, and to inform the construction of the effective models presented in Chapter 4.

2.2 Ferroelectricity and antiferroelectricity

Having established that certain structural distortions in perovskites are associated with unstable phonon modes, it is natural to ask what macroscopic physical quantity emerges when such an instability condenses, and what microscopic mechanism is at its origin. A central quantity of interest is the electric polarization $\mathbf{P}$, defined as the electric dipole moment per unit volume of the crystal. When atoms displace from their centrosymmetric positions along a polar mode, the resulting charge asymmetry gives rise to a net polarization. Depending on how this polarization orders across the crystal, whether it is uniform or spatially modulated, qualitatively different collective behaviors emerge. This section introduces the two main classes of polar order relevant to this thesis: ferroelectricity, in which the spontaneous polarization is uniform and switchable by an external electric field, and antiferroelectricity, which involves a more subtle, spatially modulated ordering.

2.2.1 Ferroelectricity

A crystal is defined as *ferroelectric* when it has at least two equivalent stable orientation of polarization in the absence of applied electric field and can be shifted from one to the other by an applied electric field (Figure 2.6) [23]. The great majority of known ferroelectrics are associated to a paraelectric high symmetry phase stable at high temperature. As a result, typical ferroelectrics exhibit a spontaneous polarization P_s which decreases with increasing temperature and disappears at a Curie temperature T_c , as illustrated by the evolution of

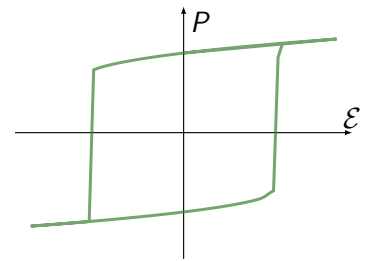


Figure 2.6: Schematic representation of a ferroelectric hysteresis loop, showing the evolution of the polarization P as a function of the applied electric field $\mathcal{E}$.

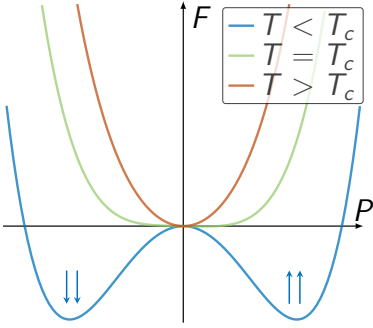


Figure 2.7: Illustration of the free energy landscape of a prototypical ferroelectric for temperatures below, equal and above the Curie temperature.

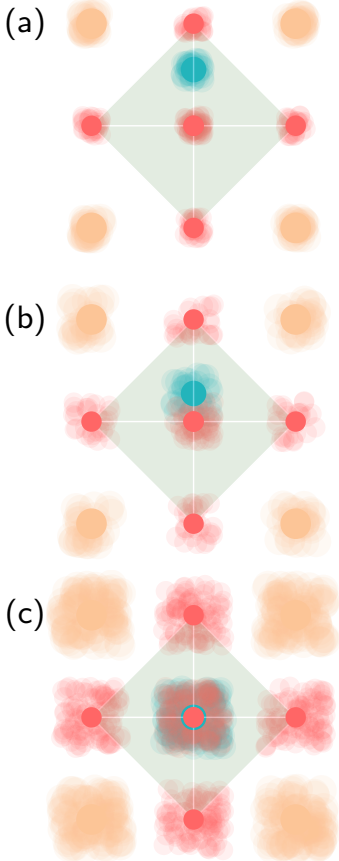


Figure 2.8: Illustration of the displacive mechanism of the ferroelectric phase transition upon increasing temperature. As the temperature increases, the amplitude of thermal fluctuations grows, progressively reducing the effective polar distortion until the system recovers its centrosymmetric configuration on average above T_c .

the free energy landscape shown in Figure 2.7. This transition is associated typically with a divergence of the dielectric permittivity ε following the Curie-Weiss law [24],

$$\varepsilon = \frac{C}{T - T_0} \quad (2.8)$$

where C is the Curie constant, where T_0 is the Curie-Weiss temperature and is equal to T_c when the ferroelectric to paraelectric transition is continuous.

The ferroelectric phase transition is commonly associated with the condensation of a soft phonon mode at the Γ point of the Brillouin zone. Two distinct, yet not mutually exclusive, microscopic are usually evoked to explain this transition.

In the *displacive* picture, illustrated in Figure 2.8, the ferroelectric ground state is stabilized by a polar distortion in which atoms displace from their centrosymmetric positions toward configurations that minimize the total free energy. This off-centering shortens specific interatomic bonds and optimizes the relevant interactions. As the temperature is raised, thermal fluctuations cause the atoms to explore an increasingly large region of space. This effectively means that configurations in which atoms are closer together, and thus experience stronger repulsive interactions, become thermally accessible. The average interatomic distances are consequently renormalized, reducing the energetic gain associated with the polar distortion, and the system progressively recovers its centrosymmetric configuration upon heating.

Within this framework, and considering the simplest case in which the polar instability is driven by a single phonon mode, the restoring force associated with that mode hardens continuously with temperature. Since the squared frequency ω^2 of a phonon mode is proportional to the curvature of the energy surface (see Section 2.1.2) along the corresponding coordinate, this hardening implies a linear relationship $\omega^2 \propto (T - T_c)$, which is the essence of the soft-mode theory introduced by Cochran [25]. The mode is said to *soften* upon cooling: its frequency decreases continuously until it reaches zero at T_c , at which point the restoring force vanishes and the system condenses into the polar phase. This softening is directly reflected in the dielectric response, providing a microscopic foundation for the divergence of the static dielec-

tric permittivity following the Curie-Weiss law introduced in Eq.(2.8).

In the *order-disorder* picture, by contrast, the relevant atomic displacements are already present locally above the transition temperature. When the thermal energy is sufficiently large to overcome the barrier separating equivalent polar configurations, the system fluctuates between them as illustrated in Figure 2.9. In the time average, these rapid switching events result in a centrosymmetric structure, even though the instantaneous local symmetry remains broken. The transition temperature thus marks the onset of long-range correlations between these local distortions rather than the appearance of the distortions themselves.

In practice, these two pictures are not mutually exclusive but rather constitute two complementary descriptions of the same underlying physics. Depending on how thermal averaging is performed, a given ferroelectric transition may appear predominantly displacive or order-disorder, even though the same phenomenon is being described. The distinction is more clear-cut in systems where the local polarization is fixed in magnitude and cannot vanish, so that the transition is genuinely of the order-disorder type, analogous to magnetic ordering. In oxide perovskites, however, the polarization can locally collapse to zero, which blurs the boundary between the two pictures: the displacive viewpoint emphasizes the softening of a collective mode toward a high-symmetry average structure, while the order-disorder viewpoint describes the same situation as a disordered ensemble of locally polarized configurations whose orientations average out. The two pictures thus coexist, and the choice between them is largely a matter of perspective rather than of physical content.

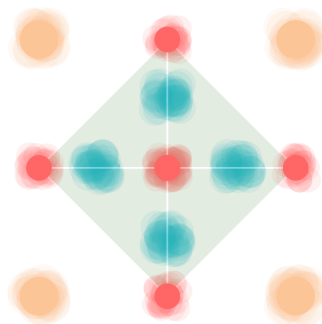


Figure 2.9: Illustration of the order disorder phase transition. At high temperature the B atom in turquoise has enough energy to switch between all the equivalent polar configurations. On average, the turquoise atom is located at the center of the cell

Type of ferroelectricity

Ferroelectrics can be classified according to the nature of the interactions driving the polar instability. The Landau framework provides a natural language for this classification, as each type of ferroelectric corresponds to a distinct form of the internal energy expansion, as described below.

Proper ferroelectricity – In proper ferroelectrics, such as BaTiO_3 or PbTiO_3 , the spontaneous polarization $\mathbf{P}$ is itself the primary order parameter of the transition. The paraelectric

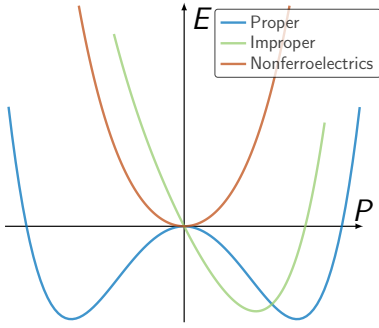


Figure 2.10: Schematic illustration of the polar mode energy landscape for three classes of materials. In proper ferroelectrics, the energy surface exhibits a double-well profile with a negative curvature at the origin ($\omega^2 < 0$), reflecting an intrinsic polar instability. In improper ferroelectrics, the polar mode is stable ($\omega^2 > 0$) but its well is shifted away from zero through coupling with a non-polar primary order parameter, inducing a finite polarization. In non-ferroelectrics, the energy surface is a single well centered at $\xi = 0$, with no instability or induced polarization.

phase hosts an unstable polar phonon mode ξ whose energy surface takes the form of a double well,

$$E(\xi) \propto \omega^2 \xi^2 + \beta \xi^4, \quad (2.9)$$

with $\omega^2 < 0$, directly reflecting the negative curvature of the energy surface along the polar coordinate introduced in Section 2.1.2. The condensation of this mode drives the system into the ferroelectric ground state, with $P \propto \xi$ acting as the primary order parameter of the transition.

Although a polar instability at the zone center is present in most ABO_3 perovskites, it generally competes with non-polar zone-boundary modes ϕ , such as oxygen octahedral rotations, through a positive biquadratic coupling of the form $E \propto \alpha \xi^2 \phi^2$ ($\alpha > 0$), which tends to suppress the ferroelectric instability. As discussed in Section 2.1.1, compounds with $t < 1$ are particularly prone to such competing rotational instabilities, so that their ground state is typically a non-polar $Pbnm$ phase [22]. Proper ferroelectricity thus most commonly arises for $t > 1$, where instabilities of rotation are not dominating.

The microscopic origin of the polar instability depends on the nature of the active cation. In B-type ferroelectrics ($t > 1$), such as BaTiO_3 , the instability is driven by a partial hybridization between O-2p and B-d states, which weakens the short-range repulsive forces and gives rise to anomalously large Born effective charges [26]. The resulting enhancement of long-range dipolar interactions then overcomes the short-range restoring forces, in line with Cochran's picture [25]. When the A-site cation is comparatively too small ($t < 1$), the dominant structural instabilities are instead the antiferrodistortive rotations of the oxygen octahedra discussed above, rather than a polar distortion. A genuine ferroelectric instability driven by the A site is found mainly in compounds containing lone pairs, where the stereochemical activity of the cation lone pair drives an off-centering through a more local, electronic mechanism [13].

The condensation of the polar mode is invariably accompanied by a macroscopic lattice distortion: the strain η appears as a secondary order parameter of the transition, linearly enslaved to the polar mode through a coupling term of the form $E \propto g \eta \xi^2$ in the energy surface. This term renormalizes the curvature of the polar energy surface, effectively softening or

hardening the polar mode depending on the sign of the applied strain, and is at the origin of the piezoelectric response of ferroelectric materials, whereby an applied mechanical stress induces a polarization and, conversely, an applied electric field produces a lattice strain. It also implies that ferroelectrics are far more sensitive to mechanical boundary conditions than magnetic materials, where the spin-lattice coupling is comparatively weak. This strong sensitivity to strain is precisely what underpins the field of strain engineering, in which epitaxial mismatch between its ferroelectric film and its substrate is exploited to tune the polar properties, and stabilize otherwise inaccessible phases [27].

(Hybrid) improper ferroelectricity – In improper ferroelectrics, the polar mode ξ does not exhibit any intrinsic instability ($\omega^2 > 0$), but its appearance induced as a secondary order parameter through its linear coupling with a non-polar primary order parameter ϕ ,

$$E \propto \lambda \phi^n \xi. \quad (2.10)$$

The condensation of ϕ shifts the polar well and induces a finite polarization $P \propto \xi$. A notable consequence is that the dielectric response does not diverge at T_c , in contrast to proper ferroelectrics.

Hybrid improper ferroelectrics are a special case in which the polarization is induced not by one but by two distinct non-polar modes ϕ_1 and ϕ_2 through a trilinear coupling,

$$E \propto \lambda \phi_1 \phi_2 \xi, \quad (2.11)$$

a mechanism particularly relevant in layered perovskites and superlattices [28]. In both cases, switching $\mathbf{P}$ necessarily requires switching one of the primary order parameter, offering a practical route to manipulate non-polar structural degrees of freedom that would otherwise be insensitive to electric stimuli.

Triggered ferroelectricity – Triggered ferroelectrics, first proposed by Holakovský [29], share with improper ferroelectrics the absence of an intrinsic polar instability in the reference structure. However, rather than a linear coupling,

the polarization is here induced through a biquadratic coupling with a non-polar primary order parameter ϕ ,

$$E \propto \alpha \phi^2 \xi^2, \quad \alpha < 0, \quad (2.12)$$

whose condensation renormalizes the curvature of the polar well from positive to negative, effectively triggering a ferroelectric instability that was absent in the paraelectric phase.

Hyperferroelectricity – Hyperferroelectrics are proper ferroelectrics that remain polar even under open-circuit boundary conditions, *i.e.*, in the presence of an unscreened depolarizing field. This unusual robustness translates into an unstable longitudinal optical (LO) mode in addition to the conventional transverse optical (TO) instability.

2.2.2 Antiferroelectricity

The concept of antiferroelectricity was introduced by Kittel in 1951 [30] by analogy with antiferromagnetism. Just as the latter is characterized by a staggered magnetic order in which neighboring spins align antiparallel, Kittel proposed that an analogous staggered electric order could exist, in which two (or more) symmetry-related sublattices carry equal but opposite electric dipole moments, yielding a macroscopically non-polar state with vanishing net polarization, as illustrated in Figure 2.11. Within the same year, experimental evidence was provided by Shirane and co-workers, who reported characteristic double hysteresis loops in the polarization-field response of PbZrO_3 [31], a material that remains the archetypal antiferroelectric nowadays.

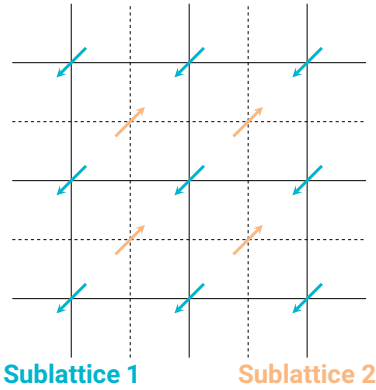


Figure 2.11: Illustration of Kittel-type antiferroelectrics defined by two sublattices with equal and opposite polarization.

This purely structural definition, however, proves insufficient to uniquely identify antiferroelectrics, since not all antipolar crystals share the same physical behavior. According to classical textbooks [23, 32], antiferroelectrics are more precisely defined as antipolar systems whose free energy is closely comparable to that of a ferroelectric modification of the same crystal, and which may therefore be switched from the antipolar to a polar phase by application of a sufficiently large electric field. This energetic proximity to a ferroelectric phase is the key distinguishing criterion, and manifests

experimentally through the appearance of characteristic double hysteresis loops in the polarization versus electric field response (Figure 2.12), as well as large dielectric anomalies near the transition temperature.

In the book entitled *Functional Metal Oxides* [33], Karin Rabe argues that the definition of antiferroelectricity should rest on energetic grounds independently of any further structural criterion, beyond the necessary condition of a vanishing net polarization. While the classical picture of two sublattices with opposite polarizations remains a useful intuition, it is neither necessary nor sufficient: a system presenting a well-defined antipolar distortion does not qualify as an antiferroelectric unless a competing ferroelectric phase lies sufficiently close in energy to be accessible under applied field. Conversely, a system with a more complex or less obvious antipolar order may well be antiferroelectric provided this energetic condition is met. The definition thus hinges not on the detailed structural character of the ground state, but on the topology of the energy landscape in the vicinity of the antiferroelectric phase.

Yet the energetic criterion alone, however physically transparent, is not without its own ambiguities. As pointed out by Catalan and co-workers [34], any system in which an antipolar state lies close in energy to a polar one and can be field-switched into the latter would formally qualify, including ferroelectric thin films or superlattices in which depolarizing fields drive the formation of antiparallel domain structures (see Section 2.3). In such systems, the net macroscopic polarization vanishes and a double hysteresis loop can be observed upon application of an electric field [34], yet no one would classify them as antiferroelectrics in the traditional sense. The reason is that the antipolar state in these systems is not an intrinsic homogeneous phase of the crystal: it is a multidomain state of a ferroelectric, where the polarization is locally finite in each domain and the apparent cancellation is purely a consequence of domain averaging. This observation motivates a more complete and modern definition of antiferroelectricity, recently proposed by Catalan and co-workers [34], which rests on three simultaneous criteria. First, the antiferroelectric must possess a ground state characterized by a *periodic antipolar arrangement of electric dipoles arising from atomic displacements with reference to a higher symmetry paraelectric phase*. This structural criterion is essential: the antipolar order must be a genuine

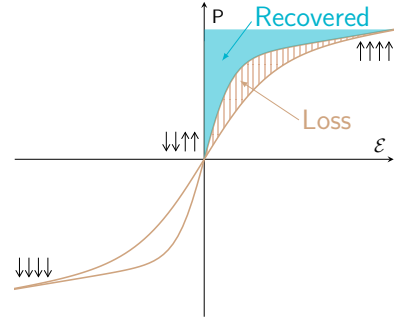


Figure 2.12: Illustration polarization versus electric field double hysteresis loop in antiferroelectrics. The Turquoise (resp. orange) part of the graph is the energy recovered (resp. lost) while releasing the applied electric field.

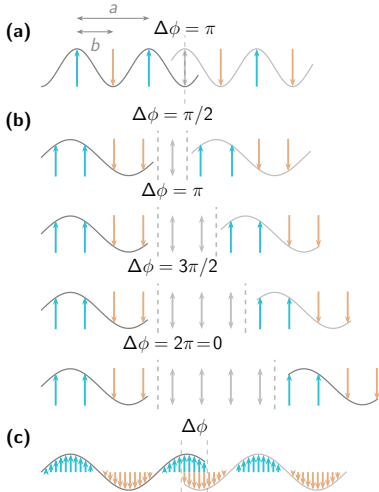


Figure 2.13: Illustration of translational boundaries in antiferroelectrics, adapted from [34]. Each panel corresponds to a distinct phase shift $\Delta\phi$ in the antipolar polarization wave $P(x)$. Panel (a) shows the classical antiphase boundary ($\Delta\phi = \pi$) arising in systems with a simple up-down modulation ($N = 2$). Panel (b) illustrates the three distinct translational boundaries ($\Delta\phi = \pi/2, \pi, 3\pi/2$) compatible with a $\uparrow\uparrow\downarrow\downarrow$ modulation ($N = 4$), as found in PbZrO_3 . Panel (c) shows the general case as a function of $\Delta\phi$.

property of the homogeneous crystal, not a consequence of domain formation. Second, the antiferroelectric must be able to accommodate *antiphase boundaries*, also called translational boundaries, which correspond to phase shifts in the periodic modulation of the antipolar distortion. Following the formalism introduced by Catalan and co-workers [34], the antiferroelectric order may be described as a spatial polarization wave along some direction x ,

$$P(x) = P_0 \sin\left(\frac{2\pi}{a}x + \phi\right), \quad (2.13)$$

where a is the periodicity of the antipolar modulation, P_0 is the amplitude, and ϕ is a spatial phase. A translational boundary is then defined as a discontinuity in ϕ , a phase shift $\Delta\phi$ in the polarization wave, as illustrated in Figure 2.13. If the antiferroelectric unit cell contains N dipoles separated by a distance b such that $a = Nb$, the phase shifts compatible with the continuity of the underlying paraelectric lattice are quantized as

$$\Delta\phi = 2\pi \frac{nb}{a}, \quad n \leq N. \quad (2.14)$$

In the simplest case of an up-down modulation ($N = 2$), the only non-trivial phase shift is $\Delta\phi = \pi$, defining the classical antiphase boundary. In PbZrO_3 , where the modulation is $\uparrow\uparrow\downarrow\downarrow$ ($N = 4$), three distinct translational boundaries exist, corresponding to phase shifts of $\pi/2, \pi$, and $3\pi/2$. Such boundaries are topologically protected: removing one implies that the entire dipole sequence of one of the adjacent domains must change. They are intrinsically distinct from the ordinary domain walls of a ferroelectric, where a wall separates regions of opposite polarization but the local order parameter remains structurally identical on both sides. The existence of translational boundaries is therefore a direct structural fingerprint of the underlying periodic antipolar order, and is absent in multidomain ferroelectrics. Third, the antiferroelectric must be capable of undergoing a *reversible voltage-induced transition to a polar phase*, manifested as a double hysteresis loop in the polarization-field response.

The conjunction of these three criteria cleanly resolves the ambiguity raised above. Systems such as $\text{PbTiO}_3/\text{SrTiO}_3$ superlattices, in which depolarizing fields stabilize antiparallel nanodomains and double hysteresis can be engineered [34], satisfy the energetic criterion of Rabe and exhibit a vanishing

net polarization, but fail the second structural criterion: no translational boundaries exist, because there is no periodic antipolar modulation at the unit cell level to begin with. Catalan *et al.* therefore classify such systems as *pseudo-antiferroelectrics* or *synthetic antiferroelectrics*, a terminology that acknowledges their functional similarity to antiferroelectrics while distinguishing them from materials in which the antipolar order is a genuine property of the crystal structure [34].

This classification is summarized in Figure 2.14, which makes clear that materials satisfying all three criteria simultaneously, and thus qualifying as antiferroelectrics in the strict sense, are in fact remarkably scarce. Far more common are materials that meet only one or two of the criteria, and that consequently share only part of the antiferroelectric phenomenology. Which specific properties such a material exhibits depends precisely on which criteria it fulfills. This observation is central to Chapter 7, where it is shown how a compound that is not antiferroelectric in any conventional sense can be turned into a synthetic antiferroelectric displaying some of the functional properties of genuine antiferroelectrics.

Properties of ferroelectrics and antiferroelectrics

The polar order characteristic of ferroelectric and antiferroelectric materials is not merely a structural curiosity: it underpins a wide range of physical phenomena of both fundamental and technological relevance. In ferroelectrics, the coupling between the spontaneous polarization and other degrees of freedom gives rise to a rich landscape of functional responses. Among the most prominent are the piezoelectric effect, whereby mechanical stress induces an electric polarization and conversely an applied field produces a mechanical deformation, and the pyroelectric effect, whereby a change in temperature produces a change in spontaneous polarization [23]. Beyond these classical responses, ferroelectrics and antiferroelectrics support a variety of phenomena that have attracted considerable attention in recent decades. Ferroelectric tunnel junctions exploit the polarization dependence of the tunneling barrier to achieve large electroresistance ratios, offering new routes toward non-volatile memory [35]. The bulk photovoltaic effect in non-centrosymmetric ferroelectrics generates a photocurrent whose direction and magnitude are controlled by the polarization state [36]. Spin-orbit coupling in polar systems gives rise to the Rashba effect, linking the

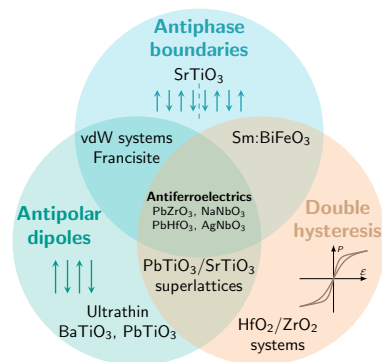


Figure 2.14: Venn diagram illustrating the classification of materials with respect to the three criteria defining antiferroelectricity, as proposed by Catalan and co-workers [34]: the presence of antipolar dipole arrangements, the ability to accommodate antiphase boundaries, and the observation of a double hysteresis loop under applied electric field. Genuine antiferroelectrics lie at the intersection of all three criteria. Adapted from [34]

electric polarization to the spin texture of charge carriers and enabling electrically tunable spin-to-charge conversion [37]. In multiferroic materials, where ferroelectric and magnetic orders coexist, magnetoelectric coupling enables the mutual control of electric polarization by a magnetic field and of magnetization by an electric field [38]. The proximity of antiferroelectric and ferroelectric phases in energy, discussed in Section 2.2.2, makes antiferroelectrics particularly attractive for energy storage and energy harvesting applications, where the large strain associated with the field-induced antipolar-to-polar switching can be exploited [39]. More recently, the discovery of ferroelectric metals [40] has challenged the conventional wisdom that metallic screening is incompatible with ferroelectric order, opening a new chapter in the understanding of polar instabilities.

Among this broad collection of properties, two are of particular relevance to the work presented in this thesis and are introduced in detail in the following subsections: the flexoelectric effect, which generalizes piezoelectricity to inhomogeneous strain configurations, and the electrocaloric effect, which couples the polarization to thermal degrees of freedom and is central to the study of field-driven caloric responses.

Piezoelectricity and flexoelectricity – Piezoelectricity is one of the most well-established electromechanical couplings in crystalline solids. In a piezoelectric material, a uniform mechanical strain η_{jk} produces a macroscopic electric polarization P_i at linear order according to

$$P_i = \sum_{jk} e_{ijk} \eta_{jk}, \quad (2.15)$$

where e_{ijk} is the third-rank piezoelectric tensor. Conversely, an applied electric field E_i induces a mechanical deformation of the crystal. Piezoelectricity requires the absence of an inversion center and is therefore restricted to the twenty non-centrosymmetric crystal classes. Ferroelectrics, being polar and non-centrosymmetric by definition, are piezoelectric, and some of the largest piezoelectric coefficients reported in single crystals are found in perovskite ferroelectrics near morphotropic phase boundaries [41].

Flexoelectricity generalizes this coupling to the case of inhomogeneous deformations [42, 43]. Rather than coupling

polarization to uniform strain, it couples polarization to a strain gradient $\partial\eta_{jk}/\partial x_l$. The constitutive relation reads

$$P_i = \sum_{jkl} \mu_{ijkl} \frac{\partial\eta_{jk}}{\partial x_l}, \quad (2.16)$$

where μ_{ijkl} is the fourth-rank flexoelectric tensor. A fundamental distinction from piezoelectricity is that flexoelectricity is symmetry-allowed in *all* dielectric crystals, including centrosymmetric ones, since a strain gradient necessarily breaks inversion symmetry locally even in a crystal whose unit cell possesses an inversion center. This universality makes flexoelectricity a coupling of broad relevance across all crystal classes.

The physical origin of flexoelectricity lies in the fact that a non-uniform deformation shifts the relative positions of positive and negative charge centers differently in adjacent unit cells, thereby generating a net dipolar response. In many perovskite oxides, large flexoelectric coefficients arise from the proximity to a polar instability, which renders the crystal highly polarizable and therefore strongly responsive to any symmetry-breaking perturbation, including inhomogeneous strain. Flexoelectricity is of particular relevance at the nanoscale, where strain gradients can be very large, and it plays an important role in the physics of domain walls, thin films under non-uniform epitaxial constraint, and curved membranes [44, 45]. This coupling will play a direct role in the results presented in this thesis: it accounts for the emergence of specific polarization components within the domain walls examined in Chapter 5, and it provides the mechanism through which acoustic phonons can nucleate and dynamically manipulate polar textures, as shown in Chapter 6.

Electrocaloric effect – The electrocaloric effect refers to the reversible adiabatic temperature change ΔT experienced by a polar dielectric upon application of an external electric field [23]. It belongs to the broader family of caloric effects, which have attracted considerable attention as solid-state alternatives to conventional gas-compression refrigeration [46]. The effect is particularly large in ferroelectric and antiferroelectric materials, owing to their anomalously large dielectric responses and the field-driven phase transitions that can be

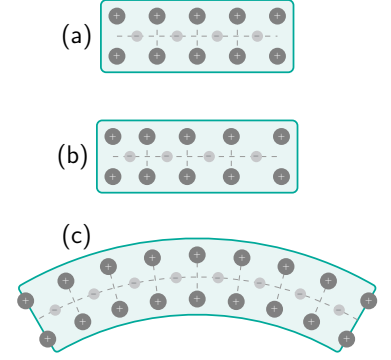


Figure 2.15: Schematic illustration of the flexoelectric effect in a centrosymmetric ionic chain. (a) In the unstrained reference configuration, the centers of positive and negative charge coincide and no polarization arises. (b) Under an inhomogeneous tetragonal strain, the vertical compression varies along the chain: the resulting strain gradient displaces the positive and negative charge centers differently from cell to cell and generates a net polarization. (c) The same effect is produced by bending, where the strain gradient arises from the curvature of the structure. In both (b) and (c), it is the gradient of the strain, rather than the strain itself, that breaks inversion symmetry and gives rise to a flexoelectric polarization.

induced in the vicinity of the Curie temperature [47]. The physical mechanism is rooted in the coupling between the electric polarization and the entropy of the system: the application of a field modifies the polar order and, under adiabatic conditions, this entropy change must be compensated by a temperature variation of the system. Depending on the phase and the direction of the applied field relative to the spontaneous polarization, this temperature change can be either positive (normal electrocaloric effect) or negative (inverse electrocaloric effect).

The electrocaloric response is quantified here following the perturbative framework introduced by Graf and Íñiguez [47]. This framework is the one employed in Chapter 7 to evaluate the electrocaloric response of CaTiO_3 and to predict its dependence on the orientation of the applied electric field. The starting point is the standard thermodynamic expression for the adiabatic temperature change, obtained via a Maxwell relation between the field derivative of the entropy and the pyroelectric vector $\pi_\alpha = (\partial P_\alpha / \partial T)_\mathcal{E}$,

$$\begin{aligned} \Delta T(\mathcal{E}_\alpha) &= - \int_0^{\mathcal{E}_\alpha} \frac{T}{C_E} \left(\frac{\partial S}{\partial \mathcal{E}'_\alpha} \right)_T d\mathcal{E}'_\alpha \\ &= - \int_0^{\mathcal{E}_\alpha} \frac{T}{C_E} \left(\frac{\partial P_\alpha}{\partial T} \right)_\mathcal{E} d\mathcal{E}'_\alpha, \end{aligned} \quad (2.17)$$

where S , T and C_E are respectively the entropy, temperature, and heat capacity at constant field. The polarization P_α is then expanded as a Taylor series in the applied field $\mathcal{E}_\alpha$,

$$P_\alpha = P_\alpha^{(0)} + \epsilon_0 \chi_{\alpha\alpha}^{(1)} \mathcal{E}_\alpha + \epsilon_0 \chi_{\alpha\alpha\alpha}^{(2)} \mathcal{E}_\alpha^2 + \dots, \quad (2.18)$$

where $P_\alpha^{(0)}$ is the spontaneous polarization and the $\chi^{(n)}$ are the diagonal components of the n -th order dielectric susceptibility tensor. Taking the temperature derivative at constant field yields a corresponding expansion for the pyroelectric vector,

$$\pi_\alpha = \pi_\alpha^{(0)} + \pi_{\alpha\alpha}^{(1)} \mathcal{E}_\alpha + \pi_{\alpha\alpha\alpha}^{(2)} \mathcal{E}_\alpha^2 + \dots, \quad (2.19)$$

where $\pi_\alpha^{(0)}$ is the spontaneous pyroelectric coefficient arising from the temperature dependence of the zero-field polarization, and the higher-order coefficients are related to the temperature derivatives of the dielectric susceptibilities ($n > 0$),

$$\pi^{(n)} = \epsilon_0 \left(\frac{\partial \chi^{(n)}}{\partial T} \right)_\mathcal{E}. \quad (2.20)$$

Substituting into Eq. (2.17) and approximating T and C_E by their zero-field values $T^{(0)}$ and $C_E^{(0)}$, a standard approximation valid away from phase transitions where $|\Delta T| \ll T^{(0)}$ [47], the adiabatic temperature change is decomposed into a hierarchy of contributions,

$$\begin{aligned} \Delta T(\mathcal{E}_\alpha) &\approx -\frac{T^{(0)}}{C_E^{(0)}} \left[\pi_\alpha^{(0)} \mathcal{E}_\alpha + \frac{1}{2} \pi_{\alpha\alpha}^{(1)} \mathcal{E}_\alpha^2 + \frac{1}{3} \pi_{\alpha\alpha\alpha}^{(2)} \mathcal{E}_\alpha^3 + \dots \right] \\ &= \Delta T^{(1)} + \Delta T^{(2)} + \Delta T^{(3)} + \dots \end{aligned} \quad (2.21)$$

The sign of each contribution, and therefore the normal or inverse character of the electrocaloric response, is fully determined by the sign of the corresponding pyroelectric coefficient. As summarized in Table 2.1, in the paraelectric phase ($T > T_c$) no spontaneous polarization is present and the response is dominated by $\Delta T^{(2)} \propto \pi_{\alpha\alpha}^{(1)}$; since the linear susceptibility decreases with temperature above T_c following the Curie-Weiss law, $\pi_{\alpha\alpha}^{(1)} < 0$ and the temperature change is positive (normal effect) regardless of the field direction. In an antiferroelectric state the spontaneous polarization also vanishes, but the susceptibility now increases toward T_c from below, so $\pi_{\alpha\alpha}^{(1)} > 0$ and $\Delta T < 0$ (inverse effect). In a ferroelectric phase with spontaneous polarization $P_z^{(0)} > 0$, a field applied parallel to the polar axis yields a dominant linear contribution $\Delta T^{(1)} \propto \pi_z^{(0)} \mathcal{E}_z > 0$, while a perpendicular field or an antiparallel field produces cooling.

Table 2.1: Expected signs of the leading contributions to $\Delta T(\mathcal{E}_\alpha)$ across different phases and field orientations [47]. The orientation of $\mathcal{E}$ is given compared to $\mathbf{P}^{(0)}$.

Phase	$\mathcal{E}$	$\Delta T^{(1)}$	$\Delta T^{(2)}$
PE	any	0	+
AFE	any	0	−
FE	$\perp$	0	−
	$\uparrow\uparrow$	+	−
	$\uparrow\downarrow$	−	−

2.3 Topological phases in polar oxides

As discussed in Section 2.2.1, ferroelectricity in polar oxides is associated with the condensation of an unstable polar mode of the high-symmetry reference structure, most commonly located at the Γ point of the Brillouin zone [13]. In the simplest picture, this condensation leads to a homogeneous distortion of the crystal and the emergence of a macroscopic polarization. In real materials, however, the polarization is generally not uniform throughout the sample: in bulk systems it typically breaks up into domains separated by domain walls, while in nanostructures, where electrostatic and elastic boundary conditions play a more prominent role, a richer variety of inhomogeneous polar textures can emerge [18]. The study of

such textures, their formation, and their response to external stimuli constitutes a central theme of this thesis, and is addressed in [Chapter 5](#) and [Chapter 6](#).

2.3.1 Physical origin

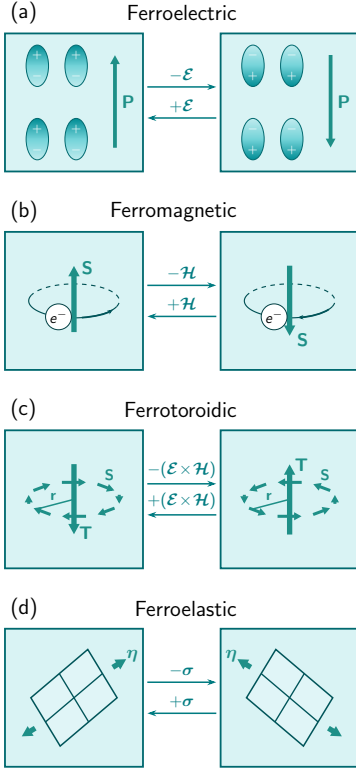


Figure 2.16: The four primary ferroic orders and their response to a conjugate field. (a) Ferroelectric order: a spontaneous electric polarization $\mathbf{P}$, switchable by an electric field $\pm\mathcal{E}$. (b) Ferromagnetic order: a spontaneous magnetization characterized by the spin $\mathbf{S}$ of the orbiting electron, switchable by a magnetic field $\pm\mathcal{H}$. (c) Ferrotoroidic order: a toroidal moment $\mathbf{T}$ arising from a vortex-like circulation of spins $\mathbf{S}$ around a toroid of radius r , switchable by the magnetoelectric product $\pm(\mathcal{E} \times \mathcal{H})$. (d) Ferroelastic order: a spontaneous strain η , switchable by an applied stress $\pm\sigma$. In each panel, the two degenerate states related by the conjugate field are shown side by side.

The origin of such textures is twofold. First, and most fundamentally, ferroic order parameters arise from the breaking of a symmetry of the high-symmetry parent phase, which generates several energetically equivalent variants of the low-symmetry phase. This is the case for ferroelectrics, ferromagnets, ferroelastics, and ferrotoroidics, all of which admit two or more equivalent polarities that can be interconverted by an external field [48]. As a material is cooled through its phase transition, different regions of the sample may independently select different polarities, spontaneously dividing into *domains* separated by *domain walls*. The symmetry of these domain walls reflects simultaneously the broken symmetry of the ferroic phase and the full symmetry of the parent paraelectric phase. In a prototypical perovskite undergoing a cubic-to-rhombohedral transition, for instance, polarization can orient along any of the eight equivalent $\langle 111 \rangle$ directions, giving rise to domain walls separating regions whose polar axes are 71° , 109° , or 180° apart and to complex inhomogeneous polar textures [18, 48].

Second, beyond this symmetry-breaking origin, additional physical mechanisms can actively drive the formation of inhomogeneous polar patterns. In massive systems, the combination of several domain walls already gives access to non-trivial polar arrangements, while strain gradients, through flexoelectric coupling, and the coupling of the polarization to other lattice degrees of freedom provide further routes towards inhomogeneous textures. The range of accessible configurations broadens considerably once surfaces and interfaces come into play, as in thin films, superlattices, and freestanding membranes: incomplete screening of the polarization charges then imposes electrostatic boundary conditions, with the associated depolarizing field, while epitaxial constraints add elastic boundary conditions. The number of competing mechanisms thus grows with the structural complexity of the system, so that nanostructures offer a particularly wide range of accessible polar textures, without this precluding the emergence of non-trivial textures in massive systems,

where fewer mechanisms are at play. Underlying all of these situations, the energy cost associated with polarization gradients penalizes abrupt spatial variations and thereby sets the internal structure and characteristic width of the resulting textures.

Thin films and superlattices are particularly fertile grounds for such textures, and serve as the main illustrative framework in what follows.

Electrostatic interactions

The dominant interaction driving the formation of inhomogeneous polar patterns in ferroelectric nanostructures is of electrostatic origin. Any spatially varying polarization field $\mathbf{P}(\mathbf{r})$ gives rise to a bound charge density

$$\rho_b(\mathbf{r}) = -\nabla \cdot \mathbf{P}(\mathbf{r}), \quad (2.22)$$

while at a free surface ($\mathbf{D} \equiv \epsilon_0 \mathbf{E} + \mathbf{P} = \mathbf{0}$), the component of the polarization normal to the interface produces a surface bound charge density

$$\sigma_b = \mathbf{P} \cdot \hat{\mathbf{n}}, \quad (2.23)$$

where $\hat{\mathbf{n}}$ is the outward unit normal, as illustrated in Figure 2.17 (a). These unscreened surface charges are the source of a large depolarizing field $\mathbf{E}_{\text{dep}}$, which is oriented antiparallel to $\mathbf{P}$ and acts to suppress the polar distortion. In a proper ferroelectric thin film under open-circuit electrical boundary conditions, this depolarizing field is typically large enough to destabilize the ferroelectric state entirely.

A first route to preserve polar order is to place the film between metallic electrodes under short-circuit conditions (Figure 2.17 (b)). The free charges at the electrode surfaces generate a screening field $\mathbf{E}_{\text{scr}}$ that compensates $\mathbf{E}_{\text{dep}}$. This compensation is perfect only for ideal electrodes. Indeed, Junquera and Ghosez demonstrated that real metallic electrodes provide only partial screening, such that below a critical thickness the polar mode switches from unstable to stable, quenching the ferroelectric state entirely [49].

A second route, applicable under open-circuit conditions, is the spontaneous formation of domains with alternating polarization orientations, separated by domain walls (Figure

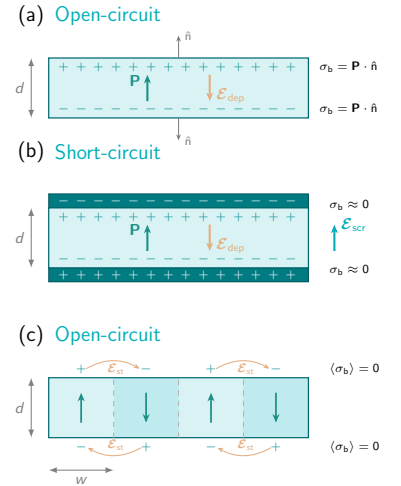


Figure 2.17: Illustration of the electrical boundary conditions in a ferroelectric thin film of thickness d . (a) Open-circuit conditions: unscreened surface bound charges σ_b generate a depolarizing field $\mathbf{E}_{\text{dep}}$ antiparallel to $\mathbf{P}$. (b) Short-circuit conditions: metallic electrodes provide a screening field $\mathbf{E}_{\text{scr}}$. (c) Domain formation with alternating polarization orientations of width w , reducing the average bound charge to zero but giving rise to a stray field $\mathbf{E}_{\text{st}}$. Adapted from Ref. [18]

2.17 (c)). The opposite polarity of adjacent domains causes their surface bound charges to cancel on average, $\langle \sigma_b \rangle = 0$, thereby reducing the depolarizing field and the associated electrostatic energy. This gain, however, comes at a cost: each domain wall represents a region where the polarization must rotate or reverse between two symmetry-equivalent ground-state configurations, which require an energy cost known as the domain wall energy. The equilibrium domain width w results from the balance between these two competing contributions and is described by the Landau-Kittel law [23]:

$$w \propto d^{1/2}, \quad (2.24)$$

where d is the film thickness. The square-root dependence reflects the fact that the electrostatic energy scales as w/d while the domain wall energy density scales as $1/w$, so that minimization over w yields this characteristic scaling.

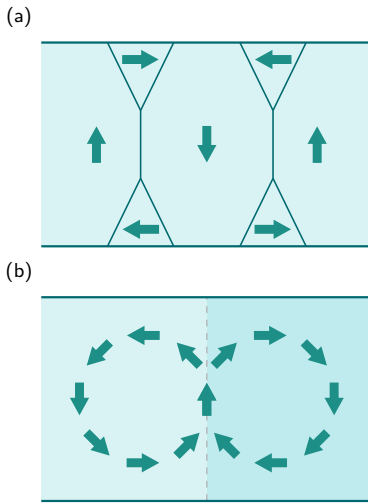


Figure 2.18: Two flux-closure configurations minimizing the electrostatic energy in ferroelectric thin films. (a) Flux-closure domain pattern built from 90° and 180° domain walls. (b) Polar vortex arising from a continuous rotation of the polarization. Adapted from Ref. [18]

Even when the average bound charge vanishes, a stray field $\mathcal{E}_{\text{st}}$ persists near the surfaces between adjacent domains of opposite polarity [50, 51], as illustrated in Figure 2.17 (c). This stray field tends to tilt the polarization in the vicinity of the surface, promoting the formation of 90° domain walls [52]. Although such configurations carry an additional energy cost associated with polarization gradients, polarization anisotropy, and elastic energy, they enforce the continuity of the normal component of polarization across the domain wall, so that the local bound charge density vanishes identically rather than merely on average. This condition, $\nabla \cdot \mathbf{P} = 0$, is more stringent than the cancellation achieved by 180° walls, and leads to a greater reduction of the electrostatic energy. One way to satisfy this condition is through the formation of flux-closure configurations, as illustrated in Figure 2.18 (a), analogous to those observed in magnetic systems, where the polarization rotates through a succession of 90° and 180° domain walls arranged to close the polarization flux. To reduce the energy cost associated with the sharp domain walls imposed by the large polarization anisotropy, the system may instead adopt a continuous rotation of the polarization, forming a vortex, as depicted in Figure 2.18 (b).

The same principles applies when, instead of a vacuum interface, the ferroelectric is part of a heterostructure with a dielectric layer. In this case, Eq. (2.23) can be rewritten as

$$\sigma_b = (\mathbf{P}_{\text{FE}} - \mathbf{P}_{\text{DE}}) \cdot \hat{\mathbf{n}}, \quad (2.25)$$

where the indices denote the two materials. Any discontinuity in the normal component of $\mathbf{P}$ across the interface therefore gives rise to bound charges and, consequently, to a depolarizing field, in direct analogy with the free-surface case. Crucially, however, the ferroelectric and dielectric layers are now in direct contact and can couple to one another (Figure 2.19). The strength and nature of this coupling depend sensitively on the dielectric properties of the surrounding material and on the periodicity of the superlattice.

At short periodicities, the ferroelectric layers are too thin to accommodate the large polarization gradients, anisotropy energy, and elastic energy required to form vortices or flux-closure configurations [53]. Instead, the ferroelectric and dielectric layers remain electrostatically coupled across the interface, and the system responds by developing a continuous out-of-plane polarization component that interpolates between the two materials, thereby reducing the discontinuity in $\mathbf{P} \cdot \hat{\mathbf{n}}$. Alternatively, both layers may align their polarization in-plane, parallel to the interface, which trivially suppresses the bound charge.

As the periodicity increases, the layers thicken and the electrostatic coupling between the ferroelectric and dielectric weakens. The polarization now has sufficient space to rotate gradually, and the energy balance shifts: the cost of domain formation decrease compared to the electrostatic gain, eventually favoring the formation of vortices or flux-closure configurations [18, 54].

Elastic interactions

As introduced in Section 2.2.1, the strong coupling between polar and elastic degrees of freedom makes ferroelectrics highly sensitive to mechanical boundary conditions. In thin film geometry, epitaxial growth on a cubic substrate with a slightly different lattice parameter imposes a biaxial in-plane strain

$$\eta = \frac{a_{\text{sub}} - a_{\text{film}}}{a_{\text{film}}}, \quad (2.26)$$

where a_{sub} and a_{film} are the lattice parameters of the substrate and the film, respectively. This coherent strain is maintained up to a critical thickness beyond which misfit dislocations nucleate and the film progressively relaxes toward its bulk lattice parameter. Within the coherent regime, the epitaxial

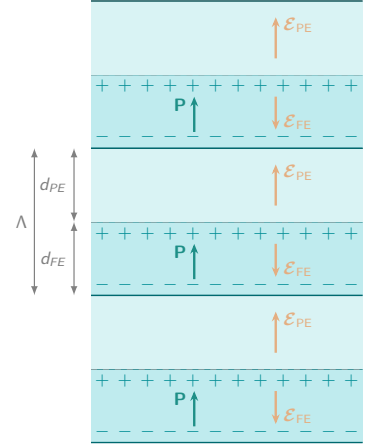


Figure 2.19: Illustration of a ferroelectric/dielectric heterostructure of periodicity Λ . The discontinuity in the normal component of polarization across the interface generates bound charges, giving rise to depolarizing fields $\mathcal{E}_{\text{FE}}$ and $\mathcal{E}_{\text{DE}}$ in the ferroelectric and dielectric layers respectively, in direct analogy with the free-surface case. Adapted from Ref. [18]

strain renormalizes the energy landscape, shifting the transition temperature, reorienting the preferred polarization direction, or even inducing polar order in otherwise paraelectric materials. As a general rule, sufficiently large compressive biaxial strains favor an out-of-plane (c) over an in-plane (a) polar phase, or vice versa.

Beyond this homogeneous contribution, the strain is rarely perfectly uniform: strain gradients develop in the vicinity of interfaces, misfit dislocations, and film edges, as well as in bent or freestanding membranes. They also arise intrinsically wherever the polarization itself varies in space, such as across domain walls and within polar textures, since the polarization is elastically coupled to the lattice. Such gradients couple back to the polarization through the flexoelectric effect introduced in [Section 2.2.2](#), providing an additional, symmetry-independent route to locally modify the polar state and to stabilize inhomogeneous textures.

In ferroelectric/dielectric heterostructures, the elastic boundary conditions further couple to the electrostatic ones discussed above. The energy balance between the elastic cost of polarization gradients and the electrostatic gain of flux-closure configurations depends sensitively on the epitaxial strain state, making the periodicity-driven crossover between homogeneous and topological polar phases tunable through the choice of substrate.

2.3.2 Topology

The physical ingredients discussed above give rise to a rich variety of inhomogeneous polar configurations, such as simple domain structures, flux-closure patterns or vortices, among others. Classifying and characterizing these configurations in a systematic way calls for a mathematical framework: topology. In the context of ordered phases, topology provides a language to distinguish field configurations that cannot be continuously deformed into one another, and to assign them invariant quantitative descriptors known as topological charges. The following section introduces only the concepts strictly necessary to follow the results presented in this manuscript; a more thorough treatment can be found in Refs. [\[18, 55–57\]](#).

At its core, topology is the branch of mathematics concerned with the properties of geometric objects that are preserved

under continuous deformations (stretching, twisting, bending, or contracting) but not under more drastic operations such as cutting, tearing, or piercing. Two objects are said to be topologically equivalent, or *homeomorphic*, if one can be continuously deformed into the other without any such operation. Formally, a homeomorphism between two topological spaces $\mathcal{X}$ and $\mathcal{Y}$ is a bijective continuous function $f : \mathcal{X} \rightarrow \mathcal{Y}$ whose inverse f^{-1} is also continuous. For instance, the closed unit disk D^2 is homeomorphic to the square $[-1, 1]^2$. Whenever two spaces are homeomorphic, all their topological properties are identical and can be transposed from one to the other by means of f . The surface of a cube and that of a sphere are homeomorphic in this sense. The surface of a torus (see Figure 2.20 (c)), however, is fundamentally different: the hole that characterizes it cannot be removed by any continuous deformation, making it topologically distinct from the sphere.

The central tool for studying topological spaces is the concept of *homotopy*. Formally, a homotopy between two continuous functions $f, g : \mathcal{X} \rightarrow \mathcal{Y}$ is a continuous function $H : \mathcal{X} \times [0, 1] \rightarrow \mathcal{Y}$ satisfying $H(x, 0) = f(x)$ and $H(x, 1) = g(x)$ for all $x \in \mathcal{X}$, with fixed endpoints $f(0) = g(0)$ and $f(1) = g(1)$. Intuitively, H describes a continuous deformation between f and g : two functions are homotopic if one can be continuously deformed into the other. A simple example is the fact that any close loop on the surface of a sphere can be continuously deformed to a constant point as illustrated in Figure 2.20 (b). A concrete illustration is provided by wrapping an elastic band around different surfaces, as shown in Figure 2.20. On an infinite cylinder $\mathbb{S}^1 \times \mathbb{R}$, the number of times the band winds around the cylinder cannot be changed by any continuous deformation: a band winding once cannot be deformed into one winding twice, nor into one that does not encircle the cylinder at all. This integer-valued invariant is called the *winding number* w , and all configurations sharing the same winding number belong to the same homotopy class (Figure 2.20 (a)). The situation is qualitatively different on a sphere $\mathbb{S}^2$: any closed loop on its surface can be continuously contracted to a point, so that all loops are homotopic, and there is only a single homotopy class (Figure 2.20 (b)). On a torus $\mathbb{T}^2$, by contrast, two independent winding numbers are required to fully classify all closed loops (one for the toroidal direction and one for the poloidal direction) reflecting the richer topology of the surface (Figure 2.20 (c)).

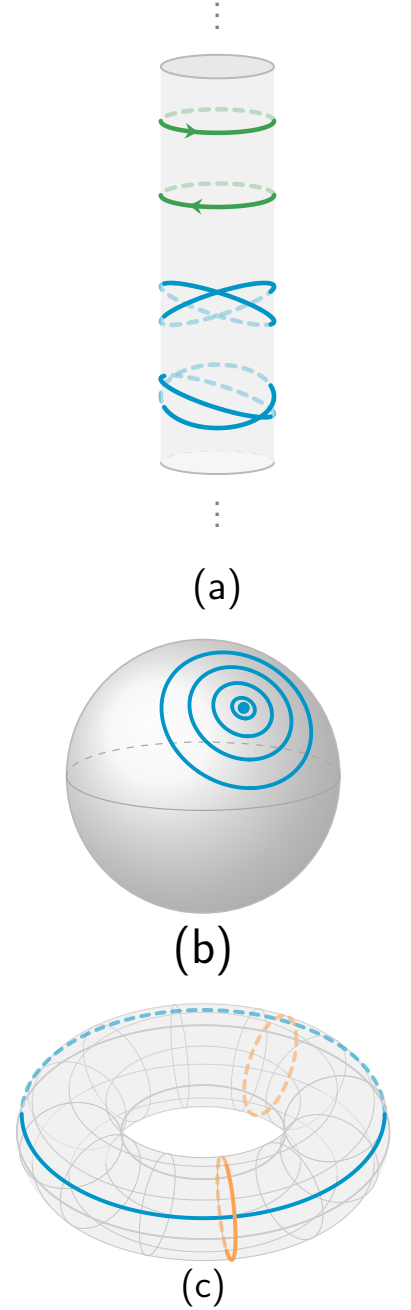


Figure 2.20: Illustration of homotopy classes using an elastic band wrapped around different surfaces. (a) On an infinite cylinder $\mathbb{S}^1 \times \mathbb{R}$, the winding number w is a topological invariant that cannot be changed by any continuous deformation. (b) On a sphere $\mathbb{S}^2$, all closed loops are contractible to a point, yielding a single homotopy class. (c) On a torus $\mathbb{T}^2$, two independent winding numbers are required to classify all closed loops. Adapted from Ref. [18]

The set of homotopy classes of closed loops on a topological space $\mathcal{X}$, labeled by the winding number w , forms the first homotopy group, or *fundamental group*, $\pi_1(\mathcal{X})$. For the cylinder, $\pi_1(\mathbb{S}^1 \times \mathbb{R}) \cong \mathbb{Z}$, reflecting the integer-valued winding number; for the sphere, $\pi_1(\mathbb{S}^2) = \{0\}$, consistent with the fact that all loops are contractible; and for the torus, $\pi_1(\mathbb{T}^2) \cong \mathbb{Z} \times \mathbb{Z}$, since two independent integers are needed to describe its closed loops. This construction generalizes naturally: the n -th homotopy group $\pi_n(\mathcal{X})$ classifies the homotopy classes of mappings from the n -dimensional sphere $\mathbb{S}^n$ into the order-parameter space $\mathcal{X}$. The relevant value of n is fixed not by the dimensionality D of the system alone, but also by the dimensionality d_s of the topological object to be classified: a singularity of dimension d_s embedded in a D -dimensional system is enclosed by a sphere of dimension $n = D - d_s - 1$, so that $\pi_n(\mathcal{X})$ provides the appropriate topological invariant, as discussed below.

2.3.3 Topological defects

In the context of condensed matter physics, the topological space $\mathcal{X}$ introduced above takes a concrete physical meaning: it is the order-parameter space, *i.e.*, the set of all values that the order parameter can take. The order parameter itself is defined throughout the system, assigning to every point of real space a value in $\mathcal{X}$. A topological defect is a region, an isolated point, line, or surface, around which the order-parameter field cannot be smoothly deformed into a uniform configuration. What characterizes such a defect is not the behavior of the field at its core, but the way the field winds around it. Away from the core, along this surface, the order parameter does not vanish and can therefore be normalized [58], so that only its orientation is retained: each point of the surface is thereby mapped onto a point of $\mathcal{X}$. The defect is topologically protected when this map cannot be continuously deformed into a trivial one, for which the orientation is uniform. Its existence is then not accidental but dictated by the topology of $\mathcal{X}$, which, together with the dimensionality of the system and that of the defect, determines which defects are allowed and how they are classified.

To fix ideas, consider three paradigmatic examples illustrated in Figure 2.21. In the Ising ferromagnet, the spin has a fixed

magnitude and can only point up or down, so $\mathcal{X}$ consists of two disconnected points, $\mathbb{S}^0$ (Figure 2.21 (a)). In the XY model, the spin can point in any direction within a given plane while maintaining a fixed magnitude, so $\mathcal{X}$ is a circle, $\mathbb{S}^1$ (Figure 2.21 (b)). Finally, in the Heisenberg model, the spin can point in any direction in three-dimensional space, sweeping the surface of a sphere, $\mathcal{X} = \mathbb{S}^2$ (Figure 2.21 (c)).

The type of defect that can appear depends on the dimensionality d of the order-parameter space, with $d = 1, 2, 3$ for the Ising, XY, and Heisenberg models respectively, independently of the physical dimension D of the system (one can even have $d > D$).

In the Ising case ($d = 1$), the order parameter can only point up or down and cannot be continuously deformed from one orientation to the other. Any boundary between domains of opposite polarity therefore hosts a *domain wall* where the order parameter vanishes. This defect is a point when $D = 1$, as illustrated in Figure 2.21 (d), a line when $D = 2$, and a plane when $D = 3$.

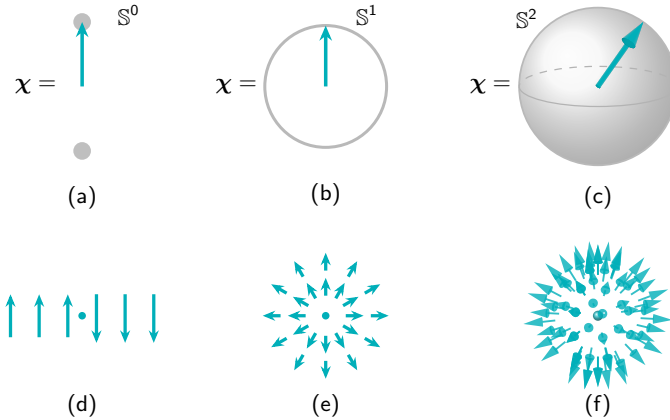


Figure 2.21: Order-parameter spaces $\mathcal{X}$ for the (a) Ising, (b) XY, and (c) Heisenberg models, together with representative topological defects in each case. (d) In the Ising model, the two-valued order parameter forces a point defect (domain wall) wherever the polarization reverses sign, here illustrated in one dimension. (e) In the XY model ($\chi = \mathbb{S}^1$ and $D = 2$), the simplest topological defect is a vortex. (f) In the Heisenberg model ($\chi = \mathbb{S}^2$ and $D = 3$), the analog is the hedgehog or Bloch point, a three-dimensional point defect.

In the XY model ($d = 2$), the order parameter can rotate continuously in the plane, but configurations that wind around a closed loop cannot be unwound without passing through a singularity. The resulting defect is a *vortex*, illustrated in Figure 2.21 (e), whose core is a point when $D = 2$ and a line when $D = 3$.

In the Heisenberg model ($d = 3$), the order parameter can point in any direction in space, but certain configurations that wrap around a closed surface similarly require a singular

point to exist. A possible realization when $D = 3$ is the *Bloch point*, illustrated in Figure 2.21 (f), where the order parameter points radially outward in all directions from the defect core.

These three cases are representative of the topological defects encountered in ferroic materials. We now discuss each of them in more detail.

Domain walls – Domain walls are ubiquitous in ferroic materials, regardless of the nature of the order parameter: polarization, strain, magnetization, or toroidal moment. Owing to the energy degeneracy of the possible orientations of the order parameter on cooling from the paraelectric phase, ferroic materials spontaneously develop domain structures. Regions of uniform order are called *domains*, and the boundaries between adjacent domains are called *domain walls* [48]. The internal structure of a domain wall depends critically on the dimensionality d of the order-parameter space. When $d = 1$, as in the Ising model, there is no alternative: passing from one domain to the other requires the order parameter to vanish at the wall, producing a genuine singularity. This is the *Ising* domain wall illustrated in Figure 2.22 (a).

When $d > 1$, the situation changes drastically. Although an Ising wall remains possible, the order parameter now has the freedom to rotate continuously across the wall without ever vanishing. If this rotation occurs in the plane of the wall, the configuration is called a *Bloch* domain wall (Figure 2.22 (c)); if it occurs perpendicular to the wall, it is called a *Néel* domain wall (Figure 2.22 (b)) [48]. As a consequence, when $d > 1$, a domain wall carries no topological protection: the order parameter can rotate continuously from one domain orientation to the other without creating any singularity, and a multidomain configuration can in principle be continuously deformed into a single-domain state. Domain walls in this case are said to be topologically trivial.

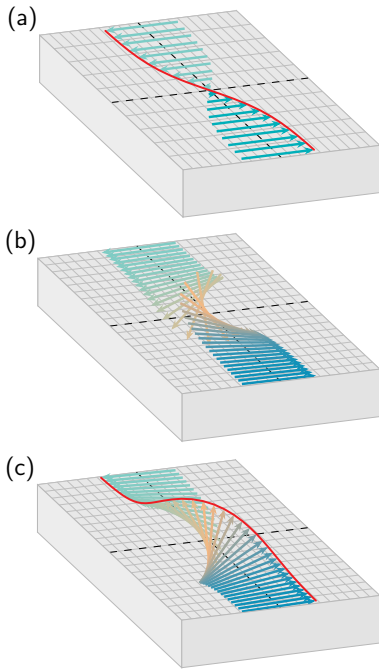


Figure 2.22: Illustration of the three possible domain-wall structures for $d > 1$ and $D = 1$: (a) Ising, (b) Néel, and (c) Bloch domain walls. The red curve traces the amplitude of the order parameter across the wall. Adapted from Ref. [48]

(anti)vortices – Vortices are topological defects arising when the order-parameter space is $\mathbb{S}^1$ or $\mathbb{S}^1 \times \mathbb{R}$, as in the examples of Figure 2.20 (a) and Figure 2.21 (b). They appear naturally in ferroelectric/dielectric heterostructures [54], where the order parameter rotates continuously around a defect, as illustrated in Figure 2.21 (e) and Figure 2.23.

Each vortex is characterized by a winding number w , which counts the number of times the order parameter winds around the singularity along a closed loop $\mathcal{L}$, as illustrated in Figure 2.23 (b). It is defined as

$$w = \frac{1}{2\pi} \oint_{\mathcal{L}} \frac{d\theta}{d\ell} \cdot d\ell, \quad (2.27)$$

where θ is the angle of the order parameter along the loop. Importantly, w is independent of the choice of $\mathcal{L}$, as long as $\mathcal{L}$ encloses one and the same singularity: the loop can be freely deformed without changing w , provided it does not cross any singularity. When several singularities are enclosed, the winding number measured along $\mathcal{L}$ is the sum of the individual winding numbers of the enclosed defects. As discussed in Section 2.3.2, all configurations sharing the same winding number can be continuously deformed into one another. For instance, the vortices in Figure 2.23 (a),(c)–(e) all share $w = +1$ and are therefore topologically equivalent, while the antivortex in Figure 2.23 (f), with $w = -1$, belongs to a distinct homotopy class and cannot be reached by any continuous transformation.

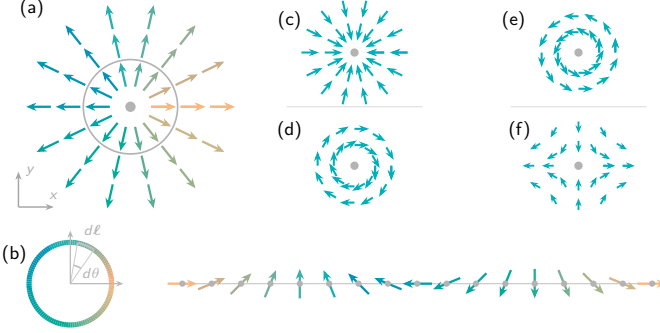


Figure 2.23: Representative vortex and antivortex configurations. (a) Generic vortex with winding number $w = +1$. (b) Definition of w along a closed loop $\mathcal{L}$ enclosing the singularity. (c) Curl-free vortex ($\nabla \cdot \mathbf{P} \neq 0$, $\nabla \times \mathbf{P} = 0$). (d) Divergence-free vortex ($\nabla \cdot \mathbf{P} = 0$, $\nabla \times \mathbf{P} \neq 0$), energetically favored in polar systems. (e) Additional $w = +1$ configuration. (f) Antivortex with $w = -1$, belonging to a distinct homotopy class. Adapted from Ref.[18]

where θ is the angle of the order parameter along the loop. Importantly, w is independent of the choice of $\mathcal{L}$, as long as $\mathcal{L}$ encloses one and the same singularity: the loop can be freely deformed without changing w , provided it does not cross any singularity. When several singularities are enclosed, the winding number measured along $\mathcal{L}$ is the sum of the individual winding numbers of the enclosed defects.

Topological equivalence does not imply energetic degeneracy, however. When the order parameter is a dipole, the vortices in Figure 2.23 (c) and Figure 2.23 (d) are energetically very different. The vortex in Figure 2.23 (d) satisfies $\nabla \cdot \mathbf{P} = 0$

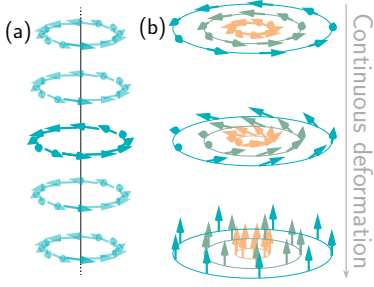


Figure 2.24: Continuous deformation of a vortex into a monodomain state when $d > 2$ in a three-dimensional system ($D = 3$). (a) The order parameter rotates out of the vortex plane along the extra dimension, progressively tilting toward a uniform orientation. (b) The resulting monodomain state, reached without passing through any singularity. Adapted from Ref. [18]

and $\nabla \times \mathbf{P} \neq 0$, while the one in Eq. Figure 2.23 (c) satisfies $\nabla \cdot \mathbf{P} \neq 0$ and $\nabla \times \mathbf{P} = 0$. As recalled from Eq. (2.22), a nonzero divergence of the polarization leads to the accumulation of bound charges at the defect core, which is energetically costly. The curl-dominated vortex of Figure 2.23 (d) is therefore strongly favored in polar systems.

As for domain walls, increasing the dimensionality of the order-parameter space unlocks additional degrees of freedom that allow the vortex to be continuously unwound. When $d > 2$, the vortex extends into a tube whose core is now a line defect. Along this extra dimension, the order parameter can rotate out of the vortex plane and tilt progressively toward a uniform orientation, deforming the configuration into a monodomain state without ever passing through a singularity, as illustrated in Figure 2.24 (b). The vortex is therefore topologically trivial when $d > 2$.

Bloch point and hopfion – When the order-parameter space is $\mathbb{S}^2$ ($d = 3$), the relevant homotopy group governing point defects in a three-dimensional system ($D = 3$) is $\pi_2(\mathbb{S}^2) \cong \mathbb{Z}$. This non-trivial group implies the existence of topologically protected point defects, known as Bloch points (or hedgehogs), in which the order parameter points radially outward from a central singularity in all directions, thereby wrapping $\mathbb{S}^2$ exactly once, as illustrated in Figure 2.25.

As established above, both domain walls and vortices are topologically trivial when $d = 3$: the additional degree of freedom available to the order parameter always allows a continuous deformation toward a uniform state. The Bloch point is the simplest configuration that escapes this triviality. It is a genuine point singularity, where the order parameter is forced to vanish at the defect core. Its topological charge is given by the degree of the mapping $\mathbf{n} : \mathbb{S}^2 \rightarrow \mathbb{S}^2$ evaluated on a small sphere surrounding the singularity. Introducing the Pontryagin charge density $\mathbf{q}$, whose i -th component is $q_i = \frac{1}{8\pi} \varepsilon_{ijk} \mathbf{n} \cdot (\partial_j \mathbf{n} \times \partial_k \mathbf{n})$, this charge is expressed as

$$Q = \frac{1}{4\pi} \oint_S \mathbf{q} \cdot d\mathbf{S} = \frac{1}{8\pi} \oint_S \varepsilon_{ijk} \mathbf{n} \cdot (\partial_j \mathbf{n} \times \partial_k \mathbf{n}) dS_i, \quad (2.28)$$

where $\mathbf{n}(\mathbf{r})$ is the unit vector of the order parameter, ε_{ijk} is the antisymmetric Levi-Civita tensor, and Einstein summation

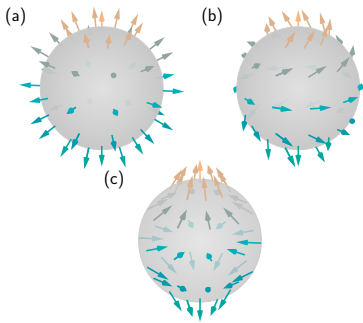


Figure 2.25: Three representative Bloch point configurations mapped onto $\mathbb{S}^2$. (a,b) Two distinct textures with topological charge $Q = +1$, differing in the rotation path of the order parameter between the poles. (c) A configuration with $Q = -1$, in which the sense of rotation is reversed.

convention is implied over i, j, k . The integral is evaluated over any closed surface $\mathcal{S}$ enclosing the defect core, and Q is independent of the choice of $\mathcal{S}$ provided it fully encloses the singularity. The radial hedgehog configuration, in which the order parameter points outward everywhere, is the prototypical example of a defect with $Q = +1$; reversing the order parameter yields the antihedgehog, with $Q = -1$. These are, however, only particular representatives of their respective classes, which contain many other, non-radial configurations of the same charge.

As established for domain walls and vortices in the preceding sections, a key question is whether these configurations can be continuously deformed into a monodomain state. For Bloch points, this is impossible as any configuration with $Q \neq 0$ is topologically protected and cannot be unwound without passing through a singularity.

2.3.4 Solitons

In contrast to topological defects, topological solitons carry no singularity: the order parameter remains continuous and well-defined everywhere. In addition, solitons always converge to a homogeneous order in the far-field region. A useful way to visualize the relationship between solitons and their associated defects is through stereographic projection, which maps the far-field boundary of a soliton onto a point and thereby establishes a correspondence with the homotopy classes introduced earlier.

(anti)skyrmions and (anti)merons – Skyrmions and anti-skyrmions are typical topological solitons arising when the order-parameter space is a sphere $\mathcal{X} = \mathbb{S}^2$, corresponding to $d = 3$. Two distinct types of skyrmion exist, distinguished by the way the order parameter rotates between the two poles of $\mathcal{X}$, as illustrated in Figure 2.26.

In the Néel skyrmion, the order parameter remains normal to the surface of the sphere $\mathcal{X}$ at every point, rotating radially from the north pole to the south pole through the meridians (Figure 2.26 (c)). In the stereographic projection onto the plane, this corresponds to a radial rotation of the order parameter from pointing up at the center to pointing down at the periphery, passing through the equatorial plane.

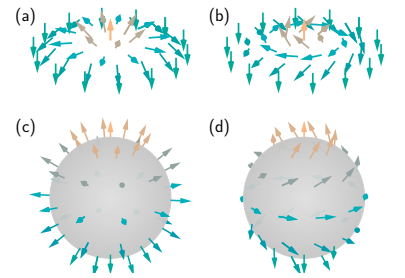


Figure 2.26: Skyrmion configurations via stereographic projection of the order-parameter space $\mathbb{S}^2$ onto the plane. (a,b) Stereographic projection of the north and south hemispheres, illustrating how the far-field boundary maps to a point. (c) Néel skyrmion, in which the order parameter rotates radially from the core to the periphery. (d) Bloch skyrmion, in which the in-plane component winds azimuthally around the core. Both carry a skyrmion number $N = +1$.

In the Bloch skyrmion, the order parameter rotates tangentially along the equator of the sphere, winding around the azimuthal direction as it travels from the north pole to the south pole (Figure 2.26(d)). In the stereographic projection, this corresponds to a vortex-like rotation of the in-plane component of the order parameter.

The topological charge of a skyrmion is obtained by mapping the order-parameter configuration within the area of the soliton onto the order-parameter space, and counting the number of times this mapping wraps around $\mathbb{S}^2$. It is given by

$$N = \frac{1}{4\pi} \iint \mathbf{n}(\mathbf{r}) \cdot \left(\frac{\partial \mathbf{n}(\mathbf{r})}{\partial x} \times \frac{\partial \mathbf{n}(\mathbf{r})}{\partial y} \right) dx dy, \quad (2.29)$$

where N is called the skyrmion number, $\mathbf{n}(\mathbf{r})$ is the unit vector of the order parameter and the integrand is called the Pontryagin charge density. A skyrmion carries $N = +1$, meaning the order parameter wraps once around $\mathbb{S}^2$, while an antiskyrmion carries $N = -1$. For $D = 3$, skyrmions are forming tubes similar the vortex line exemplified in Section 2.3.3.

The topological charge is not necessarily an integer. A meron is a half-skyrmion with $N = \pm 1/2$, in which the order parameter covers only one hemisphere of $\mathcal{X}$. Unlike skyrmions, merons do not satisfy the far-field homogeneity condition and are therefore not topological solitons in the strict sense. They typically appear in bound pairs whose combined topological charge is that of a full skyrmion, restoring the homogeneous far-field order at the scale of the pair.

2.3.5 Topology of spins and electric dipoles

Before discussing topological protection in detail, it is worth pausing on a specificity of polar systems with respect to their magnetic counterparts, in which topological textures such as vortices and skyrmions were first predicted and observed [59, 60].

In magnetic systems, the spin is a rigid unit vector constrained to $\mathbb{S}^2$: its magnitude is fixed and it can rotate freely in any direction at essentially no cost. The order-parameter space is therefore isotropic, and smooth rotations between different orientations are energetically inexpensive. In polar systems,

the situation is fundamentally different for two reasons. First, the electric polarization can in principle vanish, meaning that the order-parameter space is not strictly $\mathbb{S}^2$ but includes the origin. However, it is common practice to renormalize each electric dipole to unit length [58], treating the polar pattern as an effective distribution of spins and thereby recovering the $\mathbb{S}^2$ topology that underpins the classification introduced above. In practice, the vanishing of the polarization is unlikely far below the Curie temperature, where the magnitude of the polarization is well established. Second, and more importantly, the polarization couples strongly to the elastic degrees of freedom through electrostriction and piezoelectricity. This coupling makes polar systems highly anisotropic: rotating the polarization away from its equilibrium orientation requires distorting the lattice simultaneously, which carries a significant elastic energy cost. For this reason, it was long believed that polar topology would be essentially limited to domain walls, the only topological objects that do not require the polarization to rotate continuously over extended regions.

In recent years, however, a plethora of experimental and theoretical evidence has demonstrated the existence of vortices, skyrmions, and other non-trivial polar textures in ferroelectric nanostructures and heterostructures [18]. These discoveries have attracted considerable attention, in part because polar objects are in principle significantly smaller than their magnetic counterparts. The stronger anisotropy and the shorter characteristic length scales of polar systems translate directly into higher potential storage densities, making topological polar textures promising candidates for next-generation memory devices.

2.3.6 Topological protection

The topological textures introduced above attract considerable interest because they are said to be topologically protected: small external perturbations such as thermal fluctuations, applied voltages, or mechanical stimuli cannot destroy them. At the same time, these objects can be displaced or deformed by such stimuli, which makes them particularly attractive for technological applications. A canonical example is the racetrack memory, in which topologically stable objects

serve as mobile information carriers that can be driven along a magnetic or polar track.

This protection is a direct physical consequence of the topological invariance introduced in [Section 2.3.2](#). Since the topological charge cannot change continuously, any transformation that would bring a non-trivial texture to a uniform state must pass through a singular, high-energy configuration. In energetic terms, the topological charge acts as a barrier: destroying the object requires an energy cost that is large enough to be inaccessible under typical external stimuli.

A concrete illustration is provided by a vortex with winding number $w = +1$ in a polar system with $d = 2$. Annihilating this vortex and reaching a monodomain state requires the polarization to pass through a head-to-head configuration at some point during the transformation. Such a configuration carries a non-zero divergence $\nabla \cdot \mathbf{P} \neq 0$, which gives rise to an accumulation of bound charges and an associated electrostatic energy cost that is prohibitively large. The vortex is therefore robust against all but the strongest external perturbations.

This reasoning also clarifies why topological protection is not universal. As discussed in [Section 2.3.3](#), when $d = 3$, a vortex can be continuously unwound into a monodomain state by rotating the order parameter out of the vortex plane, without ever passing through a singular configuration. In this case, no high energy barrier exists and the object carries no topological protection.

Computational methods 3

The physical phenomena described in the preceding sections, ranging from subtle structural instabilities and polar phase transitions to the formation and dynamics of topological textures, all emerge from the collective behavior of electrons and ions in complex oxide materials. Describing these phenomena at the theoretical level requires a hierarchy of complementary approaches, each offering a different balance between accuracy and computational tractability.

At the most fundamental level, the behavior of a material is entirely determined by the quantum mechanical interactions between its electrons and nuclei. Methods that solve these interactions from first principles, without any empirical input, provide the highest level of accuracy and predictive power. However, the computational cost of such approaches scales steeply with system size, restricting their applicability to unit cells or small supercells containing at most a few hundred atoms, and to static or short-time-scale calculations. Many of the phenomena of interest here, such as the nucleation and dynamics of topological textures or finite-temperature phase transitions, involve length and time scales that are orders of magnitude beyond this reach.

Bridging a gap requires coarser descriptions that retain the essential physics while dramatically reducing the computational cost. As illustrated in Figure 3.1, the different approaches available span many orders of magnitude in both length and time scales, from first-principles calculations operating at the nanometer and picosecond scale, to second-principles and Landau-Ginzburg-Devonshire models reaching the millimeter and millisecond regime. In this section, the most relevant methods used throughout this thesis are introduced from the bottom up, following this hierarchy of length and time scales. The presentation draws from the textbooks by Giustino [61] and Martin [62] for the first-principles foundations, and from the review by Ghosez and Junquera [13] for the coarser-scale approaches.

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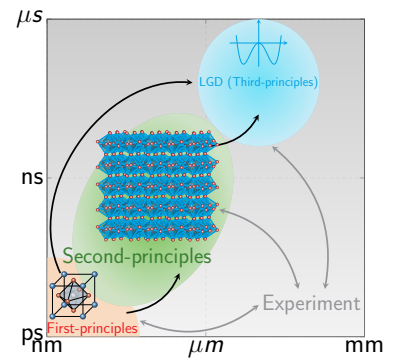


Figure 3.1: schematic overview of the length and time scales accessible to the different theoretical approaches discussed in this thesis, from first-principles methods at the atomic scale to phenomenological models at the mesoscopic scale. Adapted from [13].

3.1 First-principles methods

The fundamental properties of matter, and in particular those of condensed-matter systems, originate from the interactions between electrons and atomic nuclei. Understanding these interactions is at the heart of quantum mechanics, which provides a unified framework to describe the structure, stability, and dynamics of materials. In the stationary regime, such systems are governed by the time-independent Schrödinger equation

$$\hat{H} \Psi = E \Psi, \quad (3.1)$$

where $\hat{H}$ denotes the Hamiltonian operator that contains the kinetic and potential energy terms of all particles, and E is the corresponding energy eigenvalue. The solution, the many-body wavefunction Ψ , contains the complete information about the quantum state of the system. Although exact in principle, solving this equation for realistic materials is computationally intractable due to the complexity arising from the simultaneous motion of all electrons and nuclei. Consider a set of N_e electrons with mass m_e and charge $-e$ at positions $\{\mathbf{r}_i\}$, interacting with N_I nuclei of atomic number Z_I , mass M_I , and positions $\{\mathbf{R}_I\}$. Throughout this thesis, atomic units are used ($\hbar = m_e = e = 1$), in which Z_I and M_I reduce to dimensionless integers and the Hamiltonian takes the form [62],

$$\begin{aligned} \hat{H} = & - \sum_{i=1}^{N_e} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N_e} \sum_{I=1}^{N_I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \\ & - \sum_{I=1}^{N_I} \frac{1}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}. \end{aligned} \quad (3.2)$$

where the first and fourth terms are the kinetic energies of the electrons and nuclei respectively, the second term is the Coulombic electron-nucleus attraction, the third term is the Coulombic electron-electron repulsion, and the last term is the Coulombic nucleus-nucleus repulsion. In this equation, the nuclear kinetic energy scales with the inverse of the nuclear mass, $1/M_I$. Since nuclei are more than a thousand times heavier than electrons, their kinetic contribution is correspondingly much smaller. Owing to this large mass difference, the electrons move much faster than the nuclei and can be assumed to adjust instantaneously to any nuclear configuration, remaining in their ground state as the nuclei

move. Consequently, the nuclear kinetic energy $\hat{T}_n$ operator can be neglected in the Hamiltonian. This is the essence of the Born–Oppenheimer approximation [63]. Under this approximation, the Hamiltonian no longer contains differential operators acting on the nuclear coordinates. As a result, the nuclear positions can be treated as fixed parameters when solving the electronic Schrödinger equation, and the Coulomb interaction between nuclei becomes a constant for a given set of nuclei positions $\{\mathbf{R}\}$. At fixed nuclear positions, the Hamiltonian can then be separated into two parts: the ionic part, $\hat{H}_n$, containing only terms that depend on the nuclei, and the electronic part, $\hat{H}_e$,

$$\hat{H} = \hat{H}_n + \hat{H}_e. \quad (3.3)$$

Thus, it remains to solve the electronic part of the Schrödinger equation. Since the Born–Oppenheimer approximation leads to a separable Hamiltonian, the total wavefunction can be approximated as

$$\Psi(\mathbf{r}, \mathbf{R}) \approx \psi(\mathbf{r}, \mathbf{R})\chi(\mathbf{R}), \quad (3.4)$$

where $\psi(\mathbf{r}, \mathbf{R})$ is the electronic wavefunction for fixed nuclear positions $\mathbf{R}$, and $\chi(\mathbf{R})$ is the nuclear wavefunction describing the motion of the ions on the Born–Oppenheimer potential energy surface. Once the Born–Oppenheimer approximation is applied, the total problem reduces to solving the electronic Schrödinger equation for fixed nuclear positions $\{\mathbf{R}_I\}$. By repeating this for successive nuclear arrangements, one obtains the electronic energy as a function of nuclear positions, defining the Born–Oppenheimer potential energy surface (PES) on which the nuclei move. Minimizing along this surface with respect to nuclear coordinates yields the equilibrium geometry of the system, while its curvature gives access to vibrational properties.

However, determining $\psi(\mathbf{r}, \mathbf{R})$ exactly remains intractable due to the electron–electron interactions, particularly in solids where the number of electrons can reach $N_e \sim 10^{23}$. Additional reformulation are therefore required. One of the most successful and widely used is *Density Functional Theory* (DFT), which is introduced in the following section.

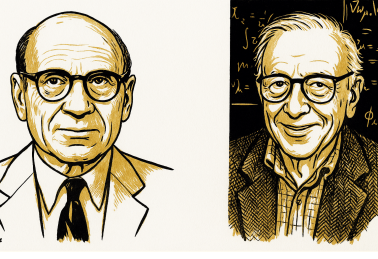


Figure 3.2: Illustrated portraits of Walter Kohn (left) and John A. Pople (right), laureates of the 1998 Nobel Prize in Chemistry. The artwork is inspired by the Nobel Foundation's modern visual style. AI-generated illustration (ChatGPT, 2025) based on portraits from the Nobel Foundation archives.

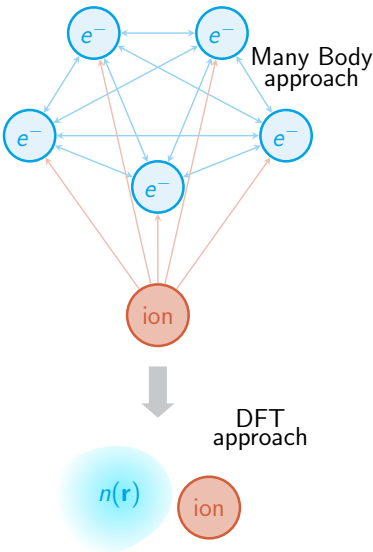


Figure 3.3: Schematic illustration of the conceptual shift from the many-body approach to density functional theory. In the many-body picture, all electrons are treated explicitly as interacting particles. In the DFT picture, the interacting system is replaced by a fictitious system of non-interacting electrons moving in an effective potential, with all many-body effects absorbed into the exchange-correlation functional

3.1.1 Density functional theory

In the previous section, the many-body wavefunction was introduced. Being a function of $3N_e$ variables, it is impossible to determine exactly. However, by reformulating the problem in terms of the electronic density $n(\mathbf{r})$ and introducing an auxiliary system of non-interacting electrons, it becomes possible to access the ground-state energy of the system. The theoretical foundation of Density Functional Theory was laid in the 1960s by Walter Kohn together with Pierre Hohenberg [64], and later by Walter Kohn and Lu Jeu Sham [65]. The first work established that the energy and all associated fundamental properties of the electronic ground state are a functional of the ground-state electron density. The second work showed that the electronic density of the interacting system can, in principle, be exactly reproduced by a fictitious system of non-interacting particles moving in an effective potential that depends on the density. This result enables a self-consistent solution of the many-body electronic problem via the non-interacting system. The density of this fictitious system is simply the sum of the densities of the single-particle wavefunctions $\phi(\mathbf{r})$ of the non-interacting electrons.

$$n(\mathbf{r}) = \sum_{i=1}^{N_{occ}} |\phi_i(\mathbf{r})|^2, \quad \langle \phi_i | \phi_j \rangle = \delta_{ij}, \quad (3.5)$$

where N_{occ} is the number of occupied states.

This section is dedicated to presenting the two theorems that underpin density functional theory, explaining how the ground-state energy is obtained in practice, and discussing how this framework is adapted to the context of solid-state physics.

As established in the previous section, the Born-Oppenheimer approximation reduces the full quantum mechanical problem to the determination of the electronic wavefunction $\psi(\mathbf{r}, \mathbf{R})$ introduced in Eq. (3.4). The ground-state energy of the electronic system is given by the expectation value of the electronic Hamiltonian $\hat{H}_e$ over this wavefunction,

$$E_e = \langle \psi | \hat{H}_e | \psi \rangle. \quad (3.6)$$

Changing the wavefunction ψ leads to a change in the energy of the electronic system. Thus, the energy of the electronic system is a functional of ψ .

This result is general for any electronic state. However, the problem remains: the total energy of the electronic system still requires knowledge of the electronic many-body wavefunction ψ . It is at this point that the work of Hohenberg and Kohn becomes particularly relevant [64]. The Hohenberg-Kohn theorem states that the ground-state electron density $n(\mathbf{r})$ uniquely determines the external potential $V_{en}(\mathbf{r})$, up to an additive constant, and hence the full many-body Hamiltonian and its ground-state wavefunction ψ . Consequently, Hohenberg and Kohn proved that the *ground-state* total energy of the electronic system is a unique functional of the density $F[n(\mathbf{r})]$. This implies that the ground-state density can be regarded as a fundamental variable of the problem: all properties of the ground state can, in principle, be obtained from a single density functional, independent of the specific system under consideration.

So far, the functional $F[n(\mathbf{r})]$ remains unknown. Following the constrained-search formulation of Levy [66, 67], the ground-state electronic energy can be expressed as a variational principle,

$$\begin{aligned} E_e &= \min_{n(\mathbf{r})} \left\{ \int d\mathbf{r} n(\mathbf{r}) V_{en}(\mathbf{r}) + \min_{\psi \rightarrow n(\mathbf{r})} \left\{ \langle \psi | \hat{T}_e + \hat{V}_{ee} | \psi \rangle \right\} \right\} \\ &= \min_{n(\mathbf{r})} \left\{ \int d\mathbf{r} n(\mathbf{r}) V_{en}(\mathbf{r}) + F[n] \right\} \end{aligned} \quad (3.7)$$

where $\hat{T}_e$ is the kinetic energy operator of the electrons and $\hat{V}_{ee}$ is the Coulombic electron-electron repulsion operator introduced in Eq. 3.2. The inner minimization defines the universal functional $F[n]$.

Kohn and Sham [65] then proposed to decompose the unknown kinetic and electron-electron contributions into tractable terms plus a remainder. Specifically, $\hat{T}_e$ is replaced by the kinetic energy of a fictitious system of non-interacting electrons $\{\phi_i(\mathbf{r})\}$ with the same density, and $\hat{V}_{ee}$ is as the classical Hartree electrostatic repulsion. All remaining many-body effects, namely the difference between the true kinetic energy and the non-interacting one, and the non-classical part of the electron-electron interaction, are gathered into a single unknown term $E_{xc}[n]$, called the exchange-correlation energy,

$$\begin{aligned}
E[n] = & \int d\mathbf{r} n(\mathbf{r}) V_{en}(\mathbf{r}) + \sum_i \int d\mathbf{r} \phi_i^*(\mathbf{r}) \frac{\nabla^2}{2} \phi_i(\mathbf{r}) \\
& + \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n].
\end{aligned} \tag{3.8}$$

The ground-state energy can be obtained by applying a variational principle [64],

$$\left. \frac{\delta F[n]}{\delta n} \right|_{n_0} = 0. \tag{3.9}$$

Applying this variational principle with a Lagrange multiplier to enforce the orthonormality of the single-particle wavefunctions, $\langle \phi_i | \phi_j \rangle = \delta_{ij}$, leads to the Kohn-Sham equations [65],

$$\begin{cases}
\left[-\frac{1}{2} \nabla^2 + V_{en}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}) \\
V_H(\mathbf{r}) = \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\
V_{xc}(\mathbf{r}) = \left. \frac{\delta E_{xc}[n]}{\delta n} \right|_{n(\mathbf{r})}
\end{cases} \tag{3.10}$$

where $\hat{V}_H$ and $\hat{V}_{xc}$ are the Hartree and exchange correlation potentials respectively. The last remaining piece of the puzzle is the knowledge of the exchange-correlation functional. Indeed, with E_{xc} and $\hat{V}_{xc}$, all many-body effects are in principle included. However, in practice, nobody knows this functional that would give the exact electronic ground-state energy and density. The problem is now to construct sufficiently simple and accurate approximations to $E_{xc}[n]$.

Since the introduction of the Kohn-Sham equations, many efforts have been made to construct exchange-correlation functionals, which can be organized into a hierarchy of increasing non-locality and computational cost, as illustrated in Figure 3.4. Historically, functionals that depends only on the electronic density have been called the *local density approximation* (LDA) [68, 69].

This approximation estimates the exchange correlation energy by locally evaluating the exchange correlation energy of the homogeneous electron gas,

$$E_{xc}^{LDA}[n] = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{xc}^{hom}[n(\mathbf{r})] \quad (3.11)$$

where ε_{xc}^{hom} is the exchange and correlation of the homogeneous electron gas. In this approximation, the exchange part is known analytically, and the correlation is parametrized using Monte-Carlo simulations [70]. Later, this initial approximation has been supplemented by the *general gradient approximation* (GGA) incorporating the local gradients of the electronic density. Then, the *meta*-GGA incorporate higher-order derivatives of the density [71], mainly $\nabla^2 n(\mathbf{r})$. Finally, hybrid functionals mix exchange–correlation terms depending on the density with orbital-explicit expressions to evaluate the exchange energy [72]. Building upon this, double-hybrid functionals further incorporate a perturbative treatment of electron correlation, thus combining DFT exchange–correlation with wavefunction-based correlation for improved accuracy [73].

Once the level of exchange correlation has been chosen, the Kohn-Sham equations finally become solvable. Indeed, the ground-state electronic energy is obtained self-consistently following the scheme in Figure 3.5. For a given ionic configuration, a first wavefunction is used to calculate a first electronic density, which is used to calculate the Hartree potential $\hat{V}_H$ and the exchange correlation potential $\hat{V}_{xc}$. It is then possible to solve the Kohn-Sham equations 3.8, evaluate a new wavefunction and then a new electronic density. If the density is equal to the previous density within the tolerance, the self-consistent field (SCF) cycle stops. If not, the new and the old densities are mixed. The new density is used to evaluate $\hat{V}_H$ and $\hat{V}_{xc}$ and the SCF restarts.

The formalism presented above can be applied to a wide range of systems, such as molecules, clusters, crystals, and disordered systems. This manuscript focuses exclusively on crystals, in which the constituent atoms are arranged periodically in space, forming a lattice characterized by translational symmetry. All the information on the crystal is then contained within a single unit cell: the position $\mathbf{R}_{l\kappa}$ of any atom is obtained by combining the lattice vector $\mathbf{R}_l = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$, which locates its unit cell, with its position $\mathbf{r}_\kappa$ within that cell (Figure 3.6),

$$\mathbf{R}_{l\kappa} = \mathbf{R}_l + \mathbf{r}_\kappa. \quad (3.12)$$

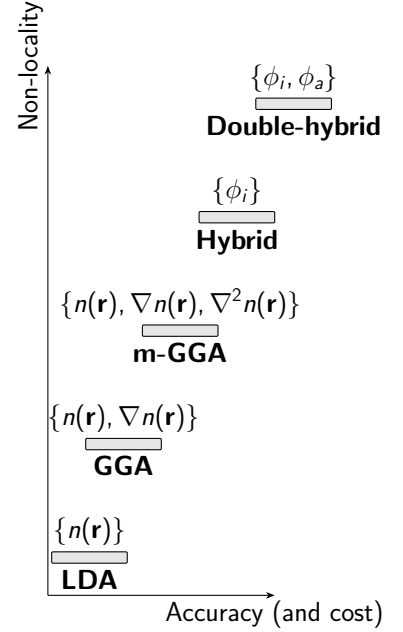


Figure 3.4: Hierarchy of exchange–correlation approximations in DFT, arranged by increasing non-locality and computational cost. Each rung of the ladder introduces additional ingredients: the local density $n(\mathbf{r})$ in the LDA, its gradient $\nabla n(\mathbf{r})$ in the GGA, higher-order derivatives in the meta-GGA, and explicit dependence on the occupied orbitals $\{\phi_i\}$ and unoccupied orbitals $\{\phi_a\}$ in hybrid and double-hybrid functionals respectively.

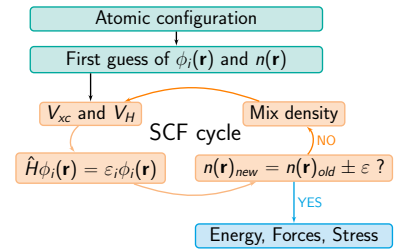


Figure 3.5: Self-consistent field scheme used to solve the Kohn-Sham equations. The gray boxes are the input needed to start the self-consistent field cycle. The orange boxes are the steps of the self-consistent field cycle, and the blue box is the output of the self-consistent field cycle.

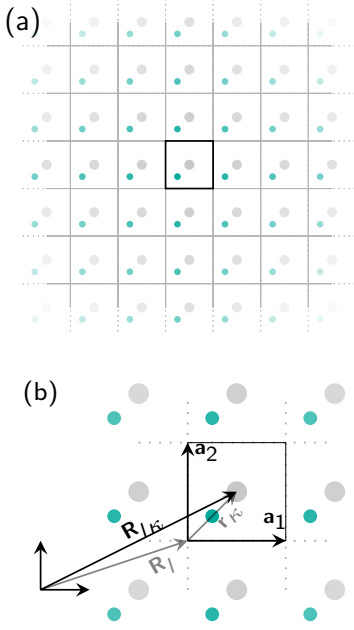


Figure 3.6: Schematic representation of (a) a periodic crystal. (b) The position of any atom in the crystal is uniquely determined by the lattice vector $\mathbf{R}_l = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$ locating its unit cell and its position $\mathbf{r}_k$ within that cell, such that $\mathbf{R}_{l,k} = \mathbf{R}_l + \mathbf{r}_k$.

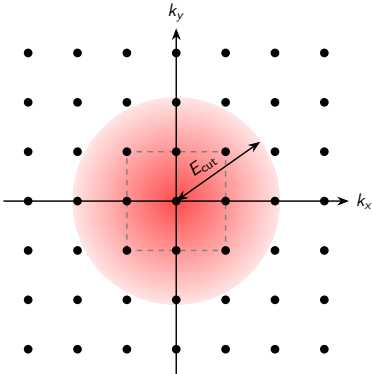


Figure 3.7: Illustration of the plane-wave energy cutoff scheme in reciprocal space. Only plane waves whose kinetic energy satisfies $\frac{1}{2}|\mathbf{k} + \mathbf{G}|^2 \leq E_{\text{cut}}$ are retained in the basis set, corresponding to reciprocal lattice vectors $\mathbf{G}$ lying within a circle of radius $\sqrt{2E_{\text{cut}}}$ in two dimensions. Increasing E_{cut} systematically improves the completeness of the basis set at the cost of a larger number of plane waves.

Because the potential shares the periodicity of the lattice, the Hamiltonian is invariant under all lattice translations. This invariance has a direct consequence on the form of the electronic wavefunctions, formalized by the *Bloch theorem* [74]: the eigenstates can be chosen so that, under a lattice translation, they are left unchanged up to a phase factor. Equivalently, each *Bloch function* can be written as the product of a plane wave of wavevector $\mathbf{k}$ and a function $u_{n\mathbf{k}}(\mathbf{r})$ that has the periodicity of the lattice. Imposing Born–von Kármán periodic boundary conditions over a supercell of N unit cells of volume Ω_0 quantizes the allowed wavevectors $\mathbf{k}$ and fixes the normalization of the Bloch functions,

$$\phi_{n\mathbf{k}}(\mathbf{r}) = (N\Omega_0)^{-1/2} e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}), \quad \langle u_{m\mathbf{k}} | u_{n\mathbf{k}} \rangle = \delta_{mn} \quad (3.13)$$

To take advantage of the periodicity of the crystal in the DFT formalism, the electronic density can be expressed in terms of the periodic functions introduced above:

$$n(\mathbf{r}) = \frac{1}{8\pi^3} \int_{\text{BZ}} d\mathbf{k} \sum_n^{\text{occ}} u_{n\mathbf{k}}^*(\mathbf{r}) u_{n\mathbf{k}}(\mathbf{r}) \quad (3.14)$$

The numerical integration over the Brillouin zone would *a priori* require a large number of $\mathbf{k}$ -points. However, the electronic wavefunction is almost identical for $\mathbf{k}$ -points close to each other. This limits the number of $\mathbf{k}$ -points needed to obtain accurate density. The $\mathbf{k}$ -point mesh has to be converged. This convergence can systematically be improved by increasing the number of $\mathbf{k}$ -points in the grid. Moreover, because the Bloch functions are periodic, they are usually written as a Fourier series, and the electronic wave function can be written as:

$$\phi_{n\mathbf{k}}(\mathbf{r}) = (N\Omega_0)^{-1/2} \sum_{\mathbf{G}} C_{n,\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \quad (3.15)$$

where $\mathbf{G}$ is a reciprocal space vector and $C_{n,\mathbf{k}}(\mathbf{G})$ is the Fourier transform of $u_{n\mathbf{k}}(\mathbf{r})$. This transformation leads to the fact that $u_{n\mathbf{k}}(\mathbf{r})$ has been expanded in a planewave basis set which consists of an infinite summation of reciprocal space vectors. Fortunately, this sum can be truncated by taking reciprocal plane waves that have a kinetic energy lower than an energy cutoff $E_{\text{cut}} \geq \frac{1}{2}|\mathbf{k} + \mathbf{G}|^2$.

As for the $\mathbf{k}$ -point grid mesh, this energy cutoff has to be

converged, and the error linked to this approximation can always be reduced by increasing the number of planewaves. The use of a plane-wave basis naturally introduces two practical difficulties. The first concerns the treatment of the tightly bound core states, which would require a prohibitively large number of plane waves to be represented accurately. The second arises from the rapid oscillations of the valence wavefunctions close to the nuclei. The first limitation is overcome by the frozen-core approximation, in which the total electronic density is separated into frozen core and active valence contributions. The core electrons are assumed to remain essentially unchanged by the surrounding chemical environment and are therefore excluded from the self-consistent cycle. The second limitation is handled through the construction of pseudopotentials, where the true ionic potential is replaced by a smoother effective potential acting only on the valence electrons. Modern pseudopotentials are now systematically generated and validated from first-principles in well-maintained databases such as PSEUDOJOJO [75], ensuring high accuracy and transferability across chemical environments.

3.1.2 The +U correction

Standard DFT exchange-correlation functionals based on the local density or generalized gradient approximations are known to fail in describing materials with strongly correlated *d* and *f* electrons, often incorrectly predicting insulating transition-metal oxides to be metallic [76]. A widely used correction to this problem is the DFT+*U* method [77–80], which supplements the DFT total energy with a Hubbard-like term acting on the correlated orbitals,

$$E_{\text{DFT}+U} = E_{\text{DFT}}[n(\mathbf{r})] + E_{\text{Hub}}[n_{m,m'}^{I\sigma}] - E_{\text{DC}}[n^{I\sigma}], \quad (3.16)$$

where E_{DFT} is the uncorrected DFT energy functional of the electronic density $n(\mathbf{r})$, E_{DC} is a double-counting term that removes the correlation energy already included in the DFT functional, and E_{Hub} is the Hubbard correction depending on the occupation matrix $n_{m,m'}^{I\sigma}$, where *I* labels the correlated atomic site, σ denotes the spin, and *m*, *m'* index the correlated orbitals within that site. The value of *U* is in practice often determined semi-empirically, by testing different values against experimental observables. Although this ap-

proach is sometimes criticized, it may be noted that most exchange-correlation functionals are themselves validated through semi-empirical testing. Alternatively, self-consistent schemes for the determination of U from first principles have been proposed [81, 82]. In this work, DFT+ U is employed exclusively for the construction of the training set of YNiO_3 (Section 4.3.6), where the Hubbard U correction is applied to the Ni d states to correctly reproduce the insulating character of this material.

3.1.3 Density Functional Perturbation Theory

Density Functional Theory provides a robust and powerful framework for computing the ground-state electronic energy of a system for a fixed configuration of atomic nuclei. By calculating this energy across a sufficient number of nuclear configurations, one can, in principle, map out the Born-Oppenheimer energy surface, which governs the system's adiabatic dynamics. While this static picture is foundational, a vast class of physical phenomena is not described by the energy itself, but rather by the system's response to external perturbations. Properties such as vibrational frequencies, elastic constants, dielectric susceptibilities, and piezoelectric coefficients are all defined by how the total energy changes when the system is slightly displaced from its equilibrium ground state. To access these properties, one must move beyond a simple enumeration of ground-state energies and develop a formalism capable of treating the system's behaviour in the vicinity of its minimum energy configuration. The conceptual foundation of DFPT rests upon the well-established framework of quantum mechanical perturbation theory. The approach begins with a reference system, typically the solved Kohn-Sham system from a standard DFT calculation, for which the unperturbed Hamiltonian, its wavefunctions, and eigenvalues are assumed to be known. A perturbation is then introduced, characterised by a small, dimensionless parameter λ , which represents a modification to the external potential. The goal is to determine the perturbed wavefunctions and their corresponding energies. This is achieved by expressing all quantities (the Hamiltonian, the wavefunctions, and the energies) as power series expansions in λ . Substituting these series into the perturbed Schrödinger equation and collecting terms of the same order in λ yields a

hierarchical set of equations. Solving these equations order-by-order provides the corrections to the wavefunctions and energies.

A profoundly important result that emerges from this formalism is the $2n + 1$ *theorem* [83]. This theorem states that the knowledge of the perturbed electronic wavefunctions up to a given order n is sufficient to determine the energy corrections up to order $2n + 1$. For example, the unperturbed ground-state wavefunction (order $n = 0$) alone determines the first-order energy correction, such as the forces and the stress. Furthermore, the first-order correction to the wavefunctions ($n = 1$) is sufficient to calculate the energy up to third order ($2n + 1 = 3$). This theorem drastically reduces the computational cost of obtaining high-order response properties, as it avoids the need to explicitly calculate high-order wavefunction corrections for many properties of interest. The power of perturbation theory has been integrated into the DFT framework by Gonze and co-workers [83–86]. In this context, the Hohenberg-Kohn theorems guarantee that the electron density becomes a functional of the perturbation parameter, λ , and consequently, so does the total energy. The $2n + 1$ theorem has been shown to hold within this DFPT framework, ensuring its computational efficiency. The formalism can be further generalised to handle multiple, distinct perturbations applied concurrently to the same reference system. This allows for the calculation of *mixed derivatives* of the energy with respect to different perturbation parameters.

As introduced above, a large range of physical quantities can then be accessed through DFPT framework. The energy can be written in a power series around the energy reference E^0

$$E(\lambda) = E^0 + \sum_i \left. \frac{\partial E}{\partial \lambda_i} \right|_0 \lambda_i + \frac{1}{2} \sum_{i,j} \left. \frac{\partial^2 E}{\partial \lambda_i \partial \lambda_j} \right|_0 \lambda_i \lambda_j + \dots \quad (3.17)$$

and the first, second, and third derivatives of the energy can be obtained using DFPT formalism.

Such perturbations typically include atomic displacements u , homogeneous strain η , and a static external electric field $\mathcal{E}$. Table 3.1 summarizes the physical quantities that can be accessed at first and second order with respect to these perturbations. At first order, each perturbation gives rise to a specific physical response: atomic displacements lead

Table 3.1: Overview of physical quantities related to first- and second-order derivatives of the total energy accessible on the first-principles level through DFPT. The perturbation parameter λ takes the values of an atomic displacement u , a homogeneous strain η , or an electric field $\mathcal{E}$.

λ	1 st	2 nd Order		
		u	η	$\mathcal{E}$
u	f	K	Λ	Z^*
η	σ	Λ	C	e^0
$\mathcal{E}$	P	Z^*	e^0	ϵ_∞

to the forces F acting on the atoms, homogeneous strain produces the stress tensor σ acting on the unit cell, and an external electric field induces a spontaneous polarization P . At second order, the corresponding derivatives define key response tensors. The second derivative with respect to atomic displacements yields the interatomic force-constant matrix K [86], that with respect to strain gives the elastic tensor C [87], and that with respect to the electric field, provides the clamped-ion dielectric tensor ϵ_{∞} . In addition to these pure responses, mixed derivatives between different perturbations describe important coupling effects. The derivative with respect to both u and η defines the internal strain-displacement coupling Λ , which quantifies the forces induced on atoms by strain and, conversely, the stress generated on the cell by atomic displacements. The derivative with respect to u and $\mathcal{E}$ corresponds to the Born effective charge tensor Z^* [86], which characterizes the polarization induced by atomic displacements or, equivalently, the forces produced by an electric field. Finally, the derivative with respect to η and $\mathcal{E}$ yields the piezoelectric tensor e^0 , which describes the polarization generated by strain or, equivalently, the stress induced by an applied field.

In principle, once the first-order derivatives of the wavefunctions are available, one can also access third-order derivatives of the total energy with respect to the same set of perturbations. These higher-order responses describe a wide range of physical effects. For instance, third derivatives with respect to three atomic displacements provide the third-order force constants, which are directly related to anharmonic effects and thermal properties. Mixed derivatives involving electric fields lead to various nonlinear optical responses: the electro-optic tensor (involving two electric fields and one static field) and the Raman tensor, which corresponds to derivatives with respect to two electric fields and one atomic displacement, describing how the dielectric polarizability changes under a vibrational mode. A particularly relevant example is the flexoelectric tensor [88, 89] introduced in Section 2.2.2 of Chapter 2, which quantifies the polarization induced by a strain gradient. This tensor can be viewed as a higher-order extension of the piezoelectric effect: while the piezoelectric tensor e^0 relates a homogeneous strain to polarization, the flexoelectric tensor describes the same coupling when the strain varies spatially. In centrosymmetric materials where the piezoelectric effect is forbidden by symmetry, the flexoelectric response thus

represents the leading electromechanical coupling.

3.2 Second-principles effective potentials

While density-functional theory provides a powerful and predictive framework to investigate materials properties from first principles, its direct application remains restricted to relatively small system sizes and short time scales. Many phenomena of interest in ferroic and functional oxides, such as domain formation, topological textures, long-wavelength structural instabilities, or finite-temperature phase transitions, emerge at length and time scales that are beyond the practical reach of standard DFT simulations [90]. To overcome these limitations, one typically constructs effective models whose parameters are derived from first-principles calculations. The central idea is to retain the same input-output structure as DFT, namely mapping an atomic configuration onto an energy, forces, and stresses, but to bypass the computationally expensive SCF cycle entirely. Instead, the Kohn-Sham equations are replaced by an analytical or data-driven representation of the potential-energy surface, trained on first-principles data, as illustrated in Figure 3.8. We collectively refer to such DFT-derived effective descriptions as *second-principles* models. The terminology reflects the fact that these approaches are fitted to first-principles data and, within the subspace on which they are trained, can in principle reproduce DFT accuracy while enabling simulations at vastly larger spatial and temporal scales.

In the following, we briefly review several representative frameworks before detailing the specific formalism employed in this work. This section is partly inspired by Refs. [13, 91], to which the reader is referred for a more comprehensive overview and additional references.

3.2.1 Lennard-Jones potential

The simplest class of interaction models used in atomistic simulations are pair potentials, which describe the energy as a function of the distance between two particles only. Among them, the Lennard-Jones potential, originally introduced by

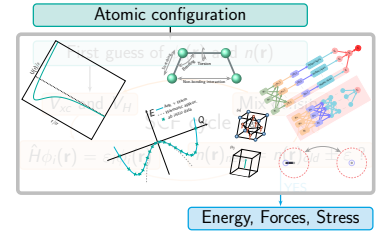


Figure 3.8: Illustration of the second-principles spirit. The second-principles potential (e.g. Lennard-Jones, shell model, ReaxFF, effective hamiltonian, fully atomistic taylor expansion or deep neural network) replace the time consuming treatment of the electron of the *ab-initio* approach.

John Lennard-Jones [92], provides a minimal yet effective description of short-range repulsion and intermediate-range attraction between neutral atoms or molecules.

In its general form, the potential combines a repulsive and an attractive power law,

$$U(r) = \frac{A_n}{r^n} - \frac{B_m}{r^m}, \quad (3.18)$$

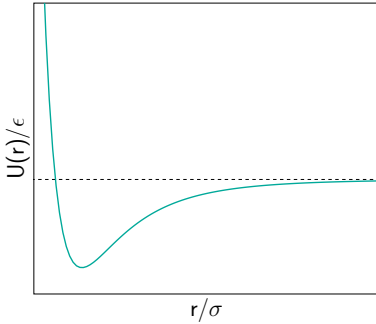


Figure 3.9: Lennard-Jones potential energy surface describing the interaction between two inert gas atoms. ϵ and σ as been obtained from Ref. [93].

where r is the interparticle distance and the coefficients A_n and B_m determine the strength of the repulsive and attractive interactions, respectively. The repulsive term reflects the strong overlap-driven energy increase at short distances, commonly associated with the Pauli exclusion principle [94], whereas the attractive contribution represents van der Waals interactions [95].

A particularly common choice (e.g. for noble gases) is the so-called 12-6 form [96],

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (3.19)$$

where ϵ sets the depth of the potential well and σ defines the distance at which the interaction energy vanishes. For a system containing many particles, the total interaction energy is obtained by summing such pair contributions over all atomic pairs (i, j) , where ϵ_{ij} and σ_{ij} are species-dependent interaction parameters. This analytical form is both flexible and computationally inexpensive, which explains its widespread use in atomistic simulations. In practice, ϵ and σ can be fitted to reproduce experimental thermodynamic data or reference *ab initio* calculations for simple systems such as noble gases, within the range where the pairwise approximation remains valid. Because the energy expression is fully analytical, the associated forces are straightforward to compute, making the potential particularly suitable for large-scale molecular dynamics simulations.

Several alternative pair potentials have been proposed to better reproduce specific classes of materials or interaction regimes. Notable examples include the Mie potential [97], which generalizes the Lennard-Jones form through adjustable exponents, and the Buckingham potential [98], which replaces the repulsive power law by an exponential term at the cost of one extra parameter. Although these forms may offer

improved realism for particular systems, the Lennard–Jones potential remains the most widely used pair interaction due to its simplicity, computational efficiency, and its ability to reproduce the qualitative behavior.

3.2.2 Reactive force fields

Reactive force fields provide an intermediate description between quantum-mechanical approaches and conventional empirical potentials. Among them, the **ReaxFF** (Reactive Force Field), introduced by van Duin, Goddard and co-workers [99], was specifically designed to enable atomistic simulations of chemically reactive systems at a computational cost much lower than quantum methods, while retaining a realistic description of bond formation and breaking. In contrast to traditional force fields, where the bonding topology must be fixed in advance, **ReaxFF** relies on a bond-order formalism in which bond strengths are continuously determined from interatomic distances. This allows bonds to deform, dissociate, and form dynamically during a simulation, while electronic effects are treated implicitly through environment-dependent interaction terms. As a result, the method can describe reactive processes such as chemical transformations, diffusion, or interfacial reactions within large-scale molecular dynamics simulations. Because of this flexibility, **ReaxFF** involves a relatively complex functional form with many parameters. These parameters are typically optimized against extensive training datasets including structural, energetic, and kinetic information, most often obtained from first-principles calculations such as density-functional theory, although experimental data can also be used. Once parameterized, the model can be applied to a wide range of environments and phases, making it suitable for studying complex materials and reactive processes beyond the accessible scales of quantum-mechanical simulations.

In this framework [100], illustrated in Figure 3.11, the total energy is decomposed into bond-related and environment-dependent contributions,

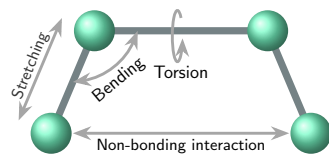


Figure 3.10: Schematic representation of the four classes of interatomic interactions in the **ReaxFF** framework: bond stretching between two atoms, valence-angle bending involving three atoms, torsional strain between four atoms, and non-bonding interactions comprising long-range electrostatic and van der Waals contributions.

$$E_{\text{System}} = E_{\text{Bond}} + E_{\text{Over}} + E_{\text{Angle}} + E_{\text{Torsion}} + E_{\text{vdW}} + E_{\text{Coulomb}} + E_{\text{Specific}}. \quad (3.20)$$

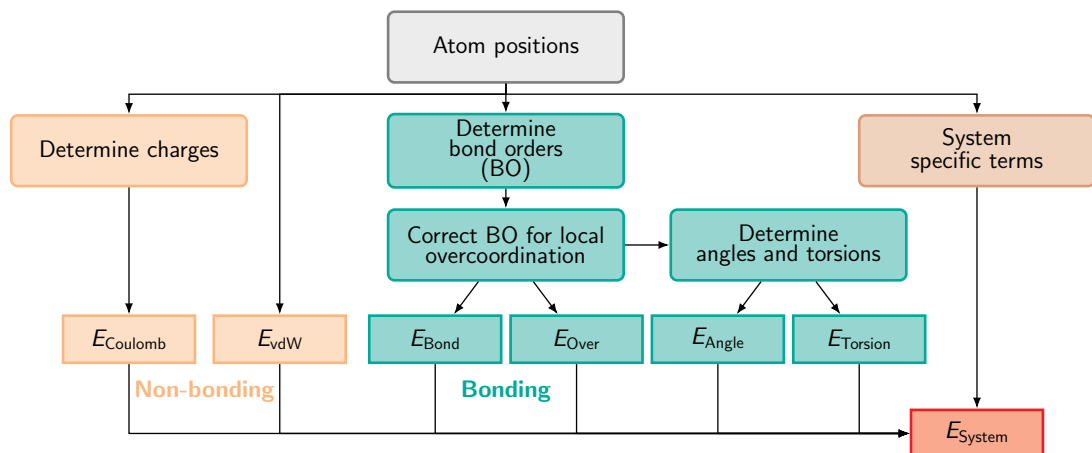


Figure 3.11: Workflow for the determination of each energy contribution in the **ReaxFF** framework. Starting from the atomic positions, the bond orders and atomic charges are first determined self-consistently, from which the bonding (E_{bond} , E_{over}), angular (E_{angle} , E_{tors}), and non-bonding (E_{Coulomb} , E_{vdW}) contributions are evaluated before being summed into the total energy E_{System} . Adapted from [100].

Here, E_{bond} depends on interatomic distances and represents bond formation energies. E_{angle} and E_{tors} account for three-body valence-angle strain and four-body torsional strain (see Figure 3.10). E_{over} introduces a penalty that limits overcoordination according to valence rules (for instance, increasing the energy if a carbon atom exceeds four bonds). E_{Coulomb} and E_{vdW} describe long-range electrostatic and dispersion interactions between all atoms, while E_{specific} gathers additional system-dependent terms required to capture effects such as lone pairs or hydrogen bonding.

The parameters entering these energy terms are typically derived from **DFT** calculations. Because the energetic contributions are explicitly resolved, **ReaxFF** can closely reproduce first-principles results while remaining computationally much less demanding. The parametrization strategy focuses on matching reference interaction distances and forces, ensuring that the model reproduces *ab initio* forces accurately in the physically relevant region of configuration space.

Since then, **ReaxFF** has been widely applied across diverse fields. In computational chemistry, it is commonly used to investigate the reactivity of organic systems [101]. It has also been extended to inorganic materials such as ferroelectric perovskite oxides [102, 103], to electrochemical problems including sodium-induced degradation of graphite cathodes in batteries [104], and to large-scale simulations of char combus-

tion under different atmospheres [105], involving systems of tens of thousands of atoms. More recently, it has successfully described proton transfer between H_3O^+ and OH^- in water, highlighting its suitability for modeling acid–base chemistry in aqueous environments [106].

3.2.3 Shell model

Another widely used approach to model ionic materials at the atomistic scale is the shell model [107], which provides a simple phenomenological description of ionic polarizability. In this framework, each ion is represented by two charged particles: a massive core and a massless electronic shell coupled through an effective spring (see Figure 3.12), such that the relative displacement between the two mimics the deformation of the electronic cloud in response to the local environment, thereby introducing an explicit description of polarization effects.

Electrostatic interactions act between all cores and shells, except within the same ion, while short-range interactions are typically defined between shells only. These short-range terms effectively account for the interactions not captured by the Coulomb contribution, including Pauli repulsion associated with electron-density overlap as well as dispersion forces. Various analytical forms can be employed for this purpose, such as Born–Mayer, Buckingham, Rydberg, or Morse-type potentials [108].

The core–shell coupling is often described using an isotropic harmonic spring, although anharmonic or anisotropic terms can be introduced when a more accurate description of polarization or hybridization effects is required. Model parameters, including effective charges, short-range potential coefficients, and core–shell coupling constants, are generally fitted to experimental measurements or first-principles calculations, targeting structural properties, energies, forces, vibrational frequencies, or dielectric responses. Owing to its balance between physical interpretability and computational efficiency, the shell model has been successfully applied to a broad range of ionic and partially covalent materials [13].

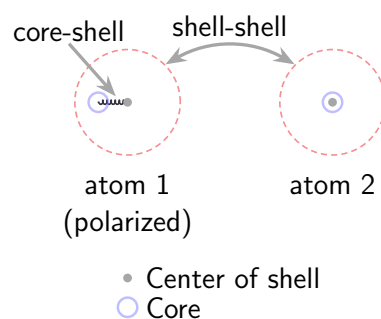


Figure 3.12: Schematic representation of the shell model for two polarized ions. Each ion is described by a massive core and a massless electronic shell coupled through an effective spring, along with the core–shell and shell–shell interactions between neighboring ions.

Bond-valence model

Another classical approach for modeling ionic and partially covalent solids is the bond–valence model [109–111], which is based on the idea that each atom tends to realize a preferred atomic valence in a stable structure. Within this framework, the valence V of an atom is distributed among the bonds it forms with its neighbors. Each bond is assigned a bond valence s_{ij} , related to the bond length R_{ij} through the exponential relation [112],

$$s_{ij} = \exp\left(\frac{R_0 - R_{ij}}{b}\right), \quad (3.21)$$

where R_0 is a bond-type-dependent reference length and b is a softness parameter. The total valence of an atom is then obtained as the sum over all its neighbors,

$$V_i = \sum_j s_{ij}, \quad (3.22)$$

and a structure is considered chemically stable when this sum matches the formal oxidation state of each ion. This simple concept has proven effective for rationalizing and predicting a wide range of crystal structures, particularly in oxide materials [113, 114].

In atomistic simulations, the bond–valence model can be formulated as an energy-based potential written as

$$E_{BV} = E_b + E_c + E_r + E_a, \quad (3.23)$$

where E_b represents the bond–valence contribution enforcing the preferred local valence V_i , E_c is the Coulomb interaction between ions, E_r denotes a short-range repulsive term preventing unphysical overlaps, and E_a accounts for angular-dependent interactions that stabilize the local bonding geometry.

The parameters entering these terms are commonly determined by fitting to experimental structural data or to first-principles results, for instance by reproducing relative energies of competing structures, equilibrium geometries, or atomic forces obtained from DFT calculations. Thanks to its physically transparent formulation and modest computational cost, the bond–valence approach provides an efficient intermediate description between simple pairwise poten-

tials and more elaborate reactive or polarization-based force fields.

3.2.4 Coarse-grained approach: effective hamiltonian

A common strategy to model complex systems across many fields is the use of coarse-grained descriptions. In biology, for instance, coarse graining is routinely employed to reduce molecular complexity: instead of tracking every atom, groups of atoms are represented as larger effective units such as amino acids, carbohydrates, or entire proteins. This reduction of microscopic detail allows one to focus on the collective behavior relevant at larger spatial and temporal scales. Such approaches have been widely used, in particular, to investigate protein folding mechanisms [115].

The same philosophy can be applied in condensed-matter physics and materials science. Instead of retaining all atomic degrees of freedom, one can construct reduced models that keep only the most relevant collective variables. In ferroelectric systems, these variables are typically local modes associated with structural instabilities, as illustrated in Figure 3.13. Such local modes may be defined approximately from the eigendisplacement of the unstable soft phonon, or more rigorously constructed as lattice Wannier functions corresponding to the unstable phonon branch [116]. By integrating out the remaining microscopic fluctuations, the system can then be described using a limited set of physically meaningful variables that capture the dominant structural distortions and energetics. Within this framework, effective Hamiltonians provide a systematic coarse-grained description in which the Born–Oppenheimer energy surface is parameterized in the restricted subspace spanned by the local modes ξ_i (lattice degrees of freedom) and the macroscopic strain η (elastic degrees of freedom). The total energy is thus written as

$$E(\xi_i, \eta) = E^{\text{self}}(\xi_i) + E^{\text{dpl}}(\xi_i) + E^{\text{short}}(\xi_i) + E^{\text{elast}}(\eta) + E^{\text{int}}(\xi_i, \eta), \quad (3.24)$$

where ξ_i denotes the local mode in cell i and η the homogeneous strain. The local-mode self-energy E^{self} is expressed as a Taylor expansion of the energy around the reference high-symmetry phase in terms of the local-mode amplitudes.

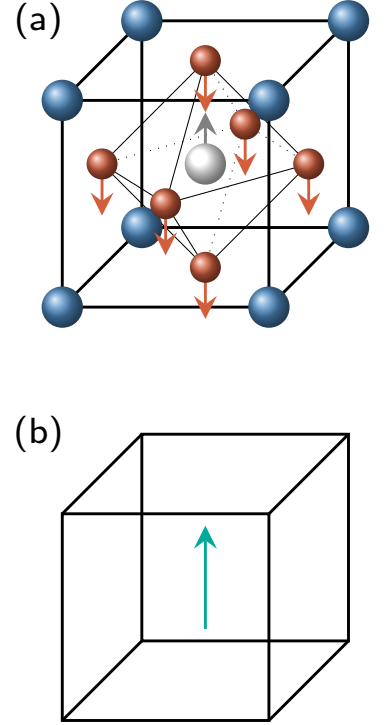


Figure 3.13: Illustration of coarse-grained approach in effective hamiltonian. (a) Sketch of atomic displacements creating a polar distortion in ABO_3 perovskite structure (b) Local mode substituting the atomic displacements.

Symmetry constraints typically suppress odd-order contributions, and the expansion is usually truncated at fourth order, yielding the commonly adopted polynomial form

$$E^{\text{self}}(\xi_i) = \sum_i \left[\alpha \xi_i^2 + \beta \xi_i^4 + \gamma \left(\xi_{ix}^2 \xi_{iy}^2 + \xi_{iy}^2 \xi_{iz}^2 + \xi_{iz}^2 \xi_{ix}^2 \right) \right]. \quad (3.25)$$

The second contribution, E^{dpl} , corresponds to the long-range part of the dipole-dipole interaction present in semiconductors and insulators. By nature, this interaction is infinite range.

$$E^{\text{dpl}}(\{\xi_i\}) = \frac{\bar{Z}^2}{\epsilon_\infty} \sum_{i < j} \frac{\xi_i \cdot \xi_j - 3(\mathbf{R}_{ij} \cdot \xi_i)(\mathbf{R}_{ij} \cdot \xi_j)}{R_{ij}^3} \quad (3.26)$$

where $\mathbf{R}_{ij}$ is the vector connecting the center of cell i with the center of cell j , ϵ_∞ is the high-frequency dielectric tensor and $\bar{Z}$ is the mode effective charge [86] which quantifies the change of polarization induced by a given local mode ξ_i ,

$$\bar{Z}_{i\alpha} = \sum_{k\beta} Z_{k\beta}^* \xi_{ik\beta}. \quad (3.27)$$

The third term, E^{short} , is the short-range interaction between the local modes and can be written as

$$E^{\text{short}}(\{\xi_i\}) = \sum_{i \neq j} \sum_{\alpha\beta} J_{i\alpha j\beta} \xi_{i\alpha} \xi_{j\beta} \quad (3.28)$$

where $\mathbf{J}$ represent the interaction matrix between local modes which decay with distance.

Then, the elastic energy, E^{elast} , can be written, using Voigt notation [117], as

$$E^{\text{elast}}(\boldsymbol{\eta}) = \frac{N}{2} \sum_{ab} C_{ab} \eta_a \eta_b \quad (3.29)$$

where $\mathbf{C}$ is the elastic tensor.

Finally, the last term entering into account is the coupling between the strain and the local modes

$$E^{\text{int}}(\{\xi_i\}, \eta) = \frac{1}{2} \sum_i \sum_a \sum_{\alpha\beta} g_{ia\alpha\beta} \eta_a \xi_{i\alpha} \xi_{i\beta} \quad (3.30)$$

where $\mathbf{g}$ is the strength of coupling between the strain and the local mode.

The parameters entering the Hamiltonian are typically derived from first-principles calculations, ensuring that the reduced model maintains a quantitative connection to the underlying electronic structure. This approach was first introduced for ferroelectric materials by Rabe and Joannopoulos in the study of GeTe [118], and was later generalized, formalized by Zhong, Vanderbilt, and Rabe for BaTiO₃ [119] and systematized by Wagmare and Rabe [116]. Their work established the modern effective-Hamiltonian framework, which has since become a powerful tool to investigate phase transitions, finite-temperature behavior, and electromechanical properties of ferroic and functional materials.

3.2.5 Second-principles interatomic potentials: MULTIBINIT

Among the second-principles approaches introduced above, the framework implemented in MULTIBINIT [120, 121] is the one employed for the vast majority of the results presented in this thesis, and will therefore be described in greater detail than the other methods.

The conceptual foundations of this approach were laid by Wojdeł, Hermet, Ljungberg, Ghosez and Íñiguez in 2013 [120], where the idea of a systematic polynomial expansion of the Born-Oppenheimer energy surface in terms of lattice degrees of freedom was first formalized. MULTIBINIT was subsequently developed as an ambitious platform aiming to unify all relevant degrees of freedom within a single framework, tightly integrated with the ABINIT software [122]. The present implementation is the result of cumulative efforts from successive members of the PHYTHEMA group. The present thesis has contributed to this effort through extensive use, systematic validation, and the identification and resolution of numerous issues in the implementation.

Reference structure – As introduced above, the second-principles approach relies on a Taylor expansion of the energy

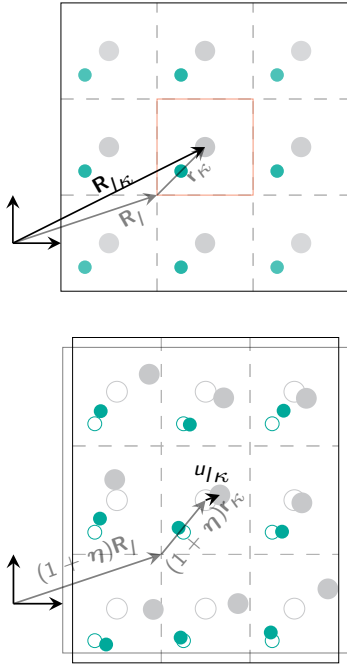


Figure 3.14: (Top) Illustration of the reference cell (red). The simulation box (black) consists of a repetition of the reference cell. (Bottom) Distorted structure with both atomic displacement and homogeneous strain (the undistorted structure is superimposed to guide the eyes).

around a reference structure (**RS**), taking into account all lattice degrees of freedom. The first step in constructing such a model is therefore the choice of this reference structure. If the goal of the model is to describe and study the anharmonicity of a given phase, the most natural choice for the reference structure is the local minimum corresponding to that phase. If, however, the objective is to describe phase transitions, competition between phases, or domain structures, the reference structure should instead correspond to a high-symmetry configuration common to several lower-symmetry phases. The reference structure, depicted in [Figure 3.14](#), is fully described by the unit cell vectors $\mathbf{R}_l$ and the atomic positions within the cell $\mathbf{r}_k$ introduced in equation (3.12). All possible crystal configurations can then be expressed in terms of atomic and strain distortions, $\mathbf{u}_{l\kappa}$ and $\boldsymbol{\eta}$, with respect to the reference structure:

$$\mathbf{R}_{l\kappa\alpha} = \sum_{\beta=1}^3 (\delta_{\alpha\beta} + \eta_{\alpha\beta})(\mathbf{R}_{l\beta} + r_{\kappa\alpha}) + u_{l\kappa\alpha}, \quad (3.31)$$

where α and β denote Cartesian coordinates. Within this framework, any possible distortion can be described, including unstrained configurations ($\boldsymbol{\eta} = 0$) with atomic displacements, homogeneous strain states where the atoms remain at their reference relative positions ($\mathbf{u}_{l\kappa} = 0$), inhomogeneous strain captured by nonzero atomic displacements ($\mathbf{u}_{l\kappa} \neq 0$), and, more generally, configurations exhibiting both finite strain and atomic displacements.

Polynomial expansion of lattice degrees of Freedom – Once this structural framework is established, the total energy E_{tot} of the system can be expressed as the sum of the energy of the reference configuration, $E(\mathbf{R}^0)$, and the energy deviation with respect to the reference structure, $E_{\text{eff}}(\mathbf{R})$,

$$E_{\text{tot}}(\mathbf{R}) = E(\mathbf{R}^0) + E_{\text{eff}}(\mathbf{R}). \quad (3.32)$$

Then, writing the energy deviation using the notation of Eq. (3.31),

$$E_{\text{eff}}(\{\mathbf{u}_{l\kappa}, \boldsymbol{\eta}\}) = E_p(\{\mathbf{u}_{l\kappa}\}) + E_s(\boldsymbol{\eta}) + E_{sp}(\{\mathbf{u}_{l\kappa}\}, \boldsymbol{\eta}) \quad (3.33)$$

where ‘ p ’ stands for phonon and ‘ s ’ for strain. Let us now focus on each term separately. It is common to write the

energy deviation from the reference structure due to atomic distortions as a Taylor series:

$$E_p(\{\mathbf{u}_{l\kappa}\}) = \sum_{n=2}^{\infty} \frac{1}{n!} \sum_{kl\kappa\nu\alpha\beta\dots} K_{kl\kappa\nu\alpha\beta\dots}^{(n)} u_{k\kappa\alpha} u_{l\nu\beta} \dots \quad (3.34)$$

where the tensor $\mathbf{K}^{(n)}$ is the n -th derivative of the energy with respect to atomic displacement

$$K_{kl\kappa\nu\alpha\beta\dots}^{(n)} = \left. \frac{\partial^n E_{\text{eff}}}{\partial u_{k\kappa\alpha} \partial u_{l\nu\beta} \dots} \right|_{RS} \quad (3.35)$$

Notably, the reference structure is a stationary point of the PES, which implies that $\mathbf{K}^{(1)} = 0$. Moreover, $\mathbf{K}^{(2)}$ is the interatomic force constant matrix that can be accessed using DFPT or finite difference, as introduced in the previous section. The range of interaction captured by the interatomic force-constant $\mathbf{K}^{(2)}$ is determined by the q -point mesh in DFPT framework and the supercell size in finite difference (typically spanning supercells of up to ten unit cells). If the reference structure is an insulator, the long-range atomic interaction created by electric dipoles caused by atomic displacements can be analytically calculated beyond the supercell size or the q -point mesh. This approach allows one to split the interatomic force constant into a short-range (SR) contribution and a long-range (LR) dipole-dipole (DD) part,

$$K_{kl\kappa\nu\alpha\beta}^{(2)} \approx K_{kl\kappa\nu\alpha\beta}^{(2),SR} + K_{kl\kappa\nu\alpha\beta}^{(2),DD} \quad (3.36)$$

where $\mathbf{K}^{(2),SR}$ is non-zero in the size of the supercell or the q -point mesh and zero outside as shown in Figure 3.15. The long-range part of the dipole-dipole interaction, $\mathbf{K}^{(2),DD}$, is defined up to infinity by [86]:

$$K_{0l\kappa\nu\alpha\beta}^{(2),DD} = \sum_{\gamma\delta} Z_{\kappa\alpha\gamma}^* Z_{\nu\beta\delta}^* \left(\frac{(\epsilon_{\infty}^{-1})_{\gamma\delta}}{D^3} - 3 \frac{\Delta_{\gamma} \Delta_{\delta}}{D^5} \right) \det(\epsilon_{\infty})^{-1/2} \quad (3.37)$$

where $\Delta_{\alpha} = \sum_{\beta} (\epsilon_{\infty}^{-1})_{\alpha\beta} \delta r_{\beta}$ and $D = \sqrt{\Delta \cdot \Delta \mathbf{r}}$ with $\Delta \mathbf{r}$ the vector separating two atoms in the simulation box.

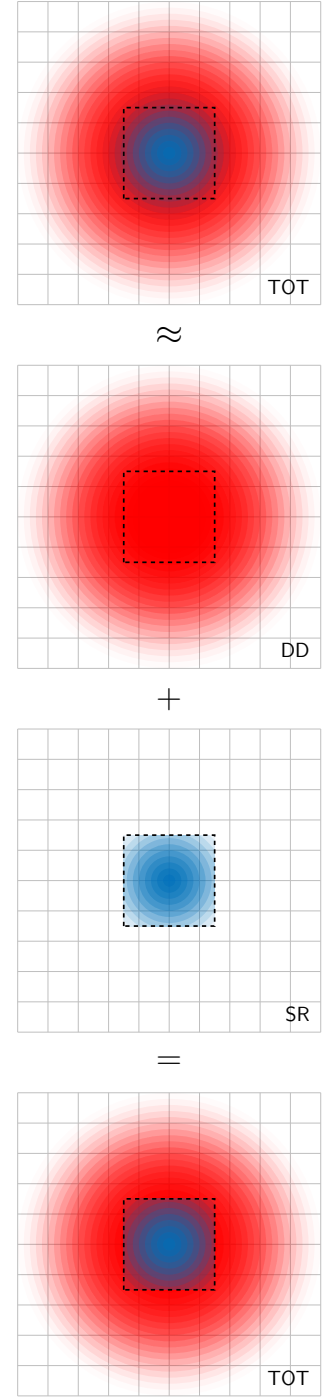


Figure 3.15: Schematic representation of the dipole-dipole (DD, red) and short-range (SR, blue) contributions to the total interatomic force constants (IFC). When activating the explicit treatment of DD interactions, the latter are computed analytically and infinite range while the SR IFC are obtained by subtracting the DD part from the total IFC and their range limited to that of a supercell defined by the q -point grid used for the calculations.

It turns out that $\mathbf{K}^{(2),DD}$ can be calculated in reciprocal space by an Ewald summation technique [86, 119]. By taking the Fourier transform of $\mathbf{K}^{(2),DD}$

$$\tilde{K}_{\kappa\nu\alpha\beta}^{(2),DD}(\mathbf{q} = \Gamma) = \sum_{l=1}^{\infty} K_{0l\kappa\nu\alpha\beta}^{(2),DD} e^{i\mathbf{0} \cdot \mathbf{R}_l}, \quad (3.38)$$

where the exponential factor reduces to unity since $\mathbf{q} = \Gamma = \mathbf{0}$, and the sum therefore runs over all lattice vectors $\mathbf{R}_l$ without any phase modulation. $\tilde{K}_{\kappa\nu\alpha\beta}^{(2),DD}$ captures the interaction of atom κ and ν and all their periodic images until infinity onto a single interaction as illustrated in Figure 3.16 (b). This mapping allows one to replace a sum over supercells up to infinity and restrict the index atom κ and ν with the size of the largest box between simulation and short-range box.

Within this formalism, the harmonic contribution to $E_p(\{\mathbf{u}_{l\kappa}\})$ can be written as,

$$\begin{aligned} E_p^{Har}(\{\mathbf{u}_{l\kappa}\}) = & \frac{1}{2} \sum_{\nu \in SC} \sum_{\alpha=1}^3 u_{0\nu\alpha} \sum_{\beta=1}^3 \left(\sum_{l\kappa \in SR} K_{0l\nu\kappa\alpha\beta}^{(2),SR} \right. \\ & \left. + \sum_{\kappa \in SC} \tilde{K}_{\nu\kappa\alpha\beta}^{(2),DD}(\mathbf{q} = \Gamma) \right) u_{l\kappa\beta} \end{aligned} \quad (3.39)$$

It means that all the atoms in the simulation box are harmonically coupled to each other. In practice, the full interatomic force constant matrix $K^{(2)}$ of the reference structure is read from a DFPT calculation (from a so called .ddb file). Then, the dipole-dipole interaction $\tilde{K}^{(2),DD}$ is calculated and subtracted from $K^{(2)}$ to get $K^{(2),SR}$. Then, $\tilde{K}^{(2),DD}$ is recalculated for the simulation box and added to $K^{(2),SR}$.

Finally, the force constant matrix and the Born effective charges must comply with the acoustic sum rule (ASR). The first one guarantees that the total energy is invariant upon a rigid translation of the crystal ($u_{k\kappa\alpha} = u_{l\nu\alpha} \forall \kappa, \nu \in SC$ and $\alpha \in [1, 3]$). This rule is fulfilled when the sum over one atom index κ vanishes, *i.e.*,

$$\sum_{\kappa} K_{0l\kappa\nu\alpha\beta}^{(2)} = 0 \quad \forall \alpha, \beta, \nu, l. \quad (3.40)$$

This is not *a priori* the case in DFPT. The strategy to impose the ASR is to derive that the self interaction element ($\kappa = \nu$)

to be the negative sum of the pairwise interaction ($\kappa \neq \nu$)

$$K_{0l\kappa\kappa\alpha\beta}^{(2)} = - \sum_{\kappa \neq \nu} K_{0l\kappa\nu\alpha\beta}^{(2)}, \forall \kappa, \quad (3.41)$$

and impose the symmetry of $\mathbf{K}^{(2)}$

$$K_{0l\kappa\nu\alpha\beta}^{(2)} = K_{0l\nu\kappa\beta\alpha}^{(2)}. \quad (3.42)$$

The second [ASR](#) guarantees that no net dipole is created by a rigid displacement of all atoms in the crystal. This implies that the sum of the Born effective charge over the entire simulation box must vanish,

$$\sum_{l\kappa} Z_{l\kappa\alpha\beta}^* = 0 \quad \forall \alpha, \beta \quad (3.43)$$

The second contribution to the harmonic energy is the elastic energy $E_s(\boldsymbol{\eta})$. The homogeneous strain tensor $\eta_{\alpha\beta}$ contains symmetric and antisymmetric parts. It is convenient to exclude the anti-symmetric part, which reflects a rigid rotation of the whole crystal, and to use Voigt notation [117] to reduce the two Cartesian indices α, β to a single index $a = 1, \dots, 6$. In this notation, $E_s(\boldsymbol{\eta})$ can be expressed as a Taylor series:

$$E_s(\boldsymbol{\eta}) = \sum_{n=2}^{\infty} \frac{N}{n!} \sum_{ab\dots} C_{ab\dots}^{(n)} \eta_a \eta_b \dots \quad (3.44)$$

where N is the number of repetitions of the unit cell and the tensor $\mathbf{C}^{(n)}$ is the n -th derivative of the energy with respect to the strain,

$$C_{ab\dots}^{(n)} = \frac{1}{N} \left. \frac{\partial^n E_{\text{eff}}}{\partial \eta_a \partial \eta_b \dots} \right|_{RS}. \quad (3.45)$$

For the same reason as for $\mathbf{K}^{(1)}$, $\mathbf{C}^{(1)} = 0$, and the harmonic term $\mathbf{C}^{(2)}$ corresponds to the elastic tensor introduced in the previous section.

Finally, the strain-phonon interaction energy $E_{sp}(\{\mathbf{u}_{l\kappa}\}, \boldsymbol{\eta})$ can also be expressed as a Taylor series:

$$E_{sp}(\{\mathbf{u}_{l\kappa}\}, \boldsymbol{\eta}) = \sum_{m,n=1}^{\infty} \frac{1}{(m+n)!} \sum_{ab\dots} \sum_{\substack{kl\kappa\nu \\ \alpha\beta\dots}} \Lambda_{ab\dots kl\kappa\nu\alpha\beta\dots}^{(m,n)} \eta_a u_{k\kappa\alpha} \dots \quad (3.46)$$

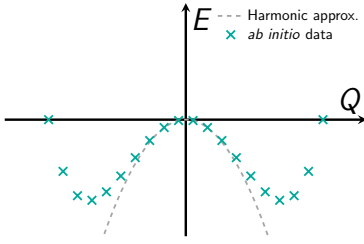


Figure 3.17: Schematic representation of the harmonic approximation (dashed) of the Born-Oppenheimer energy surface. The crosses represent a sample of *ab initio* data points. While exact at the reference structure, the harmonic approximation progressively deviates from the true Born-Oppenheimer energy surface for larger distortions.

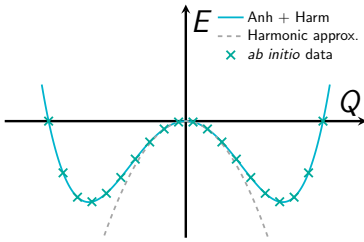


Figure 3.18: Schematic representation of the second-principles approach to the Born-Oppenheimer energy surface. The harmonic contribution (dashed) is kept exact from DFPT calculations, while the anharmonic correction (solid) is fitted to the residual *ab initio* data (crosses), i.e. the difference between the true energy surface and the harmonic approximation.

where the tensor Λ is the (m, n) -th mixed derivative of the energy with respect to the strain and atomic displacements,

$$\Lambda_{ab\cdots kl\kappa\nu\alpha\beta\cdots}^{(m,n)} = \frac{\partial^{n+m} E_{\text{eff}}}{\partial \eta_a \cdots \partial u_{k\kappa\alpha} \cdots} \Big|_{RS}. \quad (3.47)$$

The lowest-order coupling term $\Lambda^{(1,1)}$ corresponds to the strain-phonon tensor introduced in the previous section.

At this stage, the information around the reference structure is known and exact at the harmonic level. This is not sufficient to fully describe the Born-Oppenheimer energy surface around the reference structure as shown in Figure 3.17. To do so, one needs to add anharmonic contribution to the Taylor expansion of the energy as illustrated in Figure 3.18. However, the number of independent tensors (3.35), (3.45) and (3.47) are generally too large to calculate all of them, even at low order. This implies that restricting the order and range of interatomic anharmonic interactions is not enough and an efficient algorithmic way of finding the most important interaction is needed. Moreover, as in the harmonic approximation, $K^{(2)}$ and $\Lambda^{(m,n)}$ have to comply with the ASR. Imposing such ASR is more complicated at higher order and turns out to be impossible considering that take into account only the most important interaction. Fortunately, it is possible to find an alternative way to write E_p and E_{sp} where the ASR is automatically satisfied at all orders. Instead of expanding the energy in terms of displacement, we expand it as a function of displacement differences:

$$E_p^{anh}(\{\mathbf{u}_{l\kappa}\}) = \sum_{n=3}^N \frac{1}{n!} \sum_{kl\kappa\nu\alpha\beta\cdots} \hat{K}_{kl\kappa\nu\alpha\beta\cdots}^{(n)} (u_{k\kappa\alpha} - u_{l\nu\beta}) \cdots \quad (3.48)$$

where $\hat{K}^{(n)}$ are the anharmonic force-constant tensors. Similarly, the anharmonic strain-phonon interaction is written as

$$E_{sp}^{anh}(\{\mathbf{u}_{l\kappa}\}, \boldsymbol{\eta}) = \sum_{\substack{m,n=1 \\ m+n \geq 2}}^{M,N} \frac{1}{(m+n)!} \sum_{ab\cdots} \sum_{kl\kappa\nu\alpha\beta\cdots} \hat{\Lambda}_{ab\kappa\nu\alpha\beta\cdots}^{(m,n)} \eta_a (u_{k\kappa\alpha} - u_{l\nu\beta}) \cdots \quad (3.49)$$

where $\hat{\Lambda}^{(m,n)}$ are the anharmonic strain-phonon coupling

tensors. Using displacement differences instead of bare displacements automatically fulfils the **ASR**, since any rigid translation of the crystal results in a null contribution to E_p^{anh} and E_{sp}^{anh} . The main counterpart of this approach resides in the fact that the number of independent anharmonic coefficients to determine increases.

Algorithmic anharmonic term generation – Now that the polynomial expansion of lattice degrees of freedom has been introduced, the next task is to find an algorithmic way of generating the anharmonic terms and grouping together the symmetry-equivalent ones.

The first step of this procedure relies on the definition of a set of independent anharmonic coefficients complying with the crystal symmetry of the reference structure. Consequently, the irreducible anharmonic coefficients will consist in a set of equivalent terms which are called symmetry adapted terms (**SATs**) [120]. During the preparation of the manuscript, we reviewed and fixed remaining issues in the implementation of the **SATs** generation in **MULTIBINIT**. We take into account the

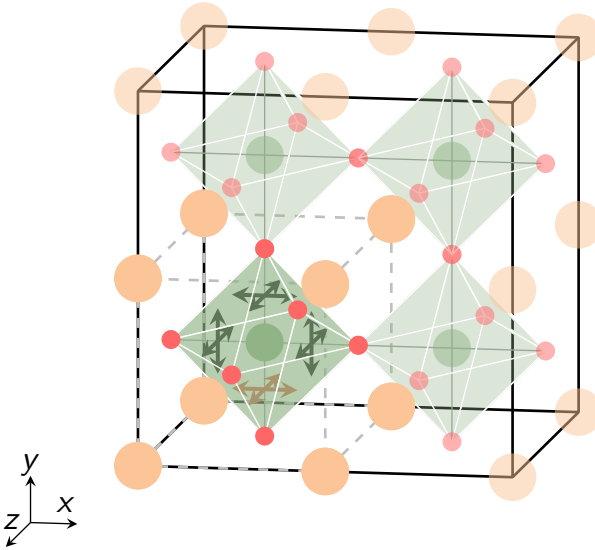


Figure 3.19: Illustration of a symmetry-adapted term (**SATs**) of the type $(B_x^{[000]} - X_{3x}^{[000]})^2 (B_y^{[000]} - X_{3y}^{[000]})^2$ in an ABX_3 perovskite structure. The highlighted cell (dashed box) is the reference unit cell located at $[000]$, surrounded by its periodic images shown at reduced opacity. Each arrow, centered on the bond between atoms i and j , represents a displacement difference $(u_{i\alpha} - u_{j\alpha})$ along the Cartesian direction α . Double arrows indicate that the corresponding displacement difference enters the term squared, which reflects the invariance of the **SATs** under mirror-plane reflections. Red and black arrows distinguish the two independent displacement pairs entering the coupling term.

set of symmetry operations $\{\mathbf{S}|\mathbf{t}\}$ of the reference structure where $\mathbf{S}$ is a 3×3 matrix that represent the point symmetry and $\mathbf{t}$ is a translation vector, both expressed in the chosen reference frame. Then, if we apply $\{\mathbf{S}|\mathbf{t}\}$ to any vector $\mathbf{x}$, we

obtain a transformed vector given by,

$$x'_\alpha = \sum_\beta S_{\alpha\beta} x_\beta + t_\alpha \quad (3.50)$$

Since, $\{\mathbf{S}|\mathbf{t}\}$ is a symmetry operation of the **RS**, it has to fulfill

$$\{\mathbf{S}|\mathbf{t}\}(\mathbf{R}_l + \mathbf{r}_\kappa) = \mathbf{R}'_l + \mathbf{r}'_\kappa. \quad (3.51)$$

This means that for any atom κ in the cell l , there must exist an atom κ' in cell l' of the same atomic species that satisfies relation (3.51). Equation (3.51) simply expresses the invariance of the **RS** under the action of its space-group symmetries $\{\mathbf{S}|\mathbf{t}\}$. As a direct consequence of the invariance of the **RS**, the atomic distortions $\mathbf{u}_{l\kappa}$ and homogeneous strain $\boldsymbol{\eta}$ with respect to the reference positions must transform consistently under the same symmetry operations

$$u'_{l'\kappa'\alpha} = \sum_\beta S_{\alpha\beta} u_{l\kappa\beta} \quad (3.52)$$

$$\eta'_{\alpha\beta} = \sum_{\gamma\delta} S_{\alpha\gamma} \eta_{\gamma\delta} (S^{-1})_{\delta\beta} \quad (3.53)$$

Naturally, since $\mathbf{u}'_{l\kappa}$ and $\boldsymbol{\eta}'$ are related to $\mathbf{u}_{l\kappa}$ and $\boldsymbol{\eta}$ by symmetry, they should produce the same energy changes,

$$E_{\text{eff}}(\{\mathbf{u}'_{l\kappa}, \boldsymbol{\eta}'\}) = E_{\text{eff}}(\{\mathbf{u}_{l\kappa}, \boldsymbol{\eta}\}) \quad (3.54)$$

In the current implementation of MULTIBINIT, **SATs** are generated through a four-step procedure. The first step consists in enumerating all elementary distortions with respect to the **RS**, including atomic displacements pairs and homogeneous strain, within a cutoff radius r_{cut} controlled by the parameter `fit_cutoff`. The full set of space-group symmetry operations $\{\mathbf{S}|\mathbf{t}\}$ of the **RS** is applied to these distortions in order to group them into symmetry-equivalent distortions. Each group of distortions is then assigned a unique irreducible label.

The second step consists of recursively combine all the irreducible distortions from the lowest polynomial order to the higher one using the keyword `fit_rangePower`. Thereby, in order to reduce the number of possible combinations, we impose that one of the irreducible atoms of the perovskite reference structure must appear in all products. As a result, only terms constructed around a fixed irreducible atomic site

are generated. The anharmonic coefficients obtained in this way can thus be interpreted as describing all anharmonic interactions within a local neighborhood, or interaction shell, centered on a single atom,

$$\hat{K}_{klm\cdots\kappa\nu\delta\cdots\alpha\beta\cdots}^{(n)}(u_{k\kappa\alpha} - u_{l\nu\alpha})(u_{k\kappa\beta} - u_{m\delta\beta})\cdots \quad (3.55)$$

The third step, required to obtain the complete set of symmetry-adapted combinations, is the most computationally demanding one. Indeed, a given combination of p irreducible distortions does not, in general, exhaust all the irreducible combinations that can be constructed from the corresponding sets of symmetry-equivalent distortions. In order to generate the missing coefficients associated with a given combination of irreducible atomic displacement pairs, a dedicated two-step procedure is employed. First, a symmetry operation $\{\mathbf{S}|\mathbf{t}\}$ is applied to one of the p irreducible atomic displacement pairs, transforming it into a symmetry-equivalent distortion. This transformed distortion is then combined with the remaining $p - 1$ untransformed irreducible distortions to form a new candidate combination. Second, all symmetry operations of the **RS** are successively applied to this new combination, allowing all p distortions to be transformed simultaneously. If the resulting set can be mapped onto an already existing irreducible combination, it is grouped with this existing combination; otherwise, it is retained and stored as a new irreducible combination. This procedure is recursively applied over all symmetry operations of the reference structure and over all p irreducible entities involved in the initial combination, including both atomic displacement pairs and homogeneous strain components. The total number of generated irreducible combinations strongly depends on the local coordination of the central atom and its nearest-neighbor environment.

In the final step of the **SATs** generation, the full set of symmetry-equivalent combinations is constructed for each representative irreducible combination and associated with a single anharmonic coefficient. As a consequence of the crystal symmetries, some symmetry-adapted terms may vanish identically. These symmetry-forbidden contributions are therefore eliminated, leading to a further reduction in the number of independent irreducible coefficients.

Algorithmic anharmonic term selection – Having constructed the complete set of symmetry-adapted anharmonic terms allowed by the reference structure, the remaining challenge is no longer one of completeness, but of relevance. The objective of a second-principles model is not to retain the full polynomial expansion of the lattice degrees of freedom up to a given order and interaction cutoff, but rather to identify and keep only the most physically important anharmonic contributions. Indeed, the number of SATs grows rapidly with both the polynomial order and the interaction range, making a systematic inclusion of all allowed terms impractical. We therefore adopt an algorithmic strategy to select, from the full space of symmetry-allowed interactions, a reduced subset of dominant anharmonic SATs, which are subsequently determined by fitting to a targeted set of *ab initio* data.

The selection and determination of these coefficients rely on the algorithm introduced by Escorihuela-Sayalero and co-workers [121], which consists of two essential ingredients: (i) the computation of anharmonic coefficients and (ii) the selection of the most relevant terms among them. In practice, the determination of the anharmonic coefficients is performed using a least-squares fitting procedure. The quantities fitted are *ab initio* energies, atomic forces, and stresses, computed for a set of atomic configurations forming the training set (TS).

Within our second-principles framework, the energy of a given atomic configuration is directly obtained by evaluating Eq. (3.33). Atomic forces are then naturally obtained as derivatives of the energy with respect to atomic displacements,

$$f_{l\kappa\alpha} = - \left. \frac{\partial E}{\partial u_{l\kappa\alpha}} \right|_{\mathbf{u}, \eta}. \quad (3.56)$$

The stresses σ acting on the simulation cell are defined as derivatives of the energy with respect to strain,

$$\sigma_a = \frac{1}{V} \left. \frac{\partial E}{\partial \eta_a} \right|_{\mathbf{u}, \eta}, \quad (3.57)$$

where V is the volume of the atomic configuration. It is important to emphasize that the derivative of the energy with respect to strain is computed under the constraint that the *relative* atomic coordinates are kept fixed. This definition

of the stress slightly differs from that originally presented by Escorihuela-Sayalero and co-workers [121]. In MULTIBINIT, we instead adopt the convention commonly used in solid-state physics textbooks [62]. In particular, the strain η applied to compute the stress does not have the same meaning as the deformation parameters defining the distorted reference structure, which are denoted here by η_a in Eq.(3.57). Appendix A provides a detailed derivation of the stress expressions and discusses their practical implementation. These expressions were independently rederived, reimplemented, and systematically tested within the present thesis.

To determine the values of the selected anharmonic coefficients, we introduce a goal function (GF) that quantifies the discrepancy between the anharmonic contributions obtained from the TS and those predicted by the second-principles polynomial expansion.

In the present implementation, only the anharmonic contributions are included in the minimization procedure. The harmonic part of the model is determined independently and with high accuracy from DFPT calculations, and is therefore removed from the total *ab initio* quantities prior to fitting. As a result, the fitting procedure targets exclusively the genuinely anharmonic part of the potential energy surface. For a given atomic configuration $s \triangleq (\{\mathbf{u}\}, \eta)$, the anharmonic energy is defined as

$$E^{\text{Anh}}(\text{TS}, s) = E^{\text{tot}}(\text{TS}, s) - E_0(\mathbf{R}^0) - E^{\text{har}}(s), \quad (3.58)$$

where $E_0(\mathbf{R}^0)$ is the energy of the reference structure and $E^{\text{har}}(s)$ denotes the harmonic contribution evaluated for the same configuration. Analogous definitions apply to the anharmonic components of the forces and stresses.

The GF depends on a set of p anharmonic coefficients $\Theta_p \triangleq \{\theta_1, \dots, \theta_p\}$, where each coefficient θ_i corresponds to one of the anharmonic parameters $\hat{\mathbf{K}}^n$, $\hat{\mathbf{A}}^{(n,m)}$, or $\hat{\mathbf{C}}^n$ associated with given SATs. It is defined as a weighted least-squares functional involving anharmonic energies, atomic forces, and

stresses,

$$\begin{aligned}
 G(\Theta_p, \text{TS}) = & \frac{w_1}{N_1} \sum_s \Omega^{-1}(s) \beta(s) [E^{\text{Anh}}(\text{TS}, s) - E^{\text{Anh}}(\Theta_p, s)]^2 \\
 & + \frac{w_2}{N_2} \sum_{skl\alpha} \beta(s) [f_{l\kappa\alpha}^{\text{Anh}}(\text{TS}, s) - f_{l\kappa\alpha}^{\text{Anh}}(\Theta_p, s)]^2 \\
 & + \frac{w_3}{N_3} \sum_{sa} \Omega^2(s) \beta(s) [\sigma_a^{\text{Anh}}(\text{TS}, s) - \sigma_a^{\text{Anh}}(\Theta_p, s)]^2,
 \end{aligned} \tag{3.59}$$

The prefactors w_1 , w_2 , and w_3 are user-defined weights, adjustable through the `fit_factors` keyword in `MULTIBINIT`, allowing one to tune the relative importance of energies, forces, and stresses in the fit. The normalization constants N_1 , N_2 , and N_3 are chosen as 1, $3N_{\text{at}}^{\text{TS}}$, and 6, respectively, where $N_{\text{at}}^{\text{TS}}$ is the number of atoms in the training set configurations. This choice compensates for the much larger number of force and stress data points compared to a single energy value per configuration. The factor $\Omega(s)$ was introduced by Shepard and co-workers [123] to balance the relative contributions of forces and stresses and depends on the volume of configuration s . Its inclusion ensures that stresses and forces enter the GF on comparable footing. In addition, each configuration s is assigned a statistical weight $\beta(s)$, designed to control the relative influence of different regions of configuration space. Strongly distorted structures typically exhibit large forces and stresses and can otherwise dominate the fit. However, for lattice-dynamical and finite-temperature simulations, it is often desirable to describe accurately the vicinity of (meta)stable configurations. To this end, we adopt a Maxwell–Boltzmann-like weighting function,

$$\beta(s) = \exp \left[-\frac{\sum_{i\alpha} |f_{i\alpha}(\text{TS}, s)|}{\alpha_w} \right], \tag{3.60}$$

where α_w is a tunable parameter specified via the `fit_weight_T` keyword. The weights $\beta(s)$ are subsequently normalized such that $\sum_s \beta(s) = n_s$, where n_s is the total number of configurations in the training set. This procedure enhances the contribution of configurations close to equilibrium while still retaining information from more distorted structures.

The GF defined in Eq. (3.59) is a quadratic function of the coefficients Θ_p and can thus be interpreted as a p -dimensional paraboloid. The optimal set of anharmonic coefficients is obtained by minimizing $G(\Theta_p, \text{TS})$ with respect to all θ_i ,

leading to the stationarity conditions

$$\frac{\partial G(\Theta_p, TS)}{\partial \theta_i} = 0 \quad \forall i \in \{1, \dots, p\}. \quad (3.61)$$

A detailed discussion of the mathematical properties of such goal functions can be found in Refs. [120, 121].

The second component of the algorithm proposed by Escorihuela-Sayalero and co-workers [121] concerns the selection of the most relevant anharmonic terms. Previous second-principles studies [120, 121] have shown that a realistic and predictive model can typically be achieved using only a few tens of anharmonic symmetry-adapted terms. Identifying this small subset from the full space of allowed interactions is, however, a highly nontrivial combinatorial problem.

If N_{SAT} symmetry-adapted terms are generated for a given cutoff radius r_{cut} and polynomial order, the number of possible combinations of p terms is

$$N_{\text{comb}} = \binom{N_{\text{SAT}}}{p}. \quad (3.62)$$

Even for moderate cutoffs, N_{comb} rapidly becomes astronomically large. For example, selecting $p = 30$ terms from the set of third- and fourth-order anharmonic interactions (including strain–phonon couplings) within a cutoff $r_{\text{cut}} = \frac{\sqrt{3}}{2} a_p$ in a perovskite structure yields $N_{\text{comb}} \sim 10^{147}$, rendering any exhaustive search infeasible.

To overcome this limitation, the iterative selection algorithm introduced in Ref. [121] is employed and schematically illustrated in Figure 3.20. In the first iteration, each individual anharmonic coefficient θ_i is fitted independently by minimizing $G(\theta_i, TS)$, and the term yielding the largest reduction of the GF is selected. In subsequent iterations, new candidate sets are constructed by adding one additional term to the previously selected set, and the coefficients are reoptimized at each step. This procedure is repeated until either a target number p of coefficients is reached, specified by the `fit_ncoeff` keyword, or a convergence criterion on $G(\Theta_p, TS)$ is satisfied. Within this approach, the total number of combinations that must be tested is drastically reduced.

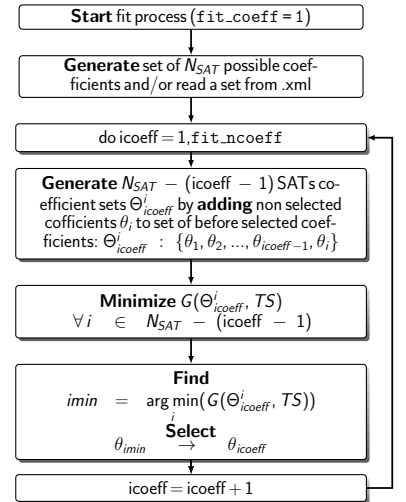


Figure 3.20: Schematic illustration of the iterative term selection algorithm proposed by Escorihuela-Sayalero and co-workers [121] as implemented in MULTIBINIT. At each iteration, the anharmonic term θ_i whose inclusion most reduces the goal function G is added to the selected set, until the target number of coefficients `fit_ncoeff` is reached.

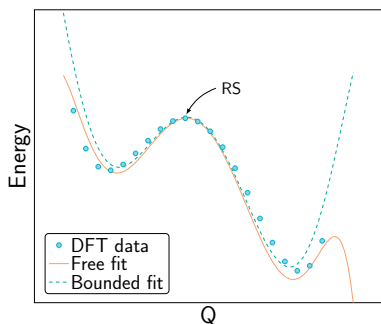


Figure 3.21: Schematic illustration of the bounding procedure. The free fit is represented by the solid line and is not bounded from below. The Bounding process assure that the model is bounded from below and produce the dashed line.

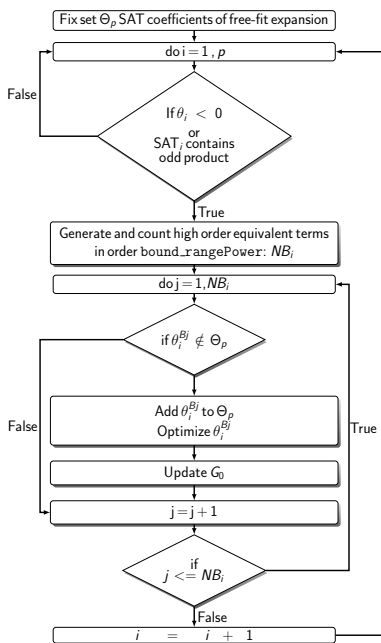


Figure 3.22: Illustration of the bounding algorithm. The algorithm is activated by the keyword `bound_model`. At the beginning an input set Θ_p of anharmonic SAT coefficients are fixed. For each divergent term θ_i a set NB_i of equivalent even higher-order term is added. x and y are representatives of any irreducible atomic displacement pair or homogeneous strain in the example. In a second loop the NB_i SAT bounding coefficients are added to the initial set and optimized

Algorithmic Bounding of the Polynomial Expansion – After the fitting stage (unconstrained fit), the resulting set of SATs often leads to an effective potential that is not bounded from below. In such situations, the energy of the model diverges towards large negative values for sufficiently large distortions, rendering the model physically meaningless and unusable in practice. Increasing the size or diversity of the TS is generally insufficient to resolve this issue, as the dimensionality of the anharmonic parameter space remains prohibitively large.

An additional strategy is therefore required to enforce the stability of the model while preserving the quality of the initial fit. The principle of the bounding algorithm is to identify anharmonic terms that may induce an unbounded behavior and to systematically stabilize them by introducing higher-order SATs with positive coefficients. This procedure ensures that the effective potential remains bounded from below without significantly degrading the accuracy of the fitted model in the physically relevant region of configuration space.

Therefore, each SATs appearing in the free-fit is examined for its propensity to induce a negative divergence at large distortion amplitudes. A SATs is classified as divergent if it involves odd powers, or if it corresponds to an even-order term with a negative fitted coefficient. Such terms can potentially destabilize the effective potential and must therefore be treated explicitly.

For each divergent SATs, a set of higher-order, even bounding SATs is constructed. This set includes even terms generated from all symmetry-allowed multipliers of the divergent SATs, as well as even analogs of the divergent term itself, provided that their polynomial order lies within the prescribed bounding range (see Figure 3.22). The lower and upper bounds of this range are controlled by the `bound_rangePower` keyword in MULTIBINIT. In practice, bounding terms are typically introduced at polynomial orders two or four higher than the maximum order included in the free fit.

To enforce the boundedness of the potential, the coefficients associated with these higher-order bounding SATs must be constrained to positive values, while preserving as much as possible the accuracy of the model with respect to the TS. A simple and robust iterative optimization strategy is then applied. At the beginning of the procedure, the coefficients

Θ_p of the free-fit polynomial are fixed. A loop over the free-fit SATs is then initiated. When a divergent free-fit SATs is detected, its associated set of N higher-order equivalent bounding SATs, denoted $\{B_j\}$, is generated. A second loop is subsequently performed over these bounding terms.

At each iteration, a single bounding SATs is added to the polynomial, and its coefficient $\theta_i^{B_j}$ is optimized independently, where i labels the divergent free-fit SATs among the initial p terms, and j labels the corresponding bounding term. Prior to the optimization, a consistency check is performed to ensure that the bounding SATs is not already present in the polynomial, as multipliers originating from different free-fit terms can lead to equivalent symmetry-adapted interactions.

The optimization of $\theta_i^{B_j}$ is carried out by analyzing the behavior of the goal function as a function of this single coefficient, while all other coefficients are held fixed. In this context, the GF becomes a one-dimensional quadratic function, $G(\theta_i^{B_j}, \text{TS})$, which is considered relative to its initial value G_0 at the beginning of the bounding iteration. The value $G(\theta_i^{B_j} = 0, \text{TS})/G_0 = 1$ provides one point on this parabola by construction. Two additional evaluations of the GF are performed at positive trial values of $\theta_i^{B_j}$, allowing the parabola to be fully determined and its minimum to be identified analytically.

If the minimum of the parabola occurs at a positive value $\theta_i^{B_j} > 0$, this value is retained, as it simultaneously improves the description of the TS and contributes to stabilizing the potential. If, on the contrary, the minimum lies at a negative value of $\theta_i^{B_j}$, a positive coefficient is instead selected such that the relative increase of the GF satisfies $G(\theta_i^{B_j}, \text{TS})/G_0 = G_P > 1$ (see Figure 3.22 and Figure 3.23). This choice explicitly trades a controlled loss of accuracy for the enforcement of boundedness.

After fixing $\theta_i^{B_j}$, the reference value G_0 is updated, and the loop over the remaining bounding SATs associated with the same divergent free-fit term is continued. The penalty factor G_P must remain close to unity in order to avoid a cumulative degradation of the model accuracy when multiple bounding terms are introduced. In MULTIBINT, the default value is $G_P = 1.001$, and it can be adjusted by the user via the `bound_penalty` keyword.

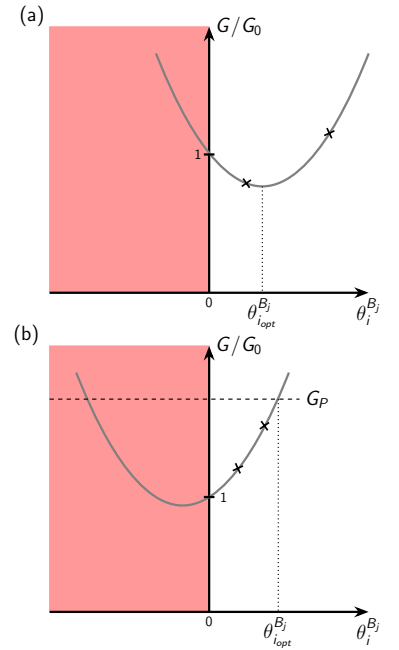


Figure 3.23: Scheme of the bounding procedure. For each created bounding term, there are two possible scenarios: (a) if the coefficient $\theta_{i,opt}^{B_j}$ that minimize the GF is positive, we keep it (b) if the coefficient $\theta_{i,opt}^{B_j}$ that minimize the GF is negative, we force it to be positive. the value of the coefficient is chosen to be positive and to keep the ratio G/G_0 under a threshold fixed by `bound_penalty`

As an alternative bounding strategy, all single-body SATs of a given range of higher even polynomial orders can be added simultaneously, and their coefficients optimized using a bounded-variable least-squares algorithm, with positivity constraints imposed on these higher-order terms. This option can be enabled by setting the corresponding `fit_max_nbody` parameter to `-1` for the selected bounding orders.

Model mixing for chemically inhomogeneous systems –

The second-principles framework described above is constructed around a single reference structure and a corresponding set of symmetry-adapted anharmonic interactions. In its standard formulation, it is therefore naturally suited to describe bulk crystalline materials with a well-defined chemical composition.

However, many systems of current interest, such as superlattices, heterostructures, or compositionally modulated materials, involve spatial variations of the chemical environment. In such cases, constructing a fully new second-principles model for the entire heterostructure would be computationally demanding and conceptually redundant when reliable bulk models of the constituent materials are already available.

In chemically inhomogeneous systems, a model-mixing strategy can be adopted, following the methodology introduced in Ref. [91]. In this approach, an effective model is constructed by combining pre-existing second-principles models of the bulk constituents. The interaction parameters are locally interpolated according to the chemical environment of each atom, ensuring consistency with the second-principles formalism.

We assume that reliable bulk second-principles models have been previously constructed for a set of materials labeled by an index c . Each bulk model provides a complete set of interaction tensors $\mathbf{K}^{(n),c}$, $\mathbf{\Lambda}^{(m,n),c}$, and $\mathbf{C}^{(n),c}$, as well as the corresponding Born effective charges and dielectric tensors.

In the mixed system, each atom ($l\kappa$) is assigned a chemical label $\mu_{l\kappa}$ identifying the bulk model to which it belongs. To characterize its local chemical environment, we consider a set of neighboring atoms within a predefined cutoff. Let $\mathcal{N}_{l\kappa}$ denote the number of neighbors of atom ($l\kappa$). For each bulk model c , we define

$$n_{l\kappa}^c = \sum_{(l'\nu) \in \mathcal{N}_{l\kappa}} \delta_{\mu_{l'\nu}, c} \quad (3.63)$$

where $\delta_{\mu_{l'\nu}, c}$ is equal to 1 if atom $(l'\nu)$ belongs to bulk model c , and 0 otherwise. By construction,

$$\mathcal{N}_{l\kappa} = \sum_c n_{l\kappa}^c. \quad (3.64)$$

We then introduce the local chemical weight

$$p_{l\kappa}^c = \frac{n_{l\kappa, c}}{\mathcal{N}_{l\kappa}}, \quad \sum_c p_{l\kappa}^c = 1, \quad (3.65)$$

which quantifies the fraction of neighbors of atom $(l\kappa)$ belonging to bulk model c . These weights define the local chemical environment and are used to interpolate the interaction coefficients entering the second-principles interatomic potential. For the pure part of the model (where the $p_{l\kappa}^c = 1$) the bulk interactions are recovered, and when $p_{l\kappa}^c \neq 1$ the interaction is interpolated between different models. If a particular interaction is missing in one model the coefficient for that interaction in averaging is set to zero.

We first consider the purely phononic part of the energy, expressed in terms of the displacement differences as introduced above. For an n -body anharmonic interaction involving atoms $(l\kappa), (k\nu), \dots$, the corresponding interaction tensor in the mixed model is defined as a weighted average over the bulk models:

$$\mathcal{K}_{\kappa\nu l\kappa\alpha\beta\dots}^{(n)} = \frac{1}{2N} \sum_c \hat{K}_{\kappa\nu l\kappa\alpha\beta\dots}^{(n), c} (p_{l\kappa}^c + p_{k\nu}^c + \dots), \quad (3.66)$$

where the sum is over different models that we have, $\hat{K}^{(n), c}$ is the interaction coefficient order n for bulk model c and N accounts for the number of bodies involved in the calculation of the parameter.

The harmonic phononic energy is then given by the (3.39) where the short-range part $K^{(2), SR}$ is replaced by the corresponding $\mathcal{K}^{(2), SR}$ following the interpolation procedure described above. The long-range dipole-dipole contribution is constructed from effective Born charges and a mixed high-frequency dielectric tensor. In analogy with Eq. (3.37), we

write

$$\mathcal{K}_{0l\kappa\nu\alpha\beta}^{(2),DD} = \sum_{\gamma\delta} \mathcal{Z}_{\kappa\alpha\gamma}^* \mathcal{Z}_{\nu\beta\delta}^* \left(\frac{(\epsilon_\infty^{-1})_{\gamma\delta}}{D^3} - 3 \frac{\Delta_\gamma \Delta_\delta}{D^5} \right) \det(\epsilon_\infty)^{-1/2} \quad (3.67)$$

The effective Born charge of atom ($l\kappa$) is approximated as

$$\mathcal{Z}_{l\kappa\alpha\beta}^* = \sum_c p_{l\kappa}^c \mathcal{Z}_{l\kappa\alpha\beta}^{*,c} \sqrt{\frac{(\epsilon_\infty)_{\alpha\beta}}{(\epsilon_\infty^c)_{\alpha\beta}}} \quad (3.68)$$

where $\mathcal{Z}_{l\kappa\alpha\beta}^{*,c}$ and $\epsilon_{\infty,c}$ are the Born effective charge tensor and dielectric tensor of bulk model c , respectively. The mixed dielectric tensor ϵ_∞ is approximated from the bulk values according to the geometry of the superlattice, where l_c denotes the fraction of unit cells of bulk model c in the superlattice. For a layered system, an arithmetic average is used for the in-plane components,

$$\epsilon_\infty^m = \sum_c l_c \epsilon_\infty^c, \quad (3.69)$$

while a harmonic average is used for the direction perpendicular to the interface,

$$(\epsilon_\infty^m)^{-1} = \sum_c l_c (\epsilon_\infty^c)^{-1}. \quad (3.70)$$

The same interpolation strategy is applied to the strain-phonon interaction tensors. For a mixed derivative of order (m, n) involving m strain components and n atomic displacements, we define

$$\mathcal{L}_{ab\kappa\nu\alpha\beta\cdots}^{(n,m)} = \frac{1}{2N} \sum_c \hat{\Lambda}_{ab\kappa\nu\alpha\beta\cdots}^{(n,m),c} (p_{l\kappa,c} + p_{kv,c} + \cdots) \quad (3.71)$$

This construction ensures that the strain-phonon couplings continuously interpolate between bulk behaviors while remaining consistent with the structure of the second-principles expansion introduced in Eq. (3.46).

Finally, the purely elastic part of the energy is constructed by interpolating the elastic constants of the bulk models. Denoting by n^c the number of unit cells of material c in the

mixed system, we approximate

$$C_{ab}^{(n)} = \sum_c n^c \hat{C}_{ab}^{(n),c} \quad (3.72)$$

where $\hat{C}_{ab}^{(n),c}$ are the order n elastic constants of bulk model c .

In practical applications to heterostructures or superlattices, the bulk constituents generally possess different equilibrium lattice parameters. Since each second-principles model is defined as a polynomial expansion around its own reference structure, a direct mixing of the models requires that their reference cells be made compatible.

Before performing the interpolation of the interaction parameters described above, it is therefore necessary to reformulate each bulk model around a common reference lattice. This can be achieved by systematically redefining the strain degrees of freedom and consistently transforming the polynomial expansion of the energy.

Each bulk second-principles model is constructed with respect to its own reference lattice, and therefore its strain variable, denoted $\eta^{(r)}$, is defined relative to that bulk reference. For the purpose of model mixing, we introduce a common reference lattice for the heterostructure, and define the corresponding strain tensor $\eta^{(m)}$. The two strain tensors are related by the lattice mismatch between the bulk and mixing references. Proceeding in a manner analogous to the derivation presented above for the stress definitions, one finds

$$\eta_{\alpha\beta}^{(r)} = \Delta\eta_{\alpha\beta} + (\delta_{\alpha\beta} + \Delta\eta_{\alpha\beta})\eta_{\alpha\beta}^{(m)}, \quad (3.73)$$

where $\Delta\eta$ denotes the misfit strain between the bulk and mixing reference structures.

Since the second-principles model is a polynomial expansion around the reference structure, replacing $\eta^{(r)}$ by its expression in terms of $\eta^{(m)}$ generates additional terms in the energy functional. The constant contributions simply shift the reference energy and can be discarded, while the linear and higher-order terms proportional to $\Delta\eta$ lead to a systematic renormalization of the elastic, strain-phonon, and higher-order coupling coefficients.

We first consider the harmonic elastic energy,

$$E_s^{Har}(\{\boldsymbol{\eta}^{(r)}\}) = \frac{N_{SC}}{2} \sum_{ab} \mathcal{C}_{ab} \eta_a^{(r)} \eta_b^{(r)}. \quad (3.74)$$

Substituting Eq. (3.73) into this expression yields additional linear and quadratic terms in $\boldsymbol{\eta}^{(m)}$. Besides the original quadratic contribution, the expansion generates: (i) linear strain terms proportional to $\Delta\boldsymbol{\eta}$, (ii) modified quadratic terms proportional to $\Delta\boldsymbol{\eta}$, (iii) a constant energy shift proportional to $\Delta\eta_a\Delta\eta_b$. The constant contribution only shifts the reference energy and can therefore be discarded. The linear and quadratic corrections can be absorbed into renormalized coefficients, which are added to the anharmonic sector of the model.

A similar procedure applies to the harmonic strain–phonon coupling,

$$E_{sp}^{Har} = \sum_{l\kappa\alpha a} \mathcal{L}_{l\kappa\alpha a} u_{l\kappa\alpha} \eta_a^{(r)}. \quad (3.75)$$

Replacing $\boldsymbol{\eta}^{(r)}$ by its expanded form produces additional phonon and strain–phonon contributions proportional to $\Delta\boldsymbol{\eta}$. These terms effectively renormalize the phonon and strain–phonon coefficients and are incorporated into the model in the same manner as for the purely elastic part.

The same transformation is applied to all strain and strain–phonon terms in both the harmonic and anharmonic sectors. As a result, each bulk model is consistently reformulated around a common reference lattice, leading to a systematic renormalization of its coefficients while preserving the polynomial structure of the energy functional. Once expressed in compatible reference cells, the bulk models can be straightforwardly combined within the model-mixing framework to construct effective potentials for heterostructures.

3.2.6 Machine learning interatomic potential

Machine-learning interatomic potentials (MLIP) provide an alternative strategy to construct accurate atomistic models directly from first-principles data. Although the idea of learning potential-energy surfaces using flexible statistical models dates back several decades, with early demonstrations already appearing in the 1990s [124], these approaches remained for

a long time relatively marginal in the atomistic-simulation community. Earlier assessments often emphasized their drawbacks [120]: the resulting potentials could be mathematically complex, difficult to interpret physically, and potentially limited in transferability, since they primarily interpolate within the region of configuration space covered by the training data. In addition, the computational overhead associated with early implementations further slowed their adoption.

This situation has changed dramatically over the past decade, and especially since the early 2020s [125–128]. Progress in machine learning, the rapid growth of available first-principles datasets [129, 130], and advances in computational resources have collectively transformed MLIP into practical and widely used tools [128, 131–135]. Modern architectures can now achieve near first-principles accuracy while retaining computational costs orders of magnitude lower than direct electronic-structure calculations. As a result, MLIP are increasingly becoming standard instruments for large-scale atomistic simulations, enabling the study of complex materials, long time scales, and large system sizes that were previously inaccessible, while maintaining a close connection to *ab-initio* reference data.

In the following, we briefly introduce the general principles behind MLIP before discussing the specific framework adopted in this work.

Deep potential – Machine-learning interatomic potentials such as DEEPM [136] are based on deep feedforward neural networks [137], whose goal is to approximate an unknown target function f^* from data.

These models are called *networks* because they can be represented as a directed acyclic graph describing how successive transformations are composed,

$$f(\mathbf{x}) = f^{(L)} \circ f^{(L-1)} \circ \dots \circ f^{(1)}(\mathbf{x}), \quad (3.76)$$

where each function $f^{(\ell)}$ corresponds to one layer. The total number of layers defines the *depth* of the model — hence the term *deep learning* — and the last transformation produces the *output layer*. The qualifier *feedforward* indicates that information propagates in a single direction, from the input representation to the output, without feedback or recurrent

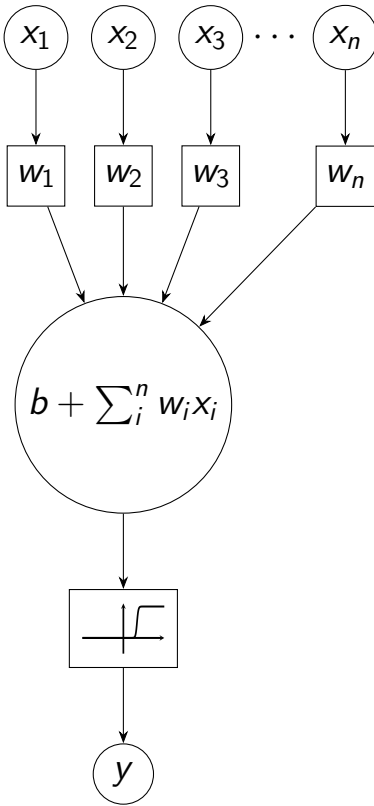


Figure 3.24: Schematic representation of an individual neuron. The neuron receives a vector of inputs $\{x_i\}$, computes a weighted sum with learnable weights $\{w_i\}$ and bias b , and applies a non-linear activation function σ to produce its output y .

connections. During training, the model output $f(\mathbf{x})$ is required to match reference values $y \approx f^*(\mathbf{x})$, provided for each input $\mathbf{x}$. While the training data specify the desired output y , they do not impose how the intermediate transformations should behave. The learning algorithm must therefore determine how to organize these internal representations so as to produce accurate predictions. For this reason, the intermediate layers are referred to as *hidden layers*.

Each layer is composed of elementary units called *neurons*. An individual neuron performs a simple (non-)linear transformation on its inputs: it receives a vector of inputs $\{x_i\}$ computes a weighted sum, adds a scalar bias b , and finally applies an *activation function* $\sigma(\mathbf{x}; \mathbf{w}, b)$. The output of a single neuron can be expressed as,

$$y = \sigma \left(b + \sum_i^n w_i x_i \right) \quad (3.77)$$

where the weights w_i and the bias b are the learnable parameters adjusted during the training process to minimize the prediction error.

In a neural network, these individual neurons are organized into layers where the outputs of one layer serve as the inputs for the next. The architecture begins with an input layer, which does not perform computations but simply holds the input data. It is followed by one or more hidden layers and a final output layer. To compute a prediction, the network performs a forward pass: starting from the input, the activations are computed layer by layer. For a given layer ℓ , the activation of each neuron is stored, as it becomes the necessary input for calculating the weighted sums of layer $\ell + 1$.

The power of this hierarchical structure relies entirely on the choice of the activation function. If a linear activation function were used for all neurons, the entire multi-layer network would collapse into a single linear transformation. This is a fundamental result of linear algebra: the composition of two linear functions is itself a linear function. In this scenario, adding more layers would provide no additional representational power over a single-layer model.

By introducing non-linear activations such as sigmoid, hyperbolic tangent functions or the Rectified Linear Unit (ReLU), defined as $\text{ReLU}(z) = \max(0, z)$, the network gains the ability to approximate complex, non-linear boundaries. Conceptually,

non-linear units can be combined to represent Boolean logic gates such as AND, OR, and NOT. Since any computational circuit can be built from these primitive gates, a sufficiently large neural network acts as a programmable functional approximator.

This is formalized by the Universal Approximation Theorem [138], which states that a feedforward network with at least one hidden layer and a non-linear activation function can approximate any continuous function to any desired degree of accuracy, provided it has enough neurons.

Rather than manually designing the connections to mimic a specific circuit, the network "learns" the optimal weights and biases through training. This process involves defining a loss function (or cost function) that measures the discrepancy between the network's prediction $f(x)$ and the training data.

The aforementioned principles can be applied to build **MLIP** as it is done in **DEEPMD**, which is designed to preserve the physical symmetries of atomic systems. In this framework, the total potential energy E of a system containing N atoms is decomposed into a sum of local atomic contributions:

$$E = \sum_{i=1}^N E_i, \quad (3.78)$$

where each atomic energy E_i is the output of a dedicated feedforward neural network that maps the local environment of atom i to a scalar value as shown in **Figure 3.25**.

For each atom i , the network only considers neighbors j located within a spherical cutoff radius R_c . Since raw Cartesian coordinates are not invariant under rotation or translation,

the relative positions are transformed into a standardized set of descriptors $\{D_{ij}\}$ which serve as the input layer.

For each neighbor j within the sphere, the spatial information is encoded as a four-component vector:

$$\mathbf{D}_{ij} = \left\{ \frac{1}{R_{ij}}, \frac{x_{ij}}{(R_{ij})^2}, \frac{y_{ij}}{(R_{ij})^2}, \frac{z_{ij}}{(R_{ij})^2} \right\}, \quad (3.79)$$

where R_{ij} is the distance between atoms i and j and $\{x_{ij}, y_{ij}, z_{ij}\}$ are the relative coordinates defined in a local frame of refer-

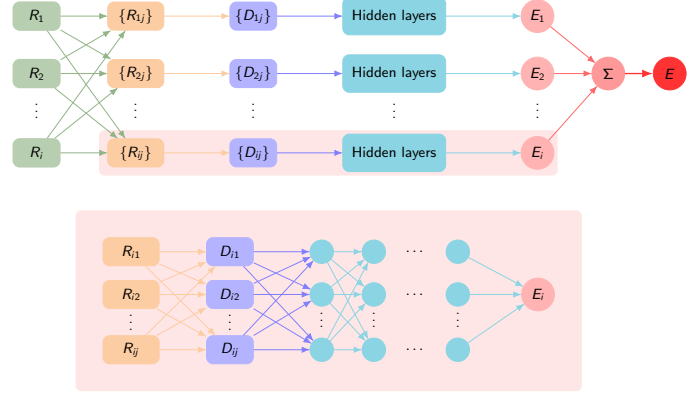


Figure 3.25: Illustration of the neural network architecture implemented in DEEPMD [136]. The frame in the box is an enlargement of a deep neural network. The relative position of all neighbors with respect to atom i , $\{R_{ij}\}$, is first converted to $\{D_{ij}\}$ which serves as the input layer and then passed to the hidden layers used to compute E_i . Adapted from Ref. [136]

ence. This transformation ensures that the input is invariant to the global orientation of the system.

The neural network is structured as a composition of multiple fully connected hidden layers:

$$\mathcal{L}_i^{out} \circ \mathcal{L}_i^{N_h} \circ \mathcal{L}_i^{N_h-1} \circ \dots \circ \mathcal{L}_i^1(\{D_{ij}\}) \quad (3.80)$$

Each hidden layer $\mathcal{L}^p$ performs a linear transformation followed by a non-linear activation function, in general the activation function is typically hyperbolic tangent. The final output layer $\mathcal{L}_i^{out}$ is a linear transformation that yields the scalar atomic energy E_i .

The model parameters are optimized using the Adam stochastic gradient descent method. The training utilizes a "multi-task" loss function L that simultaneously accounts for errors in energy, forces, and the virial tensor:

$$L(p_\epsilon, p_f, p_\xi) = p_\epsilon \Delta\epsilon^2 + \frac{p_f}{3N} \sum_i |\Delta\mathbf{F}_i|^2 + \frac{p_\xi}{9} \|\Delta\xi\|^2, \quad (3.81)$$

where $\Delta\epsilon$, $\Delta\mathbf{F}_i$ and $\Delta\xi$ are the root-mean-square errors of the energy, forces, and virial, respectively. The gradients required for the forces and virial are computed analytically via backpropagation. This simultaneous training on multiple physical properties provides a strong regularization, ensuring physical consistency across the predicted potential energy surface.

In this thesis, MLIP are employed for the construction of atomistic models detailed in Chapter 4 and further exploited in Chapter 8.

3.2.7 Temperature dependent effective potential

As discussed in Section 2.1.2, the harmonic approximation gives access to the curvature of the Born–Oppenheimer energy surface, from which phonon dispersion curves can be derived. These curves are particularly useful for assessing the dynamical stability of a given material: a negative curvature along a phonon branch signals that the corresponding mode is unstable. Whether computed via DFPT or finite differences, however, these approaches share a fundamental limitation: they probe the potential energy surface strictly at zero temperature.

This limitation becomes especially problematic when the phase of interest is only thermodynamically stable above a finite critical temperature T_c . Such a phase is experimentally well defined and accessible, yet a harmonic phonon calculation performed within it will inevitably produce imaginary frequencies. These imaginary modes are artifacts of the zero-temperature framework rather than genuine physical instabilities of the material.

To overcome this difficulty, one must build an effective interatomic potential that accounts for finite-temperature effects from the outset. This is the central idea behind the Temperature Dependent Effective Potential (TDEP) method [139, 140], which replaces the static internal energy used in the harmonic approximation by the free energy, thereby incorporating the thermal fluctuations that govern structural stability at finite temperature.

The starting point of the method is a model Hamiltonian that describes the lattice dynamics in harmonic form:

$$\hat{H} = U_0 + \sum_i \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2} \sum_{ij\alpha\beta} u_{i\alpha} K_{ij\alpha\beta} u_{j\beta}, \quad (3.82)$$

where $\mathbf{p}_i$ and $\mathbf{u}_i$ are the momentum and displacement of atom i relative to its thermally averaged position at a given temperature, respectively. The interatomic force constants $K_{ij\alpha\beta}$ and the baseline energy U_0 are unknown quantities that remain to be determined.

As emphasised above, the TDEP method is formulated in terms of the free energy F rather than the internal energy U . Within the quasiharmonic framework, the free energy

separates into two contributions:

$$F = U - TS = F_{\text{el}} + F_{\text{vib}}. \quad (3.83)$$

The first term, F_{el} , is the electronic contribution obtained from DFT calculations using the Mermin functional [141]. The second term, F_{vib} , captures the vibrational contribution and, in the harmonic approximation, takes the form

$$F_{\text{vib}} = \int_0^\infty g(\omega) \left[k_B T \ln \left(1 - e^{-\frac{\hbar\omega}{k_B T}} \right) + \frac{\hbar\omega}{2} \right] d\omega, \quad (3.84)$$

where $g(\omega)$ is the phonon density of states. The first term inside the integral accounts for the thermal population of phonon modes, while the second corresponds to the zero-point energy contribution.

The key insight of **TDEP** is to determine the force constants not from a static calculation at the equilibrium geometry, but from a molecular dynamics simulation that naturally samples the thermally relevant region of the potential energy surface. In a canonical-ensemble molecular dynamics run, the system explores configurations weighted by the Boltzmann distribution at temperature T . The simulation gives direct access to the instantaneous forces, displacements, and potential energies at each time step. However, it does not provide the entropy directly. This is precisely the gap that **TDEP** fills through its model Hamiltonian, which gives access to the phonon density of states and, from it, the vibrational entropy.

Within the **TDEP** framework, the potential energy at each time step t is modelled as

$$U_{\text{TDEP}}(t) = U_0 + \frac{1}{2} \sum_{ij\alpha\beta} K_{ij\alpha\beta} u_{i\alpha}(t) u_{j\beta}(t), \quad (3.85)$$

where U_0 is the potential energy of the thermally averaged structure. The force constants $K_{ij\alpha\beta}$ are obtained by minimising the difference between the forces predicted by this harmonic model and those computed along the molecular dynamics trajectory. Physically, this amounts to finding the best harmonic approximation to the potential energy surface as experienced by the atoms at temperature T , rather than at the static equilibrium geometry. Because the molecular dynamics trajectory samples configurations according to their thermal weight, the resulting force constants naturally encode the ef-

fective stiffness felt by the ions at that temperature (including the implicit effects of anharmonicity on the curvature of the energy landscape).

Once the force constants are known, the baseline energy U_0 is fixed by requiring that the average potential energy of the model match that of the molecular dynamics:

$$U_0 = \left\langle U_{\text{MD}}(t) - \frac{1}{2} \sum_{ij\alpha\beta} K_{ij\alpha\beta} u_{i\alpha}(t) u_{j\beta}(t) \right\rangle. \quad (3.86)$$

The physical intuition behind this expression is straightforward: U_0 absorbs all the potential energy that is not captured by the harmonic thermal fluctuations. By subtracting the harmonic contribution from the instantaneous molecular dynamics energy, one isolates a quantity whose time fluctuations are far smaller than those of U_{MD} itself, leading to a more rapidly converging estimate of the baseline energy.

The **TDEP** free energy is then assembled by combining this baseline energy with the vibrational free energy computed from the **TDEP** phonon density of states:

$$F_{\text{TDEP}} = U_0 + F_{\text{vib}}. \quad (3.87)$$

In this expression, the phonon density of states entering F_{vib} is evaluated using the temperature-dependent force constants, so that the vibrational entropy and zero-point energy reflect the effective potential landscape at the temperature of interest.

To assess the residual error of this approach, one can invoke thermodynamic integration via the Kirkwood coupling parameter λ [142], yielding the formally exact free energy:

$$F = U_0 + F_{\text{vib}} + \int_0^1 \langle U_{\text{MD}} - U_{\text{TDEP}} \rangle_\lambda d\lambda. \quad (3.88)$$

The last term quantifies the degree of anharmonicity that escapes the harmonic model. Since **TDEP** is designed to capture as much of the physics as possible within a harmonic framework, this correction is expected to be small. Numerical tests by Hellman and co-workers [140] confirm that, for systems of practical size (of the order of a hundred atoms), the anharmonic correction is indeed negligible compared to the intrinsic accuracy of the method.

Example: one-dimensional anharmonic oscillator— To build intuition for the **TDEP** procedure, it is instructive to consider a simple one-dimensional potential that combines a harmonic well with a localised anharmonic perturbation:

$$U(x) = \frac{1}{2}k(x - x_0)^2 + \alpha e^{-\beta(x-x_0)^2}. \quad (3.89)$$

Here k sets the harmonic stiffness, while α and β control the amplitude and width of the Gaussian perturbation, respectively. The parameter x_0 denotes the equilibrium position, which may itself depend on temperature.

In the standard harmonic approximation, one evaluates the second derivative of $U(x)$ at the zero-temperature equilibrium position $x = 0$, yielding the force constant

$$K = \left. \frac{d^2U}{dx^2} \right|_{x=0} = k + 2\alpha\beta(2\beta x_0^2 - 1)e^{-\beta x_0^2}. \quad (3.90)$$

This expression shows that the curvature at the origin can become negative for certain values of α and β , producing an imaginary harmonic frequency even though the potential supports stable oscillations at finite temperature as illustrated in **Figure 3.26**. The problem is clear: the harmonic approximation probes the energy surface only at a single point which is a static equilibrium and entirely misses the effective stiffness experienced by a thermally excited particle.

The **TDEP** approach resolves this by placing a particle in the full potential and running a molecular dynamics simulation at the temperature of interest. The trajectory provides a set of N_t instantaneous forces, positions, and energies $\{F_t, x_t, E_t\}$. These data are then used to fit an effective harmonic potential of the form

$$U(x) = \hat{K}^{(0)} + \frac{1}{2}\hat{K}^{(2)}(x - x'_0)^2, \quad (3.91)$$

where x'_0 is the temperature-dependent equilibrium position. The effective force constant $\hat{K}^{(2)}$ is determined by a least-squares fit of the model forces $\hat{K}^{(2)}(x_t - x'_0)$ to the true forces F_t . Geometrically, this corresponds to fitting a straight line through the force-versus-displacement data sampled along the trajectory—the slope of that line gives the effective spring constant at temperature T .

The equilibrium position x'_0 is found self-consistently: start-

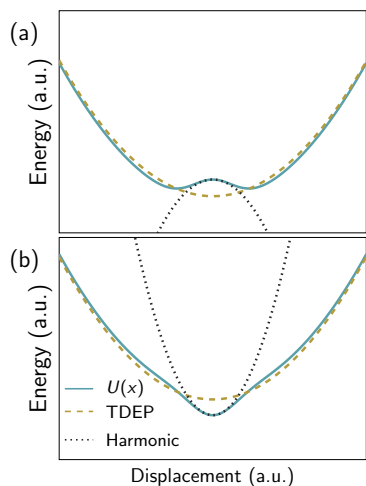


Figure 3.26: Illustration of the **TDEP** procedure applied to a one-dimensional anharmonic potential (black). The standard harmonic approximation evaluated at the static equilibrium (dashed) fails to capture the effective stiffness at finite temperature, while the **TDEP** effective potential (colored) correctly reproduces the thermally sampled curvature.

ing from an initial guess, one extracts $\hat{K}^{(2)}$ and computes the residual force at x'_0 . This residual force is then used to update x'_0 in a steepest-descent fashion, and the process is repeated until convergence. Once the equilibrium position is determined, the baseline energy is obtained by requiring the model to reproduce the average potential energy of the simulation:

$$\hat{K}^{(0)} = \left\langle E_t - \frac{1}{2} \hat{K}^{(2)} (x_t - x'_0)^2 \right\rangle. \quad (3.92)$$

The resulting effective potential has a remarkable property: even though it is strictly harmonic in form, it implicitly encodes the anharmonicity of the true potential to the extent that it is thermally probed. Unlike the Taylor expansion around the static minimum, which requires increasingly high-order terms to capture the shape of the potential away from equilibrium, the **TDEP** fit adapts its curvature and centre to the region of phase space that matters at the temperature of interest. This is what makes the method particularly well suited to dynamically unstable systems, where the harmonic approximation predicts imaginary frequencies while **TDEP** recovers real, physically meaningful phonon modes.

In this thesis, the **TDEP** method is employed to compute finite-temperature phonon dispersions, with its most significant application to the study of the structural phase transition in YNiO_3 , as detailed in **Chapter 8**.

Construction and validation of second-principles models

4

A substantial part of this thesis has been devoted to the systematic construction and validation of atomistic models for perovskite materials. Building reliable models is not a peripheral task: it is a prerequisite for any meaningful large-scale simulation, and the quality of the physical conclusions drawn in the following chapters rests directly on the predictive accuracy of the models described here. The construction workflow has been applied as consistently as possible across all materials, following the general methodology introduced in [Section 3.2.5](#) and [Section 3.2.6](#). The training set construction strategy is detailed in [Section 4.1](#). The materials covered span a broad range of physical complexity: from BaHfO_3 , a simple cubic dielectric with no structural instability, to canonical ferroelectrics such as BaTiO_3 and PbTiO_3 , to more subtle cases including the quantum paraelectric SrTiO_3 and the incipient ferroelectric CaTiO_3 , and finally to YNiO_3 , a rare-earth nickelate exhibiting a metal-to-insulator transition, for which a [MLIP](#) model was developed. The author also contributed to the construction of a deep-learning potential for the antiferroelectric PbZrO_3 [[143](#)], though this model is not directly employed in the simulations presented in this manuscript. All other models have been used in one or several of the publications associated with this work, and constitute the computational foundation upon which the results reported in the subsequent chapters are built.

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Related publications

2. Phys. Rev. B 108 (13), 134117
3. Phys. Rev. B 110 (5), 054109
9. Phys. Rev. B 112 (10), 104324
10. Phys. Rev. B 112 (14), 144101
12. Phys. Rev. B 112 (22), 224103

4.1 Generation of the training set

The construction of a physically motivated training set is a central step in any second-principles interatomic potential construction workflow. This workflow is common to all the models presented in this manuscript. The strategy exploits the structure of the model itself: since the harmonic part of the potential is obtained exactly from [DFPT](#), the phonon dispersion curves are available before any training set is constructed and directly reveal the curvature of the Born-Oppenheimer surface along every lattice degree of freedom. In particular, any imaginary frequency identifies a direction

of negative curvature, signaling a structural instability of the reference structure.

Step 1: Identification of the energy minima – Starting from the unstable modes identified in the phonon dispersion curves, all possible combinations are condensed using (Q)AGATE software [144] and used as starting points for *ab initio* structural relaxations typically in $2 \times 2 \times 2$ supercells of the reference structure. Each combination that converges to a local minimum is retained. Not all combinations yield a minimum, and symmetry-equivalent phases must be considered separately since the energy barriers between two phases are not necessarily the same depending on the path taken.

Step 2: Interpolation between the reference structure and the minima – Once all local minima have been identified, linear interpolations are performed between the reference structure and each minimum, and between all pairs of minima, following

$$\alpha S_1 + \frac{(\alpha_{\max} - \alpha) S_2}{\alpha_{\max}}, \quad \alpha \in [0; \alpha_{\max}], \quad (4.1)$$

where S_1 and S_2 are the starting and ending structures, α is the interpolation fraction, and $\alpha_{\max}$ is chosen so that the interpolated structures remain within the energy window $[E_{\text{GS}}; E_{\text{RS}} + |E_{\text{GS}}|]$, where E_{GS} is the ground-state energy and E_{RS} is the energy of the reference structure, for interpolations from the reference structure to the minima. For interpolations between minima, $\alpha_{\max}$ is set to 1 to avoid spurious phase-mixing effects. All interpolated structures are characterized at the *ab initio* level to obtain energies, forces, and stresses. Extrapolations beyond the minima ($\alpha_{\max} > 1$) are also included in order to provide information on the shape of the potential energy surface beyond the minima, which is essential to ensure that the fitted model remains bounded from below.

Step 3: Phonon and strain noise – To ensure that the training set covers configurations around the interpolation paths and the minima, random structures are generated by combining two types of perturbations applied to each relaxed structure. First, a random strain is applied by composing

a tetragonal distortion matrix $\eta(\varepsilon, \delta_1)$ and a shear matrix $\mathcal{S}(\delta_2)$, where ε controls the amplitude of the homogeneous volumetric deformation, δ_1 the tetragonal distortion, and δ_2 the shear amplitude, all drawn randomly. To explore deformations along arbitrary crystallographic directions, each matrix is additionally rotated by an independently drawn permutation matrix $\mathcal{O}$ chosen from $\{\mathbb{I}, R_{xy}, R_{xz}, R_{yz}\}$ [145]. The deformed cell matrix is obtained by successively applying these matrices to the lattice vector matrix $\mathcal{R}$,

$$\mathcal{R} \leftarrow \mathcal{R} \mathcal{O}_2 \mathcal{S} \mathcal{O}_1 \eta. \quad (4.2)$$

Second, random atomic displacements $\mathbf{u}$ are generated by populating phonon modes of the reference structure at a chosen temperature following a Bose-Einstein distribution [146],

$$\Delta u_{\kappa\alpha} = \left(\frac{M_p}{M_\kappa} \right)^{1/2} \sum_\nu (-1)^{\nu-1} e_{\kappa\alpha,\nu} l_\nu \left(\frac{2}{e^{\hbar\omega_\nu/k_B T} - 1} + 1 \right)^{1/2}, \quad (4.3)$$

where M_p is the mass of the proton, M_κ is the mass of atom κ , $e_{\kappa\alpha,\nu}$ the $\kappa\alpha$ component of the ν -th normalized eigenvector of the dynamical matrix with associated vibrational frequency ω_ν , and $l_\nu = \sqrt{\hbar/(2M_p\omega_\nu)}$ the zero-point amplitude of the ν -th mode.

Step 4: Iterative refinement and bounding – The training set obtained from the previous steps is used to fit a first model. In practice, the energy landscape contains too many degrees of freedom to be sampled exhaustively, and a restricted training set typically produces some anharmonic terms with negative coefficients or odd powers that cause the model to diverge toward $-\infty$ for large atomic displacements. When this occurs, the model is analyzed to identify the offending terms, and additional bounding terms of higher order with positive coefficients are added following the automatic bounding procedure of Section 3.2.5. The corrected model is then used to run molecular dynamics simulations at increasing temperatures, whose trajectories are compared against *ab initio* calculations to identify poorly described regions of the energy landscape. The training set is enriched accordingly and the model is refitted. This procedure is repeated until the model passes the systematic validation described below.

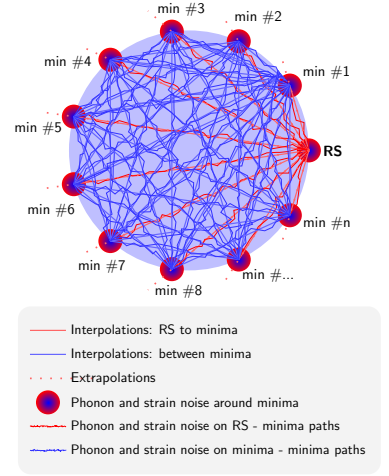


Figure 4.1: Schematic illustration of the training set construction strategy on a subset of the Born-Oppenheimer surface. Identified energy minima are connected by linear interpolation paths, and phononic and strain noise configurations are superimposed around each minimum and along each path to ensure a representative sampling of the thermodynamically relevant region of configuration space.

The resulting training set illustrated in Figure 4.1 is physically motivated and targeted: rather than sampling the Born-Oppenheimer surface uniformly, it concentrates on the low-energy subspace that is thermodynamically relevant, and its construction is driven at every step by the information already available from the harmonic model.

4.2 Systematic validation of models

Once a model has been fitted and bounded, it must be validated before being used for production simulations. A systematic three-step procedure that probes the quality of the model at increasing levels of complexity is followed consistently for all models presented in this manuscript.

Step 1: Training set and test set reproduction – The first step consists in verifying that the model reproduces the energies, forces, and stresses contained in the training set. The goal function values before and after fitting provide a first quantitative estimate of the quality of the fit. To guard against overfitting and assess the predictive power of the model, a test set is constructed by running a molecular dynamics simulation with the model and recalculating a fraction of the trajectory at the *ab initio* level. Good agreement between the model and DFT on these unseen structures confirms that the model is predictive in the region of phase space explored by the molecular dynamics. It should be noted, however, that when small supercells are employed for the molecular dynamics, the temperatures assigned to the test sets are best understood as indicative of the thermal energy injected into the system rather than as the actual thermodynamic phase explored, owing to the well-known sensitivity of structural phase transition temperatures to supercell size [147].

Step 2: Relaxation of metastable phases – The second step verifies that the model predicts the correct sequence of local minima. All phases identified during the training set construction are relaxed using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [148–151] as implemented in MULTIBINIT, and the resulting energies and atomic distortions are compared against DFT. This step ensures that the ground state is correctly identified and that no spurious inversion of metastable

phases occurs, which would compromise the description of phase transitions.

Step 3: Phonon dispersion curves – The third step probes the curvature of the energy around a phase of interest, typically the experimental ground state, by computing phonon dispersion curves with finite differences and comparing them against DFPT. Good agreement on the phonon dispersion or density of states ensures that the thermal activation of the modes will be correctly described in finite-temperature simulations.

All models produced during this thesis that pass this validation procedure are made publicly available on the University dataverse (<https://dataverse.uliege.be>) together with a validation passport that summarizes all three steps of the procedure, reports the goal function values, and documents any limitations or known issues encountered during the fitting and bounding process. Depending on the material and the intended application, additional tests are included in the passport, such as the sequence of phase transitions, domain wall energies, or other quantities relevant to a complete characterization of the model. This practice is intended to ensure the reproducibility of the results presented in this manuscript and to make the models directly reusable by the broader community.

4.3 Second-principles interatomic potentials

The methodology outlined in Section 4.1 and Section 4.2 is now applied to a broad range of perovskite materials, each selected to address a distinct set of physical phenomena investigated in the following chapters.

4.3.1 Barium Hafnate

Barium hafnate, BaHfO_3 , is an ABO_3 perovskite oxide in which the A site is occupied by a Ba^{2+} cation and the B site by a Hf^{4+} cation. With a Goldschmidt tolerance factor of $t = 1.016$ [152], BaHfO_3 sits at the center of the perovskite structural diagram illustrated in Figure 2.3, in the ideal cubic

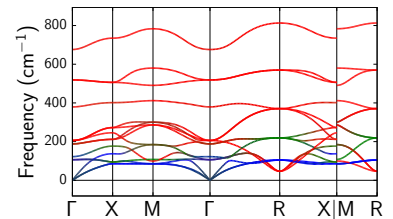


Figure 4.2: Phonon dispersion curves of BaHfO_3 in the cubic $Pm\bar{3}m$ phase at 0 K.

region, alongside BaZrO_3 ($t \approx 1.0$) [153]. This near-perfect geometric compatibility between ionic sizes explains why BaHfO_3 retains its cubic $Pm\bar{3}m$ symmetry over the entire accessible temperature range, from melting at $T_m \approx 2893$ K [152] down to the lowest temperatures, without exhibiting any structural instability. This absence of any structural phase transition is atypical within the perovskite family [22], and is confirmed by the absence of any soft mode in the phonon dispersion curves, as illustrated in Figure 4.2. This lack of structural complexity has kept BaHfO_3 comparatively understudied with respect to the broader perovskite family, in which a wider variety of structural instabilities and functional properties arise.

It is precisely this simplicity that makes BaHfO_3 an ideal candidate for the construction and validation of a second-principles interatomic potential, serving as a straightforward introductory case before tackling more complex materials. In the absence of any competing instability, the model does not need to reproduce a sequence of structural phase transitions, allowing one to focus entirely on the quality of the energy surface representation around a single minimum. For this reason, BaHfO_3 is used as the tutorial material in the official MULTIBINIT documentation [154], and constitutes the natural starting point of the series of models presented in this section.

Harmonic interactions – The harmonic part of the model was obtained from DFPT calculations performed with the ABINIT software package [122], using the GGA with the PBEsol exchange-correlation functional [155] and a plane-wave pseudopotential approach. Optimized norm-conserving pseudopotentials from the PseudoDojo server [75, 156] were employed, treating Ba $5s^25p^66s^2$, Hf $5s^25p^65d^26s^2$, and O $2s^22p^4$ electrons as valence states. A plane-wave energy cutoff of 55 Ha was adopted, together with a $8 \times 8 \times 8$ Γ -centered Monkhorst-Pack [157] k -point mesh for the five-atom cubic unit cell, with the sampling adapted to the supercell size to maintain a comparable level of convergence. The dynamical matrices were computed on a $8 \times 8 \times 8$ q -point mesh for the relaxed cubic $Pm\bar{3}m$ phase. In addition to the interatomic force constants, the DFPT calculations provided the dielectric constant, Born effective charges, elastic constants, and strain-phonon coupling coefficients, the latter vanishing identically by symmetry in the cubic reference structure. The dielectric

constant and Born effective charges are used to construct the long-range dipole-dipole interaction, while the elastic constants enter in the harmonic description of the strain degrees of freedom.

Training set generation – Following the construction procedure outlined in [Section 4.1](#), the simplicity of BaHfO_3 renders the first two steps essentially trivial. Since the energy landscape reduces to a single global minimum with positive curvature in all directions, the cubic $Pm\bar{3}m$ phase is the only equilibrium structure, and no interpolation between competing minima is required. The training set therefore consists exclusively of phononic and strain noise, built from 150 configurations sampled around the cubic reference: 50 structures generated at 50 K, 50 at 100 K, and 50 at 500 K. This deliberately broad temperature range ensures that the model correctly describes the curvature of the energy surface from the harmonic regime at low temperature up to the strongly anharmonic displacements relevant at high temperature. The energies, forces, and stresses of all configurations were computed using the same *ab initio* settings as described above, on a $2 \times 2 \times 2$ supercell of 40 atoms, with the k -point mesh reduced to $4 \times 4 \times 4$ to maintain a comparable sampling density of the Brillouin zone.

Generation of the interatomic potential – With the training set in hand, the next step consists in constructing an interatomic potential capable of reproducing the first-principles data it contains. The quality of the harmonic approximation alone can first be assessed by evaluating the goal function on the training set before any fitting, as reported in the second column of [Table 4.1](#). Although the harmonic part is exact with respect to DFPT, it proves insufficient to reproduce the training set data accurately, as evidenced by the large values of G_E , G_f , and G_σ .

The anharmonic part of the model was therefore obtained by fitting to the training set. SATs up to fourth order were generated using a cutoff radius of 3.44 Å (compared to a cubic lattice parameter of 4.14 Å), including third- and fourth-order phonon-displacement and strain-phonon coupling terms, while elastic interactions were retained at second order. A selection of 20 anharmonic SATs was identified through goal-function minimization using the algorithmic selection

Table 4.1: Goal function values ($eV^2/\text{\AA}^2$) of the energy, forces and stresses for each step of the construction of the models of BaHfO_3 : before the fit process (TS evaluated with the harmonic part), after the fit process (20 SATs), after the bounding process (110 SATs for BaHfO_3)

	Harmonic part	Unbounded	Bounded
G_E	2.278×10^{-3}	4.940×10^{-5}	2.194×10^{-5}
$G_{f+\sigma}$	3.973×10^{-2}	3.894×10^{-3}	4.106×10^{-3}
G_f	2.471×10^{-2}	2.948×10^{-3}	3.052×10^{-3}
G_σ	1.502×10^{-2}	9.463×10^{-4}	1.054×10^{-3}

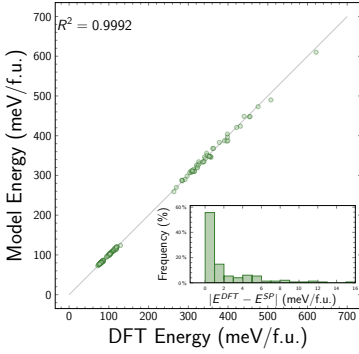


Figure 4.3: Comparison between the bounded model and DFT energies for the configurations contained in the training set of BaHfO_3 . The solid line indicates perfect agreement between the model and DFT. The inset shows the distribution of the absolute errors. Energies are reported relative to the cubic reference structure.

presented in Section 3.2.5. As shown in the third column of Table 4.1, the addition of these terms reduces the goal function by orders of magnitude with respect to the harmonic baseline, confirming that the fitted model captures the dominant anharmonic contributions.

The bounding procedure described in Section 3.2.5 was then applied to ensure that the model remains bounded from below at large atomic displacements. Bounding terms of order 6 and 8 were added automatically, introducing 110 additional SATs into the model. As shown in the fourth column of Table 4.1 and illustrated in Figure 4.3, this procedure preserves the quality of the fit to an excellent degree, leaving the goal function essentially unchanged while eliminating any risk of divergence. The final model thus comprises 130 SATs in total.

Validation of the model – The validation of the model follows the three-step procedure outlined in Section 4.2. For BaHfO_3 , however, steps two and three are trivially satisfied by construction. Since the energy landscape possesses a single stationary point, no metastable phase relaxation is required, and the comparison with DFPT phonon dispersion curves in the cubic reference structure is exact by definition: the interatomic-force constant are taken directly from DFPT and preserved unchanged in the model, so the phonon dispersion curves of the reference phase are reproduced with perfect accuracy by construction.

The non-trivial part of the validation therefore reduces to step 1: assessing whether the model generalizes beyond the training set. A test set was constructed by running hybrid Monte Carlo (HMC) [158, 159] simulations with the model at 50 K, 300 K, and 1000 K, and recalculating 1% of each trajectory at the *ab initio* level. The goal function evaluated on these unseen structures is reported in Table 4.2. The model reproduces the test set data with good accuracy at 50 K and 300 K, while a moderate degradation is observed at

	TS	Test set		
		50K	300K	1000K
G_E	2.19×10^{-5}	9.16×10^{-7}	1.76×10^{-5}	5.34×10^{-4}
$G_{f+\sigma}$	4.11×10^{-3}	2.67×10^{-4}	4.57×10^{-3}	7.72×10^{-2}
G_f	3.05×10^{-3}	1.15×10^{-4}	3.26×10^{-3}	5.39×10^{-2}
G_σ	1.05×10^{-3}	1.51×10^{-4}	1.31×10^{-3}	2.33×10^{-2}

Table 4.2: Goal function values ($eV^2/\text{\AA}^2$) of the energy, forces and stresses for each test set produced by running MD with the model of BaHfO₃ (50 K, 300 K and 1000 K).

1000 K, where the thermal displacements explore regions of the potential energy surface that are not sampled by the training set. As illustrated in Figure 4.4, panel (a) confirms that the model correctly tracks the instantaneous DFT energies along the HMC trajectories at all three temperatures, with no systematic drift. Panel (b) further shows that the model versus DFT energy comparison remains largely linear across the entire temperature range, with the test set points closely following the training set trend. The agreement is excellent at 50 K and 300 K, and remains satisfactory at 1000 K despite the larger displacements, demonstrating the predictive character of the potential in the physically relevant regime.

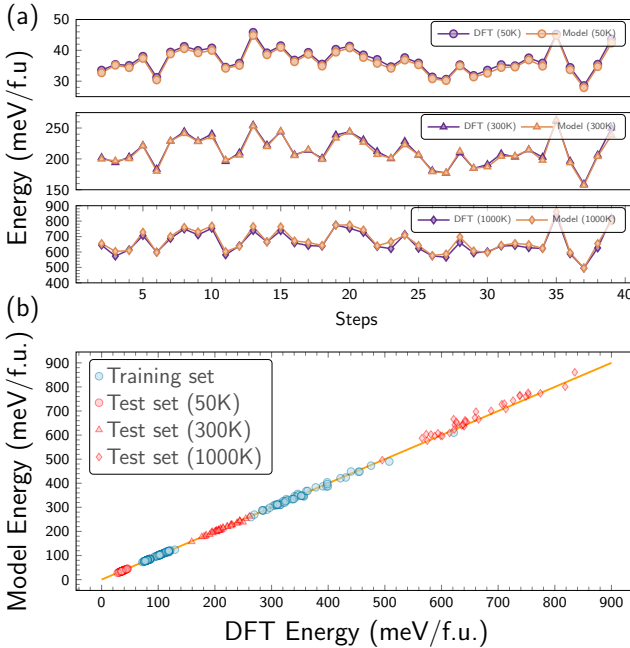


Figure 4.4: Validation of the BaHfO₃ model against *ab initio* data. (a) Time evolution of the energy along representative segments of the hybrid Monte Carlo trajectories at 50 K, 300 K, and 1000 K, comparing the model predictions with the DFT recalculations. (b) Model versus DFT energies for the training set and the three test sets generated at 50 K, 300 K, and 1000 K. The solid line indicates perfect agreement. Energies are reported relative to the cubic reference structure.

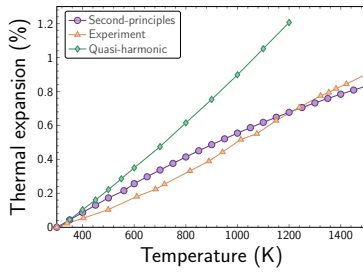


Figure 4.5: Thermal expansion of BaHfO₃ as a function of temperature, comparing the second-principles model with experimental data [152] and the quasi-harmonic approximation [160].

Finite-temperature simulations – As a first application of the model, the thermal expansion of BaHfO₃ was investigated through HMC simulations performed on a supercell of 20480 atoms, with 40 Monte Carlo trial trajectories of 1000 molecular dynamics time steps each, spanning the temperature range from 300 K to 1500 K. The resulting volumetric thermal expansion coefficient $\alpha_V = 2.097 \times 10^{-5} \text{ K}^{-1}$ is in excellent agreement with the experimental value of $2.079 \times 10^{-5} \text{ K}^{-1}$ [152], and significantly improves upon the quasi-harmonic estimate of $3.213 \times 10^{-5} \text{ K}^{-1}$ [160], as illustrated in Figure 4.5. This result confirms that the explicit treatment of anharmonicity in the second-principles framework is essential for an accurate description of thermal properties, even in a structurally simple material such as BaHfO₃.

4.3.2 Strontium Titanate

Strontium titanate, SrTiO₃, is one of the most extensively studied perovskite oxides, having played a central role in the history of condensed matter physics. It was indeed SrTiO₃ that provided some of the first experimental evidence for soft-mode driven structural phase transitions [161], quantum paraelectricity [162], two-dimensional electron gases at oxide interfaces [163], and unconventional superconductivity at remarkably low carrier densities [16, 164]. This remarkable breadth of physical phenomena stems from the delicate balance between competing instabilities that characterizes this material.

With a Goldschmidt tolerance factor of $t = 1.001$, SrTiO₃ sits at the center of the structural diagram illustrated in Figure 2.3, making it one of the closest realizations of the ideal cubic perovskite structure. Above the critical temperature, it adopts the cubic $Pm\bar{3}m$ phase. Upon cooling, it undergoes an antiferrodistortive (AFD) phase transition at $T_c \approx 105 \text{ K}$ [161], driven by the condensation of oxygen octahedra rotations at the R -point of the Brillouin zone, which lowers the symmetry to the tetragonal $I4/mcm$ phase. Below 4 K, quantum fluctuations prevent the polar soft mode from fully condensing, causing the static dielectric constant to saturate at an exceptionally large but finite value rather than diverging as would be expected for a true ferroelectric transition [162].

This behavior establishes SrTiO_3 as the archetypal quantum paraelectric.

From the perspective of model construction, SrTiO_3 represents a qualitatively different challenge compared to BaHfO_3 . The cubic reference phase is no longer a global minimum of the energy landscape but rather an unstable stationary point, as evidenced by the several soft modes visible in its phonon dispersion curves (Figure 4.6): an out-of-phase oxygen octahedra rotation at the R -point, which drives the cubic-to-tetragonal $I4/mcm$ transition at $T_c \approx 105$ K; a weaker in-phase rotation instability at the M -point; and a polar instability at the Γ -point. The latter is in direct competition with the rotations, a consequence of the tolerance factor being close to unity. Upon cooling it is the R -point instability that condenses first, driving the cubic-to-tetragonal transition while the polar mode remains uncondensed down to the lowest temperatures. However, this delicate balance makes SrTiO_3 extremely sensitive to external perturbations: epitaxial strain alone is sufficient to tip it into a ferroelectric phase, even at room temperature [165]. The model must therefore correctly reproduce not only the curvature of the potential energy surface around the distorted ground state but also the energy barriers separating the symmetry-equivalent minima and the coupling between oxygen octahedra rotations, polar, and strain degrees of freedom that govern its rich structural energy landscape.

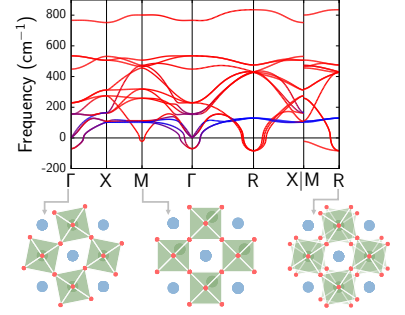


Figure 4.6: Phonon dispersion curves of SrTiO_3 in the cubic $Pm\bar{3}m$ phase at 0 K, with atomic participation highlighted by color: Sr (blue), Ti (green), and O (red). Imaginary frequencies appear at the Γ point, corresponding to a polar instability involving mainly Ti and O displacements, at the M point, corresponding to in-phase oxygen octahedra rotations, and at the R point, corresponding to the antiferrodistortive out-of-phase oxygen octahedra rotations. The atomic displacement patterns associated with each unstable mode are illustrated below the dispersion curves.

Harmonic interactions – The harmonic part of the model was obtained from DFPT calculations performed with the ABINIT software package [122], using the GGA with the PBEsol exchange-correlation functional [155] and a plane-wave pseudopotential approach. Optimized norm-conserving pseudopotentials from the PseudoDojo server [75, 156] were employed, treating Sr $4s^2 4p^6 5s^2$, Ti $3s^2 3p^6 3d^2 4s^2$, and O $2s^2 2p^4$ electrons as valence states. A plane-wave energy cutoff of 45 Ha was adopted, together with a $8 \times 8 \times 8$ Γ -centered Monkhorst-Pack [157] k -point mesh for the five-atom cubic unit cell, with the sampling adapted to the supercell size to maintain a comparable level of convergence. The dynamical matrices were computed on a $8 \times 8 \times 8$ q -point mesh for the relaxed cubic $Pm\bar{3}m$ phase. In addition to the interatomic force constants, the DFPT calculations provided the dielectric

constant, Born effective charges, elastic constants, and strain-phonon coupling coefficients, the latter vanishing identically by symmetry in the cubic reference structure. The dielectric constant and Born effective charges are used to construct the long-range dipole-dipole interaction, while the elastic constants enter in the harmonic description of the strain degrees of freedom.

Training set generation – Following the construction procedure outlined in Section 4.1, the richer energy landscape of SrTiO₃ requires a more elaborate training set than that of BaHfO₃. Starting from the unstable cubic $Pm\bar{3}m$ reference phase, the soft modes identified from the phonon dispersion curves were used to drive structural relaxations via the BFGS algorithm, combining the unstable modes at Γ , M , and R in all relevant combinations in order to systematically map the energy landscape and identify the distinct local minima. The energies, forces, and stresses of all configurations were computed using the same *ab initio* settings as described above, on a $2 \times 2 \times 2$ supercell of 40 atoms, with the k -point mesh reduced to $4 \times 4 \times 4$ to maintain a comparable sampling density of the Brillouin zone. The resulting phases are summarized in Table 4.3. These results are in good agreement with previous theoretical results [166].

A noteworthy observation is that the DFT lowest-energy minimum at 0 K is not the experimentally observed $I4/mcm$ phase but rather a polar phase, with Cc and $Ima2$ lying slightly below it in energy. This confirms the quantum paraelectric character of SrTiO₃: in the absence of quantum fluctuations, the ground state at 0 K carries a finite polarization, and it is only the zero-point motion of the ions that stabilizes the non-polar $I4/mcm$ phase at low temperature [167]. Furthermore, the rotation amplitude of the $I4/mcm$ phase predicted at 0 K amounts to 5.64° , significantly larger than the experimental value of approximately 2° [168]. This overestimation is a known limitation of the PBEsol functional, which has been reported to systematically overestimate octahedra tilt amplitudes in SrTiO₃ [169].

Interpolations and extrapolations between the identified stationary points in Table 4.3 were then performed to ensure adequate coverage of the potential energy surface between the minima. Phononic noise was subsequently added by sampling thermal displacements in the $I4/mcm$ phase at 15,

25, 50, and 100 K. The final training set comprises 2064 *ab initio* configurations.

Space group	ΔE	ϕ_x	ϕ_y	ϕ_z	P
$Pm\bar{3}m$	-	-	-	-	-
$P4/mbm$	-0.046	-	-	+1.6	-
$P4mm$	-0.526	-	-	-	16.4
$Amm2$	-0.638	-	-	-	18.0
$R3m$	-0.682	-	-	-	18.5
$R\bar{3}c$	-6.673	-3.08	-3.08	-3.08	-
$Imma$	-6.905	-3.84	-3.84	-	-
$I4/mcm$	-7.375	-5.64	-	-	-
$Ima2$	-7.651	-	-	-5.6	14.2
Cc	-7.660	-0.45	-0.45	-5.6	14.8

Table 4.3: Summary table of all the identified minima in SrTiO_3 in GGA-PBEsol. For all identified minima, the energy compared to the reference structure $Pm\bar{3}m$ ΔE (meV/f.u.) is reported, the tilt ϕ of the oxygen octahedra (degrees) and the module of the polarization ($\mu\text{C}/\text{cm}^2$)

Generation of the interatomic potential – With the training set in hand, the next step consists in constructing an interatomic potential capable of reproducing the first-principles data it contains. The quality of the harmonic approximation alone can first be assessed by evaluating the goal function on the training set before any fitting, as reported in the second column of Table 4.4.

	Harmonic part	Unbounded	Bounded
G_E	3.834×10^{-5}	2.454×10^{-8}	1.900×10^{-8}
$G_{f+\sigma}$	4.438×10^{-3}	3.078×10^{-5}	3.010×10^{-5}
G_f	6.542×10^{-4}	2.259×10^{-5}	2.217×10^{-5}
G_σ	3.784×10^{-3}	8.185×10^{-6}	7.927×10^{-6}

Table 4.4: Summary table of the mean squared displacement ($eV^2/\text{\AA}^2$) of the energy, forces and stresses for each step of the construction of the models of SrTiO_3 : before the fit process (TS evaluated with the harmonic part, after the fit process (20 SATs), after the bounding process (73 SATs).

Although the harmonic part is exact with respect to DFPT, it proves insufficient to reproduce the training set data accurately, as evidenced by the relatively large values of G_E , G_f , and G_σ .

The anharmonic part of the model was therefore obtained by fitting to the training set. SATs up to fourth order were generated using a cutoff radius equal to the cubic lattice parameter of 3.88 Å, including third- and fourth-order phonon-displacement and strain-phonon coupling terms, while elastic interactions were retained at second order. A selection of 20 anharmonic SATs was identified through goal-function

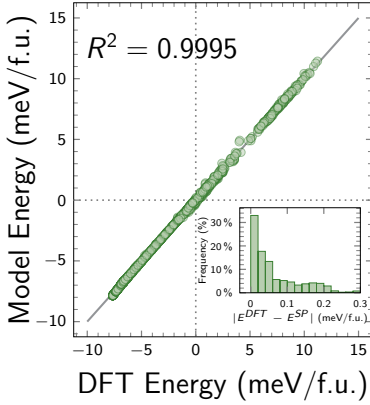


Figure 4.7: Comparison between the bounded model and **DFT** energies for the configurations contained in the training set of SrTiO_3 . The solid line indicates perfect agreement between the model and **DFT**. The inset shows the distribution of the absolute errors. Energies are reported relative to the cubic reference structure.

Table 4.5: Goal function values ($\text{eV}^2/\text{\AA}^2$) of the energy, forces and stresses for each test set produced by running **HMC** with the model of SrTiO_3 (10 K, 50 K and 100 K).

minimization. As shown in the third column of [Table 4.4](#), the addition of these terms reduces the goal function by several orders of magnitude with respect to the harmonic model alone.

The bounding procedure described in [Section 3.2.5](#) was then applied to ensure that the model energy remains bounded from below at large atomic displacements. Bounding terms were added automatically, introducing 53 additional **SATs** into the model. As shown in the fourth column of [Table 4.4](#) and illustrated in [Figure 4.7](#), this procedure preserves the quality of the fit to an excellent degree, leaving the goal function essentially unchanged and an excellent linear agreement between model and **DFT** energies ($R^2 = 0.9995$) and a distribution of absolute errors tightly peaked around zero, while eliminating any risk of divergence. The final model thus comprises 73 **SATs** in total.

Validation of the model – The validation of the model follows the three-step procedure outlined in [Section 4.2](#). Unlike BaHfO_3 , all three steps are non-trivial here. First, a test set was constructed by running **HMC** simulations with the model at 10 K, 50 K, and 100 K on a $2 \times 2 \times 2$ supercell of 40 atoms, and recalculating 1% of each trajectory at the *ab initio* level.

	TS		Test set		
			10K	50K	100K
G_E	1.90×10^{-8}	2.35×10^{-8}	1.03×10^{-6}	7.98×10^{-5}	
$G_{f+\sigma}$	3.01×10^{-5}	1.61×10^{-4}	9.78×10^{-4}	3.03×10^{-3}	
G_f	2.22×10^{-5}	1.36×10^{-4}	7.96×10^{-4}	2.50×10^{-3}	
G_σ	7.93×10^{-6}	2.52×10^{-5}	1.82×10^{-4}	5.29×10^{-4}	

The goal function evaluated on these unseen structures is reported in [Table 4.5](#) and the model versus **DFT** energy comparison is illustrated in [Figure 4.8](#). The model reproduces the test set data with good accuracy across the entire temperature range, with the goal function remaining close to the one obtained for the training set.

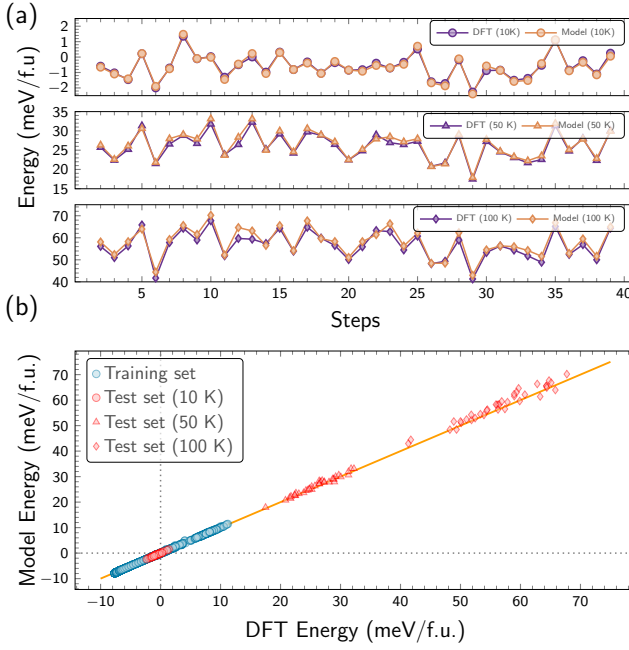


Figure 4.8: Validation of the SrTiO₃ model against *ab initio* data. (a) Time evolution of the energy along representative segments of the hybrid Monte Carlo trajectories at 10 K, 50 K, and 100 K, comparing the model predictions with the DFT recalculations. (b) Model versus DFT energies for the training set and the three test sets generated at 10 K, 50 K, and 100 K. The solid line indicates perfect agreement. Energies are reported relative to the cubic reference structure.

In the case of SrTiO₃, the $2 \times 2 \times 2$ supercell is already in the cubic $Pm\bar{3}m$ phase at 50 K, so that the test sets at 10 K and 50 K both probe the energy surface in the vicinity of the $I4/mcm$ and cubic phases, which is precisely the region of interest for finite-temperature simulations of this material. The test set at 100 K, which samples larger displacements, further confirms that the model remains predictive at higher thermal amplitudes.

Having validated the first step, all phases identified during the training set construction were relaxed using the BFGS algorithm and compared against DFT. As shown in Figure 4.9, the model correctly reproduces the sequence of local minima, with energy differences with respect to DFT below 0.21 meV/f.u. for all phases. The structural distortions, projected onto the phonon modes of the cubic reference, are also accurately reproduced, with a maximum discrepancy below 0.045 Å/f.u.

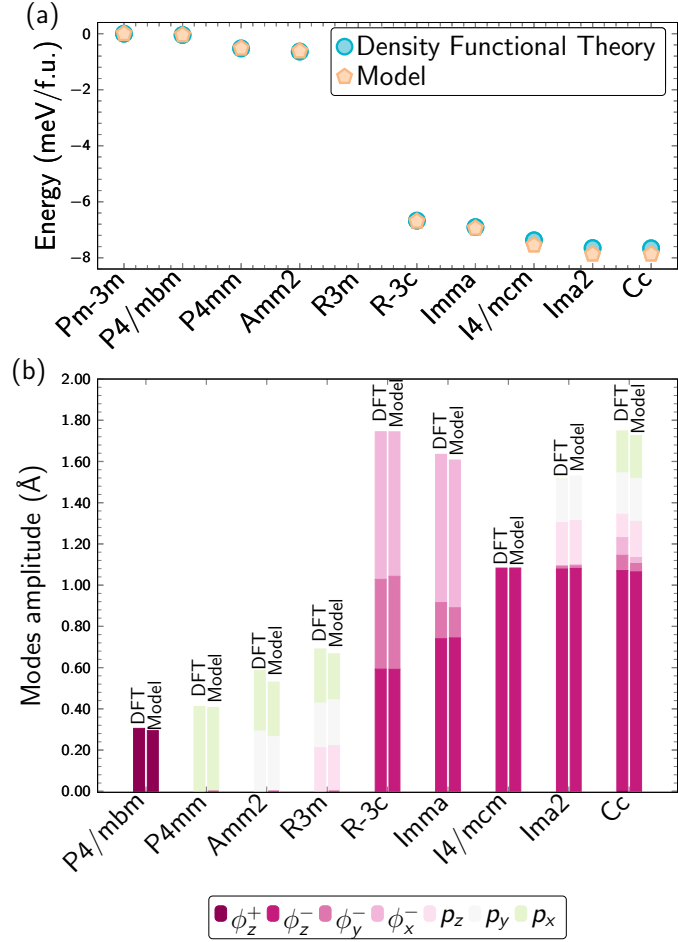


Figure 4.9: Comparison between DFT and model for all identified metastable phases of SrTiO₃. (a) Energies relative to the cubic $Pm\bar{3}m$ reference. (b) Amplitudes of the distortion modes (Å/f.u.).

Finally, the phonon dispersion curves and the density of states were computed in the experimental $I4/mcm$ ground state using finite differences with PHONOPY [170] and compared against DFPT, as shown in Figure 4.10. The model reproduces both the dispersion branches and the density of states with good accuracy, ensuring that the thermal activation of vibrational modes will be correctly described in finite-temperature simulations. Importantly, the model preserves the soft mode at the Γ point of the $I4/mcm$ phase, correctly capturing the quantum paraelectric character of SrTiO₃.

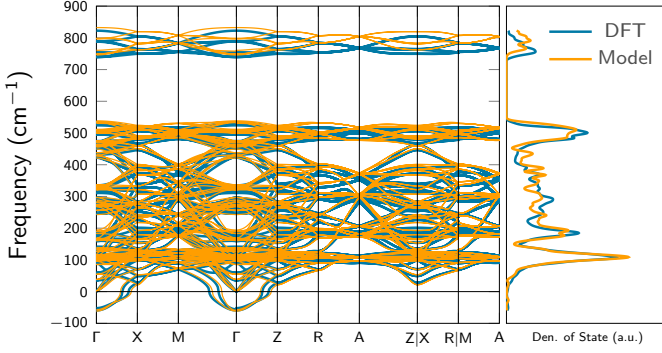


Figure 4.10: Comparison between the **DFT** and the model (finite difference method) of the phonon dispersion curves and the density of states of SrTiO_3 in the experimental ground state $I4/mcm$ (40 atoms cell).

Finite-temperature simulations – The validated model is now used to investigate the finite-temperature properties of SrTiO_3 , focusing on the $I4/mcm \rightarrow Pm\bar{3}m$ structural phase transition. **HMC** simulations were performed on supercells of 8640 atoms with 40 Monte Carlo trial trajectories of 1000 molecular dynamics time steps. In the vicinity of the critical temperature, larger supercells of 20480 atoms with 4000 time steps were employed to reduce finite-size effects and properly capture the fluctuations at the phase transition.

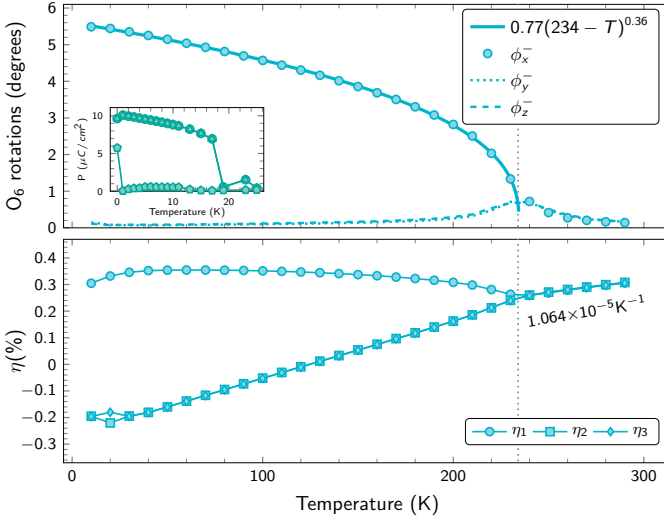


Figure 4.11: Evolution of the oxygen octahedra rotation amplitude ϕ and the strain η with temperature, obtained from **HMC** simulations. The dashed line shows a power-law fit $\phi \propto (T_c - T)^{0.36}$. The strain evolves linearly with ϕ^2 , as expected for the secondary order parameter of a proper ferroelastic transition. The thermal expansion coefficient α_l of the high-temperature cubic phase is indicated in the right panel. The inset shows the emergence of a finite polarization at low temperature.

As illustrated in **Figure 4.11**, the model predicts a phase transition from $I4/mcm$ to $Pm\bar{3}m$ at $T_c^{\text{sim}} \approx 230$ K, with the rotation amplitude following a power-law $\phi \propto (T_c - T)^{0.36}$, characteristic of a second-order transition. The strain, which acts as the secondary order parameter, evolves linearly with

the rotation amplitude squared, as expected for a proper ferroelastic transition, and the thermal expansion of the cubic phase is well reproduced with $\alpha_l = 1.064 \times 10^{-5} \text{ K}^{-1}$ [171]. The inset of Figure 4.11 (a) further reveals the emergence of a small but finite polarization at low temperature, consistent with the polar instability identified in Table 4.3 and confirming the quantum paraelectric character of SrTiO_3 : in the absence of quantum fluctuations, the classical ground state at 0 K is polar.

The shift between T_c^{sim} and the experimental value of 105 K results from two distinct sources. First, neglecting zero-point quantum fluctuations in classical molecular dynamics simulations is known to overestimate T_c [172, 173]. Second, the choice of exchange-correlation functional plays a critical role: as demonstrated by Verdi and co-workers [174], no single functional can simultaneously reproduce the correct transition temperature, the experimental rotation amplitude, and the softening of the polar mode. The PBEsol functional used here predicts a T_c that is too high and overestimates the octahedra tilt amplitude, while the Random Phase Approximation (RPA) functional [175], despite giving the best description of the polar soft mode, significantly overestimates T_c . The rSCAN meta-GGA functional [176] offers the best compromise for the transition temperature but at the cost of a poorer description of the ferroelectric instability.

The importance of quantum nuclear effects has been further demonstrated through isotope substitution. Using RPA-based MLIP combined with path-integral molecular dynamics, Schmidt and co-workers [177] showed that O^{16} remains paraelectric even when quantum fluctuations are included, while the heavier O^{18} isotope, whose reduced zero-point motion tips the balance, recovers a standard soft-mode driven ferroelectric transition, consistent with experimental observations. These results underscore that a quantitatively accurate description of SrTiO_3 requires the simultaneous treatment of quantum nuclear motion, isotopic effects, and a high-level electronic-structure description.

These limitations being well identified and rooted in the treatment of quantum nuclear effects and the choice of exchange-correlation functional, they are not expected to affect the description of the pressure dependence of the phase transition, which is governed by classical structural energetics. Despite this systematic overestimation of T_c , the

model correctly captures the physical trends under pressure, as shown in Figure 4.12. The stabilization of the $I4/mcm$ phase with increasing pressure is well reproduced, with a dT_c/dP slope in excellent agreement with the experimental value of 0.054 GPa/K [178]. When the experimental phase boundary is rigidly shifted in temperature to match T_c^{sim} at zero pressure, it aligns closely with the model predictions across the entire pressure range.

The temperature dependence of the phonon dispersion curves in the cubic phase was further investigated using the TDEP method [140, 179], as shown in Figure 4.13. The dispersion curves were computed at temperatures ranging from T_c^{sim} to $3T_c^{\text{sim}}$, revealing that all modes are stable well above T_c^{sim} and that, upon cooling toward T_c^{sim} , two distinct soft modes emerge progressively: the R_4^+ antiferrodistortive mode associated with out-of-phase oxygen octahedra rotation and the Γ_5^- polar mode. The R_4^+ mode softens and reaches near-zero frequency first, consistent with the fact that it is this mode that drives the phase transition, while the Γ_5^- mode remains finite throughout the cubic phase, reflecting the competition between these two modes.

The temperature dependence of these two modes is quantified in Figure 4.14, where ω^2 is plotted as a function of temperature and compared against experimental data from Shirane *et al.* [161] and Yamanaka *et al.* [180]. The linear temperature dependence of ω^2 , characteristic of Cochran's soft-mode theory [25], is well reproduced by the model for both modes, in good agreement with the PBEsol results reported by Verdi and co-workers [174] using the stochastic self-consistent harmonic approximation (SSCHA) [181].

As expected, the R_4^+ mode softens continuously upon cooling and extrapolates to zero at T_c^{sim} . Below T_c , the system enters the tetragonal $I4/mcm$ phase, where the three-fold degeneracy of the R_4^+ mode is lifted by the reduced symmetry into a two-fold degenerate branch and a non-degenerate branch. Both branches harden upon further cooling. Meanwhile, the Γ_5^- polar mode continues to soften below T_c and eventually reaches zero frequency at low temperature, signaling a second instability toward a polar phase. This is fully consistent with the sequence of phase transitions identified in Figure 4.11, where the ground state of SrTiO_3 is polar, as expected in the absence of quantum fluctuations.

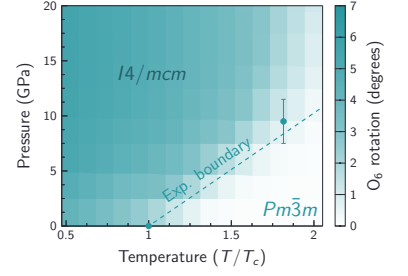


Figure 4.12: Pressure-temperature phase diagram of SrTiO_3 , showing the evolution of the oxygen octahedra rotation amplitude with temperature and pressure from HMC simulations. The color scale encodes the rotation amplitude in degrees. The dashed line represents the experimental phase boundary [178], rigidly shifted in temperature to match T_c^{sim} at zero pressure, with the experimental slope of $dT_c/dP = 0.054$ GPa/K preserved. The solid circles are the experimental data points.

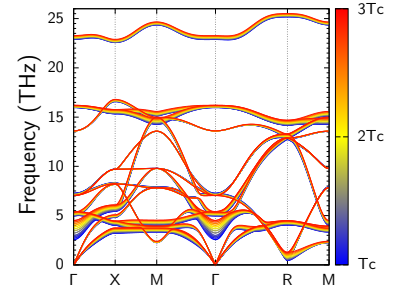


Figure 4.13: Temperature-dependent phonon dispersion curves of SrTiO_3 in the cubic $Pm\bar{3}m$ phase, computed using the TDEP method [179] at temperatures ranging from T_c to $3T_c$. The color scale encodes temperature. The progressive hardening of the soft modes at R and Γ with increasing temperature is clearly visible.

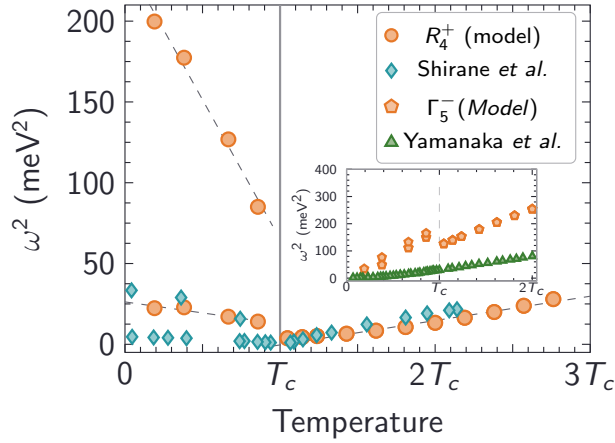


Figure 4.14: Evolution of ω^2 as a function of temperature for the R_4^+ antiferrodistortive mode (main panel) and the Γ_5^- polar mode (inset), compared against experimental data from Shirane and co-workers [161] and Yamanaka and co-workers [180]. The linear temperature dependence of ω^2 is illustrated by the dashed lines.

The second-principles model for SrTiO_3 constructed in this section is made publicly available and can be retrieved following Ref. [182]. It has been used in several subsequent studies: directly to investigate the multimodal topological textures arising from coupled structural orders in SrTiO_3 [183] and the mechanical coupling between polar topologies and oxygen octahedra rotations in $\text{PbTiO}_3/\text{SrTiO}_3$ heterostructures [184], and in combination with the PbTiO_3 model of Section 4.3.3 to study domain wall structures and polar textures in $\text{PbTiO}_3/\text{SrTiO}_3$ heterostructures (Chapter 5) [185].

4.3.3 Lead Titanate

Lead titanate, PbTiO_3 , is a prototypical ferroelectric perovskite with a Goldschmidt tolerance factor of $t = 1.001$, placing it in the ideal cubic region of Figure 2.3, close to SrTiO_3 . Despite this geometric similarity, the two materials display strikingly different physical behaviors: while SrTiO_3 undergoes an antiferrodistortive transition and remains a quantum paraelectric, PbTiO_3 exhibits a single, strongly first-order ferroelectric phase transition from the cubic $Pm\bar{3}m$ phase to the tetragonal $P4mm$ phase at $T_c \approx 763$ K [186], with a large spontaneous polarization of ~ 0.75 C/m² and an exceptionally large tetragonality $c/a \approx 1.065$ at low temperature [187].

This behavior originates from the dual nature of the ferroelectric instability in PbTiO_3 , which is not a pure B-type fer-

roelectric like BaTiO_3 [188]. As demonstrated by Cohen [189], ferroelectricity in PbTiO_3 involves two distinct covalent mechanisms: the hybridization between the Ti $3d$ and O $2p$ states, responsible for the B-site off-centering common to both materials, and the hybridization between the Pb $6s$ lone pair and the O $2p$ states, which drives a large A-site displacement absent in BaTiO_3 . It is this additional Pb contribution that stabilizes the tetragonal phase and suppresses the intermediate orthorhombic and rhombohedral phases observed in BaTiO_3 , resulting in a single, direct cubic-to-tetragonal transition upon cooling.

Beyond its role as a textbook ferroelectric, PbTiO_3 has emerged as a privileged platform for the study of topological polar textures at both the bulk and heterostructure level, including ferroelectric domain walls of Ising, Bloch, and Néel character [190–192], polar skyrmions in heterostructures [193], and a rich variety of topological configurations in bulk [194, 195]. A predictive large-scale atomistic model is therefore an essential tool for investigating such phenomena, which are the subject of Chapter 5 and Chapter 6 of this thesis.

From the perspective of model construction, PbTiO_3 poses a more demanding challenge than SrTiO_3 . The dominant polar instability at Γ competes with octahedra rotation instabilities at R and M , as illustrated in Figure 4.15. Among these competing instabilities, the polar mode wins and drives the system into a ferroelectric ground state characterized by unusually large atomic displacements and a strong coupling between polarization and strain. Since the model relies on a Taylor expansion of the potential energy surface around the cubic reference structure, accurately capturing such large distortions requires a careful selection of high-order SATs. The model must therefore not only reproduce the correct energy hierarchy between the polar and antiferrodistortive minima, but also describe the strong strain-phonon coupling that is responsible for the exceptionally large tetragonality of the $P4mm$ ground state.

Harmonic interactions – The harmonic part of the model was obtained from DFPT calculations performed with the ABINIT software package [122], using the GGA with the PBEsol exchange-correlation functional [155] and a plane-wave pseudopotential approach. Optimized norm-conserving pseudopotentials from the PseudoDojo server [75, 156] were

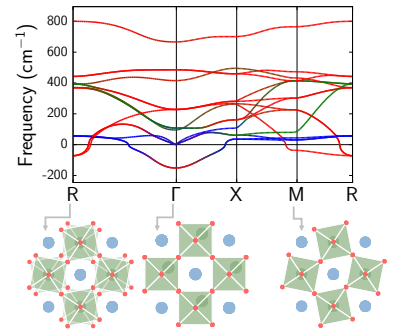


Figure 4.15: Phonon dispersion curves of PbTiO_3 in the cubic $Pm\bar{3}m$ phase at 0 K, with atomic participation highlighted by color: Pb (blue), Ti (green), and O (red). Imaginary frequencies appear at the Γ point, corresponding to a polar instability involving mainly Ti and O displacements, at the M point, corresponding to in-phase oxygen octahedra rotations, and at the R point, corresponding to the antiferrodistortive out-of-phase oxygen octahedra rotations. The atomic displacement patterns associated with each unstable mode are illustrated below the dispersion curves.

employed, treating Pb $5d^{10}6s^26p^2$, Ti $3s^23p^63d^24s^2$, and O $2s^22p^4$ electrons as valence states. A plane-wave energy cutoff of 65 Ha was adopted, together with a $8 \times 8 \times 8$ Γ -centered Monkhorst-Pack [157] k -point mesh for the five-atom cubic unit cell, with the sampling adapted to the supercell size to maintain a comparable level of convergence. The dynamical matrices were computed on a $4 \times 4 \times 4$ q -point mesh for the relaxed cubic $Pm\bar{3}m$ phase. In addition to the interatomic force constants, the DFPT calculations provided the dielectric constant, Born effective charges, elastic constants, and strain-phonon coupling coefficients, the latter vanishing identically by symmetry in the cubic reference structure. The dielectric constant and Born effective charges are used to construct the long-range dipole-dipole interaction, while the elastic constants enter the harmonic description of the strain degrees of freedom.

Training set generation – Following the construction procedure outlined in Section 4.1, the training set was built using the same strategy as for SrTiO₃: the unstable modes identified from the phonon dispersion curves of the cubic reference were combined systematically to map the energy landscape and identify all relevant local minima, which were then connected through interpolations and extrapolations, supplemented by phononic noise generated at several temperatures. The energies, forces, and stresses of all configurations were computed using the same *ab initio* settings as described above, on a $2 \times 2 \times 2$ supercell of 40 atoms, with the k -point mesh reduced to $4 \times 4 \times 4$ to maintain a comparable sampling density of the Brillouin zone. The identified phases and their structural parameters are summarized in Table 4.6, in good agreement with the first-principles reference data of Sharma *et al.* [196].

The bounding procedure, however, proved significantly more challenging than for BaHfO₃ or SrTiO₃. The large atomic displacements and strong strain-phonon coupling characteristic of PbTiO₃ led to frequent divergences during finite-temperature molecular dynamics simulations, even after the initial bounding step. To address this, the configurations at which the model energy diverged were identified, added to the training set, and the fitting and bounding procedure was repeated iteratively. Additionally, several molecular dynamics trajectories were included in the training set to better sample the regions of configuration space prone to divergence. This

iterative refinement of the training set is a direct consequence of the physical complexity of PbTiO_3 and illustrates the additional care required when constructing second-principles models for materials with large distortions. The final training set comprises 3644 *ab initio* configurations.

S.G.	a (Å)	b (Å)	c (Å)	ϕ (°)	P	ΔE
$Pm\bar{3}m$	3.92	3.92	3.92	0.0	0.0	0.0
$P4/mbm$	3.92	3.92	3.92	+2.1	0.00	-0.23
$I4/mcm$	3.91	3.91	3.93	-4.3	0.00	-3.27
$Imma$	3.91	3.92	3.92	-3.2	0.00	-3.63
$R\bar{3}c$	3.92	3.92	3.92	-2.6	0.00	-3.66
$R3m$	3.95	3.95	3.95	0.0	0.81	-59.19
$Amm2$	3.89	3.98	3.98	0.0	0.86	-64.00
$P4mm$	3.86	3.86	4.24	0.0	1.26	-85.24

Generation of the interatomic potential – With the training set in hand, the next step consists in constructing an interatomic potential capable of reproducing the first-principles data it contains. The quality of the harmonic approximation alone can first be assessed by evaluating the goal function on the training set before any fitting, as reported in the second column of Table 4.7. Although the harmonic part is exact with respect to DFPT, it proves insufficient to reproduce the training set data accurately, as evidenced by the large values of G_E , G_f , and G_σ .

The anharmonic part of the model was therefore obtained by fitting to the training set. SATs were generated using a cutoff radius of $\sqrt{3}/2$ times the cubic lattice parameter ($a = 3.92$ Å), including terms up to eighth order in atomic displacements, strain-phonon coupling, and anharmonic elastic constants up to fourth order. The inclusion of high-order elastic terms proved essential to achieve a satisfactory reproduction of the training set, reflecting the unusually large structural distortions and strong strain-phonon coupling characteristic of PbTiO_3 . A selection of 29 anharmonic SATs was identified through goal-function minimization. As shown in the second column of Table 4.7, the addition of these terms reduces the goal function by several orders of magnitude with respect to the harmonic baseline, confirming that the fitted model captures the dominant anharmonic contributions to the potential energy surface.

Table 4.6: Structure and energy of various metastable phases of PbTiO_3 designated by their space group, as relaxed in DFT. Lattice parameters are in Å, distortion amplitudes include rotations in degrees with respect to the cubic reference, the norm of polarization in C/m² using the Born effective charge of the cubic reference, and energies ΔE are in meV/f.u. with respect to the five-atom cubic reference structure.

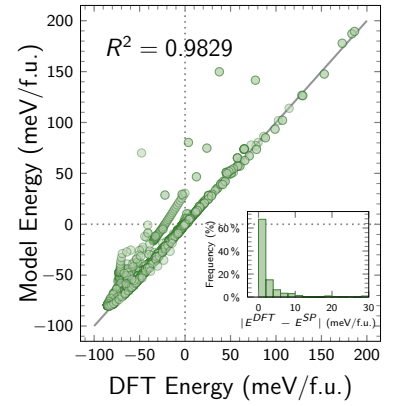


Figure 4.16: Comparison between the bounded model and DFT energies for the configurations contained in the training set of PbTiO_3 . The solid line indicates perfect agreement between the model and DFT. The inset shows the distribution of the absolute errors. Energies are reported relative to the cubic reference structure.

The bounding procedure described in Section 3.2.5 was then applied to ensure that the model energy remains bounded from below at large atomic displacements. Bounding terms were added automatically, introducing 66 additional SATs into the model. As shown in the fourth column of Table 4.7, the bounding procedure preserves the quality of the fit for the vast majority of configurations. However, as visible in Figure 4.16, a subset of high-energy structures are noticeably affected: the bounding terms introduce an additional stiffness that causes the model to overestimate the energy of configurations corresponding to large atomic displacements. This is an inherent consequence of the need to stabilize the Taylor expansion at large amplitudes, which is particularly pronounced in PbTiO₃ due to its exceptionally large polar distortions. The final model thus comprises 95 SATs in total and remains reliable for configurations within the thermally relevant range, as will be assessed more carefully during the validation procedure below.

Table 4.7: Summary table of the mean squared displacement ($eV^2/\text{\AA}^2$) of the energy, forces and stresses for each step of the construction of the models of PbTiO₃: before the fit process (TS evaluated with the harmonic part), after the fit process (29 SATs), after the bounding process (66 SATs).

	Harmonic part	Unbounded	Bounded
G_E	6.764×10^{-3}	1.860×10^{-5}	8.547×10^{-5}
$G_{f+\sigma}$	8.709×10^{-1}	1.948×10^{-3}	2.842×10^{-3}
G_f	4.362×10^{-2}	1.449×10^{-3}	2.012×10^{-3}
G_σ	8.273×10^{-1}	4.995×10^{-4}	8.295×10^{-4}

Validation of the model – The validation of the model follows the three-step procedure outlined in Section 4.2. A test set was constructed by running HMC simulations with the model at 10 K, 50 K, 100 K, 200 K, and 300 K, and recalculating 1% of each trajectory at the *ab initio* level. The goal function values evaluated on these unseen structures are reported in Table 4.8.

Table 4.8: Summary table of the mean squared displacement ($eV^2/\text{\AA}^2$) of the energy, forces and stresses for each test set produced by running MD with the model of PbTiO₃ (10 K, 50 K, 100 K, 200 K and 300 K).

	TS	Test set				
		10K	50K	100K	200 K	300 K
G_E	8.6×10^{-5}	1.0×10^{-5}	5.4×10^{-5}	1.5×10^{-4}	2.1×10^{-4}	5.4×10^{-4}
$G_{f+\sigma}$	2.8×10^{-3}	3.9×10^{-3}	1.4×10^{-2}	2.6×10^{-2}	5.0×10^{-2}	8.1×10^{-2}
G_f	2.0×10^{-3}	3.7×10^{-3}	1.3×10^{-2}	2.3×10^{-2}	3.0×10^{-2}	3.9×10^{-2}
G_σ	8.3×10^{-4}	2.2×10^{-4}	5.8×10^{-4}	3.1×10^{-3}	2.0×10^{-2}	4.2×10^{-2}

The model reproduces the test set data with good accuracy at low temperatures, while a moderate degradation of the goal function is observed at 200 K and 300 K, due to the larger atomic displacements sampled at higher temperatures. Crucially, as illustrated in Figure 4.17, the model versus DFT energy comparison remains largely linear across the entire temperature range, without any sign of the artificial stiffening observed for some high-energy training set configurations. This indicates that the problematic configurations identified during the bounding step are not visited during molecular dynamics at these temperatures, which is reassuring regarding the practical applicability of the model in the thermally relevant regime.

Then, all phases identified during the training set construction were relaxed using the BFGS algorithm and compared against DFT. As shown in Figure 4.18 (a), the model correctly reproduces the sequence of local minima across the full energy range, from the non-polar phases close to the cubic reference to the tetragonal $P4mm$ ground state, ~ 85 meV/f.u. below it. The largest energy discrepancy amounts to 0.68 meV/atom for the ground state, within the typical convergence criterion for DFT calculations. The structural distortions, projected onto the symmetry-adapted modes [197, 198] of the cubic reference, are also accurately reproduced as shown in Figure 4.18 (b), with a maximum discrepancy of 0.049 Å/f.u. across all identified phases.

Finally, phonon dispersion curves and the density of states were computed in the experimental $P4mm$ ground state using finite differences with PHONOPY [170] and compared against DFPT, as shown in Figure 4.19 and Figure 4.20. The model reproduces the overall shape of the dispersion branches with good accuracy, particularly in the low-frequency region where the thermally relevant modes are located. However, a notable feature deserves attention: the DFPT calculation reveals a softening of a low-frequency branch between the $A(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $Z(0, 0, \frac{1}{2})$ high-symmetry points. This softening suggests the proximity of the $P4mm$ phase to a competing structural modulation with a wavevector in the plane perpendicular to the polarization axis, possibly related to the formation of domain structures or modulation of the polarization, though its precise origin warrants further investigation. This soft branch is precisely what made the bounding procedure so challenging for $PbTiO_3$: adequately stabilizing the model against divergence in this region required a stronger bound-

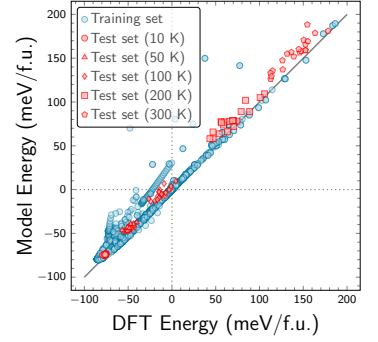


Figure 4.17: Model versus DFT energies for the training set and the three test sets generated at 10 K, 50 K, 100 K, 200 K and 300 K. The solid line indicates perfect agreement. Energies are reported relative to the cubic reference structure.

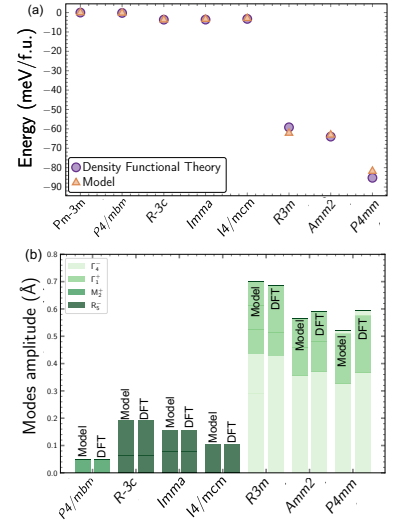


Figure 4.18: Validation against DFT of the interatomic potential for $PbTiO_3$. (a) Comparison between DFT and model energies for different (meta)-stable phases, as consistently relaxed within each approach. (b) Comparison between DFT and model distortion amplitudes for different meta- and stable phases, as consistently relaxed within each approach (Å/f.u.).

ing, which in turn introduces some stiffening of the potential and contributes to the partial degradation of the fit quality noted above.

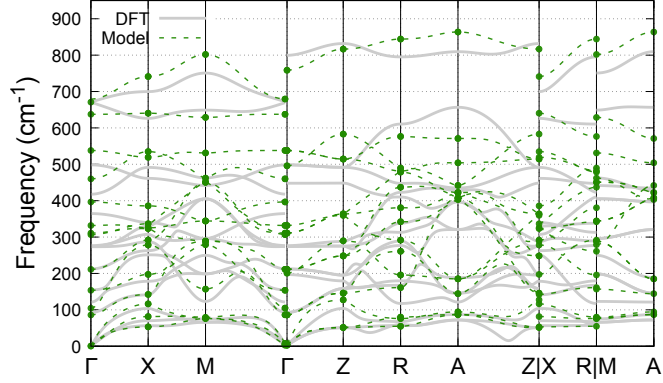


Figure 4.19: Validation against **DFT** of the interatomic potential for PbTiO_3 . Comparison between **DFT** and model of the phonon dispersion curve across the whole Brillouin zone.

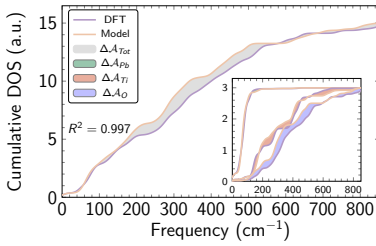


Figure 4.20: Validation against **DFT** of the interatomic potential for PbTiO_3 . Comparison between **DFT** and model cumulative total phonon density of states in the tetragonal $P4mm$ ground state. The inset shows the comparison between **DFT** and model contributions to the cumulative phonon density of states individually for each type of atoms.

Despite some discrepancy between the model and **DFT** in certain regions of the dispersion curves, the model remains fully predictive in the low-frequency regime where the thermally relevant modes are located. To quantify the overall agreement more rigorously, given these partial discrepancies, the cumulative phonon density of states is compared against **DFT** in Figure 4.20. The area-based quality factor $\Delta a = 1 - \Delta A / A_{\text{DFT}} = 0.95$, where ΔA denotes the difference in area between the model and **DFT** cumulative **DOS** normalized by the **DFT** result, confirms that the model captures the overall vibrational spectrum with good fidelity. Examining the atom-projected contributions reveals that the residual discrepancy originates primarily from the oxygen modes, while the Pb and Ti contributions are well reproduced.

Finite-temperature simulations – The validated model is now applied to investigate the finite-temperature properties of PbTiO_3 , focusing on the ferroelectric $P4mm \rightarrow Pm\bar{3}m$ phase transition. **HMC** simulations were performed in the NPT ensemble with 40 Monte Carlo trial trajectories of 1000 molecular dynamics time steps on a supercell of 8640 atoms ($12 \times 12 \times 12$), using 1000 sweeps for thermalization followed by 1000 sweeps for the production run. In the vicinity of the phase transition, larger supercells of 20480 atoms ($16 \times 16 \times 16$) with 4000 sweeps were employed to reduce finite-size effects and properly capture the critical fluctuations.

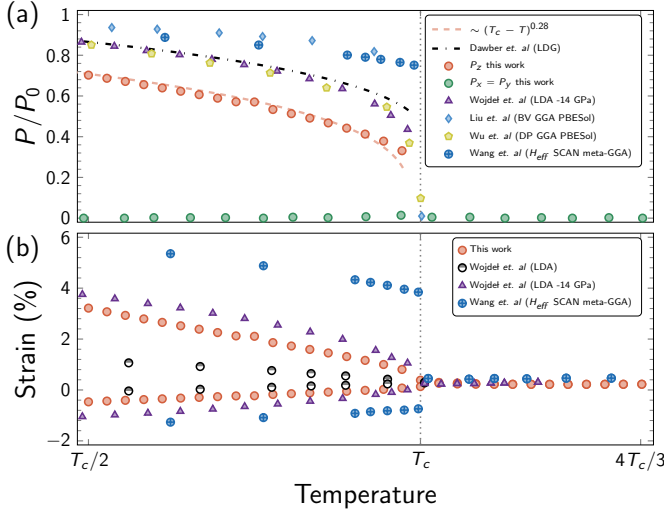


Figure 4.21: Ferroelectric $P4mm$ to paraelectric $Pm3m$ phase transition of $PbTiO_3$ in temperature as predicted by the interatomic potential. (a) Evolution of the spontaneous polarization (normalized with the polarization P_0 at 0 K) with temperature, in comparison with the results of Refs [120, 199–202]. The orange dashed curve shows a critical exponent fit of $n = 0.28$. (b) Evolution of the homogeneous strains with temperature, in comparison with the results of Refs [120, 203]. Note that the data of Ref. [120] with a negative pressure of -14 GPa have been shifted to align with the strain of the present model at T_c

As illustrated in Figure 4.21, the model predicts a first-order ferroelectric phase transition at $T_c^{\text{sim}} \approx 400$ K, significantly lower than the experimental value of 763 K. The polarization evolves with a critical exponent $n = 0.28$, and drops discontinuously at T_c , consistent with the first-order character of the transition. The strain likewise exhibits a discontinuity at T_c , in good agreement with LDA-based second-principles calculations [120] under negative pressure correction. The spontaneous polarization at 0 K reported in Figure 4.21 (a) has been estimated using the Born effective charges of the cubic phase, yielding a slightly overestimated value of $P_0 = 1.1$ C/m². Using instead the Born effective charges of the $P4mm$ phase would give an underestimated value of 0.84 C/m². The more accurate value obtained from DFT using the Berry phase approach is $P_0 = 0.99$ C/m², in good agreement with previous calculations [204]. The underestimation of T_c is a common feature of second-principles models based on PBEsol, which tends to underestimate the ferroelectric instability [120, 199, 200, 202], and is further compounded by the high-order bounding terms that stiffen the potential at large displacements. Notably, T_c^{sim} lies between the values obtained from LDA-based second-principles [120] and machine-learning meta-GGA methods [202], which respectively under- and overestimate T_c in the absence of pressure correction.

The temperature dependence of the phonon dispersion curves was investigated using the TDEP method [140, 179], as shown in Figure 4.22. Above T_c^{sim} , the system is stable in the cu-

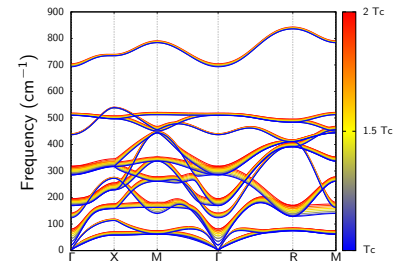


Figure 4.22: Temperature-dependent phonon dispersion curves of $PbTiO_3$ in the cubic phase above T_c (T_c denotes the critical temperature of the simulation considering $4 \times 4 \times 4$ supercell)

bic phase with no imaginary modes. Upon cooling toward T_c^{sim} , a polar mode at the Γ point softens progressively from 81 to 21 cm^{-1} , while antiferrodistortive modes at R and M simultaneously soften, though more slowly. This simultaneous softening at both the zone center and zone boundary is the hallmark of the competition between polar and rotational instabilities in materials with a tolerance factor close to unity [120], and confirms that the polar mode wins over the antiferrodistortive one in PbTiO_3 , in direct contrast to the scenario observed in SrTiO_3 .

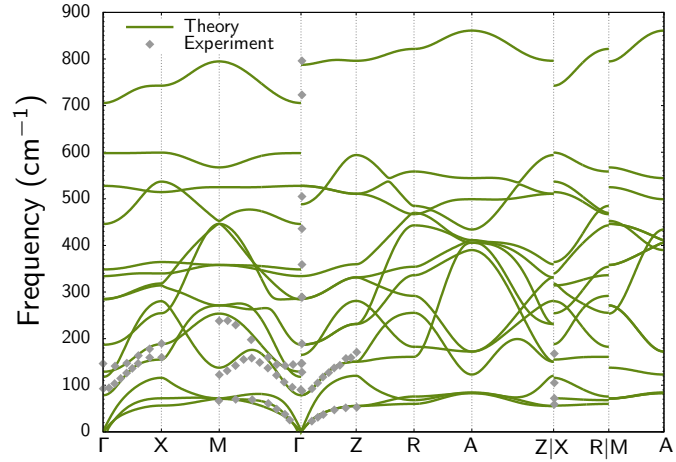


Figure 4.23: Temperature-dependent phonon dispersion curves of PbTiO_3 in the tetragonal phase at $T_{\text{exp}} = 300 \text{ K}$ in a $4 \times 4 \times 4$ supercell, compared with experimental data from Refs [205, 206].

The phonon dispersion curves in the tetragonal $P4mm$ phase were computed using **TDEP** on a $4 \times 4 \times 4$ supercell and compared against experimental data from Tomeno and co-workers [205] and Fontana and co-workers [206], as shown in **Figure 4.23**. Since the model underestimates T_c , a direct comparison at $T_{\text{sim}} = 300 \text{ K}$ would not be meaningful. Instead, the simulation was performed at a rescaled temperature $T_{\text{sim}} = (T_{\text{exp}}/T_{c,\text{exp}}) \times T_{c,\text{sim}}$, where $T_{c,\text{sim}}$ is the critical temperature predicted by the model for the $4 \times 4 \times 4$ supercell used in the **TDEP** calculation. The model shows excellent agreement with the experimental data over a wide frequency range and across all high-symmetry paths of the Brillouin zone, highlighting its predictive reliability for the description of vibrational properties at finite temperature despite the underestimation of the critical temperature.

The second-principles model for PbTiO_3 constructed in this section is made publicly available and can be retrieved following Ref. [207]. It constitutes the primary atomistic tool

employed in Chapter 5 and Chapter 6 of this thesis. In Chapter 5, it is applied directly to the study of ferroelectric domain walls and polar textures in bulk PbTiO_3 [195], and in combination with the SrTiO_3 model of Section 4.3.2 to investigate domain wall structures and polar textures in bulk and in $\text{PbTiO}_3/\text{SrTiO}_3$ heterostructures [184, 185]. In Chapter 6, it is further employed to study the dynamical manipulation of polar topologies from acoustic phonon excitations [208] and the precise control of polar textures under inhomogeneous and time-dependent electric fields [209].

4.3.4 Barium Titanate

Barium titanate, BaTiO_3 , is arguably the most studied ferroelectric perovskite oxide, having served as a cornerstone material for both fundamental research and technological applications since its discovery in the 1940s [210]. With a Goldschmidt tolerance factor of $t = 1.063$, it sits well within the B-type ferroelectric region of Figure 2.3, reflecting the excess space available to the Ti^{4+} cation within its oxygen octahedron. At high temperature, BaTiO_3 adopts the cubic $Pm\bar{3}m$ phase, and upon cooling it undergoes a rich sequence of three first-order ferroelectric phase transitions: cubic $Pm\bar{3}m$ to tetragonal $P4mm$ at 403 K, to orthorhombic $Amm2$ at 278 K, and to rhombohedral $R3m$ at 183 K [211], with the polarization successively rotating from the $\langle 001 \rangle$ to the $\langle 011 \rangle$ and $\langle 111 \rangle$ pseudocubic directions.

Unlike SrTiO_3 and PbTiO_3 , BaTiO_3 exhibits no octahedra rotation instability as shown in Figure 4.24. Its phonon dispersion curves in the cubic phase shows a single unstable branch centered on the Γ point, corresponding to the off-centering of the Ti cation within its oxygen cage. The other parts of this unstable branch are simply modulations of this same Ti-O displacement pattern, reflecting the local character of the instability. This purely polar energy landscape stands in sharp contrast to both SrTiO_3 , where antiferrodistortive and polar instabilities compete, and PbTiO_3 , where the A-site lone pair and the strong coupling with the strain provide an additional driving force.

The microscopic origin of ferroelectricity in BaTiO_3 has been the subject of extensive debate. As established by Cohen [189], the ferroelectric instability in BaTiO_3 is driven by the hybridization between the Ti $3d$ and O $2p$ states, which over-

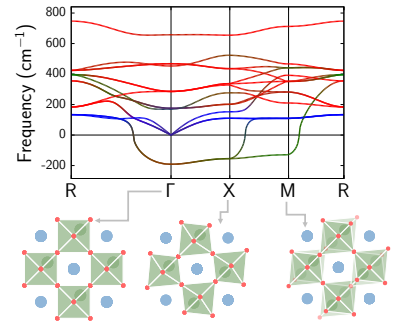


Figure 4.24: Phonon dispersion curves of BaTiO_3 in the cubic $Pm\bar{3}m$ phase at 0 K, with atomic participation highlighted by color: Ba (blue), Ti (green), and O (red). Imaginary frequencies appear at the Γ point, corresponding to a polar instability involving mainly Ti and O displacements, at the X point, corresponding to antipolar motion of Ti and O along one direction, and at the M point, corresponding to antipolar motion of Ti and O along two directions. The atomic displacement patterns associated with each unstable mode are illustrated below the dispersion curves.

comes the short-range repulsions that would otherwise stabilize the centrosymmetric phase. This balance is particularly delicate in BaTiO_3 : as shown by Ghosez and co-workers [188], the ferroelectric instability results from a subtle competition between the destabilizing long-range dipole-dipole interactions, driven by the large Born effective charges associated with Ti-O hybridization, and the stabilizing short-range forces.

The model for BaTiO_3 was developed collaboratively over several iterations, starting from an initial version described in Ref. [212]. The training set was subsequently enriched by A. Sasani, and the model was then refitted and finalized by M. Yu. The author of this thesis contributed to all stages of this process, providing guidance and performing systematic validation at each step.

Harmonic interactions – The harmonic part of the model was obtained from DFPT calculations performed with the ABINIT software package [122], using the GGA with the PBEsol exchange-correlation functional [155] and a plane-wave pseudopotential approach. Optimized norm-conserving pseudopotentials from the PseudoDojo server [75, 156] were employed, treating Ba $5s^2 5p^6 6s^2$, Ti $3s^2 3p^6 3d^2 4s^2$, and O $2s^2 2p^4$ electrons as valence states. A plane-wave energy cutoff of 40 Ha was adopted, together with a $8 \times 8 \times 8$ Γ -centered Monkhorst-Pack [157] k -point mesh for the five-atom cubic unit cell. The dynamical matrices were computed on a $4 \times 4 \times 4$ q -point mesh for the relaxed cubic $Pm\bar{3}m$ phase. In addition to the interatomic force constants, the DFPT calculations provided the dielectric constant, Born effective charges, elastic constants, and strain-phonon coupling coefficients, the latter vanishing identically by symmetry in the cubic reference structure. The dielectric constant and Born effective charges are used to construct the long-range dipole-dipole interaction, while the elastic constants enter the harmonic description of the strain degrees of freedom.

Training set generation – Following the construction procedure outlined in Section 4.1, the energy landscape of BaTiO_3 was first mapped by condensing the unstable modes identified from the phonon dispersion curves of the cubic reference, in all relevant combinations, to identify the distinct local minima. The energies, forces, and stresses of all configurations

were computed using the same *ab initio* settings as described above, on a $2 \times 2 \times 2$ supercell of 40 atoms, with the k -point mesh reduced to $4 \times 4 \times 4$ to maintain a comparable sampling density of the Brillouin zone. The resulting phases are summarized in Table 4.9. Interpolations and extrapolations between the identified stationary points were then performed to ensure adequate coverage of the potential energy surface between the minima. Unlike BaHfO₃, SrTiO₃, and PbTiO₃, where phononic noise was generated by populating phonon modes at selected temperatures, the thermal sampling for BaTiO₃ was performed directly through *ab initio* molecular dynamics simulations at temperatures ranging from 1 K to 100 K on a $2 \times 2 \times 2$ supercell of 40 atoms. The final training set comprises 1119 *ab initio* configurations.

S.G.	a (Å)	b (Å)	c (Å)	ϕ (°)	P	ΔE
$Pm\bar{3}m$	3.97	3.97	3.97	0.0	0.0	0.0
$P4/nmm$	3.97	3.97	4.02	0.0	0.0	-6.54
$Pmma$	3.97	3.96	4.03	0.0	0.0	-8.98
$Pbcm$	3.96	4.01	3.98	+0.03	0.10	-9.84
$Cmcm$	3.97	4.00	4.00	0.0	0.0	-10.63
$P4mm$	3.96	3.96	4.05	0.0	0.38	-17.27
$Amm2$	4.01	4.01	3.95	0.0	0.42	-21.66
$R3m$	3.99	3.99	3.99	0.0	0.43	-23.14

Table 4.9: Structure and energy of various metastable phases of BaTiO₃ designated by their space group, as relaxed in DFT. Lattice parameters are in Å, distortion amplitudes include rotations in degrees with respect to the cubic reference, the norm of polarization in C/m² using the Born effective charge of the cubic reference, and energies ΔE are in meV/f.u. with respect to the five-atom cubic reference structure.

Generation of the interatomic potential – With the training set in hand, the next step consists in constructing an interatomic potential capable of reproducing the first-principles data it contains. The quality of the harmonic approximation alone can first be assessed by evaluating the goal function on the training set before any fitting, as reported in the second column of Table 4.10. Although the harmonic part is exact with respect to DFPT, it proves insufficient to reproduce the training set data accurately, as evidenced by the large values of G_E , G_f , and G_σ .

The anharmonic part of the model was therefore obtained by fitting to the training set. SATs from third to fourth order were generated using a cutoff radius equal to the cubic lattice parameter of 3.97 Å, including strain-phonon coupling terms and anharmonic elastic constants. A selection of 24 SATs was identified through goal-function minimization. As shown in the second column of Table 4.10, the addition of these terms

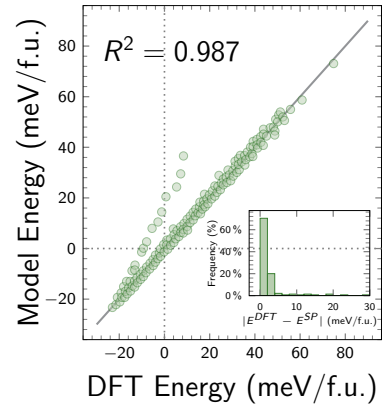


Figure 4.25: Comparison between the bounded model and DFT energies for the configurations contained in the training set of BaTiO₃. The solid line indicates perfect agreement between the model and DFT. The inset shows the distribution of the absolute errors. Energies are reported relative to the cubic reference structure.

reduces the goal function by several orders of magnitude with respect to the harmonic baseline, confirming that the fitted model captures the dominant anharmonic contributions to the potential energy surface.

The bounding procedure described in Section 3.2.5 was then applied to ensure that the model energy remains bounded from below at large atomic displacements. Bounding terms were added automatically, introducing 68 additional SATs into the model. As shown in the third column of Table 4.10, this procedure preserves the quality of the fit to an excellent degree, leaving the goal function essentially unchanged while eliminating any risk of divergence. The final model thus comprises 92 SATs in total. As illustrated in Figure 4.25, the bounded model achieves an excellent linear agreement with DFT energies ($R^2 = 0.987$), with more than 90% of the training set configurations reproduced within 1 meV/atom, which is within the typical convergence criterion of DFT calculations. A minor stiffening artifact is visible for a small subset of configurations, a direct consequence of the bounding terms.

Table 4.10: Summary table of the mean squared displacement ($eV^2/\text{\AA}^2$) of the energy, forces and stresses for each step of the construction of the models of BaTiO₃: before the fit process (TS evaluated with the harmonic part), after the fit process (24 SATs), after the bounding process (68 SATs).

	Harmonic part	Unbounded	Bounded
G_E	2.22×10^{-4}	1.48×10^{-5}	1.45×10^{-5}
$G_{f+\sigma}$	1.68×10^{-1}	5.43×10^{-3}	5.69×10^{-3}
G_f	2.93×10^{-2}	4.51×10^{-3}	4.52×10^{-3}
G_σ	1.39×10^{-1}	9.19×10^{-4}	1.27×10^{-3}

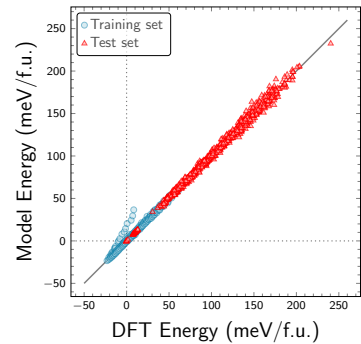


Figure 4.26: Model versus DFT energies for the training set and the three test sets generated by continuously heating from 10 K to 300 K for BaTiO₃. The solid line indicates perfect agreement. Energies are reported relative to the cubic reference structure.

Validation of the model – The validation of the model follows the three-step procedure outlined in Section 4.2.

The bounded model achieves a good fit quality on the training set, as illustrated in Figure 4.26. The test set was constructed differently from the approach used for the previous materials: rather than sampling discrete temperatures, a continuous heating simulation from 10 K to 300 K was performed, generating 861 configurations whose energies, forces, and stresses were recalculated at the *ab initio* level. As shown in Figure 4.26, the model versus DFT energy comparison is perfectly linear across the entire range, with $R^2 = 0.994$, confirming the predictive character of the potential throughout the thermally relevant regime.

All phases identified during the training set construction were relaxed using the BFGS algorithm and compared against DFT.

As shown in Figure 4.27 (a), the model correctly reproduces the sequence of local minima across the full energy range with remarkable accuracy, from the antipolar phases near the cubic reference to the polar $R3m$ ground state. The structural distortions, projected onto the symmetry-adapted modes [198] of the cubic reference, are also accurately reproduced as shown in Figure 4.27 (b), with excellent agreement between the model and DFT amplitudes for all identified phases.

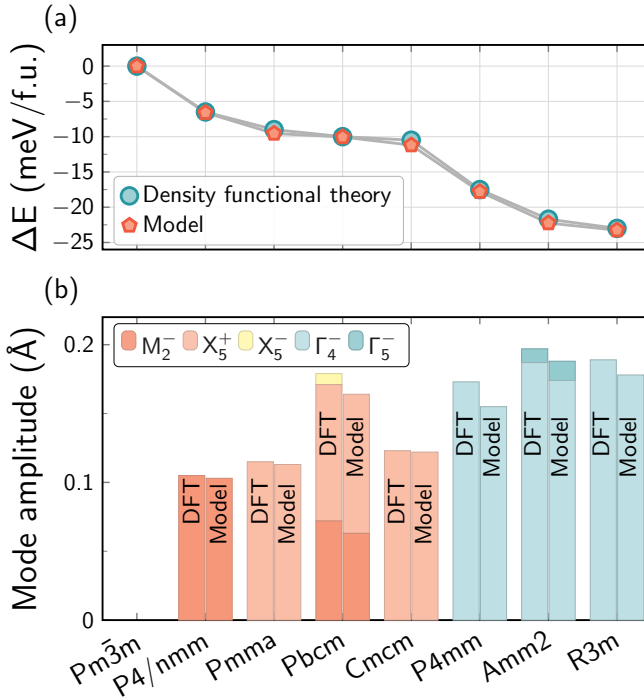


Figure 4.27: Validation against DFT of the interatomic potential for BaTiO₃. (a) Comparison between DFT and model energies for different (meta)-stable phases, as consistently relaxed within each approach. (b) Comparison between DFT and model distortion amplitudes for different meta- and stable phases, as consistently relaxed within each approach (Å/f.u.).

Phonon dispersion curves were computed using finite differences with PHONOPY [170] in the three experimentally observed phases of BaTiO₃: the tetragonal $P4mm$, orthorhombic $Am\bar{m}2$, and rhombohedral $R3m$ phases. As shown in Figure 4.28, the model is in excellent agreement with DFPT in all three phases, correctly reproducing the dispersion branches. A notable feature in panel (c) is the apparent instability of the acoustic branches in the $R3m$ phase as predicted by DFPT. This artifact is attributed to the absence of higher-order multipolar corrections to the non-analytic part of the dynamical matrix [213], which become significant in low-symmetry polar phases such as the rhombohedral phase of BaTiO₃ and are not included in the present DFPT calculation. The model,

which does not suffer from this limitation, correctly predicts stable acoustic branches in this phase. This confirms that the curvature of the potential energy surface is accurately described around each of the thermodynamically relevant phases, ensuring a reliable description of the thermal activation of vibrational modes in finite-temperature simulations.

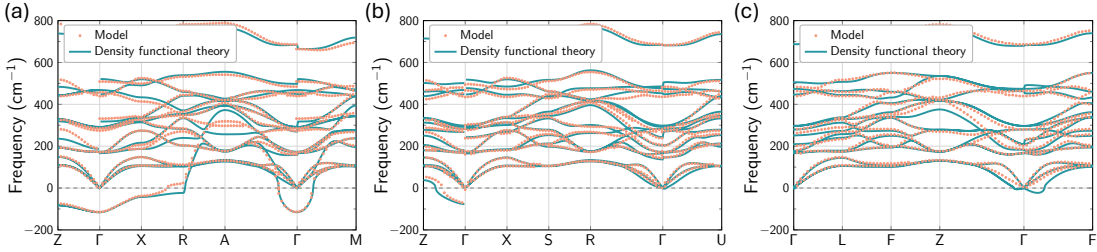


Figure 4.28: Comparison between DFPT (solid lines) and model (dots) phonon dispersion curves of BaTiO₃ in the three experimentally observed phases: (a) tetragonal $P4mm$, (b) orthorhombic $Amm2$, and (c) rhombohedral $R3m$.

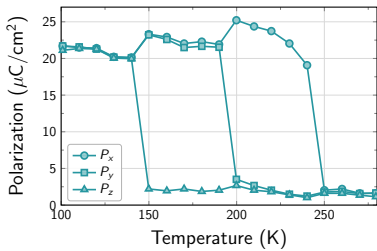


Figure 4.29: Evolution of the three polarization components P_x , P_y , and P_z with temperature, obtained from HMC simulations in the NPT ensemble. The successive discontinuous jumps identify the three first-order phase transitions $R3m \rightarrow Amm2 \rightarrow P4mm \rightarrow Pm\bar{3}m$.

Finite-temperature simulations – The validated model is applied to investigate the well-known $R3m \rightarrow Amm2 \rightarrow P4mm \rightarrow Pm\bar{3}m$ phase transition sequence of BaTiO₃ upon heating. HMC simulations were performed in the NPT ensemble, following the same protocol as for the other materials. As illustrated in Figure 4.29, the model successfully reproduces the full R-O-T-C phase transition sequence, with transition temperatures of approximately 150 K, 200 K, and 250 K for the $R3m \rightarrow Amm2 \rightarrow P4mm \rightarrow Pm\bar{3}m$ transitions, respectively. Each transition is clearly identifiable as a discontinuous jump in the polarization components, consistent with the first-order character of all three transitions. The model also correctly captures the thermal expansion of the cubic phase above T_c , demonstrating that the strain degrees of freedom are accurately described throughout the temperature range.

The predicted transition temperatures underestimate the experimental values of 183 K, 278 K, and 393 K [211], a systematic trend common to PBEsol-based atomistic models. As demonstrated for the second-principles model of Ref. [212], this offset can be compensated by applying a small negative hydrostatic pressure to correct for the underestimation of the cubic lattice constant by PBEsol, recovering transition temperatures in much better agreement with experiment.

More fundamentally, this underestimation reflects the sensitivity of the ferroelectric instability in BaTiO_3 to the choice of exchange-correlation functional. Azuma and co-workers [214] recently demonstrated that the R2SCAN meta-GGA functional combined with DFT-D4 dispersion corrections yields phase transition temperatures of 350 K, 250 K, and 160 K, in significantly better agreement with experiment, at the cost of a more computationally demanding electronic structure treatment.

The second-principles model for BaTiO_3 constructed in this section is made publicly available and can be retrieved following Ref. [215]. It serves as the primary atomistic tool in Chapter 5 and Chapter 6 of this thesis. In Chapter 5, it is applied to characterize switchable skyrmion-antiskyrmion tubes in rhombohedral BaTiO_3 [216]. In Chapter 6, it is further employed to investigate the dynamical manipulation of polar topologies from acoustic phonon excitations [208].

4.3.5 Calcium Titanate

Calcium titanate, CaTiO_3 , is the original mineral perovskite that gave its name to the entire family of ABO_3 compounds. With a Goldschmidt tolerance factor of $t \approx 0.973$, it sits well within the A-type region of Figure 2.3, reflecting the undersized Ca^{2+} cation relative to the available A-site cavity. This geometric configuration drives a strong tendency for oxygen octahedra rotations, placing CaTiO_3 among the most distorted oxide perovskites at ambient conditions. Its room-temperature and ground-state structure is the orthorhombic $Pbnm$ phase, characterized by the $a^-a^-c^+$ octahedra rotation pattern in Glazer notation [21]. Upon heating, CaTiO_3 undergoes a sequence of phase transitions before reaching the cubic $Pm\bar{3}m$ phase above 1636 K [217]. Although it is generally agreed that the tetragonal $I4/mcm$ phase precedes the cubic phase, the exact sequence of intermediate phases between $Pbnm$ and $I4/mcm$ remains debated. Based on neutron diffraction and calorimetry measurements, Kennedy and co-workers [218] and Guyot and co-workers [219] proposed an intermediate $Cmcm$ phase ($a^0b^-c^+$) between $Pbnm$ and $I4/mcm$, a result reproduced by a Landau-type phenomenological potential fitted to the same experimental data [220]. Independently, Carpenter suggested an intermediate $Imma$ phase ($a^-a^-c^0$) for the related $(\text{Ca},\text{Sr})\text{TiO}_3$ solid-solution

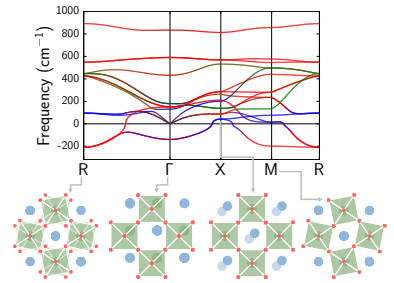


Figure 4.30: Phonon dispersion curves of CaTiO_3 in the cubic $Pm\bar{3}m$ phase at 0 K, with atomic participation highlighted by color: Ca (blue), Ti (green), and O (red). Imaginary frequencies appear at the Γ point, corresponding to a polar instability involving Ca and Ti displacement against O, at the X point, corresponding to antipolar motion of Ca and O along one direction, at the M point, corresponding to in-phase rotation of oxygen octahedra and at R corresponding to out-of-phase oxygen octahedra rotation. The atomic displacement patterns associated with each unstable mode are illustrated below the dispersion curves.

system based on a Landau-type analysis [221]. Furthermore, temperature-dependent structural measurements by Yashima and Ali [217, 222] suggested that CaTiO_3 may transform directly from $Pbnm$ to $I4/mcm$ without any intermediate phase. Overall, there is currently no consensus on the full temperature-dependent phase transition sequence of CaTiO_3 , making further theoretical investigations timely.

Despite its apparently simple non-polar character, CaTiO_3 conceals a rich and subtle physics. The $Pbnm$ ground state contains antipolar displacements of the Ca cation induced by a trilinear coupling with the in-phase and antiphase oxygen octahedra rotations through the hybrid-improper mechanism [223]. Although the dominant octahedra rotations and antipolar Ca displacements suppress the polar instability in the $Pbnm$ phase, CaTiO_3 remains an incipient ferroelectric [224] and small perturbations such as epitaxial strain are sufficient to stabilize a ferroelectric phase [225], as will be discussed in Chapter 7. This delicate balance between oxygen octahedra rotations and polar degrees of freedom makes CaTiO_3 particularly demanding to capture within a second-principles model based on Taylor-expansion. The large amplitudes of the oxygen octahedra rotation distortions place the system far from the cubic reference structure, challenging the convergence of the polynomial expansion. Moreover, the large number of unstable modes in the cubic reference structure gives rise to a rich landscape of metastable phases, imposing stringent requirements on the coverage of the potential energy surface during the construction of the model. Furthermore, the phase transition sequence upon heating remains debated, so the model must be validated against a rich set of metastable phases whose correct energetic ordering is not fully experimentally established. Finally, as pointed out above, although CaTiO_3 is nominally non-polar in its $Pbnm$ ground state, it sits close to a ferroelectric instability, such that small perturbations are sufficient to stabilize a polar phase; the model must therefore reproduce the energetics of the relevant ferroelectric phases with sufficient fidelity.

An initial second-principles model of CaTiO_3 was previously developed during the PhD work of MM. Schmitt [226]. However, significant developments of the MULTIBINIT software during the course of this thesis, in particular in the treatment of anharmonic terms and the fitting procedures, motivated a re-examination of this model. In collaboration with H. Zhang,

the anharmonic part of the potential was therefore re-fitted using the updated implementation, while the harmonic terms and the overall structure of the model were preserved. The original validation tests were systematically reproduced to ensure consistency with the previous version. The model presented here should therefore be viewed as an updated and internally consistent version of the original Schmitt model, benefiting from methodological improvements in the fitting procedure rather than representing a fundamentally new construction.

Harmonic interactions – The harmonic part of the model was obtained from DFPT calculations performed with the ABINIT software package [122], using the GGA with the Wu-Cohen exchange-correlation functional [227], which has been shown to provide excellent results for CaTiO_3 [228]. Optimized norm-conserving pseudopotentials [156] generated with the Wu-Cohen functional were employed, treating Ca $3s^2 3p^6 4s^2$, Ti $3s^2 3p^6 3d^2 4s^2$, and O $2s^2 2p^4$ electrons as valence states. A plane-wave energy cutoff of 40 Ha was adopted, together with a $8 \times 8 \times 8$ Γ -centered Monkhorst-Pack [157] k -point mesh for the five-atom cubic unit cell. The dynamical matrices were computed on a $8 \times 8 \times 8$ q -point mesh for the relaxed cubic $Pm\bar{3}m$ phase. In addition to the interatomic force constants, the DFPT calculations provided the dielectric constant, Born effective charges, elastic constants, and strain-phonon coupling coefficients, the latter vanishing identically by symmetry in the cubic reference structure. The dielectric constant and Born effective charges are used to construct the long-range dipole-dipole interaction, while the elastic constants enter the harmonic description of the strain degrees of freedom.

Training set generation – The training set for CaTiO_3 was constructed prior to the development of the systematic procedure described in Section 4.1, following an earlier and more computationally intensive approach [121]. As a first step, the unstable modes of the cubic reference structure were condensed systematically to identify the relevant local minima. The resulting phases, summarized in Table 4.11, span a wide range of structural distortions, from purely antiferrodistortive phases such as $I4/mcm$, $Cmcm$, and $Imma$, to the $Pbnm$ ground state combining rotations and antipolar

displacements, as well as purely polar phases such as $P4mm$, $Amm2$, and $R3m$ lying at much higher energies. *Ab initio* molecular dynamics simulations were then performed to explore the dynamical distortions of the material from first principles. However, this approach alone proved insufficient to adequately cover the full energy landscape: the high-energy purely polar phases are almost never spontaneously visited during such simulations, given the large energy barriers separating them from the ground state. The potential energy surface was therefore additionally sampled through linear interpolations between the various stationary phases, with the lattice parameters relaxed along each interpolation path to provide information on strain-phonon couplings. The energies, forces, and stresses of all configurations were computed at the *ab initio* level on $2 \times 2 \times 2$ supercells of the cubic reference structure. The final training set comprises 5325 *ab initio* configurations.

Table 4.11: Structure and energy of various metastable phases of CaTiO_3 designated by their space group, as relaxed in DFT. Lattice parameters are in Å (in the primitive cell) and energies ΔE are in meV/f.u. with respect to the five-atom cubic reference structure.

Space group	ΔE	a (Å)	b (Å)	c (Å)
$Pm\bar{3}m$	0.0	3.863	3.863	3.863
$R3m$	-42.0	5.422	5.422	6.751
$Amm2$	-48.4	3.821	5.423	5.545
$P4mm$	-72.1	3.803	3.803	4.018
$P4/mbm$	-224.2	5.338	5.338	3.882
$Pmc2_1$	-238.0	3.842	5.383	5.410
$I4/mcm$	-261.1	5.336	5.336	7.750
$R\bar{3}c$	-280.3	5.405	5.405	13.122
$Cmcm$	-291.6	7.564	7.643	7.635
$Imma$	-296.2	5.401	7.566	5.407
$R3c$	-303.3	5.395	5.395	13.313
$Pbnm$	-355.3	5.433	7.587	5.333

Generation of the interatomic potential – With the training set in hand, the next step consists in constructing an interatomic potential capable of reproducing the first-principles data it contains. SATs up to third and fourth order were generated using a cutoff radius equal to the cubic lattice parameter. A selection of 60 anharmonic SATs was identified through goal-function minimization, with the first 30 terms having Ca as the common atom and the subsequent 30 terms having Ti as the common atom. The bounding procedure described in Section 3.2.5 was then applied to ensure that the model energy remains bounded from below at large atomic

displacements. This step proved essential for CaTiO_3 : the unbounded 60-term model frequently encountered divergences during finite-temperature simulations. Bounding terms were added automatically, introducing 179 additional SATs into the model, without significantly deteriorating the quality of the fit. The final model thus comprises 239 anharmonic SATs in total. As illustrated in Figure 4.31, the bounded model achieves an acceptable linear agreement with DFT energies ($R^2 = 0.966$).

Validation of the model – To verify to which extent the model successfully captures the important metastable phases, structural relaxations has been performed and compared the resulting energies and lattice distortions with those calculated by DFT relaxations. As illustrated in Figure 4.32 (a), while the model slightly overstabilizes the energy of some phases, it successfully reproduces the correct energetic order.

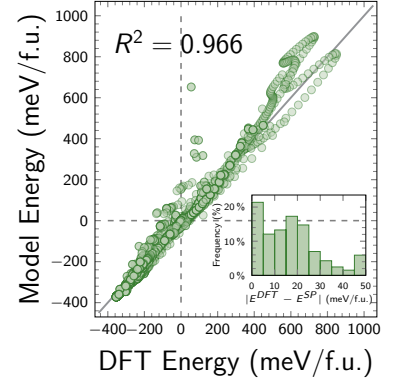


Figure 4.31: Comparison between the bounded model and DFT energies for the configurations contained in the training set of CaTiO_3 . The solid line indicates perfect agreement between the model and DFT. Energies are reported relative to the cubic reference structure.

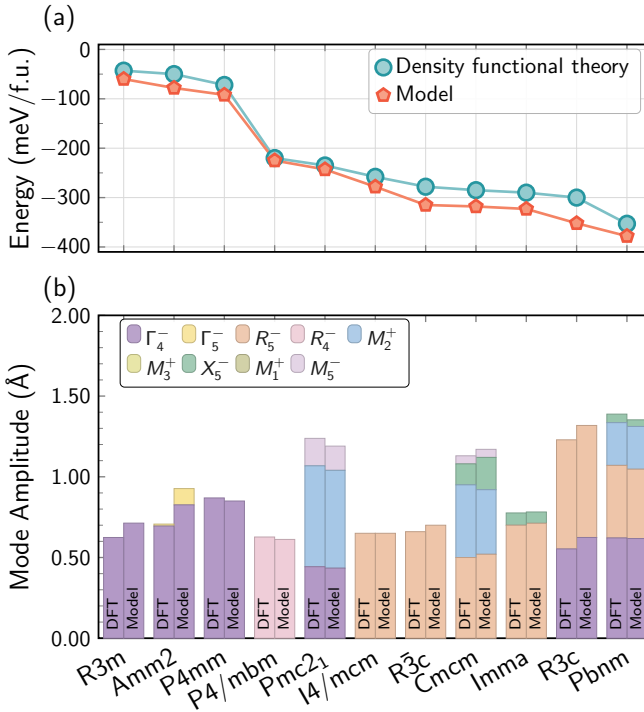


Figure 4.32: Comparisons of (a) energy, (b) lattice distortion modes and of different phases of CaTiO_3 between DFT and model-based structural relaxations. The symmetry-adapted lattice distortion modes and strain modes were analyzed with ISODISTORT [198]. The amplitudes of the lattice distortion modes are reported in the so-called “parent-cell-normalized” values.

In Figure 4.32 (b), the symmetry-adapted modes condensed [198] in different distorted phases are compared between DFT

and model-based structural relaxations. All lattice distortion modes appearing in the DFT-relaxed structures also appear in the model-relaxed structures, with comparable mode amplitudes in both cases. These results indicate that the key stationary points on the potential energy surface are well captured by the model.

The phonon dispersion curves and density of states were computed in the *Pbnm* ground state and the *R3c* metastable phase using finite differences with PHONOPY [170] and compared against DFPT, as shown in Figure 4.33. The model accurately reproduces the phonon dispersions of these strongly distorted phases, confirming that the curvature of the potential energy surface is well captured in the vicinity of the relevant stationary points.

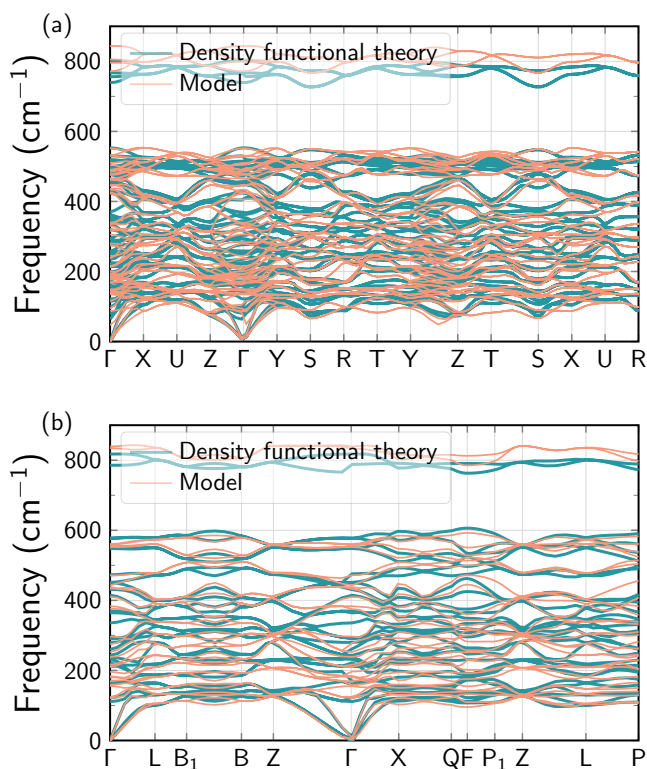


Figure 4.33: Comparisons of phonon dispersions and phonon density of states between DFPT and the model-based finite-difference calculations for (a) the *Pbnm* ground state and (b) the *R3c* metastable phase.

Finite temperature simulations – The validated model is now applied to investigate the temperature-dependent phase transitions of CaTiO₃. HMC simulations were performed in a 16×16×16 supercell, starting from the low-temperature *Pbnm*

ground state and progressively heating until the system becomes cubic. Throughout the heating process, the system stays non-polar. To monitor structural phase transitions, the evolution of octahedra rotations and lattice parameters as functions of temperature has been tracked.

The finite-temperature simulations show that the system remains in the $Pbnm$ phase at low temperatures, characterized by the $a^-a^-c^+$ rotation pattern and the lattice parameters $a = b > c$ (Figure 4.34 (a) and (b)). As the temperature increases, several phase transitions can be observed, as indicated by the changes in octahedra rotation pattern and lattice parameters. In addition, the volume of the unit cell shows rapid increases near the phase transitions, resulting in peaks in lattice dilation curve (Figure 4.34 (c)). The phase transition temperatures are estimated by these peaks in the lattice dilation curve.

Upon heating from the low-temperature $Pbnm$ phase, the first phase transition occurs around 1200 K, where the in-phase rotation ϕ_z^+ exhibits a sudden reduction and the antiphase rotations ϕ_x^- and ϕ_y^- are almost unchanged. Above this temperature, the antiphase rotations ϕ_x^- and ϕ_y^- have slightly different amplitudes, suggesting that the phase above the first transition can be identified as the $C2/m$ with $a^-b^-c^0$ rotation pattern. This $C2/m$ phase is very similar to the $Imma$ ($a^-a^-c^0$) phase suggested by Carpenter [221]; the main difference lies in the amplitudes of the antiphase rotations about the two pseudocubic axes, which are equal in the $Imma$ phase but unequal in the $C2/m$ phase.

With the temperature further increasing, the next phase transition occurs around 1550 K, where ϕ_y^- rapidly decreases and ϕ_x^- slightly increases. Above this temperature, only ϕ_x^- has a significant amplitude, indicating that the phase is $I4/mcm$ with $a^-c^0c^0$ rotation pattern. Finally, around 1900 K, the amplitude of the last rotation ϕ_x^- decreases toward zero, indicating that the system changes to the cubic $Pm\bar{3}m$ phase. Therefore, the finite-temperature simulation suggests a phase transition sequence for CaTiO_3 : $Pbnm$ ($a^-a^-c^+$) $\rightarrow$ $C2/m$ ($a^-b^-c^0$) $\rightarrow$ $I4/mcm$ ($a^-c^0c^0$) $\rightarrow$ $Pm\bar{3}m$ ($a^0a^0a^0$), where the octahedra rotations about the three pseudocubic axes disappear progressively.

The evolution of octahedra rotations with temperature is further illustrated in Figure 4.35, where the three-dimensional distributions of local oxygen octahedra rotations in the $16 \times$

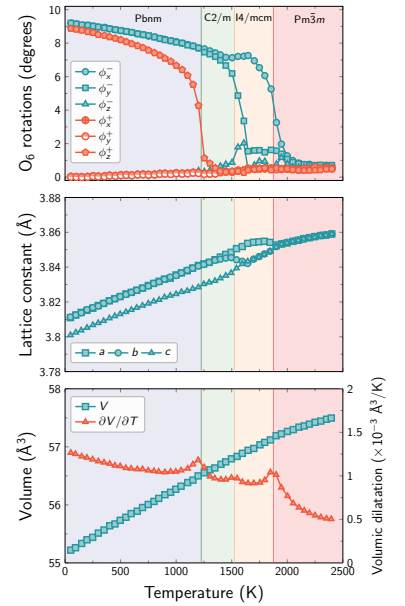


Figure 4.34: Structural phase transitions during the heating process from the $Pbnm$ ground state. (a) Oxygen octahedra rotations, (b) pseudocubic lattice parameters, and (c) unit cell volume and lattice dilation as functions of temperature. The simulation is performed in a $16 \times 16 \times 16$ super-cell using the second-principles model of CaTiO_3 .

16×16 simulation supercell are depicted. The rotations of the local oxygen octahedra are characterized using ϕ_x , ϕ_y , ϕ_z as defined by

$$\phi_x = \omega_x(-1)^{i_y+i_z}, \quad \phi_y = \omega_y(-1)^{i_z+i_x}, \quad \phi_z = \omega_z(-1)^{i_x+i_y}, \quad (4.4)$$

where ω_x , ω_y , ω_z is the rotation angle around the pseudocubic [100], [010], and [001] directions, respectively, and i_x , i_y , i_z are integers that indicate the position of the local oxygen octahedra in the directions of the three pseudocubic axes. As shown in Figure 4.35, at low temperatures (e.g., 100 K), ϕ_x and ϕ_y alternate between positive and negative values, indicating that the rotations around the pseudocubic [100] and [010] axes are antiphase. In contrast, ϕ_z does not change its sign throughout the supercell, indicating that the rotations around the pseudocubic [001] axis are in-phase. This is consistent with the $a^-a^-c^+$ rotation pattern in the low-temperature $Pbnm$ phase. As the temperature increases, the octahedra rotations around the three pseudocubic axes progressively diminish: first, the in-phase rotations around the pseudocubic [001] axis disappear, followed by the disappearance of antiphase rotations around the pseudocubic [010] axis, and then the [100] axis. Additionally, above those transition temperatures, local octahedra rotations with small amplitude persist and exhibit a layered-correlation feature. This layered-correlation feature of octahedra rotations is related to the geometric connectivity of the octahedra in the perovskite structure, which imparts strong correlation of octahedra rotations within the plane perpendicular to the rotation axis and weak correlation of the octahedra rotations between adjacent planes. As outlined at the beginning of this section, there is general consensus from experiments on the low-temperature $Pbnm$ phase, and the high-temperature $I4/mcm$ and $Pm\bar{3}m$ phases, while the potential intermediate phase between the $Pbnm$ and $I4/mcm$ phases is still under debate. The model-based simulations are consistent with experiments with regard to the $Pbnm$, $I4/mcm$, and $Pm\bar{3}m$ phases, and predicts an intermediate $C2/m$ phase between the $Pbnm$ and $I4/mcm$ phases. For comparison with experimental values, the model predicts the model predicts the disappearance of in-phase and antiphase octahedra rotations at approximately 1200 K (where the transition $Pbnm$ ($a^-a^-c^+$) $\rightarrow$ $C2/m$ ($a^-b^-c^0$) occurs) and 1900 K (where the transition $I4/mcm$ ($a^-c^0c^0$) $\rightarrow$ $Pm\bar{3}m$ ($a^0a^0a^0$) occurs), respectively. In comparison, x-ray and neutron diffrac-

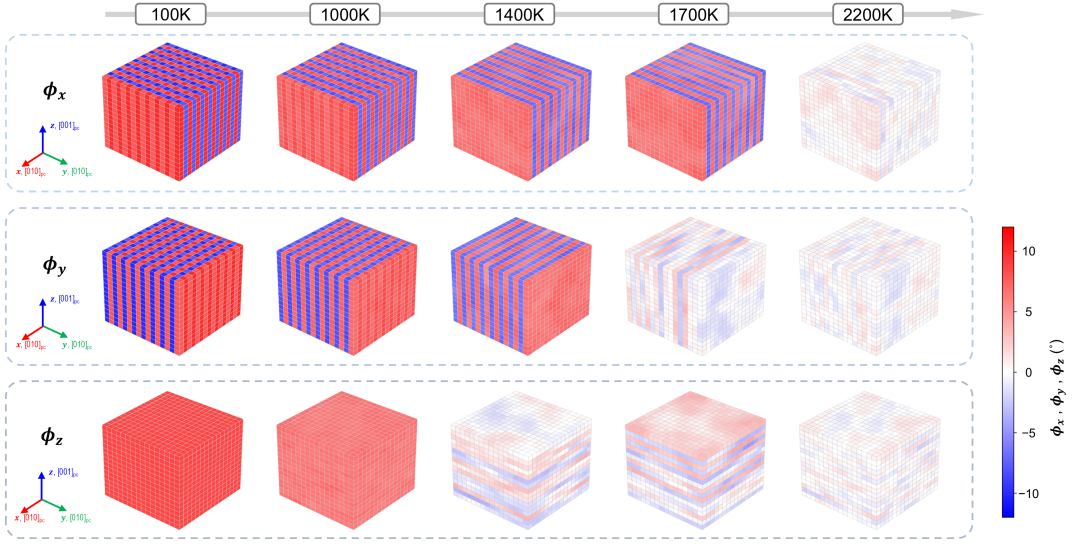


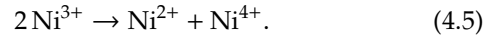
Figure 4.35: Evolution of octahedra rotations during the heating process from the $Pbnm$ ground state in CaTiO_3 . The intensity of the colors represents the amplitude of ϕ_x , ϕ_y , and ϕ_z defined by Eq. (4.4), with red and blue indicating opposite signs.

tion experiments [217, 218, 222] show that superlattice reflections associated with in-phase octahedra rotations vanish around 1500 K, while those related to antiphase rotations disappear around 1600 K. Therefore, the model appears to underestimate the temperature at which in-phase octahedra rotations vanish and overestimate the temperature at which antiphase rotations disappear.

The second-principles model for CaTiO_3 constructed in this section is made publicly available and can be retrieved following Ref. [229]. It constitutes the primary atomistic tool employed in Chapter 7 of this thesis, where it is applied to investigate the finite-temperature properties and the hidden ferroelectric $R3c$ phase of bulk CaTiO_3 [230], as well as the first-order polarization process arising in CaTiO_3 thin films grown on NdGaO_3 substrates [231]. The model was also employed to study the tuning of the CaTiO_3 energy landscape into that of antiferroelectric PbZrO_3 [232], though the results of that work fall outside the scope of the present thesis.

4.3.6 Yttrium Nickelate

RNiO_3 ($R = \text{Pr-Lu, Y}$) perovskites are well known to exhibit a metal-to-insulator transition (MIT) upon cooling, accompanied by a structural transition from the orthorhombic $Pbnm$ phase to the monoclinic $P2_1/n$ phase [233]. The critical temperature of this MIT (T_{MIT}) depends strongly on the tolerance factor t of the system, and decreases as t increases. The structural transition across the MIT is accompanied by a breathing distortion of the NiO_6 octahedra, which expand and contract according to a rock-salt pattern. This gives rise to two inequivalent Ni sites, with long and short Ni-O bonds, often described as a charge ordering of the nominal form [233]



The origin of the MIT in RNiO_3 has long been debated. It was initially interpreted as an electronic instability, of either charge-disproportionation or Mott type, driven primarily by on-site electronic correlations. Mercy and co-workers proposed instead that the transition is structurally triggered [234]. In the cubic reference structure, the breathing mode of the oxygen octahedra is stable and, in fact, the stiffest mode of the system; its energy curvature is, however, progressively renormalized by the oxygen octahedra rotations through a cooperative biquadratic coupling. When the rotations reach a critical amplitude, the breathing mode becomes unstable and condenses, opening a gap. The MIT thus takes the form of a Peierls instability that is not present in the cubic phase but is triggered by the oxygen octahedra rotations. The same work showed that this mechanism is generic across the RNiO_3 series and that an effective Landau theory correctly captures the evolution of T_{MIT} with the tolerance factor. The softening of the breathing mode has, however, not yet been observed experimentally, which raises questions about the continuous character of the structural change across the MIT. One possibility is the involvement of Raman-active modes coupling the oxygen octahedra rotations and the breathing distortion, which would render the transition more complex; a similar mechanism was recently proposed for NdNiO_3 by Gomes and co-workers [235].

In addition to the MIT, RNiO_3 compounds exhibit, upon further cooling, a magnetic transition from a paramagnetic state to an E-type antiferromagnetic order, characterized by an

up-up-down-down spin arrangement at the in-plane Ni sites. For compounds with smaller tolerance factor, the magnetic transition temperature T_N lies well below T_{MIT} , and the two transitions are decoupled. From NdNiO_3 onwards, however, T_{MIT} and T_N become entangled and coincide: for these large-cation compounds, the oxygen octahedra rotations alone are no longer sufficient to trigger the MIT, and the onset of the antiferromagnetic order assists the transition, which becomes first order [234].

Among the RNiO_3 family, YNiO_3 is of particular interest, as it exhibits a high T_{MIT} of approximately 600 K [233], while its magnetic transition occurs at a much lower temperature of approximately 150 K [234]. This large separation between the two transition temperatures allows the MIT to take place entirely within the paramagnetic regime, in the absence of long-range magnetic order. A further computational advantage of YNiO_3 is the absence of partially filled f -states, which would otherwise introduce additional complexity and computational cost.

Unlike the second-principles models presented in the previous sections, the model for YNiO_3 is constructed within the MLIP framework using the DEEPMD approach introduced in Section 3.2. In this framework, no reference structure is required, and the harmonic and anharmonic parts of the interaction are not distinguished: the potential energy surface is learned directly from a set of *ab initio* configurations through a neural network representation of the atomic interactions. The construction of the model therefore reduces to the generation of a representative training set and the optimization of the network parameters, as described below.

Training set generation – DFT calculations were performed using the DFT+ U approach with the LDA exchange-correlation functional as implemented in the ABINIT software package [122]. An on-site Coulomb repulsion was applied to the Ni 3d orbitals, with $U = 2.5$ eV and $J = 0$ eV. A plane-wave energy cutoff of 24 Ha was adopted, together with a $12 \times 12 \times 8$ Γ -centered Monkhorst-Pack [157] k -point mesh for the 20-atom unit cell, corresponding to a $\sqrt{2} \times \sqrt{2} \times 2$ supercell of the five-atom cubic $Pm\bar{3}m$ phase. Calculations on larger supercells of 40 and 160 atoms were additionally carried out for the construction of the training set, with the k -point mesh adapted accordingly to maintain a comparable

sampling density of the Brillouin zone. In all calculations, a ferromagnetic alignment of the Ni magnetic moments was imposed.

The key structural ingredients governing the properties of YNiO_3 are the oxygen octahedra rotations and the breathing distortion of the NiO_6 octahedra. Although the breathing mode appears as an unstable phonon in the $Pbnm$ structure, it corresponds to a high-frequency stable mode in the cubic $Pm\bar{3}m$ reference, and is progressively softened by the introduction of the oxygen octahedra rotation, as demonstrated by Mercy and co-workers [234] through the so-called triggering mechanism. These two degrees of freedom therefore constitute the minimal set of ingredients required to correctly describe both the ground state and the structural transition of YNiO_3 .

The training set was constructed with this physical picture in mind. The primary contribution consists of structures in which the breathing distortion amplitude is systematically varied at different oxygen octahedra rotation amplitudes, so as to map the coupling between these two key degrees of freedom across the relevant region of the potential energy surface. Additional phases beyond $Pbnm$ and $P2_1/n$ were also included, namely $Imma$ ($a^-a^-c^0$), $P4/mbm$ ($a^0a^0c^+$), and the cubic $Pm\bar{3}m$ ($a^0a^0a^0$) reference, together with interpolated and extrapolated structures between them. Finally, configurations with random strain and atomic displacement noise were added to ensure adequate coverage of the potential energy surface in the vicinity of each minimum. The final training set comprises approximately 2100 *ab initio* configurations.

Generation of the interatomic potential – The interatomic potential for YNiO_3 was constructed using the DEEPM-D-KIT software [127], employing the Deep Potential Smooth Edition descriptor, referred to as `se_e2_a`. In this descriptor, the atomic environment of each atom is encoded through an embedding network whose input consists of pairwise interatomic distances, while both radial and angular information of the neighboring environment are captured through the construction of a descriptor matrix combining the embedding outputs along all pair directions as detailed in Eq.(3.79). The resulting descriptor is by construction invariant under translation, rotation, and permutation of atoms of the same species. Interactions are restricted to neighbors within a cutoff

radius of 7.0 Å, with a smooth inner onset at 1.5 Å to avoid short-range singularities and a smooth decay to zero at the outer cutoff of 7.0 Å. The embedding network consists of three layers with 25, 50, and 100 neurons respectively, with an axis neuron dimension of 12, while the fitting network comprises three hidden layers of 240 neurons each with residual connections. All activation functions are hyperbolic tangents. The model was trained for 10^6 steps on a dataset comprising configurations from supercells of 20, 40, and 160 atoms, including dedicated configurations sampling the triggering mechanism between octahedra rotations and the breathing distortion. The loss function weights were set to progressively increase the contribution of energies relative to forces over the course of training, starting from a force-dominated regime with prefactors of 1000 on forces and 0.02 on energies, and converging to equal weights of 1 for both. The learning rate followed an exponential decay from 10^{-3} to 7.7×10^{-5} .

Validation of the model – The validation of the model follows the three-step procedure outlined in Section 4.2. The training set and test set reproductions are presented in Figure 4.36.

The model achieves excellent fit quality on the training set, with $R^2 = 0.99995$, and maintains high accuracy on the independent test set, with $R^2 = 0.9998$, confirming the predictive character of the interatomic potential on configurations not included during training.

The two experimentally observed phases, $Pbnm$ and $P2_1/n$, are then relaxed using the BFGS algorithm and compared against DFT. As reported in Table 4.12, the model accurately reproduces both the lattice parameters and the relative energetics of the two phases. The energy difference between $Pbnm$ and $P2_1/n$ is reproduced to within 0.17 meV/f.u., and the lattice parameters agree with DFT to within 0.01 Å for all axes. The monoclinic distortion angle β of the $P2_1/n$ phase is also recovered with high fidelity.

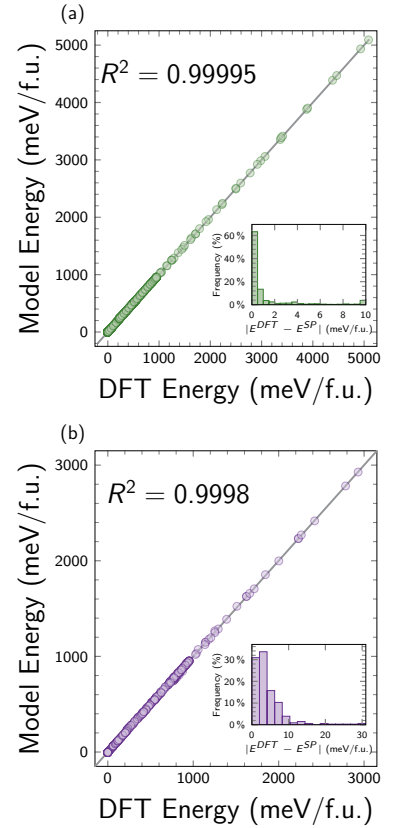


Figure 4.36: Model versus DFT energies for the structures contained in the (a) training set (b) test set of $YNiO_3$. The insets show the distribution of the absolute error in both cases.

Table 4.12: Comparison of the relaxed lattice parameters of the $Pbnm$ and $P2_1/n$ structures obtained from DFT and from the model in YNiO_3 .

	$Pbnm$		$P2_1/n$	
	DFT	Model	DFT	Model
ΔE (meV/f.u.)	9.9	9.73	0.0	0.0
a (Å)	5.0753	5.0756	5.0786	5.0793
b (Å)	5.4404	5.4345	5.4267	5.4249
c (Å)	7.2724	7.2754	7.2912	7.2878
β (deg.)	90	90	90.104	90.104

The distortion amplitudes of the two phases, projected onto the symmetry-adapted modes [198] of the cubic $Pm\bar{3}m$ reference, are compared in Figure 4.37. The model correctly captures the relative weights of the dominant R_5^- out-of-phase oxygen octahedra rotation mode and the M_2^+ in-phase oxygen octahedra rotation mode, as well as the secondary modes present in the $P2_1/n$ ground state such as the breathing R_2^- mode responsible for the metal-to-insulator transition [234].

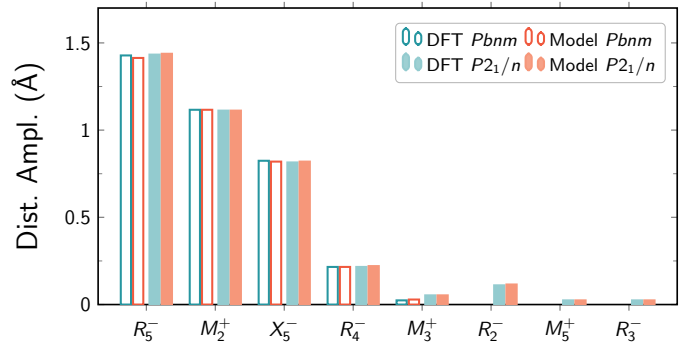


Figure 4.37: Comparison of the distortion amplitudes for the $Pbnm$ and $P2_1/n$ phases of YNiO_3 , projected onto the symmetry modes of the cubic $Pm\bar{3}m$ reference structure, as obtained from DFT and from the model.

Finally, the phonon dispersion curves of both the $Pbnm$ and $P2_1/n$ phases are compared against DFPT calculations in Figure 4.38. The model reproduces the overall phonon band structure of the $Pbnm$ phase with good accuracy across the entire Brillouin zone, correctly capturing both the acoustic branches and the distribution of optical modes up to 600 cm^{-1} . Crucially, the imaginary frequency at the Γ point of the $Pbnm$ phase, associated with the breathing distortion of the NiO_6 octahedra and responsible for the structural transition toward the $P2_1/n$ ground state, is accurately reproduced by the model. For the $P2_1/n$ ground state, the absence of any imaginary frequency in the model-based dispersion confirms that the breathing distortion is correctly stabilized,

in agreement with the DFT result. The overall agreement between model and DFT phonon dispersions in both phases validates the ability of the potential to describe the lattice dynamics of YNiO_3 in the thermodynamically relevant region of its energy landscape.

4.3.7 Lead zirconate

A second-principles model for PbZrO_3 was also developed within the group, based on the MLIP framework using the DEEPMD approach [143]. In that work, the model was employed to investigate the finite-temperature properties of antiferroelectric PbZrO_3 , including its structural phase transition and dielectric response. The model was subsequently used by collaborators to study the topology of ferroelastic domain walls in PbZrO_3 single crystals, where second-principles atomistic simulations revealed the existence of vortices and antivortices at 90° twin boundaries [236]. As the results obtained with this model fall outside the scope of the present work, the model is not discussed further.

The MLIP model for YNiO_3 constructed in this section will be made publicly available upon publication. It constitutes the primary atomistic tool employed in Chapter 8 of this thesis.

4.4 Role of long-range dipolar interactions

The second-principles and MLIP models presented in the previous sections have demonstrated their ability to reproduce the properties of polar and functional oxides with near-first-principles accuracy. However, a fundamental difference exists between these two classes of models in the way electrostatic interactions are treated. In second-principles models built within the MULTIBINIT framework, the long-range part of the dipole-dipole interactions is incorporated analytically through the Born effective charges and the dielectric tensor, as discussed in Section 3.2.5. In contrast, MLIP models such as DEEPMD [127] rely on the nearsightedness of interatomic interactions and neglect, by construction, any contribution

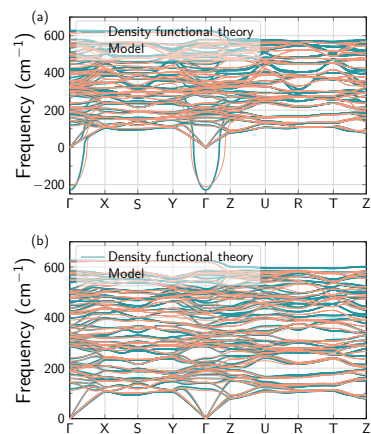


Figure 4.38: Comparisons of phonon dispersion curves between DFPT and the model-based finite-difference calculations for (a) the $Pbnm$ phase and (b) the $P2_1/n$ ground state in YNiO_3 .

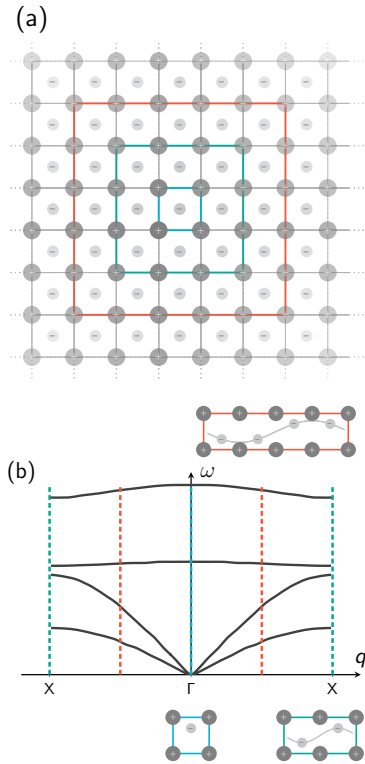


Figure 4.39: (a) Two-dimensional diatomic lattice composed of oppositely charged ions arranged on a bipartite square lattice. The primitive unit cell (blue) and a larger supercell (red) are indicated. Dark and light spheres represent ions of opposite charge. (b) Phonon dispersion relation $\omega(q)$ along the high-symmetry path $\Gamma-X-\Gamma-X$ of the Brillouin zone. The presence of two atoms per unit cell gives rise to acoustic and optical branches. Insets illustrate the corresponding eigenmodes at selected q -points.

beyond the cutoff radius defined by the training set. In practice, most MLIP models are trained on $2 \times 2 \times 2$ supercells, which limits the effective interaction range to approximately two unit cells. While non-dipolar short-range interactions are expected to decay exponentially fast beyond this range, dipole-dipole interactions are long-ranged and decay only as $1/r^3$, raising the question of whether their truncation at the scale of the training supercell introduces significant errors in the description of polar materials.

This question is particularly relevant in the context of longitudinal optical (LO) phonon modes, whose macroscopic electric field originates precisely from the long-range part of the dipole-dipole interactions and gives rise to the characteristic LO-TO splitting. When this contribution is absent from the model, the LO branches near the Γ point may be incorrectly described, potentially introducing artifacts in the phonon dispersion curves and in the energetics of specific atomic displacement patterns. At the same time, it is not *a priori* clear to what extent such artifacts affect macroscopic properties such as phase diagrams or ferroelectric switching, which are governed by the transverse optical (TO) instability and may remain well captured even within a purely short-range model.

As already detailed in Section 3.2.5 and illustrated in Figure 3.15, the DD contribution to the total IFC is evaluated analytically from the Born effective charges and the optical dielectric tensor, and extends from nearest neighbors to infinite range. It is subtracted from the total IFC to yield the remaining SR contribution, whose range is limited to that of the supercell defined by the q -point grid used in the DFPT calculation. In practice, and as illustrated in Figure 4.39, a second-principles model trained on a $2 \times 2 \times 2$ supercell therefore captures short-range interactions up to two unit cells, while the dipole-dipole correction, when activated, extends these to infinite range. This dual control, which consists in adjusting the q -point grid while toggling the analytical dipole-dipole term, allows one to systematically modulate the effective interaction range of the model and to isolate the specific contribution of long-range dipolar interactions to the material properties. Taking BaTiO_3 as a paradigmatic polar material is particularly relevant in this context, since its ferroelectric instability has historically been rationalized as a competition between short-range repulsions and long-range dipole-dipole interactions [188, 189]. One might therefore expect that truncating the long-range

part of the dipole-dipole interactions would significantly alter the description of the material. Three models are constructed and compared: M8+Dip, derived from an $8 \times 8 \times 8$ q -point mesh with analytical dipole-dipole correction and used as the reference; M2+Dip, derived from a $2 \times 2 \times 2$ mesh with analytical dipole-dipole correction; and M2, derived from a $2 \times 2 \times 2$ mesh without any dipole-dipole correction.

The influence of neglecting the long-range part of the dipole-dipole interactions on the phonon dispersion curves of BaTiO₃ is first examined. Figure 4.40 presents the phonon dispersion curves produced by the three models, each capturing a given range of interactions (arranged by rows), evaluated at different levels of resolution in the phonon band structure (arranged by columns). The resolution is varied by computing the phonon frequencies at q -points compatible with supercells of increasing size, which gives access to distortion patterns of progressively longer wavelength, not necessarily limited to the intrinsic interaction range of the model itself.

In the first column, a $2 \times 2 \times 2$ supercell is considered, which only gives access to distortion patterns associated with phonon modes at the high-symmetry points (Γ , X , ...) as schematized in Figure 4.40. The second column ($4 \times 4 \times 4$ supercell) extends this to additional intermediate points along the dispersion paths. Finally, the third column ($8 \times 8 \times 8$ supercell) further increases the number of points, offering a more detailed sampling of the phonon dispersion curves, and overlays a faint colored line representing the frequencies as predicted by the model in the infinite supercell limit.

By rows, each model is constructed using different q -point meshes for the calculation of the dynamical matrices, related to a specific range of interatomic force constants in real space. The first-row model (blue points) is derived using an $8 \times 8 \times 8$ q -point mesh, while the second-row (green points) and third-row (red points) models use a $2 \times 2 \times 2$ mesh. It is important to emphasize that, within this framework, the short-range part of the dipole-dipole interactions is inherently included up to the specified interaction range of each model. The long-range part is treated differently: it is incorporated analytically in the first two models, while the third model omits this contribution entirely. For reference, the solid blue line representing the phonon frequencies predicted by the M8+Dip model is superimposed on all panels; importantly, the long-range part of the dipole-dipole interactions is only

included in the plotted dispersion lines if the model itself accounts for this information.

Comparing M2+Dip with the reference M8+Dip first, only minor differences are observed in the phonon dispersion curves, in good agreement with the literature [237]. This suggests that beyond a range of two unit cells, the interactions are dominated by electrostatics while the short-range part nearly vanishes [238]. This observation is in line with the results of Ref. [237] where the inclusion of the point $\Lambda = (1/4, 1/4, 1/4)$ on top of the $2 \times 2 \times 2$ q -point mesh was anticipated to provide good convergence of the phonon curves.

When the long-range part of the dipole-dipole interactions is omitted (M2 model), the overall description of the phonon dispersion bands remains accurate. However, certain specific bands, particularly near the Γ point, are inadequately described, as evidenced by an extra unstable LO branch and an artificial degeneracy between the LO and TO modes of the topmost band at Γ . These discrepancies underscore the critical role of the long-range part of electrostatic interactions in accurately capturing the giant LO-TO splitting characteristic of BaTiO₃ [239, 240]. Including the long-range part of the dipole-dipole interactions corrects these inaccuracies, yielding a significantly improved representation of the phonon bands in this region. The remaining bands and the LO branches away from Γ are well described regardless of whether the long-range correction is included. Interestingly, the ferroelectric instability, intrinsic to TO modes, is very well captured even without the long-range part of electrostatic interactions. This demonstrates that the short-range part of the Coulomb interactions alone, limited to two unit cells, is sufficient to accurately describe this instability, and that in BaTiO₃, the long-range part of the Coulomb interaction does not play a significant role in its ferroelectric character. It is important to note, however, that the dipole-dipole interactions include both short-range and long-range parts, and that the competition between the so-called short-range and dipole-dipole interactions is already present in the interatomic force constants down to first neighbors [241]. The dominant contributions of the dipole-dipole interactions responsible for the ferroelectric instability are therefore already well captured within a $2 \times 2 \times 2$ supercell. This establishes that a BaTiO₃ model built with a $2 \times 2 \times 2$ training set, as is typical of MLIP approaches, will remain largely accurate

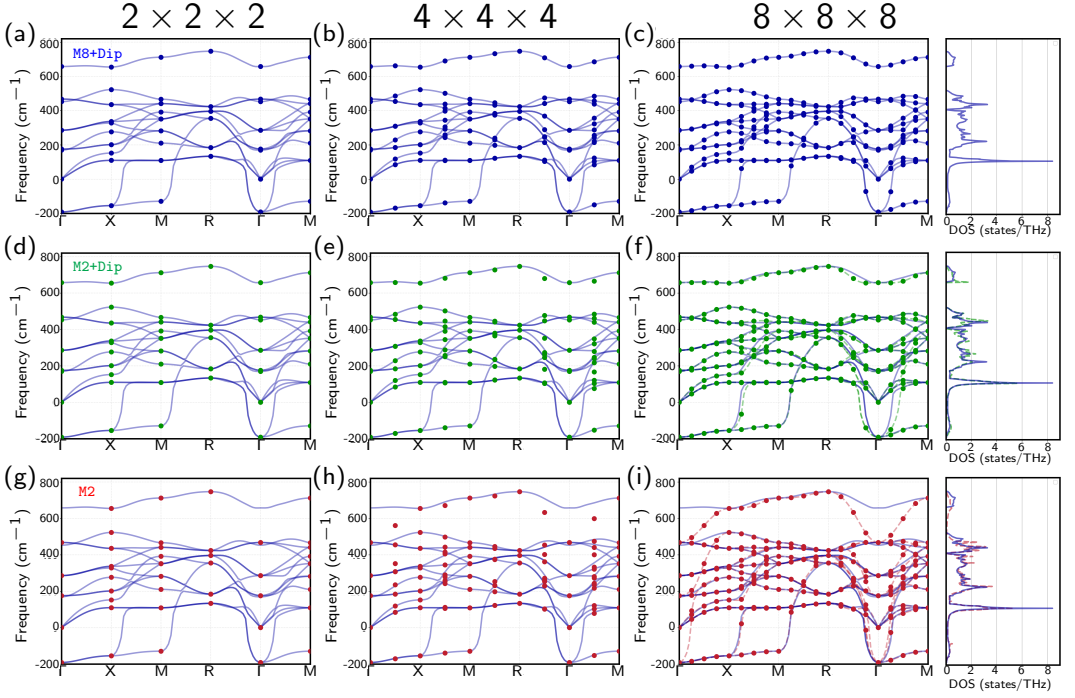


Figure 4.40: Phonon dispersion curves of BaTiO₃ obtained from three distinct models each capturing a specific range of interactions (8, 2 and 2 from top to bottom rows) with varying levels of resolution in the phonon band structure (2, 4 and 8 from left to right columns). The first two models (blue, green) include analytically the dipole-dipole interactions that extend to infinite range M8+Dip and M2+Dip, while the third (red) omits them M2. The solid blue line present in all panels represents the reference model (8×8×8 q -point mesh with analytic treatment of the dipolar interactions).

overall, with the ferroelectric instability and its chain-like character [240] preserved, except for the specific LO phonon branches near Γ . This discrepancy is unlikely to significantly impact phase transitions, as confirmed by the very similar phase transition sequence and hysteresis loops reproduced by the M2 and M8+Dip models shown in Figure 4.41 [143, 242, 243]. It must be noted, however, that this conclusion is material-dependent and the $2 \times 2 \times 2$ range cannot be taken for granted in general.

It is also worth noting that programs such as PHONOPY [170] can include the dipole-dipole correction at the postprocessing level on top of a M2-type model, thereby mimicking the phonon dispersion curves of the M2+Dip model. This is a common practice in the literature [143, 242, 243]. However, this correction is not present in the independent use of the model itself, creating the illusion that the model phonons correspond to those of M2+Dip, while in reality the model

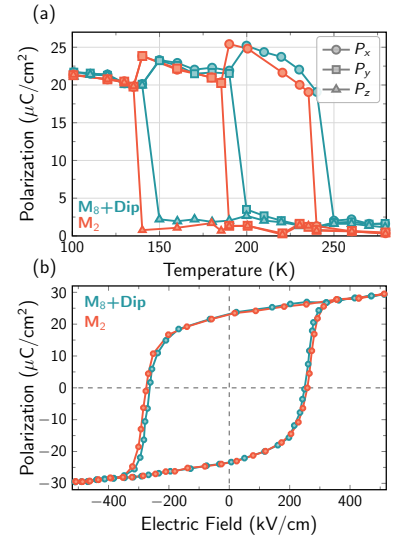


Figure 4.41: (a) Phase diagram of BaTiO₃, and (b) hysteresis loop of the $R3m$ phase at 50 K, reproduced using the M2 and M8+Dip models, as indicated in the legend. The supercell size used for the calculations was $12 \times 12 \times 12$.

operates at the M2 level during simulations.

A deeper analysis is conducted by focusing on the Γ -X branch of the phonon dispersion curve, which allows access to larger supercells. As shown in Figure 4.42, the extra unstable phonon branch predicted by the M2 model is confirmed to be an artifact arising from the absence of the long-range part of the dipole-dipole interactions: when these interactions are included, the branch stabilizes. Similarly, the high-frequency LO mode is significantly corrected, eliminating its near degeneracy with the TO mode near Γ . The remaining bands are reasonably well described in all cases. Several conclusions can be drawn at this

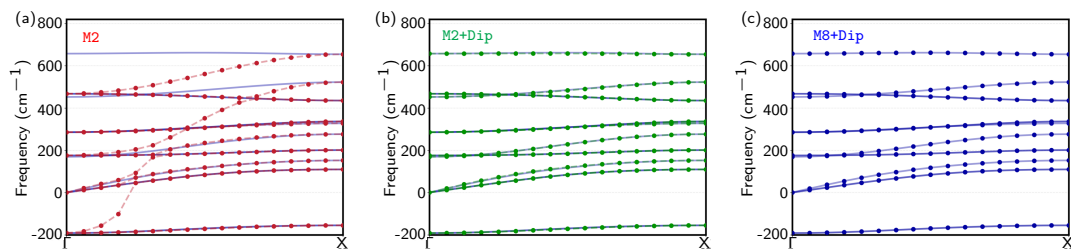


Figure 4.42: Phonon dispersion curves of BaTiO₃ along the Γ - X branch for the same three models as described in Figure 4.40. Blue lines correspond to the phonon dispersion curves computed with the reference model.

stage. First, neglecting the long-range part of the dipole-dipole interactions leads to significant inaccuracies in the description of LO modes, making their inclusion essential whenever these modes are involved in the material's distortions. Second, including these interactions not only improves accuracy but also speeds up convergence, allowing a good description of the phonon dispersion curves with a relatively coarse q -point grid. Third, a small interaction cutoff may be sufficient for a reasonable global description of the phonon dispersion curves, including the ferroelectric instability, which explains the success of MLIP methods even when trained on small supercells [242]. It must be kept in mind, however, that this interaction range is material dependent.

To further quantify the concrete deficiencies arising from the exclusion of the long-range dipole-dipole interactions, the spurious unstable LO phonon at $q = 1/20$ u.c.⁻¹ predicted by the M2 model is condensed onto a large supercell. As illustrated in Figure 4.43, the condensation of such a mode induces head-to-head and tail-to-tail domain configurations that remain metastable due to the incorrect description of the phonon branch. This polarization state is clearly unphys-

ical, as the divergence of the polarization generates bound charges that enormously increase the electrostatic energy of the system (see Eq. (2.22)). Similarly, condensing two such LO modes directed along x and y simultaneously stabilizes a lattice of center-convergent and center-divergent vortices, demonstrating that more complex polar configurations can also be affected by this spurious behavior. The energy lowering associated with these fake metastable phases is not negligible, reaching approximately 10 meV/f.u., comparable to that of the $Pmma$ phase (see Table 4.9). Properly including the long-range part of the dipole-dipole interactions stabilizes the problematic LO branch and suppresses these fake low-energy states: the original double-well potential is replaced by a steeply rising energy surface, preventing the formation of bound charges and restoring a physically correct description of the material.

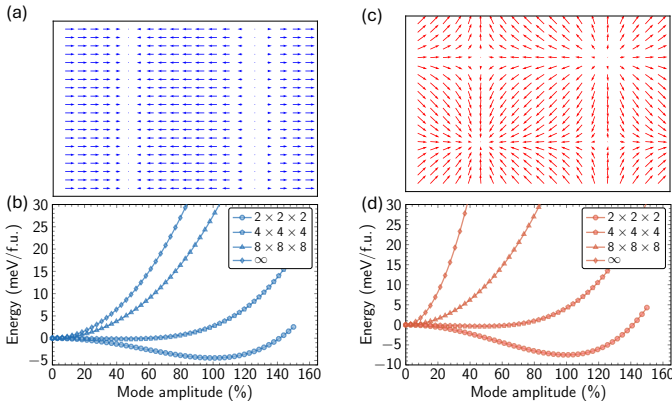


Figure 4.43: Polarization map resulting from the condensation of (a) one and (c) two LO phonon modes (directed along y and x) from the $\Gamma - X$ branch at $q = 1/20$ u.c.⁻¹ predicted by the model calculated using a $2 \times 2 \times 2$ q -point mesh and excluding the long-range part of the dipole-dipole interactions. (b,d) Energy landscapes as a function of the amplitude of the corresponding LO modes predicted by the models calculated using a $2 \times 2 \times 2$, $4 \times 4 \times 4$, $8 \times 8 \times 8$ q -point mesh without the long-range part and a $2 \times 2 \times 2$ with the long-range part of the dipole-dipole interactions as specified in the legend.

It is worth noting that the apparent minima observed when limiting the interaction range are in fact saddle points of the Born-Oppenheimer energy surface once full structural relaxation without symmetry constraints is allowed, as confirmed by finite-temperature simulations using the M2 model in which the associated configurations are found to be unstable and do not persist. This is consistent with the absence of such metastable phases in previous MLIP models restricted to short-range interactions. However, one cannot exclude the presence of spurious local minima in other materials, and at a minimum these results demonstrate that models limited to short-range interactions will significantly overstabilize head-to-head or tail-to-tail polar configurations, inevitably affecting phase competition in any context where such configurations are relevant.

In summary, as soon as longitudinal optical phonon modes are involved in the atomic displacements of the material under study, the proper treatment of the long-range part of the dipole-dipole interactions remains essential to correctly quantify the energetics. This becomes particularly relevant when studying topological textures, dynamics in large supercells, or thin films and superlattices where depolarizing fields play an important role.

4.5 Summary

This chapter has presented the construction and validation of second-principles and machine-learning interatomic potential models for a series of functional perovskite oxides, namely BaHfO_3 , SrTiO_3 , PbTiO_3 , BaTiO_3 , CaTiO_3 , and YNiO_3 , covering a broad range of physical behaviors from quantum paraelectricity and antiferrodistortive transitions to strongly first-order ferroelectricity and metal-insulator transitions.

For the second-principles models constructed within the MULTIBINIT framework, a common construction strategy has been followed: the harmonic part is obtained exactly from DFPT, the training set is built by systematically mapping the relevant regions of the potential energy surface, and the anharmonic part is determined by fitting to this set, followed by a bounding procedure to ensure stability at large distortions. Each model has been validated through a systematic three-step procedure involving training set reproduction, test set assessment, and comparison of structural and vibrational properties against DFT. The model for YNiO_3 demonstrates that this workflow can equally be adapted to the MLIP framework, here using the DEEPMD approach, while retaining the same validation standards.

Finally, the role of long-range dipole-dipole interactions has been examined systematically, using BaTiO_3 as a test case. It has been shown that their truncation, as is common in MLIP models trained on small supercells, leaves the ferroelectric instability largely unaffected but introduces spurious LO phonon branches that can stabilize unphysical head-to-head and tail-to-tail polar configurations. This result establishes a concrete limitation of short-range models for the study of topological textures and inhomogeneous polar configurations, and motivates the explicit treatment of long-range

electrostatics in the second-principles framework. All models presented in this chapter that have been the subject of a publication are made publicly available, and together constitute the primary atomistic tools employed in the subsequent chapters of this thesis.

Characterization of polar textures in perovskite oxides

5

5.1 Polar textures in bulk crystals

The background developed in Chapter 2 established that the polarization of a ferroelectric material is not necessarily uniform, and that a variety of inhomogeneous polar textures can emerge instead. Several mechanisms contribute to this. The multiplicity of energetically equivalent polar states allows the material to break up into domains separated by domain walls of different types, whose coexistence and combination can already give rise to non-trivial polar arrangements. On top of this, polarization and strain gradients, depolarizing fields, and epitaxial strain provide additional driving forces that further shape the resulting textures. This chapter is devoted to the characterization of such textures in perovskite oxides, with the aim of identifying the mechanisms that govern their internal structure and assessing how robust they are to their environment.

The chapter is organized around two complementary settings. The first part addresses polar textures in bulk crystals, where the absence of interfaces isolates their intrinsic properties. The case of 180° domain walls in PbTiO_3 is examined first, with particular attention to the in-plane Bloch component that develops at the wall center, to the ferroelectric-to-paraelectric transition occurring within the wall, and to the sensitivity of the Bloch component to mechanical boundary conditions. Because this Bloch component is itself ferroelectric, it can be manipulated and reversed, and serves as the building block for topological polar textures in tetragonal PbTiO_3 . The discussion then turns to the stabilization of skyrmion and antiskyrmion tubes that can be stabilized in rhombohedral BaTiO_3 and KNbO_3 . The second part addresses polar textures in $\text{PbTiO}_3/\text{SrTiO}_3$ heterostructures, where the confinement of the ferroelectric layer and the presence of interfaces introduce additional competing contributions. The question of whether the Bloch character of 180° domain walls persists in this geometry is examined first.

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Related publications

4. Physical Review X 14 (4), 041052
7. Physical Review B 111 (18), L180104
8. Journal of Applied Physics 138 (4)
10. Physical Review B 112 (14), 144101

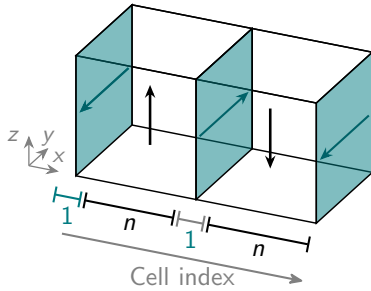


Figure 5.1: Schematic representation of the $(2n+2) \times 1 \times 1$ supercell used to model 180° ferroelectric domain walls in bulk PbTiO_3 . The black arrows indicate the orientation of the Ising polarization component P_z in each domain, pointing upward and downward in alternating halves of the supercell. The colored planes mark the positions of the two domain walls, each centered on a PbO plane and lying in the yz plane. The colored arrows indicate the Bloch polarization component P_y confined at the domain walls. The domain width is n unit cells on each side, with the domain wall itself occupying a single unit cell, as indicated by the cell index below.

5.1.1 Bloch domain wall in PbTiO_3

A domain wall separating two antiparallel polarization domains is classified according to the character of the polarization within the wall. In the Ising case, the polarization simply vanishes at the wall center with no in-plane component. When an in-plane component develops, the wall acquires a mixed character: it is termed Bloch if this component is oriented perpendicular to the domain wall normal, and Néel if it is oriented parallel to it [48], as introduced in Section 2.3.3. Early first-principles studies by Meyer and Vanderbilt [190] concluded that 180° domain walls in bulk PbTiO_3 were purely of Ising character, with no polarization component at the wall center. This picture was later revised by Wojdeł and Íñiguez [191], who proposed that the domain wall can develop a spontaneous ferroelectric component in the wall plane, with an amplitude of approximately 0.4 C/m^2 primarily driven by Pb displacements in the PbO plane, as illustrated in Figure 5.1. This in-plane component, now commonly referred to as the Bloch component, carries important physical consequences: it breaks the mirror symmetry of the domain wall and endows it with a chiral character, with direct implications for the emergence of topological polar textures in PbTiO_3 -based systems [194] detailed in Section 5.1.2.

Building on these findings, the work presented in this section reinvestigates 180° domain walls in bulk PbTiO_3 in greater depth, combining second-principles large-scale atomistic simulations [195] and first-principles calculations [244], with a particular focus on the ferroelectric-to-paraelectric transition occurring within the domain wall and on the sensitivity of the Bloch component to mechanical boundary conditions.

First-principles

Strain dependence of Bloch domain wall – The 180° stripe domain in bulk PbTiO_3 were first reinvestigated at the first-principles level using the same DFT parameters as for the construction of the PbTiO_3 model described in Section 4.3.3, with the k -point mesh adapted to the supercell dimensions. To this end, the five-atom unit cell was replicated 20 times along the $[100]$ direction, building a $20 \times 1 \times 1$ supercell of 100 atoms, as shown in Figure 5.1. The domain wall was centered on a PbO plane, which is the energetically preferred configuration with respect to the TiO_2 -centered alternative [190].

The bulk soft-mode distortion of the tetragonal phase was then superimposed on the atomic positions such that the polarization points upward in one half of the supercell and downward in the other. With this geometry, the domain wall lies in the yz plane, the Ising polarization within the domains points along z , the Bloch component at the wall lies along y , and the Néel component along x . At this point, it is important to emphasize that the systems studied in this section are bulk ferroelectrics without interfaces to dielectric or metallic layers that could give rise to bound surface charges. Besides, periodic boundary conditions are imposed in all three spatial directions. This enforces continuity of the normal component of the polarization and precludes the formation of surface charges, thereby eliminating any macroscopic depolarization field along z . In the absence of significant depolarization fields, the true ground state of the system is monodomain. The domain structures analyzed in this work should thus be viewed as metastable configurations, stabilized under the considered specific conditions.

The stability of the different domain wall configurations is characterized through three energy quantities. The Ising domain wall energy E_{DW}^{Ising} measures the energy cost of forming a 180° domain wall with no Néel or Bloch component with respect to the homogeneous ferroelectric phase, and is computed as

$$E_{DW}^{Ising} = \frac{1}{2A} \left(E_{sc}^{Ising} - 20 \times E_{bulk}^{ferro} \right), \quad (5.1)$$

where E_{sc}^{Ising} is the energy of the relaxed supercell where only the Ising domain is allowed to condense (i.e. atomic relaxation along z only), E_{bulk}^{ferro} is the reference energy of the bulk structure (without domain walls), calculated from a single perovskite unit cell in the relaxed ferroelectric phase. The factor of $1/2$ is due to the fact that in a supercell with periodic boundary conditions there are two domain walls. A represents the area of the domain wall, computed from the corresponding lattice parameter within the supercell. Since the most stable structure in bulk $PbTiO_3$ under short-circuit boundary conditions is the monodomain ferroelectric phase, E_{DW}^{Ising} is positive. Domain walls energies will be given in units of mJ/m^2 or in units of $meV/\square$, where the square " $\square$ " represents the cell surface area of the domain wall.

The second relevant magnitude is the energy gain for condensing only the Néel component at the domain wall on top of the Ising configuration (*i.e.* atomic relaxation along z and x). This is referred from now on as E_{DW}^{Neel} . It is computed applying an equivalent relation as the one described by Eq. (5.1) with E_{sc}^{Ising} replaced by E_{sc}^{Neel} , the energy of the relaxed structure allowing for a Néel component at the domain wall. During this process, the appearance of a Bloch component of the polarization at the domain wall is constrained. It is important to emphasize that the distinction that is drawn between Ising and Néel-type domains is not commonly made in the literature. In many cases, the term “Ising domain” is used even when a Néel component and the associated inhomogeneous strain relaxations along the x -direction are present. This is, for instance, the case of Refs. [185, 190, 191]. This point will be discussed further below. This practice arises because, upon structural relaxation, the Néel component develops naturally contrary to the Bloch component that requires an explicit breaking of symmetry to emerge.

Finally, if on top of the most stable Ising and Néel components of the polarization at the domain wall, the condensation of the Bloch component is allowed (*i.e.* atomic relaxation along x , y and z), E_{DW}^{Bloch} can be defined by applying an equivalent relation as the one described by Eq. (5.1), but introducing E_{sc}^{Bloch} as the energy of the most stable ferroelectric polarization (including both Néel and Bloch components). The difference between E_{DW}^{Bloch} and E_{DW}^{Neel} is particularly relevant to estimate the critical temperature upon which the Bloch component is unstable T_C^{DW} . Structural relaxation using BFGS algorithm has been performed with a convergence criteria of 2.5×10^{-3} eV/Å for the maximum component of the force on any atom and 2.5×10^{-5} eV/Å³ for the maximum component of the stress tensor. The local polarization is computed following the standard approach of Ref. [190], as the product of the Born effective charges of the cubic reference structure and the atomic displacements with respect to the centrosymmetric phase, evaluated on five-atom unit cells centered on either Pb or Ti depending on the plane.

The relaxed atomic structures of the supercell were obtained under various epitaxial strain conditions. These include: (i) full relaxation of both atomic positions and lattice vectors; (ii) relaxation with lattice constants fixed to those of the optimized bulk tetragonal ferroelectric phase (see Table 4.6); (iii) relaxation under the epitaxial constraint imposed by

a hypothetical SrTiO_3 substrate ($a = b = 3.889 \text{ \AA}$); and (iv) relaxation under strain conditions corresponding to a DyScO_3 substrate, both assuming a square surface unit cell ($a = b = 3.912 \text{ \AA}$), or an orthorhombic one ($a = 3.912 \text{ \AA}$ and $b = 3.916 \text{ \AA}$ or $a = 3.916 \text{ \AA}$ and $b = 3.912 \text{ \AA}$). The corresponding layer-resolved polarization profiles are presented in Figure 5.2.

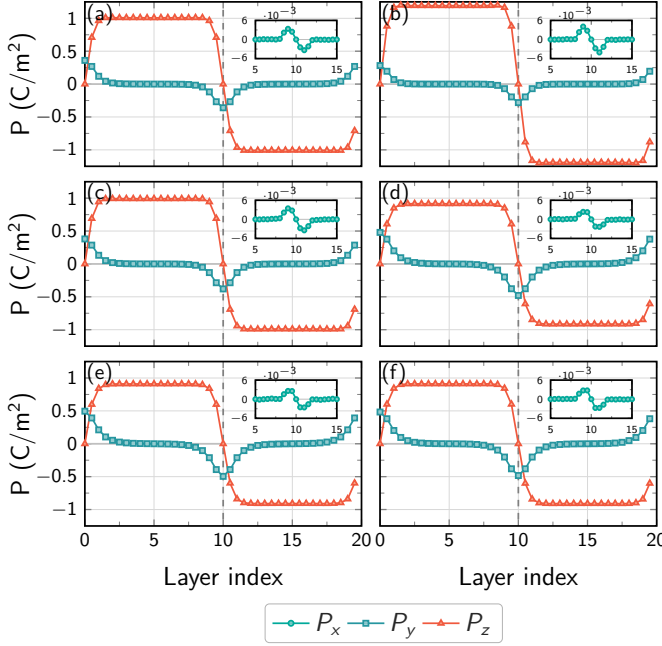


Figure 5.2: Layer-resolved polarization profiles across 180° ferroelectric domains in bulk PbTiO_3 under six different epitaxial strain conditions: (a) full relaxation of atomic positions and lattice vectors; (b) relaxation with lattice parameters fixed to those of the optimized bulk tetragonal ferroelectric phase (see Table 4.6); (c) relaxation under an epitaxial constraint mimicking a hypothetical SrTiO_3 substrate ($a = b = 3.889 \text{ \AA}$); (d) relaxation under strain corresponding to a DyScO_3 substrate with a square surface unit cell ($a = b = 3.912 \text{ \AA}$); (e) relaxation with orthorhombic DyScO_3 substrate constraints, $a = 3.912 \text{ \AA}$ and $b = 3.916 \text{ \AA}$; and (f) the same as (e) but with $a = 3.916 \text{ \AA}$ and $b = 3.912 \text{ \AA}$. Vertical dashed lines mark the position of the PbO plane at the domain wall. Inset: zoom on the P_x component around the domain wall.

The results presented in Figure 5.2 are consistent with prior findings [245], the 180° ferroelectric domain walls are atomically narrow, with a width on the order of the lattice constant. The domain wall width was extracted by fitting the polarization profile to the functional form proposed by Gureev and co-workers [246],

$$P(x) = P_0 \tanh\left(\frac{x}{\delta}\right), \quad (5.2)$$

where δ denotes the characteristic half-width of the domain wall, such that the full transition from $-P_0$ to P_0 extends over approximately 4δ . The results reveal that δ increases with the in-plane lattice parameter, ranging from $2.06 \text{ \AA}$ at $a = 3.871 \text{ \AA}$ to $2.45 \text{ \AA}$ at $a = 3.916 \text{ \AA}$, reflecting a broadening of the domain wall under tensile strain conditions as detailed in Table 5.1.

recalling that the “Ising” domain wall energies reported in Refs. [185, 190, 191] correspond to Néel wall energies in the notation adopted here, which should be kept in mind when comparing the absolute values. While this is primarily a matter of nomenclature, it is an important point when comparing energies across studies. The remaining discrepancies can be attributed to differences in the DFT functional (LDA in Ref. [190] and PBEsol in Refs. [185, 191] and in this work), pseudopotentials, and basis sets. Notably, when the same pseudopotentials are used, the agreement in energy differences improves.

When a Néel-type polarization component is allowed at the domain wall in the fully relaxed case, the energy decreases by approximately 6.0 mJ/m^2 ($6.2 \text{ meV}/\square$), in good agreement with the value of 6.4 mJ/m^2 reported in Ref. [185]. This energy gain is surprisingly large given the relatively small amplitude of the Néel polarization component, and is attributed to the relaxation of the elastic energy produced by an inhomogeneous strain at the domain wall, as discussed above.

The full development of the Bloch component leads to an additional energy reduction that strongly depends on the imposed in-plane lattice constant. In the fully relaxed structure, this reduction amounts to 4.2 mJ/m^2 ($4.2 \text{ meV}/\square$), in good agreement with Ref. [185] (6.4 mJ/m^2) and Ref. [191] (4.1 mJ/m^2). First-principles calculations reported in Ref. [244] further show that, under a tensile strain akin to that imposed by a DyScO₃ substrate, this energy reduction increases substantially, reaching approximately 10.7 mJ/m^2 ($10.6 \text{ meV}/\square$). This trend is consistent with previous studies on the phase diagram of bulk PbTiO₃ under strain, where tensile strains favor polarization rotation from the purely tetragonal *c*-phase toward phases with non-vanishing in-plane components [250, 251]. The absence of any increase in the Néel component P_x with strain reflects symmetry constraints enforcing head-to-head and tail-to-tail polarization configurations, which are electrostatically unfavorable.

This strain dependence of the Bloch energy well suggests that the critical temperature below which the Bloch component stabilizes is highly sensitive to the mechanical boundary conditions. It should however be noted that the conclusions drawn here for the DyScO₃ strain conditions must be interpreted with some caution. Under such tensile strain, bulk

PbTiO₃ is known to favor the formation of *a/c* domain structures [252, 253]. However, the periodic boundary conditions imposed in the present DFT calculations enforce a strict periodicity of the domain configuration and preclude any modulation along the *y* and *z* directions, making such *a/c* domain structures inaccessible within this computational framework. Furthermore, the supercell sizes required to properly describe these configurations would be computationally prohibitive at the DFT level. The strain-dependent trends reported here should therefore be understood as pertaining specifically to the constrained stripe domain geometry considered in this work.

Second-principles

While DFT calculations remain tractable for the supercell sizes considered above, the exploration of more complex domain configurations, larger domain widths, and finite-temperature behavior requires system sizes that quickly become prohibitive at the first-principles level. The second-principles interatomic potential constructed in Section 4.3.3 is therefore employed, providing access to much larger supercells and longer simulation times while retaining first-principles accuracy. As a preliminary validation, the domain wall energies and polarization components of the model are compared against DFT for conventional 180° and 90° domain wall configurations, using the same nomenclature as above. The results, summarized in Table 5.2, show good agreement between the model and DFT for both Ising and Ising+Néel configurations of the 180° domain wall, as well as for the 90° Ising+Néel wall following the setup of Ref. [190].

Table 5.2: Comparison of domain wall energies (mJ/m²) and maximal polarization components (μC/cm²) for a 180° Pb-centered stripe configuration with a domain width of 10 u.c. (1 × 1 × 20 u.c. simulation box) and for a 90° O-O-centered configuration with a domain width of 4 u.c. (1 × 1 × 8 u.c. simulation box). Values in parentheses correspond to DFT results for the 180° cases and to Ref. [190] for the 90° case.

Type	E_{DW}	P_x	P_y	P_z
Constrained 180° Ising	206 (200)	0.0 (0.0)	0.0 (0.0)	93 (102)
Fully relaxed 180° Ising + Néel	201 (194)	0.15 (0.37)	0.0 (0.0)	93 (102)
Fully relaxed 180° Bloch	195 (190)	0.17 (0.33)	36 (36)	93 (101)
Fixed cell 90°	39 (32.5)	3×10^{-4}	42	67

With the model validated on conventional domain wall configurations, it can be applied with confidence to the exploration of Bloch-type walls. As illustrated in Figure 5.4, and without

having been explicitly trained on such inhomogeneous configurations, the model predicts a spontaneous ferroelectric Bloch component confined at the 180° domain wall, with an amplitude of $P_y = 36 \mu\text{C}/\text{cm}^2$, in excellent agreement with the DFT result reported in Figure 5.2 and with previous theoretical predictions [191, 248]. The energy difference between the fully relaxed Ising+Néel and Bloch configurations amounts to approximately $6 \text{ mJ}/\text{m}^2$ ($6 \text{ meV}/\square$), in good agreement with DFT (Table 5.2), with the total energy difference across the supercell differing by only 3.8 meV per formula unit. The robustness of the model is further confirmed by the fact that the Bloch domain wall energy is independent of whether the Bloch components in adjacent walls are aligned or anti-aligned, consistent with the expected ferroelectric character of this component.

With the domain wall energetics and polarization components of the model validated against DFT, the structural properties of the domain wall can now be examined in greater detail. Interestingly, both layer-by-layer polarization profiles in Figure 5.2 (a) and Figure 5.4 exhibit a plateau beginning at the second TiO_2 plane, with a saturation value of P_0 lower than the bulk value reported in Table 4.6. This discrepancy arises from the competition between the c lattice parameter preferred at the domain center, where P_z saturates, and the shorter c favored near the domain wall, where P_z vanishes. The relaxed out-of-plane parameter of the full domain structure is $c = 4.122 \text{ \AA}$, i.e., 2.87% shorter than the bulk tetragonal value, with a concomitant increase of the in-plane lattice constant from $3.861 \text{ \AA}$ to $3.884 \text{ \AA}$. The local in-plane strain η_1 illustrated in Figure 5.3, exhibits a uniform tensile strain of approximately 0.54% within the domain interior. This effect diminishes as the domain width increases, since the contribution from the domain interior grows relative to the domain wall region. This sensitivity of the lattice parameters to the domain width has direct consequences on the convergence of the domain wall energies. In other words, the strong coupling between polarization and strain drives the system to locally align the tetragonality with the polarization direction. In the domain interior, where the polarization points along z , the unit cell tends to elongate along z while contracting along x and y . In contrast, within the domain wall, the polarization rotates toward the y direction, leading to a preferred elongation along y and contraction along x and z , as illustrated in Figure 5.5. This results in a competition between the structural pref-

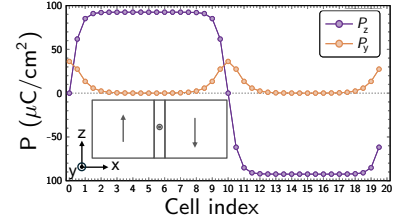


Figure 5.4: Polarization profile of $P \parallel [001]$ (P_z) (purple) and $P \parallel [010]$ (P_y) (orange) in a 180° domain structure from second-principles.

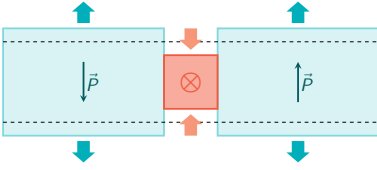


Figure 5.5: Illustration of the elastic competition between the domain and the domain wall in PbTiO_3 .

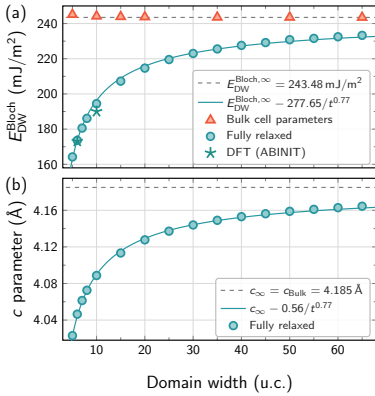


Figure 5.6: (a) Convergence of the Bloch DW energies with respect to the domain width t in the fully relaxed case, constrained to the bulk tetragonal cell parameters case and DFT fully relaxed results (green stars). The solid lines represents a power-law fit to the energies on the fully relaxed case. (b) Convergence of c lattice parameter with respect to the domain width fitted with a power-law.

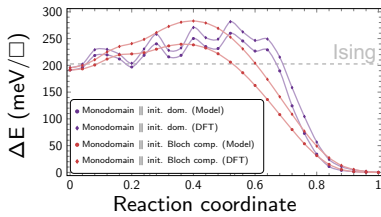


Figure 5.7: Results of NEB calculations illustrating the domain wall energy evolution along the transition from a Bloch domain wall to two distinct monodomain configurations: one with the final polarization aligned parallel to the original domain polarization and the other with the final polarization oriented perpendicular to the original domain polarization. Both NEB paths are compared against DFT calculations.

erences of the domain interior and those of the domain wall, forcing the system to adopt a compromise configuration.

For this reason, domain wall energies are inherently difficult to converge, as the associated strain relaxations are long-range in nature and DW energies evolve strongly with the domain density [254]. In the present work, stripe domain configurations are considered with a domain width $t = L/2$, where L is the supercell size along x , such that each supercell always contains two domain walls. Under fully relaxed conditions, increasing t modifies the lattice parameters and in turn influences E_{DW} as shown in Figure 5.6. Alternatively, fixing the lattice parameters to their bulk values provides a practical estimate of the isolated domain wall energy from small supercells [190]. The evolution of c and E_{DW} as a function of t , obtained from second-principles simulations, is shown in Figure 5.6. Both quantities converge slowly under full relaxation, following a power-law dependence on t . Fixing the lattice constants to their bulk values yields domain wall energies in excellent agreement with the extrapolated isolated domain wall limit, consistent with previous findings [190].

Domain wall-domain wall interaction – To investigate the mechanism by which a domain wall configuration transitions to a monodomain state, NEB calculations were performed. Two possible monodomain states exist: one aligned with the polarization in the domain interior, and another aligned with the Bloch component of the domain wall. This distinction is crucial for understanding how an applied electric field will drive the system toward a monodomain state, and provides insight into how domain walls vanish with increasing temperature. The resulting transition paths are presented in Figure 5.7.

The pathway from a Bloch domain wall to a monodomain aligned with one of the original domains (along z) involves domain wall displacement followed by annihilation, passing through several local minima as the walls approach each other. The last local minimum arises when the walls are separated by three unit cells, beyond which the system evolves continuously toward the monodomain state. This is consistent with the domain wall width of approximately 4δ , i.e., roughly two unit cells, extracted from Table 5.1: once the two walls are closer than this characteristic length, their profiles overlap

and the system can no longer sustain two distinct walls. In contrast, the transition toward a monodomain aligned with the Bloch component (along y) follows a smooth rotation of the domain polarization. Both transitions exhibit comparable energy barriers, significantly higher than that of the Bloch-to-Ising transition, suggesting that with increasing temperature the system will first undergo a Bloch-to-Ising transition before complete suppression of the domain wall, consistent with previous findings [191]. As further confirmed in Figure 5.7, the model accurately reproduces the energetics of the Bloch domain wall configuration with respect to DFT and the energy path of the transition to the monodomain state.

The interaction between domain walls as they approach each other is further examined in Figure 5.8. Significant interactions arise when the walls are separated by less than three unit cells, and their strength increases exponentially with decreasing separation, following approximately $\sim 7.2 e^{-1.2x}$, where x is the inter-wall distance. A power law of the type $2.1/x^{1.8}$ appears less appropriate by comparison. This exponential decay reflects the short-range character of direct domain wall interactions, consistent with the characteristic domain wall width of $4\delta \approx 2.5$ unit cells extracted from Table 5.1, and contrasts with the slower power-law convergence of domain wall energies with domain density, which is governed by long-range elastic relaxations [244]. Beyond four unit cells, domain walls do not interact significantly, which may cause the Bloch component to disorder with increasing temperature, complicating its experimental detection. This is a direct consequence of the ferroelectric nature of the domain wall, meaning that the relative orientation of the Bloch components in adjacent walls becomes irrelevant at larger separations.

Disorder within domain walls – The possibility of Ising line disorder within the domain wall is also investigated, following the proposal of Stepkova and co-workers in BaTiO₃ [255]. As shown in Figure 5.9, the relaxed structure inside the 180° domain wall of PbTiO₃ closely resembles the Ising line configuration predicted for BaTiO₃ [256] and observed experimentally in LiTaO₃ [257]. The Ising line configuration lies 2.95 meV/□ above the uniformly ordered Bloch configuration. This appears to be the first prediction of Ising lines in PbTiO₃, which calls for experimental verification. This finding also

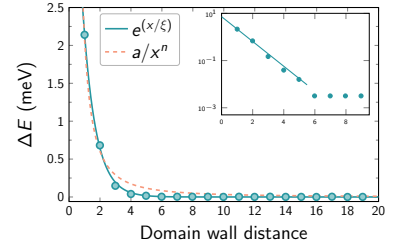


Figure 5.8: Evolution of the energy when domain walls approach each other and its fit with exponential and power laws. The inset show the same energy evolution in log scale.

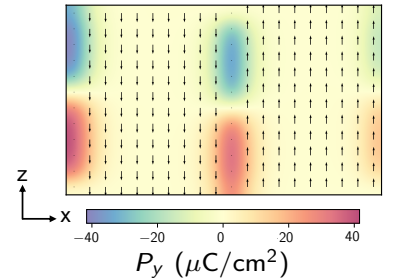


Figure 5.9: Polarization profile in x - z plane highlighting the appearance of Ising lines within the domain wall.

highlights the difficulty of detecting the Bloch component through techniques such as X-ray diffraction, which require a well-ordered Bloch component for unambiguous observation [185].

5.1.2 Topological polar textures in PbTiO_3

Recently, topological textures such as magnetic skyrmions have attracted considerable attention in magnetic materials for their potential applications in information storage and processing [258]. Their electric analogs in ferroelectrics were long considered unlikely, given the strong coupling between polarization and strain that tends to penalize polarization rotation, and the few examples reported prior to 2019 were confined to specific heterostructures [193]. Pereira Gonçalves and co-workers [194] proposed an elegant route to stabilize such textures in simple bulk ferroelectrics: consider a columnar nanodomain polarized along $+z$, embedded in a matrix of opposite polarization along $-z$. The closed 180° domain wall encircling this nanodomain naturally develops a spontaneous Bloch component that winds continuously around the domain boundary, giving rise to a non-zero topological charge $Q = 1$ and stabilizing an electric skyrmion bubble in bulk PbTiO_3 as illustrated in Figure 5.10 (a).

In the magnetism community, a distinction is sometimes drawn between skyrmions, stabilized by chiral Dzyaloshinskii-Moriya interactions, and skyrmion bubbles, stabilized by non-chiral dipolar interactions, despite both carrying the same topological charge [258]. Whether an analogous distinction applies in the ferroelectric context remains an open question. Following the convention of Ref. [194], the term skyrmion is used throughout this chapter to refer to any $Q = 1$ polar texture, without implying a specific stabilization mechanism.

Stabilization of polar skyrmionic textures – Since the second-principles model accurately reproduces the Bloch domain wall structure of PbTiO_3 , which constitutes the fundamental building block of the electric skyrmion, it can be used to stabilize and characterize such configurations. Following the procedure described in Ref. [194] (see Figure 5.10 (a)), a polar Bloch skyrmion is stabilized as shown in Figure 5.10 (c). The relaxed polarization profile exhibits a tightly

bound vortex-like arrangement, with the in-plane polarization components winding continuously around a central core polarized antiparallel to the surrounding matrix.

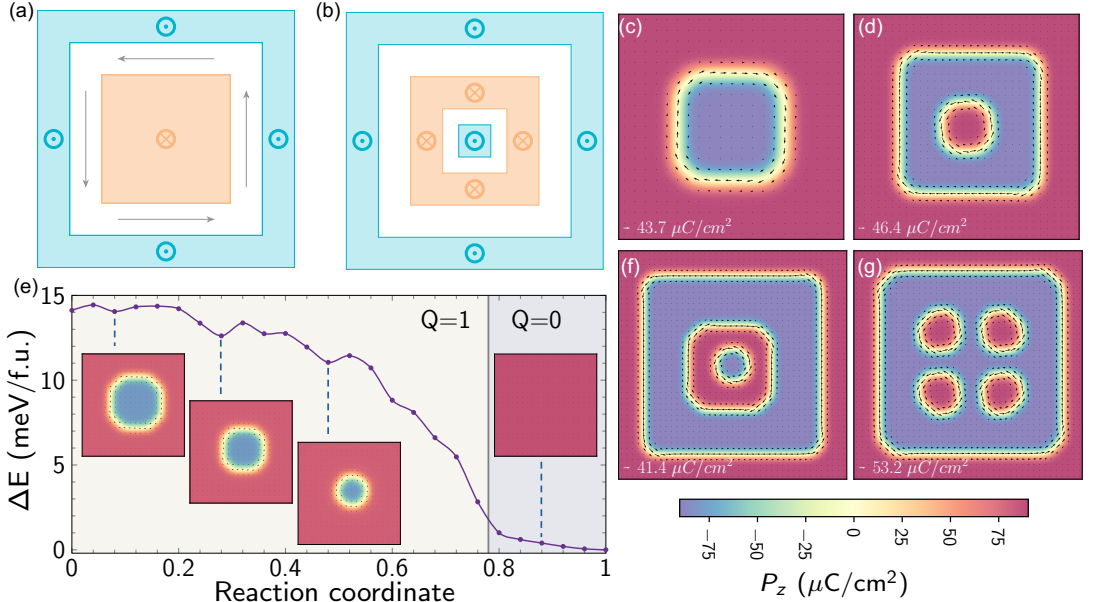


Figure 5.10: Skyrmion, skyrmionium, target-skyrmion and skyrmion bag in PbTiO_3 . (a) Sketch of a Bloch skyrmion. (b) Sketch of a skyrmionium constructed using 180° domains. (c) Relaxed Bloch skyrmion using a $20 \times 20 \times 1$ supercell, starting from the configuration of panel (a). (d) Relaxed Bloch skyrmionium using a $32 \times 32 \times 1$ supercell, starting from the configuration of panel (b). (e) Results of a NEB calculation along the path between the skyrmion and monodomain states using a $20 \times 20 \times 1$ supercell. (f) Relaxed Bloch target-skyrmion using a $41 \times 41 \times 1$ supercell. (g) Relaxed Bloch skyrmion bag using a $40 \times 40 \times 1$ supercell.

To analyze the transition from a skyrmion to a monodomain state, NEB calculation has been performed. Figure 5.10 (e) illustrates the minimum energy pathway, where the skyrmion progressively shrinks while transforming into a monodomain structure. Along this pathway, several intermediate configurations are observed, some of which correspond to distinct metastable states. This finding agrees with finite-temperature simulations. Indeed, the skyrmion remains stable up to 50 K in a $20 \times 20 \times 4$ supercell. Beyond this temperature, thermal effects induce its collapse into a monodomain state through a pinning–depinning transition. This behavior aligns with the observations of Liu and co-workers in Ref. [259].

In addition, the last minimum exhibited by the NEB calculation corresponds to a skyrmion radius of four unit cells, which is consistent with the domain wall interaction length discussed in Section 5.1.1.

Given the robustness of the model in reproducing topologies reported in the literature, additional polar textures have been explored. Following the scheme illustrated in Figure 5.10 (b), a Bloch-type skyrmionium has been constructed. This structure consists of a central core encircled by a ring of opposite polarization, yielding a net zero topological charge ($Q = 0$). The resulting stabilized configuration is shown in Figure 5.10 (d). Although topologically trivial, it exhibits a spatially complex structure with concentric domain walls that makes it physically distinct from a simple monodomain state. Analogous textures have been previously reported in ferromagnetic systems under various names, including " 2π -vortex" [260, 261] and "donut skyrmion" [262]. The term skyrmionium is usually given to a skyrmion surrounded by a domain wall of opposite topological charge [263] and it is the convention adopted here.

The term "target-skyrmion" [264] is also sometimes used for such structures but, rigorously speaking, target-skyrmion more precisely refers to multi-ring textures with nonzero topological charge. In the present work, the target-skyrmion would consist of multiple concentric polarization domains, giving rise to a nonzero topological charge. They are successfully stabilized in PbTiO_3 , as illustrated in Figure 5.10 (d). Figure 5.10 highlights the rich diversity of topological structures accessible in ferroelectrics and point to new possibilities for information encoding based on topological textures. These structures can be understood within a unified $k\pi$ -skyrmion framework, where the out-of-plane polarization component reverses k times between the center and the periphery. Within this scheme, the standard skyrmion, skyrmionium, and target-skyrmion correspond to $k = 1$, $k = 2$, and $k = 3$, respectively, reflecting increasing radial complexity and domain wall multiplicity [260]. Here, these textures are stabilized by selectively reversing the sign of P_z within the skyrmion core. By controlling the number and spatial arrangement of these reversals, we can in principle realize $k\pi$ -skyrmions with arbitrary values of k , limited only by the physical size of the system. While $k\pi$ -skyrmion textures have been observed in $\text{PbTiO}_3/\text{SrTiO}_3$ superlattices, where interfacial coupling facilitates their formation [265, 266], the results presented here demonstrate that a broader variety of topological structures can also be stabilized in bulk PbTiO_3 .

Finally, "skyrmion bags" are also sometimes reported in magnetic systems [264, 267]. They consist of several skyrmion-

like cores confined within a larger enclosing domain wall, resulting in a composite texture with higher total topological charge. They can also be stabilized in PbTiO_3 as illustrated in Figure 5.10 (g). Depending on the number of skyrmion inside the bag, the topological charge Q can take any arbitrary value.

Influence of biaxial strain – The skyrmions discussed earlier emerge from the Bloch component of the domain wall. An anti-skyrmion can thus be constructed by reversing the internal structure of this component, as shown in Figure 5.11 (a). This approach is justified by the ferroelectric nature of the Bloch component.

In the absence of strain constraints, the skyrmion is more stable than the anti-skyrmion, as shown in Figure 5.11 (b). The anti-skyrmion is not stable at finite temperature. Indeed, it transforms into a skyrmion even at low temperatures. Under epitaxial tensile strain, the energy difference between the skyrmion and the anti-skyrmion increases, as shown in Figure 5.11 (b). This is due to the enhancement of the in-plane component under tensile strain. It increases the energetic cost of the head-to-head configuration in the anti-skyrmion. However, at a critical threshold (around $3.94 \text{ \AA}$), the energy difference abruptly drops to zero. For cell parameters

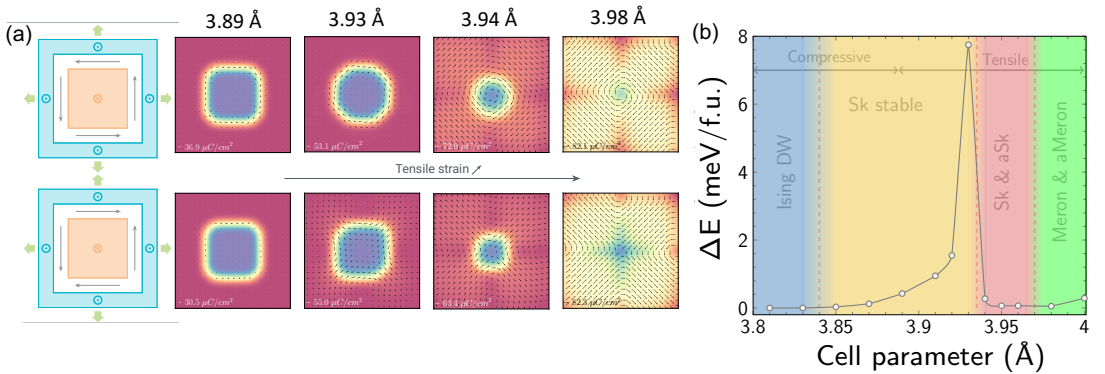


Figure 5.11: Effect of biaxial strain on the stability of skyrmion and anti-skyrmion in PbTiO_3 . (a) Sketch of the initial configuration of a skyrmion and an anti-skyrmion and the evolution of the relaxed polar texture of skyrmion and anti-skyrmion under biaxial strain. (b) Evolution of the difference of energy between skyrmion and anti-skyrmion for various values of in-plane cell parameters.

above $3.94 \text{ \AA}$, the in-plane component of the polarization extends throughout the supercell. As a result, skyrmions and anti-skyrmions become energetically degenerate. This is

due to periodic boundary conditions and the Poincaré–Hopf theorem [268] which dictates that the total vorticity in the simulation cell must vanish. As a result, vortex and antivortex textures must cancel each other. This effect is general for any skyrmion and antiskyrmion stabilized in rhombohedral phases, as discussed in greater details in Section 5.1.3. It is worth noting that, as far as can be determined from the literature, anti-skyrmions have not yet been experimentally observed in PbTiO_3 , representing an open challenge for experimental verification.

Finally, Figure 5.11 (b) also shows that at high compressive epitaxial strain, the energy difference between skyrmions and anti-skyrmions tends toward zero. Under compressive strain, the Bloch component diminishes, consistent with the strain dependence of the domain wall energetics reported in Section 5.1.1. As a result, both skyrmion and anti-skyrmion textures approach an Ising-type domain wall configuration. At high tensile strain, the out-of-plane polarization component progressively diminishes, consistent with the known tendency of bulk PbTiO_3 to adopt the $Amm2$ phase under sufficient tensile strain [251], in which the polarization lies entirely in-plane. As a result, the out-of-plane component survives only at the vortex and antivortex cores, transforming skyrmions and anti-skyrmions into merons and anti-merons respectively.

5.1.3 Skyrmion and antiskyrmion rhombohedral ferroelectrics

As seen in Section 5.1.2, a Bloch skyrmion tube is stabilized in bulk PbTiO_3 when a polar nanocolumn is embedded in a matrix of opposite polarization. The question naturally arises as to whether analogous topological structures can be stabilized in other ferroelectric perovskites, and in particular in rhombohedral systems such as BaTiO_3 . In this context, fractional Skyrme lines have been predicted in rhombohedral BaTiO_3 , confined within 180° domain walls [270], although ordinary skyrmions could not be stabilized in that work. Separately, antiskyrmion tubes with $Q = -2$ have been predicted when a columnar nanodomain is aligned along any $\langle 111 \rangle_{\text{pc}}$ polar axis [269] (see Figure 5.12), broadening the scope of topological structures accessible in this material. Here, motivated by the nanocolumn approach employed in PbTiO_3

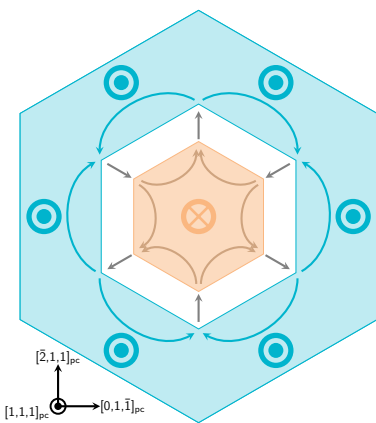


Figure 5.12: Schematic representation of the antiskyrmion tubes with $Q = -2$ reported in Ref. [269].

presented in Section 5.1.2, a $[001]_{\text{pc}}$ -oriented polar nanocolumn is constructed in rhombohedral BaTiO_3 , in which the Ti displacements responsible for the in-plane and out-of-plane polarization components are intentionally adjusted to achieve the desired initial configuration. The same DFT framework as described in Section 4.3.4, in combination with the second-principles model introduced therein, is employed throughout this section. The generality of the approach is further assessed in KNbO_3 , a rhombohedral ferroelectric analog of BaTiO_3 , for which analogous results are obtained, discussed in greater detail, and compared to those reported for PbTiO_3 under tensile strain in Section 5.1.2. The corresponding DFT calculations are performed using the ABINIT package [122]. For KNbO_3 , the GGA with the PBEsol exchange-correlation functional is employed together with a plane-wave pseudopotential approach and optimized norm-conserving pseudopotentials from the PseudoDojo server [75, 156]. The valence electron configurations are $3s^2 3p^6 4s^1$ for K, $4s^2 4p^6 4d^4 5s^1$ for Nb, and $2s^2 2p^4$ for O. A plane-wave energy cutoff of 40 Ha is used together with an $8 \times 8 \times 8$ Γ -centered k -point mesh, adapted to the supercell size.

Stabilization and topological properties of skyrmion and antiskyrmion tubes

The relaxation of these initial configurations reveals a distinctive behavior with respect to previously studied topological textures in bulk ferroelectrics. In previously studied systems such as strain free PbTiO_3 skyrmions (see Section 5.1.2), $[111]_{\text{pc}}$ -oriented antiskyrmion tubes in BaTiO_3 [269], and skyrmion lines in 180° domains in BaTiO_3 [270], the non-collinear polarization is confined to the domain wall. In contrast, as shown in Figure 5.13 (a), the Bloch character of the polarization is found to extend throughout the entire matrix of antiparallel polarization after relaxation: although the out-of-plane polar nanocolumn is confined to a few unit cells, the vortexlike disturbance of the field, reflected by the in-plane polarization components, spreads across the whole supercell.

This behavior can be attributed to two main factors: (i) the development of an in-plane polarization component reduces elastic energy, allowing each cell to locally adopt a configuration closer to the nearest $\langle 111 \rangle_{\text{pc}}$ R3m ground state, and (ii) it mitigates the formation of energetically unfavorable 180°

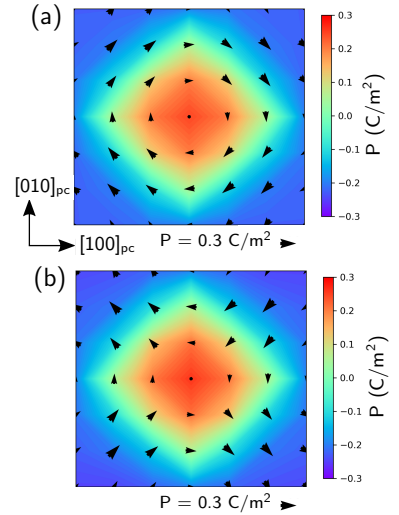


Figure 5.13: BaTiO_3 polarization map of (a) DFT equilibrium skyrmion texture obtained after relaxation of manually imposed initial Ti displacements. (b) Equilibrium antiskyrmion texture obtained after relaxation of the skyrmion texture after reverting the sign of the displacements along x . Arrows indicate the in-plane components of the polarization, whereas the color map represents the out-of-plane polarization.

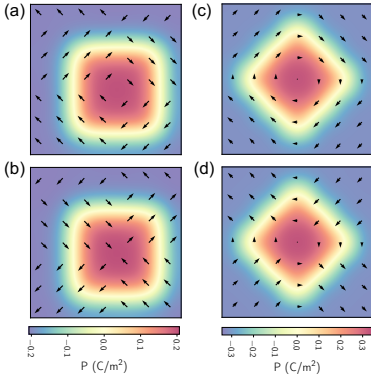


Figure 5.14: KNbO₃ polarization map with respect to the cubic reference and the unit cell centred on Nb atom in xy plane. (a) K-centered skyrmion (b) K-centered antiskyrmion (c) Nb-centered skyrmion (d) Nb-centered antiskyrmion. The colorbar represents the out-of-plane polarization P_z .

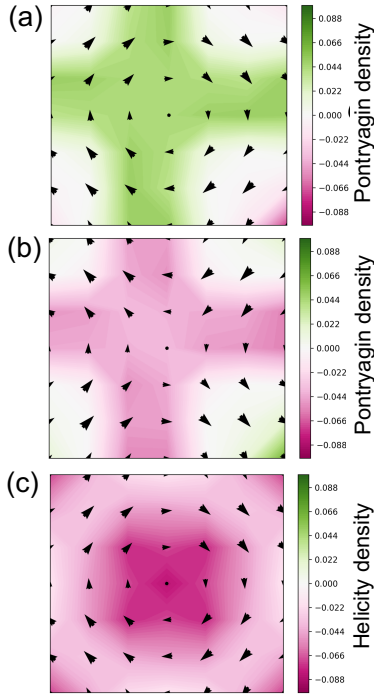


Figure 5.15: Analysis of the topological charge and helicity of the skyrmion tubes shown in Figure 5.13. Arrows indicate the direction of the in-plane polarization components. (a,b) The color map represents the Pontryagin density, integrand of Eq. (2.28) for the (a) skyrmion case and (b) antiskyrmion case. (c) The color map represents the helicity density computed as the integrand of Eq. (5.3).

domains, which would otherwise be prohibitively costly, as reported in Refs. [269, 270]. A similar behavior was reported in Ref. [194] for PbTiO₃ skyrmion tubes subject to tensile strain exceeding a critical threshold. As demonstrated in Section 5.1.2, this behavior is confirmed and extended by the present calculations: both skyrmion and antiskyrmion textures are stabilized in PbTiO₃ over the biaxial strain range $a \in [3.935, 3.970]$ Å. Together with the stabilization of analogous structures in KNbO₃ (see Figure 5.14), these results suggest that the extension of the Bloch character throughout the polarization matrix is a general feature of rhombohedral ferroelectrics rather than a peculiarity of BaTiO₃.

Having established the stabilization of these textures, their topological and chiral properties are now examined. As shown in Figure 5.15 (a), an integer value of $Q = 1$ is obtained for the polar texture shown in Figure 5.13 (a), confirming its nontrivial topological character. Unlike the antiskyrmions reported in Ref. [269], the skyrmion textures stabilized here are found to exhibit a chiral nature, a property of significant relevance for light-matter interactions with potential applications in optoelectronics [271]. Such chirality can in principle be probed experimentally by means of resonant soft X-ray diffraction-based circular dichroism measurements [272–276].

The chirality of the skyrmion tube can be quantified through the helicity [18, 273, 277, 278],

$$\mathcal{H} = \iiint \mathbf{P}(\mathbf{r}) \cdot (\nabla \times \mathbf{P}(\mathbf{r})) d\mathbf{r}, \quad (5.3)$$

which takes a non-zero value whenever the in-plane polarization rotation is coupled to a finite out-of-plane component at the core, as illustrated in Figure 5.15.

Due to the periodic boundary conditions and the Poincaré-Hopf theorem [268], the total vorticity in the simulation supercell must sum to zero. Consequently, the vortex and antivortex textures must counterbalance each other. As it can be observed in Figure 5.13 (a) and Figure 5.14 (a,c), the antivortex is located at the middle of the cell edges. One may wonder whether the center of the nanocolumn could be positioned at the antivortex core to stabilize an antiskyrmion with a topological charge of $Q = -1$ in place of a skyrmion. This can be accomplished by reversing the sign of the atomic displacements along the x -direction of the skyrmion texture

with respect to the cubic reference, effectively transforming vortices into antivortices and vice versa.

Interestingly, and in contrast to the strain-free case of PbTiO_3 (see Section 5.1.2) skyrmion, the position of the nanocolumn is found to be flexible and decoupled from the in-plane polarization components, allowing it to align with the antivortex core and stabilize an antiskyrmion, as illustrated in Figure 5.13 (b). As shown in Section 5.1.2, this flexibility is also recovered in PbTiO_3 when a sufficient biaxial tensile strain is applied, suggesting that it is the rhombohedral character of the local polarization that governs this decoupling. The DFT energy of the antiskyrmion structure is found to be nearly degenerate with that of the skyrmion (see Figure 5.16), demonstrating that rhombohedral ferroelectrics can host both skyrmion and antiskyrmion textures under identical strain and growing conditions.

Two distinct types of skyrmions and antiskyrmions are further identified, depending on whether the vortex and antivortex cores are centered at Ti or Ba sites. Although the textures are initially stabilized through intentional Ti displacements, configurations with the singularity centered at Ba sites are found to be stable as well. Notably, the Ba-centered configurations are energetically more favorable, lying 1.2 meV/f.u. below their Ti-centered counterparts in the $7 \times 7 \times 1$ supercell. This energy difference can be understood from the fact that the vortex and antivortex cores represent the intersection of two domain walls separating the up/down and left/right in-plane polarization components, which are more stable when centered on the Ba site [279]. A detailed energy analysis of both skyrmion and antiskyrmion pairs, together with NEB [280–282] calculations of the energy barriers between them, is presented in Figure 5.17.

Orientation, size effects and stability of skyrmion tubes

The energy and stability of skyrmion tubes are systematically investigated as a function of nanocolumn orientation, radius, and supercell size. Given the nearly degenerate energetics of Ba- and Ti-centered skyrmion and antiskyrmion textures established above, the analysis is carried out on the Ti-centered skyrmion configuration as a representative case. Orientation effects are examined with DFT, while stability and size effects

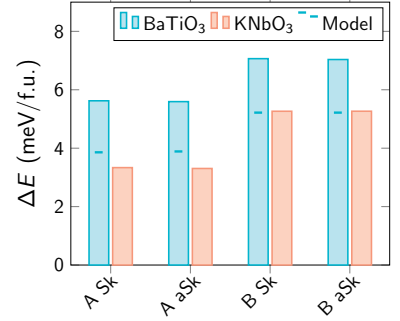


Figure 5.16: Energy comparison of skyrmion and anti-skyrmion defects centered on A and B sites for BaTiO_3 and KNbO_3 . DFT energies with respect to the rhombohedral phase are represented by vertical bars whereas second-principles energies for the BaTiO_3 model are represented by horizontal lines within the Turquoise bars.

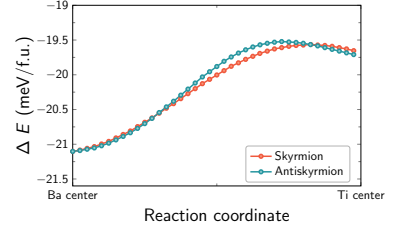


Figure 5.17: Energy barrier for the Ba to Ti centered skyrmions and antiskyrmions obtained from a NEB calculation with the second-principles model. Both curves represent the energy per formula unit with respect to the cubic reference.

are studied with the second-principles interatomic potential presented in [Section 4.3.4](#).

Size dependence of skyrmion tube energetics – The dependence of the defect energy on nanocolumn size is examined from second-principles for a fixed supercell length of $L = 21$ u.c. Stable configurations are found down to $r = 1$ u.c., as illustrated in [Figure 5.18](#), which is notably smaller than the minimum radius of 4 u.c. reported in Ref. [269], below which textures decay to a monodomain configuration. The defect energy is found to scale linearly with the square root of the nanocolumn area, with metastable states accessible at different sizes. For instance, doubling the radius from $r = 1$ to $r = 2$ u.c. raises the energy by only $\Delta E = 0.07$ meV/f.u., illustrating the fine tunability of the nanocolumn size.

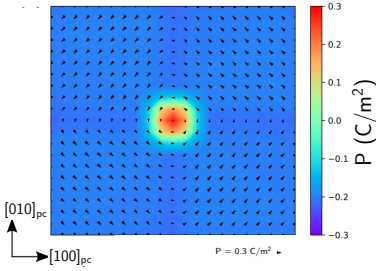
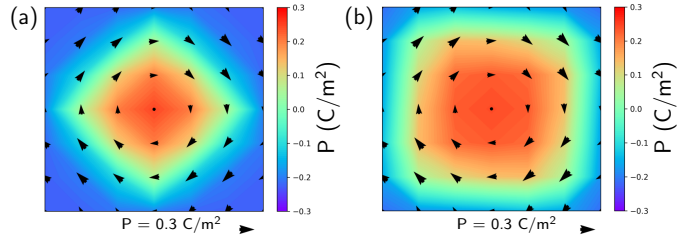


Figure 5.18: Stabilization of different skyrmion in BaTiO_3 of $r = 1$ u.c. nanocolumn stabilized with the second-principle interatomic potential using supercell sizes of $21 \times 21 \times 1$ and $7 \times 7 \times 1$.

Influence of the orientation of the nanocolumn's cross section – As the skyrmion tube is oriented along the $[001]_{\text{pc}}$ direction, its cross-section exhibits a cubic shape, in contrast to the hexagonal-like cross-sections reported in Ref. [269]. Square nanocolumns are found to align either rhombically,

Figure 5.19: Stabilization of (a) Rhombus and (b) square-like defects oriented cross sections of the nanocolumn in BaTiO_3 . Arrows indicate the in-plane components of the polarization, whereas the color map represents the out-of-plane polarization computed in a supercell of $7 \times 7 \times 1$.



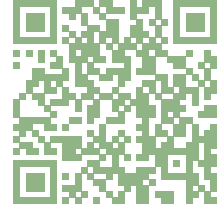
with domain walls along $\{110\}_{\text{pc}}$ as shown in [Figure 5.19](#) (a), or cubically, with domain walls along $\{100\}_{\text{pc}}$ as shown in [Figure 5.19](#) (b). Both configurations are stable, with an energy difference of 0.1 meV/f.u. in the $7 \times 7 \times 1$ supercell. However, attributing this difference solely to the domain orientation is not straightforward, as a change in orientation inevitably affects the nanocolumn area, which influences the total energy by a comparable amount, as discussed above. Overall, the energy landscape associated with varying the nanocolumn cross-section orientation is found to be extremely flat, suggesting that multiple realizations are accessible and that dynamical transitions between them are possible at finite

temperatures, as illustrated in the supplemental video[†] of Ref. [216].

Effect of the supercell size – The effect of supercell size is examined from second-principles by fixing the nanocolumn radius at $r = 2$ u.c. and varying the supercell length across $L = 7, 11, 13, 15, 17, 19, 21$ u.c. As discussed above, although the nanocolumn size is fixed, the in-plane polarization components extend across the supercell, locally resembling the $\langle 111 \rangle_{\text{pc}}$ $R3m$ configuration, leading to an asymptotic energy behavior, as shown in Figure 5.20. As the supercell grows, regions resembling the $\langle 111 \rangle_{\text{pc}}$ monodomain expand uniformly while the defect's energy contribution remains constant. This behavior is accurately described by a power-law model $E = E_d + a/(x + b)$, allowing the energy difference between the defect and the rhombohedral monodomain phase to be extrapolated to the infinite supercell limit.

The asymptotic defect energy extrapolated to the infinite supercell limit is $E_d = 0.07 \pm 0.01$ meV/f.u. above the $R3m$ ground state, lying well within the narrow energy window separating the rhombohedral and orthorhombic $Amm2$ phases. This result indicates that the defect introduces only a minor, localized energy disturbance despite inducing a large-scale disruption in the polarization pattern, confirming the metastable character of these topological textures.

Stability of the skyrmion tubes – The thermal stability of skyrmion and antiskyrmion textures is investigated by means of second-principles finite-temperature molecular dynamics simulations. Both types of textures are not found to be equally robust under thermal fluctuations. Ti-centered defects remain stable up to $T = 150$ K, corresponding to the $R3m \rightarrow Amm2$ phase transition reported in Section 4.3.4, whereas Ba-centered defects collapse already at $T = 80$ K. Beyond these thresholds, the nanocolumns collapse into a monodomain out-of-plane polarization while the in-plane vortex components persist. Despite their lower energy, Ba-centered defects exhibit a lower barrier to transitioning into the homogeneous state, as quantified by the NEB calculations presented in Figure 5.21. The corresponding transition paths are illustrated in the supplemental[†] videos of Ref. [216].



[†]Supplemental Video 1 of Ref. [216]

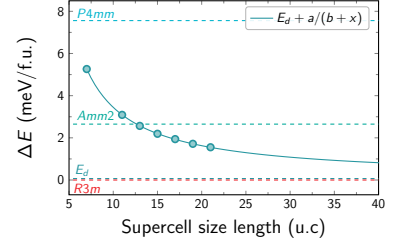


Figure 5.20: Energy dependence of a Ti-centered skyrmion tube exhibiting a nanocolumn of 2 u.c. as a function of supercell size, obtained from second-principles simulations in BaTiO₃. Points indicate the simulation data, while the solid line represents a fit to the power-law model and its asymptotic value as explained in the text. All energies are calculated with respect to the $R3m$ monodomain ground-state

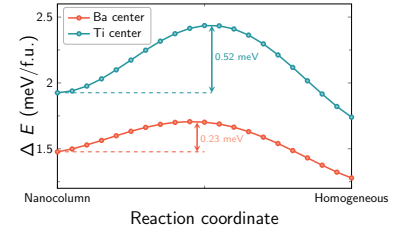
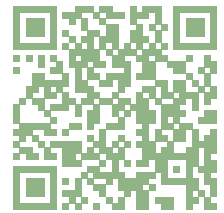


Figure 5.21: Energy barrier for the stability of Ba and Ti centered skyrmions toward an homogeneous out-of-plane polarization state obtained from a NEB calculation with the second-principles model. Blue and red curves represent the energy per formula unit with respect to the cubic reference for Ba and Ti centered defects respectively.



[†]Supplemental Videos 2 and 3 of Ref. [216]

5.2 Polar textures in heterostructures

As discussed in [Section 2.3](#), heterostructures provide a natural framework in which non-trivial topological textures can emerge spontaneously [18]. This behavior originates from the interplay between electrical, mechanical boundary conditions, which can be tuned independently, in contrast to bulk ferroelectrics.

This has been clearly illustrated in several phase-field studies. For instance, Dai and co-workers [283] investigated $(\text{PbTiO}_3)_{16}/(\text{SrTiO}_3)_{16}$ superlattices under fixed electrical boundary conditions. By varying the substrate lattice constant from 3.87 Å to 3.99 Å, a sequence of phases was obtained, evolving from c phase to a skyrmion bubble state, then to a vortex phase, and finally to an a -twin configuration. In a complementary approach, Hong and co-workers [284] considered the opposite situation, where the mechanical boundary conditions were kept fixed while the electrical boundary conditions were tuned by varying the periodicity, i.e., the value of n in $(\text{PbTiO}_3)_n/(\text{SrTiO}_3)_n$. In this case, the system was found to evolve through a sequence of phases of the form a_1/a_2 domain configuration to a vortex and finally to flux-closure by varying n from 6 to 54.

Overall, these studies demonstrate that heterostructures exhibit a much richer variety of accessible phases than bulk ferroelectrics, where similar topological structures are typically only metastable. This enhanced tunability makes them a particularly suitable platform for the stabilization and control of complex polar textures.

5.2.1 Ubiquity of Bloch domain walls in $\text{PbTiO}_3/\text{SrTiO}_3$ heterostructures

From a theoretical perspective, the presence of a Bloch component in 180° stripe domain walls in bulk PbTiO_3 appears to be a robust and intrinsic feature. As discussed in [Section 5.1](#), such non-Ising character emerges naturally from the underlying energetics of the system and is often regarded as ubiquitous in this material. However, it remains unclear whether this picture holds in PbTiO_3 heterostructures.

In $\text{PbTiO}_3/\text{SrTiO}_3$ heterostructures, the PbTiO_3 layer is confined between SrTiO_3 layers, which induces a discontinuity

of the polarization at the interface. This leads to depolarizing fields that perturb the ideal 180° domain-wall configuration by limiting its extension along the out-of-plane direction and favoring the formation of flux-closure domains [54].

Within this context, combined experimental and theoretical investigations have reported the presence of Bloch components at 180° domain walls in PbTiO_3 layers, and have suggested that these may give rise to chiral domain walls [193]. Despite these reports, direct experimental evidence remains scarce owing to the intrinsic difficulty of probing ferroelectric domain walls at the nanoscale. Moreover, other experimental studies based on different techniques, have questioned the existence of chiral domain walls in PbTiO_3 -based thin films [192, 257]. These contrasting observations suggest that the presence of Bloch components in heterostructures may be highly sensitive to external conditions. From the theoretical side, the situation also remains debated. Using the second-principles model of Wojdeł and Íñiguez constructed from LDA data [120, 191], Gómez Ortiz and co-workers investigated the evolution of polar textures as a function of layer thickness, epitaxial strain, and temperature [285, 286]. Their calculations predicted the persistence of a Bloch component of the polarization within domain walls up to room temperature, a feature that was further invoked to explain the formation of polar skyrmions [193]. In contrast, other DFT simulations of $\text{PbTiO}_3/\text{SrTiO}_3$ based on LDA did not report any Bloch component [287].

In order to clarify this issue, the second-principles models introduced in Section 4.3.2 and Section 4.3.3 are combined to construct $\text{PbTiO}_3/\text{SrTiO}_3$ heterostructures, following the methodology described in Section 3.2.5. Within this framework, the reference in-plane lattice parameter of the heterostructure is determined by minimizing the total elastic energy of the coupled SrTiO_3 and PbTiO_3 layers:

$$\frac{C_{\text{SrTiO}_3}}{2} \left(\frac{a_{\text{av}} - a_{\text{SrTiO}_3}}{a_{\text{SrTiO}_3}} \right)^2 + \frac{C_{\text{PbTiO}_3}}{2} \left(\frac{a_{\text{av}} - a_{\text{PbTiO}_3}}{a_{\text{PbTiO}_3}} \right)^2, \quad (5.4)$$

where C_{SrTiO_3} (*resp.* C_{PbTiO_3}) denotes the harmonic elastic constant of SrTiO_3 (*resp.* PbTiO_3). Minimization of this expression

yields the equilibrium lattice parameter a_{av} :

$$a_{av} = a_{\text{SrTiO}_3} a_{\text{PbTiO}_3} \left(\frac{\frac{C_{\text{SrTiO}_3}}{C_{\text{PbTiO}_3}} a_{\text{SrTiO}_3} + a_{\text{PbTiO}_3}}{\frac{C_{\text{SrTiO}_3}}{C_{\text{PbTiO}_3}} a_{\text{SrTiO}_3}^2 + a_{\text{PbTiO}_3}^2} \right). \quad (5.5)$$

In the following, $\text{PbTiO}_3/\text{SrTiO}_3$ superlattices are denoted as $(\text{PTO}_n|\text{STO}_m)_N$, where n and m denote the number of PbTiO_3 and SrTiO_3 unit cells per period, respectively, and N the number of repetitions. All the structures in this section have been relaxed using the **BFGS** algorithm in order to minimize the forces below 1×10^{-3} eV/Å and the stresses not constrained by epitaxial strain below 3.7×10^{-5} eV/Å³.

As a prototypical example, $(\text{PTO}_6|\text{STO}_6)_\infty$ heterostructures epitaxially grown on a SrTiO_3 cubic substrate is considered. For such layer thicknesses the second-principles simulations reveal that the equilibrium domain period (Λ_d) is approximately 18 unit cells. For comparison, other calculations found an equilibrium domain period of 12-14 unit cells at these thicknesses [286]. Importantly, as shown in **Figure 5.22**, while the presence of a Bloch component is observed in the domain wall for small lateral domain sizes ($P_y = 0.27$ C/m² for $\Lambda_d=8$ unit cells), this component progressively reduces with increasing Λ_d and disappears completely for domain periods larger than 14 unit cells. Consistently, the Bloch component disappears completely at periods lower than the equilibrium domain periods of superlattices with different layer thicknesses. **Figure 5.22** (c) shows a plot of the magnitude of the Bloch component as a function of domain period for bulk PbTiO_3 strained on SrTiO_3 and for superlattices with varying thickness of PbTiO_3 and SrTiO_3 , specifically $(\text{PTO}_6|\text{STO}_6)_\infty$, $(\text{PTO}_{10}|\text{STO}_6)_\infty$ and $(\text{PTO}_{10}|\text{STO}_{10})_\infty$. At the equilibrium domain period for each system (18, 26, and 24 unit cells, respectively, marked by the vertical arrows) the magnitude of the Bloch component is zero.

The absence of Bloch polarization at the domain walls of the superlattices is at odds with the predictions for bulk PbTiO_3 for which the Bloch component is largely independent of the lateral size of the domains. The disappearance of the Bloch component in heterostructures is most likely related to the finite size of the PbTiO_3 layer in the simulated $\text{PbTiO}_3/\text{SrTiO}_3$ heterostructures (in contrast to bulk PbTiO_3) and appears to originate from the interaction between the Bloch and flux-closure components of the polarization. Consecutive panels

in Figure 5.22 (a) demonstrate that, as the domain period Λ_d progressively increases, the volume occupied by the flux closure regions naturally expands to eventually cover the entire film thickness and suppress the Bloch component. In the bulk PbTiO_3 calculations with periodic boundary conditions (see Figure 5.22 (b)), which artificially remove the surface region, the Bloch component remains sizable, confirming the intrinsic Bloch nature of the domain wall in PbTiO_3 and supporting the interpretation of a surface effect in $\text{PbTiO}_3/\text{SrTiO}_3$ superlattices. Importantly, second-principles simulations further reveals that the magnitude of the Bloch component is strongly sensitive to the epitaxial strain as shown in Figure 5.22 (d). For a domain period of 12 unit cells, the Bloch component disappears when the compressive strain increase from 0 to -0.2%. From a modeling perspective, these observations mean that making reliable predictions remains challenging since the results might be very sensitive to the approximations that are used and the way the strain is treated in the simulations.

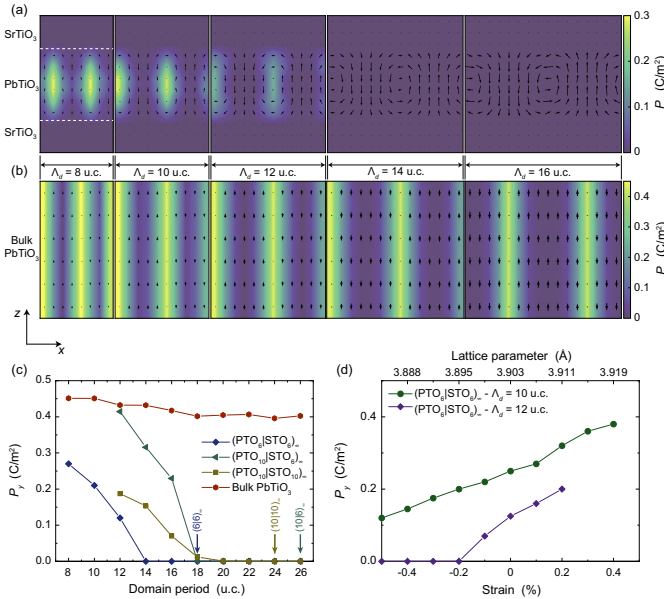


Figure 5.22: Second-principles calculations of the structure of 180° domain walls in $\text{PbTiO}_3/\text{SrTiO}_3$ heterostructures at 0 K. (a) Cross sections of a $(\text{PTO}_6|\text{STO}_6)_\infty$ heterostructure period viewed in $x-y$ plane for domain periods ranging from 8 to 16 unit cells. The color scales depict the magnitude of P_y , whereas the arrows mark the orientation of the spontaneous polarization. (b) Domain period dependence of the Bloch polarization in bulk PbTiO_3 for comparison. Note the different color scale compared to (a). (c) Plot of the magnitude of the Bloch polarization in the domain walls of bulk PbTiO_3 (red circles) and for $\text{PbTiO}_3/\text{SrTiO}_3$ heterostructures with different layer thicknesses as a function of the domain period (both systems are strained on SrTiO_3). The arrows indicate the equilibrium domain periods for the PbTiO_3 layer in each superlattice. (d) Plot of the Bloch polarization in the domain walls of the $\text{PbTiO}_3/\text{SrTiO}_3$ heterostructure as a function of strain, for a domain period of 10 (green circles) and 12 (purple diamonds) unit cells. Reprinted from Ref. [185].

Experimentally, it means that partial relaxation of the superlattice and local fluctuation of the strain (e.g., during preparation of lamellae for scanning transmission electron microscopy analysis) might strongly affect the observations.

Nevertheless, it should be noted that the use of tensile strain to attempt to stabilize the Bloch component in PbTiO_3 domain walls is associated with caveats that must be considered. Substrates that impose tensile strain on PbTiO_3 (including the rare-earth scandates) also promote the formation of a/c domains due to ferroelasticity [288]. The combination of the depolarizing field and the tensile strain induces asymmetric flux-closure arrays with net in-plane polarization, where 90° and 180° domain walls coexist [200, 289]. The ferroelastic component in the tensile strain regime could further affect the Bloch component in the 180° domain walls.

Further insight into the presence of Bloch components in $\text{PbTiO}_3/\text{SrTiO}_3$ heterostructures has been obtained through a combination of first-principles-based modelling, phase-field simulations, and experimental investigations, detailed in Ref. [185]. The first- and second-principles modelling was carried out in the present work, the phase-field simulations were performed by the group of J. Hlinka, and the experimental investigations were led by M. Hadjimichael and E. Zatterin.

The Phase-field simulations for a realistic $\text{PbTiO}_3/\text{SrTiO}_3$ heterostructure under compressive strain yielded a labyrinthine domain pattern with 180° domain walls and a domain period of about 27 unit cells, consistent with experimental observations. The domain walls exhibited a flux-closure structure, with in-plane polarization appearing only near the interfaces and no Bloch component at the domain-wall centre. Diffuse X-ray scattering patterns were computed from these simulated configurations to enable a direct comparison with experiment. Around the $hk0$ heterostructure peaks (zero out-of-plane momentum transfer), the pure flux-closure texture gave rise only to a very weak second-order diffuse signal, whereas an artificially introduced Bloch component produced strong transverse diffuse intensity. Synchrotron diffuse scattering measurements performed down to 2.2 K showed no such transverse signature at the $hk0$ reflections, ruling out any periodic Bloch polarization. In contrast, the anisotropic diffuse signal observed around the $kk1$ peaks, characterized by minima perpendicular to the in-plane momentum transfer, matched exactly the scattering fingerprint expected from the depolarization-driven flux-closure rotation. These results, fully consistent across length scales, confirm that a Bloch component is not ubiquitous in $\text{PbTiO}_3/\text{SrTiO}_3$ heterostructures and that its appearance depends critically on the boundary conditions, domain period and epitaxial strain, as highlighted

by the first- and second-principles calculations of the present work. Further details on the experimental measurements and phase-field simulations are provided in Ref. [185].

5.3 Summary

This chapter has examined polar textures in perovskite oxides across two complementary settings, bulk crystals and heterostructures, with the aim of identifying the mechanisms governing their internal structure and assessing their sensitivity to mechanical and electrical boundary conditions.

In bulk PbTiO_3 , the 180° domain wall is found to develop a spontaneous ferroelectric Bloch component at its center, driven primarily by Pb displacements in the PbO plane. This component is shown to be highly sensitive to epitaxial strain: tensile strain increases the associated energy gain substantially, while compressive strain suppresses it. The strong coupling between polarization and strain is identified as a key factor governing the convergence of domain wall energies with domain width, through long-range elastic relaxations that extend far beyond the wall core. The domain wall interior is further shown to exhibit a ferroelectric-to-paraelectric transition upon approaching the wall center, and Ising line disorder is predicted for the first time in PbTiO_3 , suggesting that the detection of the Bloch component by diffraction-based techniques may be hampered by orientational disorder of adjacent walls at finite temperature.

The ferroelectric nature of the Bloch component, confirmed by the independence of the domain wall energy on the relative alignment of Bloch components in adjacent walls, establishes it as the elementary building block for topological polar textures. In tetragonal PbTiO_3 , a polar skyrmion tube is stabilized when a columnar nanodomain is embedded in a matrix of opposite polarization, with the winding Bloch component along the domain boundary conferring a topological charge $Q = 1$. Under sufficient tensile strain, the polarization matrix acquires an extended Bloch character and antiskyrmion textures become accessible as well, alongside merons and antimerons as the system approaches the $Amm2$ phase.

In rhombohedral BaTiO_3 and KNbO_3 , both skyrmion and antiskyrmion tubes are stabilized via the same nanocolumn approach, with the key distinction that the Bloch character

extends throughout the entire polarization matrix rather than being confined to the domain wall. This behavior is attributed to the multicomponent nature of the polarization in the rhombohedral phase, which allows each unit cell to locally approach a $\langle 111 \rangle_{\text{pc}}$ ground-state configuration. Skyrmion and antiskyrmion textures are found to be degenerate and exhibit a chiral character, with Ti-centered defects remaining stable up to the $R3m \rightarrow Amm2$ phase transition temperature.

In $\text{PbTiO}_3/\text{SrTiO}_3$ heterostructures, the picture established in bulk does not carry over straightforwardly. Second-principles simulations reveal that the Bloch component present at small domain periods is progressively suppressed as the equilibrium domain period is approached, due to the competition between the intrinsic Bloch character of the domain wall and the flux-closure polarization structure induced by depolarizing fields at the interfaces. The magnitude of the Bloch component is found to be strongly sensitive to both the domain period and the epitaxial strain, suggesting that reliable predictions in this geometry require careful control of these parameters. These findings are fully consistent with synchrotron diffuse X-ray scattering measurements, which find no evidence for a periodic Bloch component at equilibrium domain periods, confirming that Bloch domain walls are not ubiquitous in $\text{PbTiO}_3/\text{SrTiO}_3$ heterostructures and that their appearance is governed by boundary conditions.

Manipulation of polar textures

6

Section 5.1 demonstrated that bulk ferroelectric perovskites host a rich variety of complex polar textures, ranging from Bloch domain walls and skyrmion tubes to antiskyrmions and merons. However, all of these structures share a fundamental limitation: in bulk materials, the true ground state is the monodomain configuration, and the topological textures discussed so far are metastable phases that were constructed by intentionally imposing specific initial atomic displacements. As a consequence, their spontaneous formation under realistic conditions remains unlikely, and experimental evidence for such textures in bulk ferroelectrics remains scarce. While complex polar textures have been observed in heterostructures and thin films [193], where electrostatic and mechanical boundary conditions naturally favor their stabilization, their direct observation and controlled engineering in bulk crystals constitutes a significant and largely unresolved experimental challenge.

Overcoming this challenge requires the development of strategies capable of actively engineering and manipulating these textures in situ. In bulk materials, the primary lever for controlling polar textures remains epitaxial strain or mechanical boundary conditions imposed by the substrate, which fix the resulting polarization pattern and leave little room for post-fabrication tunability. Early attempts at dynamical control relied on electric field or optical pulses applied over mesoscopic regions to pump polar optical phonons and stabilize hidden phases [290, 291]. While demonstrating that in situ manipulation is in principle achievable, these approaches suffer from important shortcomings: only specific phases have been stabilized so far, the correlation between pulse characteristics and the resulting polar arrangement is poorly understood, and deterministic control over the full phase diagram of topological textures remains elusive.

This chapter presents two complementary approaches to the dynamical manipulation of polar textures, both relying on the application of spatially modulated excitations rather than static boundary conditions. The first approach, detailed in Section 6.1, exploits inhomogeneous and time-dependent electric fields to achieve precise and reversible control over domain

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Related publications

5. Nano Letters 24 (43), 13783-13789
6. Phys. Rev. B 111 (13), 134107
7. Phys. Rev. B 111 (18), L180104

arrangements and topological defects, including the stabilization and switching of polar skyrmion and antiskyrmion in BaTiO₃ [209, 216] presented in Section 5.1.3. The second approach, detailed in Section 6.2, leverages the flexoelectric coupling in ferroelectric materials through acoustic phonon excitations (APEX), enabling deterministic and predictable tailoring of a broad range of polar topologies in both BaTiO₃ and PbTiO₃ [208].

6.1 Control and displacement of polar textures from inhomogeneous and time-dependent electric fields

The second-principles models for PbTiO₃ and BaTiO₃ introduced in Section 4.3.3 and Section 4.3.4 are employed here to investigate the stabilization and dynamical control of the polar textures characterized in Chapter 5. Finite-temperature molecular dynamics simulations are carried out, and the system is driven by spatially inhomogeneous and time-dependent electric fields $\mathcal{E}(\mathbf{r}, t)$ of various functional forms, which are detailed in the following subsections.

The effect of the inhomogeneous electric fields is incorporated by adding an external force on each atom. Since the Born effective charge tensor $\mathbf{Z}^*$ describes the linear relationship between the force on an atom and the macroscopic electric field [86], the force induced along β on an atom κ at position $\mathbf{r}$ by an electric field $\mathcal{E}$ in direction α is given by

$$F_{\kappa,\beta}(\mathbf{r}, t) = Z_{\kappa,\alpha\beta}^* \mathcal{E}_\alpha(\mathbf{r}, t). \quad (6.1)$$

In the following examples, the standard procedure is adopted whereby $\mathbf{Z}^*$ is computed in the reference $Pm\bar{3}m$ cubic phase in the present case.

6.1.1 Stabilization and control of polar textures in PbTiO_3

Stripe domains

The first class of inhomogeneous electric fields considered takes the cosine form

$$\mathcal{E}(\mathbf{r}) = \mathbf{A} \cdot \cos(\mathbf{k} \cdot \mathbf{r}) = \mathbf{A} \cdot \cos\left(\frac{2\pi x}{\lambda_x} + \frac{2\pi y}{\lambda_y} + \frac{2\pi z}{\lambda_z}\right), \quad (6.2)$$

where $\mathbf{k}$ controls the direction and periodicity of the spatial modulation, and $\mathbf{A}$ sets the direction and amplitude of the applied field. The relative orientation of these two vectors determines the nature of the resulting domain structure. When $\mathbf{k}$ and $\mathbf{A}$ are parallel or antiparallel, the field promotes head-to-head and tail-to-tail domain configurations, which are electrostatically unfavorable. When $\mathbf{k}$ and $\mathbf{A}$ are perpendicular, the field instead couples to transverse optical modes and stabilizes regular 180° domain walls, as illustrated in Figure 6.1 (a-c) for bulk PbTiO_3 . In the latter case, Bloch-like

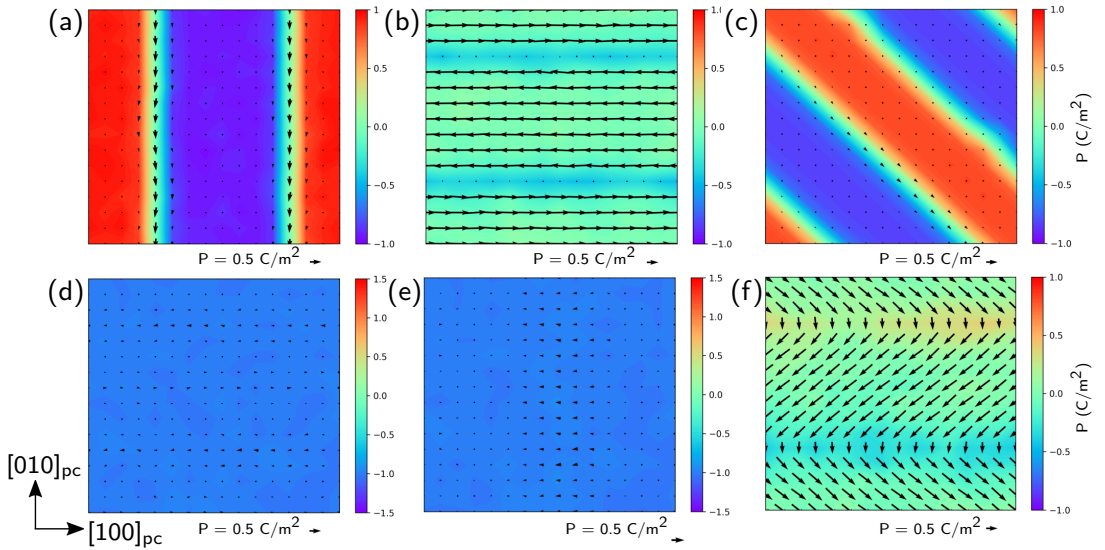


Figure 6.1: Stabilization of different domain textures in bulk PbTiO_3 after the application of an inhomogeneous electric field with the functional form of Eq. 6.2. (a) $\lambda_x = 16$ u.c. $\mathbf{A} = 0.51(0, 0, 1)$ MV/cm. (b) $\lambda_y = 16$ u.c. $\mathbf{A} = 0.51(1, 0, 0)$ MV/cm. (c) $\lambda_x = \lambda_y = 16$ u.c. $\mathbf{A} = 0.51(0, 0, 1)$ MV/cm. (d) $\lambda_y = 8$ u.c. $\mathbf{A} = 1.54(0, 0, 1)$ MV/cm (e) $\lambda_x = 16$ u.c. $\mathbf{A} = 25.7(1, 0, 0)$ MV/cm (f) in-plane tensile strain $a = b = 3.955 \text{ \AA}$ and $\lambda_y = 16$ u.c. $\mathbf{A} = 0.51(1, 0, 0)$ MV/cm. Arrows indicate the in-plane components of the polarization, whereas the color map represents the out-of-plane polarization. A reference arrow representing the scale of the in-plane polarization components is included.

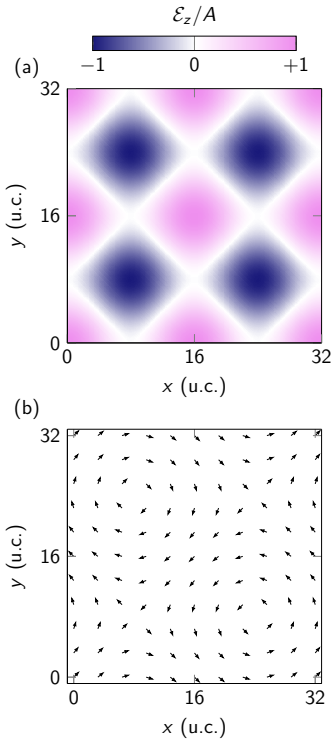


Figure 6.2: Superposed electric field used to stabilize the polar textures of Figure 6.3 (a) and (c). Colors the normalized component of the electric field along z while the arrows represent the in-plane component of the electric field.

polarization components emerge at the domain walls as a consequence of their ferroelectric character [191], a feature introduced in Section 5.1.1.

The polarization configuration obtained from the second-principles calculations does not necessarily mirror the applied electric field, as other energy contributions are inherently at play. Applying fields with very narrow periodicities or configurations that promote head-to-head and tail-to-tail domains will not necessarily produce such structures if they lead to energetically unfavorable solutions. For instance, in bulk PbTiO_3 , simulated in a $16 \times 16 \times 4$ supercell, a periodicity of $\lambda \leq 8$ u.c. does not result in 180° domain walls with the imposed periodicity. Instead, the dipoles tilt towards the direction perpendicular to the modulation, forming a more uniform pattern that minimizes gradient energies, as shown in Figure 6.1 (d). Similarly, when an electric field favoring head-to-head and tail-to-tail domains is applied, these configurations are largely suppressed at low field magnitudes. As the field strength increases, the system minimizes the electrostatic energy by lifting the dipoles towards the direction perpendicular to the modulation, thereby reducing the unfavorable bound charges arising from polarization divergence, as illustrated in Figure 6.1 (e).

Finally, when a sufficiently large tensile strain is applied to PbTiO_3 ($a = b = 3.955$ Å), the regular 180° domains evolve towards textures with a non-uniaxial polarization pattern, typically adopting a polarization wave arrangement as shown in Figure 6.1 (f). Notably, the PbO plane, which previously exhibited a ferroelectric instability along z , reorients along y while remaining perpendicular to the applied field, a response driven by elastic energy relaxation.

Stabilization of complex polar textures

More complex polar textures can be stabilized through the superposition of several electric fields of the form of Eq. (6.2). In particular, skyrmion textures can be stabilized in bulk PbTiO_3 by superposing two cosine fields, both oriented along z with amplitude $A = 0.51$ (0, 0, 1) MV/cm, but modulated along perpendicular directions x and y associated with periodicity λ_x and λ_y respectively. This promotes the formation of a square lattice of skyrmion bubbles [194], as illustrated in Figure 6.3 (a-b). It is noteworthy that the Bloch component

of the domain walls varies stochastically between individual skyrmions (Figure 6.3 (b)), demonstrating that they are not identical periodic replicas of one another and granting a distinct chiral nature to each defect.

Upon increasing the tensile strain on the system ($a = b = 3.955 \text{ \AA}$), in-plane lattices of vortices and antivortices can be stabilized, as shown in Figure 6.3 (c), through the superposition of two fields modulated along x and y with magnitudes along y and x respectively. The polarization wave previously stabilized under similar mechanical conditions (see Section 6.1.1) becomes unstable under the effect of the second modulated field, and closure textures emerge in order to comply with the imposed periodicity. This results in the evolution of the previously uniform domain wall along y into a structured wall exhibiting distinct internal domains with $P_y > 0$ and $P_y < 0$. Under the combined effect of the tensile strain and the two modulated fields, this corresponds to a transition from a uniform PbO ferroelectric domain wall [191] into an Ising line [255]. The vortex and antivortex singularities are placed at the intersection of the two domain walls, centered on a Pb

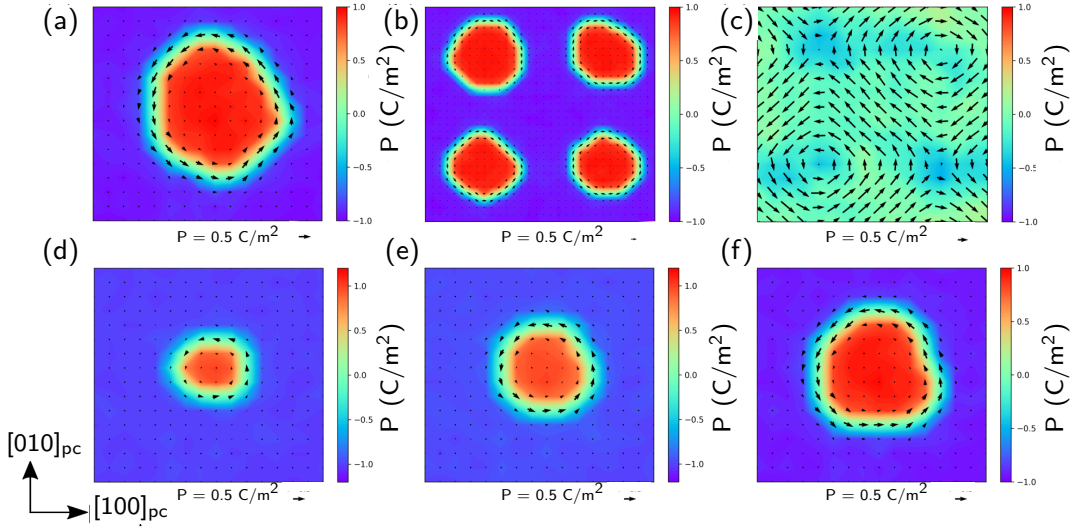


Figure 6.3: Stabilization of different textures in bulk PbTiO₃ by means of different electric fields. (a-b) Skyrmion lattice generated by the superposition of two cosine functions with periodicities of $\lambda_{1,x} = 16$ u.c. and $\lambda_{2,y} = 16$ u.c. and $\mathbf{A} = 0.51(0, 0, 1)$ MV/cm in a supercell of size $L = 16, 32$ u.c. respectively. (c) Stabilization of a vortex/antivortex lattice in epitaxially strained PbTiO₃ $a = b = 3.955 \text{ \AA}$ by the superposition of two cosine functions with periodicities of $\lambda_{1,x} = 16$ u.c. and $\lambda_{2,y} = 16$ u.c. and $\mathbf{A}_1 = 0.51(0, 1, 0)$, $(\mathbf{A}_2 = 0.51(1, 0, 0))$ MV/cm. (d-f) Individual Skyrmion defects stabilized by the effect of Gaussian pulses as achievable by an AFM tip with different values of $\sigma = 4, 5, 6$ u.c. respectively. Arrows indicate the in-plane components of the polarization, whereas the color map represents the out-of-plane polarization. A reference arrow representing the scale of the in-plane polarization components is included.

atom, and an out-of-plane polarization component develops at those points, granting a non-zero topological character to the texture and effectively forming a meron/antimeron lattice. Notably, these closure textures remain stable over large distances, allowing their nucleation with fields that do not require strong spatial modulation.

Single defects can also be stabilized by a Gaussian field applied on a homogeneous background of opposite polarity, mimicking the effect achievable with an atomic force microscopy tip as anticipated in Refs. [194, 292]. Such a field takes the general form

$$\mathcal{E}(\mathbf{r}, t) = \mathbf{A} \cdot e^{-(\mu - \mathbf{r} - \mathbf{v}t)^2 / \sigma^2}, \quad (6.3)$$

where μ is the center of the Gaussian field, σ its standard deviation, and $\mathbf{v}$ the velocity of the center of mass. By selecting different values of σ , bubble domains of different sizes can be stabilized, as shown in Figure 6.3 (d-f). However, if σ is chosen too small, the applied field is unable to nucleate any domain unless unrealistically large amplitudes are employed, and the resulting domains collapse into a monodomain phase upon removal of the bias.

6.1.2 Reversible and deterministic switching

One of the strengths of stabilizing polar textures via applied electric fields, compared to conventional methods such as strain engineering [283] or varying growth conditions [284], is the ability to actively manipulate the polar state of the material in real time. In the previous subsections, the initial structure before applying the electric field was the centrosymmetric cubic $Pm\bar{3}m$ phase for simplicity. However, as discussed below, similar control of the resulting phase is obtained when starting from an already polarized phase.

This subsection presents concrete examples in which domains along different directions or skyrmion lattices can be stabilized and dynamically switched between each other by varying the applied electric field. To illustrate this, Figure 6.4 collects the progressive evolution of the system at $T = 70$ K under different applied electric fields. Starting from a monodomain structure obtained after poling with a homogeneous field (Figure 6.4 (a)), a domain structure periodically repeated along x is nucleated by applying a field of the form of Eq. (6.2)

with $\lambda_x = 16$ u.c. and $A_z = 5.14$ MV/cm (Figure 6.4 (b)), which relaxes upon removal of the field (Figure 6.4 (c)). The domain orientation can subsequently be switched towards y by applying a softer field with periodicity $\lambda_y = 16$ u.c. and $A_z = 2.06$ MV/cm. Notably, these field-induced phases are long-lived metastable states that remain stable after the field is removed (Figure 6.4 (d)).

The domain structure can be erased by applying a homogeneous field of amplitude $A_z = 1.54$ MV/cm, or rewritten at convenience following the procedure described above. Furthermore, a transition from periodically repeated domain structures to a lattice of skyrmions can be achieved by simultaneously applying two fields modulated along x and y with $\lambda_{1,x} = \lambda_{2,y} = 16$ u.c. and $A_z = 5.14$ MV/cm (Figure 6.4 (f)). Upon removal of the field, the periodic lattice of bubble nanodomains further relaxes into a lattice of skyrmion textures, demonstrating once more the stability of the nucleated phases and the deterministic character of the control.

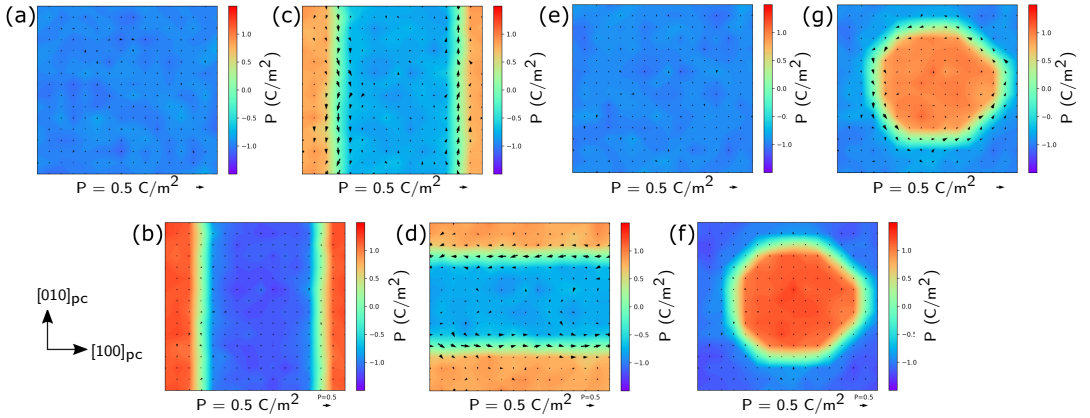


Figure 6.4: Dynamical evolution of different textures in bulk PbTiO₃ stabilized by means of electric fields. (a) Initial phase showing a monodomain configuration. (b) Domain structure under the application of a modulated electric field following Eq. (6.2) $\lambda_x = 16$ u.c. and $\mathbf{A} = 5.14(0, 0, 1)$ MV/cm (c) Relaxed domain structure after removing the electric field. (d) Relaxed opposite domain configuration after the application of a modulated field following Eq. (6.2) $\lambda_y = 16$ u.c. and $\mathbf{A} = 2.06(0, 0, 1)$ MV/cm. (e) Monodomain structure obtained under the application of a homogeneous field of magnitude 1.54 MV/cm. (f) Lattice of bubble domains after the application of two modulated fields along x and y with magnitude 5.14 MV/cm. (g) Skyrmion lattice after the relaxation of (f) under no external fields. Arrows indicate the in-plane components of the polarization, whereas the color map represents the out-of-plane polarization. A reference arrow representing the scale of the in-plane polarization components is included.

6.1.3 Dynamics of ferroelectric domains

After stabilizing domain structures and demonstrating deterministic switching between different configurations, the displacement of domain walls under time-dependent electric fields is now investigated using time-dependent electric fields. This section focuses on their mobility, examining how domain walls respond to changes in the electric field and how fast they can rearrange. In order to account for the time modulation of the electric field an extra term needs to be added to the functional form presented in Eq. (6.2) that now reads

$$\mathcal{E}(\mathbf{r}, t) = \mathbf{A} \cdot \cos\left(\frac{2\pi x}{\lambda_x} + \frac{2\pi y}{\lambda_y} + \frac{2\pi z}{\lambda_z} + \frac{2\pi t}{T}\right), \quad (6.4)$$

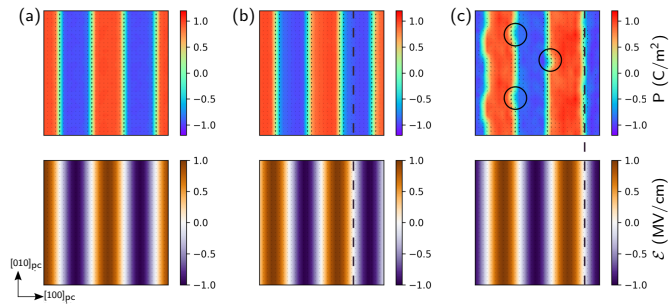
where T is the period of the time-modulation. The expected velocity of the electric field wave, corresponding to the propagation speed of its phase, is then given by

$$v = \left(1/\lambda_x^2 + 1/\lambda_y^2 + 1/\lambda_z^2\right)^{-1/2} / T, \quad (6.5)$$

which, in the most common case of a single spatial modulation, reduces to $v = \lambda/T$.

The motion of domain walls is critical to many applications involving ferroelectric materials and has been deeply studied in the context of homogeneous electric fields under the nucleation and growth framework [293–297]. However, their behavior under inhomogeneous and time-dependent electric fields, as well as the dynamics of topological textures, remains comparatively underexplored except for a few recent works [292, 298]. In Figure 6.5, the molecular dynamics re-

Figure 6.5: Domain wall motion in bulk PbTiO₃. Domain structure (upper row) and instantaneous electric field (bottom row) at (a) $t = 0$ s. (b) $t = 4.8$ ns and (c) $t = 9.3$ ns. Arrows in the dipole patterns represent the in-plane components of the polarization. The color bar in the electric field represents its normalized value along the z direction. The dashed lines in panels (b) and (c) represents the location of the node of the electric field wave and the circles in panel (c) highlight domain nucleation points.



sults are shown for the domain wall motion under an external electric field of magnitude 2 MV/cm, periodicity $\lambda_x = 16$

u.c. and velocity $v = 300$ m/s. The temporal variation of the electric field imposes a constraint on the domain walls, requiring them to adapt to the periodic changes in the electric field. However, as revealed in [Figure 6.5 \(b\)](#), a noticeable lag in their response to the field's oscillations can be observed (see dashed line), proving a delay in the reaction time of the domains to the external driving force that amounts to 4 ps at $T = 5$ K for the 16 u.c. domain periodicity. Interestingly, this lag is only present at the onset of the dynamics; once the domains begin to move, the correlation between the domain wall position and the node of the electric field wave becomes one-to-one (see dashed line in [Figure 6.5 \(c\)](#)). Moreover, this lag shows a strong temperature dependence: when the system is heated to 100 K, the lag is reduced by half, and at 200 K, it already becomes negligible. Interestingly, when the electric field is removed, the domains stop moving immediately, showing no sign of residual momentum, although this observation can be slightly influenced as a consequence of the domain propagation mechanism.

The molecular dynamics simulations confirm that domain displacement follows the diffuse boundary model as proposed in Ref. [295]. As shown by the solid circles in [Figure 6.5](#), certain regions of the domain nucleate first, and the domain wall subsequently follows this initial nucleation, rather than propagating uniformly across the domain. Therefore, if the nucleus of the new domain exceeds a critical size, it can lead to the formation of an additional domain layer even after the electric field is removed. However, this phenomenon is more related to the relaxation of the domain structure than to an inertial response. While the absence of response delay upon field removal is consistent with the findings of Ref. [299], these results complement them by demonstrating a clear response delay at the onset of domain wall motion. This asymmetry in the response delay of domains comes from the intrinsic energy barrier for nucleation.

Besides, there are scenarios where domains remain immobile due to the high activation energy associated with their motion irrespective of the wave velocity. These observations indicate, for instance, that domain mobility is strongly influenced by their size: domains with double periodicity (32 u.c.) remain static when the electric field is adjusted to match their modulation while retaining the magnitude that renders domains with a periodicity of 16 u.c. already mobile. The activation energy barrier can be mitigated by either increasing

the temperature or enhancing the magnitude of the electric field applied to the domains. Specifically, when the periodicity of the domains and the corresponding electric fields is doubled, the field magnitude should also be doubled in order to produce sufficient force on the domains, enabling their movement. This relationship between activation energy, temperature, and electric field is consistent with the predictions of the creep law [296, 297]. These adjustments enable domains to transition from an immobile to a mobile regime, allowing even larger domains to overcome their activation energy.

When the propagation speed of the electric field increases, the domain structure is unable to keep up with the rapid oscillations and eventually regions of negative electric field align with positive polarization regions. This misalignment induces a chaotic evolution in the system, leading to the fragmentation of the domain structure and marking the maximum velocity at which domains can move. In this case, with $\lambda_x = 16$ u.c. and a field amplitude of 2 MV/cm, this limiting velocity was approximately 3000 m/s, significantly higher than the 900 m/s recently reported for magnetic skyrmions [300]. If the wave velocity of the electric field is increased further, there is a threshold beyond which the domains become effectively immobile, no longer responding to the applied electric field. Interestingly, the limiting velocity at which domains lose connectivity and destabilize remains unaffected by changes in the electric field magnitude or temperature as long as the domains remain in the mobile regime. The domain structure consistently destabilizes at the same electric field velocity, marking an intrinsic upper bound on domain wall motion that is probably related with the material and the stability of the multidomain structure.

Similar characteristics, such as the lag in response and asymmetric response delay, existence of a limiting velocity (which is indeed identical to the one previously reported), and diffuse boundary nucleation, are also observed in the dynamics of bubble domains. In such a case, the motion of the bubble domains is governed by the elongation and contraction of their structure, resembling the deformation of a water droplet or the motion of an amoeba. Remarkably, the mobility of these bubble domains is isotropic, enabling them to move equivalently in any direction in response to the position of a Gaussian field, without exhibiting any preference for specific crystallographic directions. Furthermore, they can adapt to

other waveforms, such as cosine functions, maintaining their structural integrity while being displaced by these periodic perturbations under appropriate electric field magnitudes.

6.1.4 Stabilization and switching of skyrmion tubes in BaTiO₃

So far, the focus has been placed on the metastability of skyrmions and antiskyrmions in rhombohedral BaTiO₃, where these structures are constructed by intentionally imposing atomic displacements and subsequently relaxing the configurations. In this section, it is shown that these textures can be stabilized using inhomogeneous electric fields, providing an experimental pathway for their realization. In order to sta-

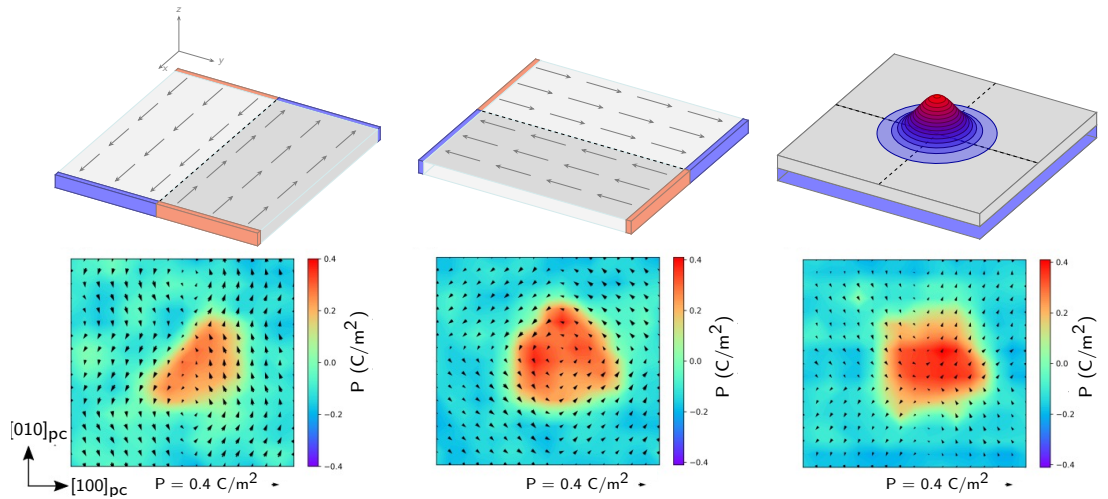
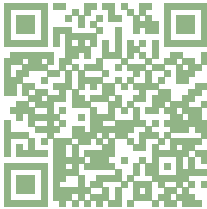


Figure 6.6: Schematic view of the computational experiment. (a-c) The black arrows denote the desired polarization direction within the material. The red and blue stripes represent electrodes, which can be sequentially activated in a stepwise manner during experimental implementations to achieve the intended polarization (a) Polarization field modulated along the x -direction and directed along y . (b) Polarization field modulated along y and directed along x . (c) Control of the out of plane components achievable by with an AFM tip. (d) Obtained structure after the application of a modulated electric field as described in the text. (e) Skyrmion texture after in-plane and out of plane components have been controlled with the application of extra fields in configurations (b) and (c). (f) Antiskyrmion texture obtained from (e) after reverting the polarity of the electric field shown in (b). Arrows indicate the in-plane components of the polarization, whereas the color map represents the out-of-plane polarization.

bilize the in-plane components of the polarization, spatially modulated electric fields are employed. In Figure 6.6 (a), an initial polarization texture is schematically illustrated. Experimentally, this could be achieved by sequentially activating contiguous electrodes in a stepwise manner, as depicted in the schematic. Numerically, an electric field of 1 MV/cm



[†]Supplemental Videos 4 of Ref. [216]

modulated along x and directed along y by a cosine function is imposed in order to comply with periodic boundary conditions, and the evolution of the system ($L = 17$ u.c.) is studied through finite-temperature simulations at $T = 10$ K. In tetragonal ferroelectrics, such electric fields will result in the stabilization of 180° domain walls with the polarization aligned along y . However, due to the rhombohedral nature of BaTiO_3 , in-plane polarization components along the x -direction will also develop as well as out-of-plane components resulting on a more complex structure (see Figure 6.6 (d)). The direction of the in-plane polarization components along the x axis can vary and show an erratic behavior as shown in Figure 6.6 (d) varying depending on the specific realization. However, applying now an electric field oriented along x and modulated along the y direction allows effective control over these in-plane components. This second field induces polarizations along the x axis, similar to those illustrated in Figure 6.6 (b). Utilizing such configuration will stabilize a vortex, while reversing the polarity of this second field will result in the stabilization of an antivortex texture, as shown in Figure 6.6 (e-f), respectively. Furthermore, this procedure can be applied recursively; by alternating the polarity of the second electric field, a controlled switching between skyrmion and antiskyrmion states can be achieved[†]. Alternatively, activating simultaneously the electrodes shown in Figure 6.6 (a) will already stabilize an antivortex texture. due to the electric fields generated between contiguous electrodes. Importantly, due to the nature of the domain-walls only Ba-centered vortex/antivortex can be stabilized in this way.

Similar to the in-plane components, the out-of-plane components will vary depending on the realization when no bias is applied to the sample. To achieve a localized nanocolumn, as shown in Figure 6.6 (e-f), a Gaussian field as achievable with an AFM tip has been applied on top of a homogeneous background of opposite polarization. Figure 6.6 (c). Experimentally, a homogeneous out-of-plane polarization could first be established via scanning, followed by local reversal to achieve the desired nanocolumn. An important aspect to highlight is that once the nanocolumn is established, it remains stable, and the switching of the in-plane components does not affect it, in agreement with the DFT results that proved the flexibility of the out-of-plane components to adjust to vortex and antivortex cores. This stability enables the transition

from skyrmion to antiskyrmion to occur without the need for an electric field applied along the z direction. Because the in-plane polarization components extend over a large scale, as discussed throughout the manuscript, highly spatially modulated electric fields are not required, facilitating the experimental implementation of this setup.

6.2 Dynamical manipulation of polar topologies from acoustic phonon excitations

The stabilization of complex polar textures through inhomogeneous electric fields, as demonstrated in Section 6.1, constitutes a powerful approach for nucleating and switching topological defects. Nevertheless, the application of spatially modulated electric fields may prove impractical in certain experimental configurations, in particular when dealing with conducting or semimetallic materials where electric fields are screened. In such cases, a mechanically-based route offers a natural alternative: rather than coupling to the polarization through the Born effective charge tensor, the same strain-mediated response can be activated through the excitation of acoustic phonons, which propagate freely regardless of the electronic character of the material [302].

Acoustic phonon excitations (APEX) constitute spatially periodic deformations of the crystal lattice that propagate as mechanical waves. In ferroelectric perovskites, ferroelectricity is strongly coupled to both homogeneous [283, 303] and inhomogeneous strains [44, 288, 304–306], as introduced in Chapter 2. The flexoelectric effect and the strong polarization-strain coupling are at the root of the effectiveness of mechanical boundary conditions in stabilizing complex polar phases. This is evidenced by the formation of complex topological structures in two-dimensional twisted freestanding layers (see Figure 6.7) [301, 307, 308], around induced cracks [309], on top of wrinkled surfaces [265], and on rippled surfaces [310]. However, in all these configurations, the mechanical boundary conditions are largely fixed and solely determined by the initial structural setup, namely the twist angle, the shape of the crack, or the surface morphology. Methods that rely on an on-demand, externally tunable strain pattern therefore remain challenging to achieve.

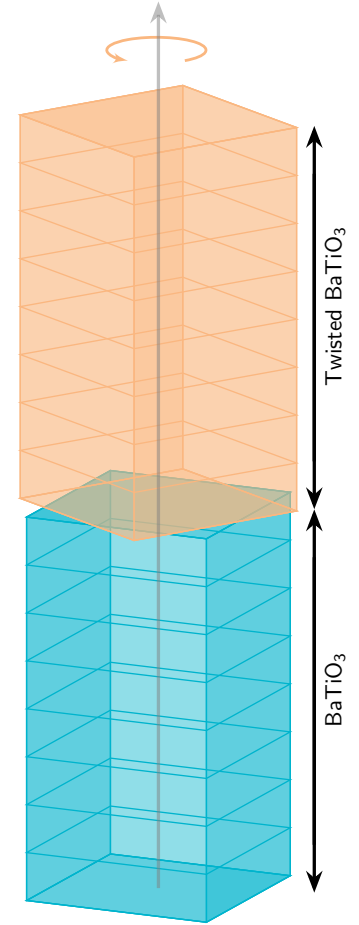


Figure 6.7: Schematic representation of the twistronics geometry employed in Ref. [301], in which a BaTiO_3 freestanding layer is twisted by a small angle relative to a reference BaTiO_3 substrate, giving rise to a moiré pattern and the associated complex polar textures at the interface.

As discussed in [Section 6.1](#), earlier attempts at dynamical control of polar textures relied primarily on the pumping of polar optical phonons through electric field or optical pulses [290, 291]. While these approaches demonstrated that in situ phase manipulation is in principle achievable, they suffer from two important limitations: only switching between specific phases has been demonstrated so far, and the relationship between the pulse characteristics and the resulting polar arrangement remains poorly understood.

The [APEX](#) approach proposed here addresses both of these shortcomings. By activating specific longitudinal and transverse acoustic modes, a spatially modulated strain field is imprinted on the material, which drives the nucleation of ferroelectric domain walls and more complex topological textures through flexoelectric coupling. The resulting polar arrangement can be anticipated a priori from the symmetry and wavevector of the pumped modes, making the method both deterministic and predictable. The results presented in this section demonstrate this approach in BaTiO_3 and PbTiO_3 as model systems, and are based on first- and second-principles simulations employing the models described in [Section 4.3.3](#) and [Section 4.3.4](#). Generalizations to other compounds exhibiting ferroelectric instabilities are in principle possible, opening a novel pathway for the discovery of materials displaying non-trivial polar topologies. These results constitute the main findings of Ref. [208].

Before discussing the consequences on the polarization pattern, the structural implications of activating [APEX](#) on the material are briefly examined. The phonon dispersion curve of PbTiO_3 in the $Pm\bar{3}m$ phase, as computed from first-principles at zero Kelvin, is shown in [Figure 6.8](#). Focusing on the Γ -X acoustic branch, two distinct mode types can be identified: the doubly degenerate transverse mode (see [Figure 6.8 \(b\)](#)) and the longitudinal mode (see [Figure 6.8 \(c\)](#)). The structural distortions generated by these [APEX](#) favor the development of head-to-head or tail-to-tail domains in the longitudinal case, and of 180° domain walls in the transverse case, consistent with the cell deformations at domain walls established from first-principles since the seminal work of Meyer and Vanderbilt [190]. With this structural picture in mind, the following subsections demonstrate how the judicious selection and combination of [APEX](#) drives the generation of various polar textures through flexoelectric coupling.

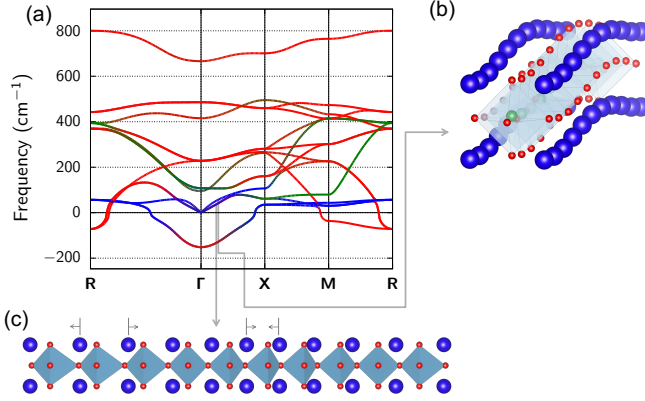


Figure 6.8: (a) Phonon dispersion curve of PbTiO₃ in the chosen $Pm\bar{3}m$ reference structure. The colors (Pb: blue; Ti: green; O: red) show the contribution of each atom to the eigenvectors. (b) Transversal APEX. (c) Longitudinal APEX. The amplitudes of the distortions have been augmented for visualization purposes.

6.2.1 Single acoustic mode

A unique transverse APEX from the Γ -X acoustic branch is first pumped into the $Pm\bar{3}m$ phase of PbTiO₃, inducing an overall distortion of 1 Å, corresponding to a maximal displacement of 0.015 Å of Pb atoms. Depending on its orientation, a significant strain gradient $\varepsilon_{xz,x}$ or $\varepsilon_{yz,y}$ is induced in the material as shown in Figure 6.9 (a2-b2). Upon the relaxation of the supercell, this strain gradient induces the formation of ferroelectric domain walls [191] through the flexoelectric effect as evidenced in Figure 6.9 (a3-b3). Indeed, depending on the wavevector of the mode $q = 1/20$ u.c.⁻¹ or $q = 1/10$ u.c.⁻¹, where u.c. stands for unit cell, the magnitude of the strain gradient varies leading to initial induced polarization values of 1.14 $\mu\text{C}/\text{cm}^2$ and 3.88 $\mu\text{C}/\text{cm}^2$ respectively. After relaxation of the supercell, typical polarization values of 93 $\mu\text{C}/\text{cm}^2$ and 84 $\mu\text{C}/\text{cm}^2$ respectively (comparable to the values reported in Section 5.1.1 in Table 5.2), are recovered inside the domain. The formation of a Bloch component within the domain wall arises from the ferroelectric nature of the domain walls introduced in Section 5.1.1, rather than being a direct result of the imposed strain gradient. The results presented are paradigmatic examples; however, other domain wall types, such as Ising or Néel, can also be engineered by pumping the longitudinal mode of the same phonon branch. Besides, the amplitude and location of the strain and strain gradient are tunable by adjusting the amplitude and phase of the acoustic wave. As shown in Figure 6.9, the size of the domains can be designed by selecting different q -points from the acoustic branch.

Remarkably, even if they remain stable across the entire Brillouin zone, pumping a phonon from the acoustic branch with positive frequency, results in a phase that is lower in energy than the initial $Pm\bar{3}m$ configuration in which the phonon was pumped. This energy lowering can be explained by the coupling of the acoustic branch and the optical soft-mode [89, 311–313] that after relaxation of the cell develops a non zero local polarization state.

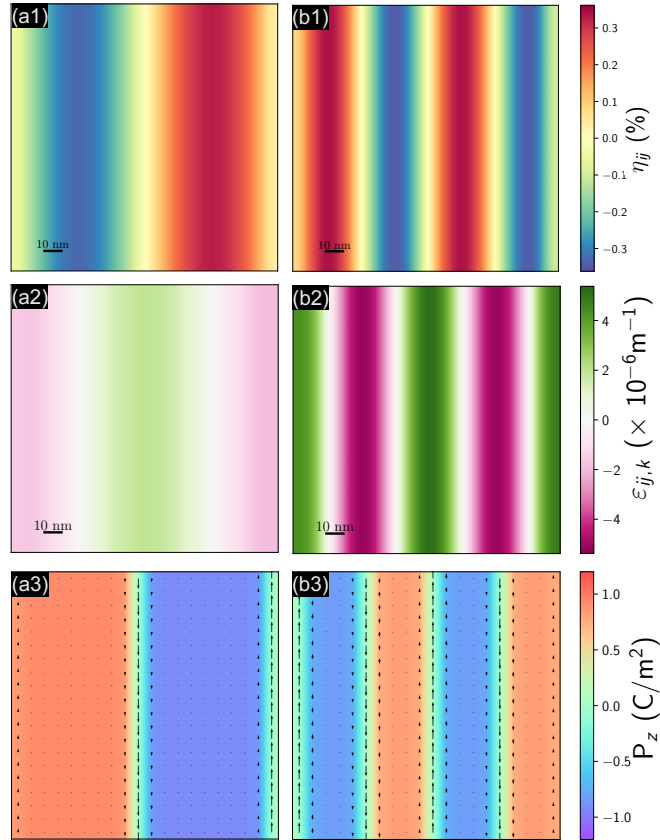


Figure 6.9: Stabilization of different domain walls in bulk PbTiO_3 after the application of an APEX of amplitude $1 \text{ \AA}$ and periodicities of $1/20$ and $1/10 \text{ u.c.}^{-1}$. (a1-b1) Shear strain, η_{xz} , produced in the material. (a2-b2) Induced strain gradients, $\varepsilon_{xz,x}$. (a3-b3) Polarization patterns after relaxation of the supercell. Arrows indicate the in-plane components of the polarization whereas the color map represents the out of plane polarization.

6.2.2 Combination of acoustic modes

Up to now, it was shown that the location and size of domains can be controlled using a unique transverse APEX. However, it is also possible to pump simultaneously more than one phonon. In this section, it is shown that mixing several APEX

can create a multitude of combinations, leading to non-trivial polar textures in both BaTiO₃ and PbTiO₃.

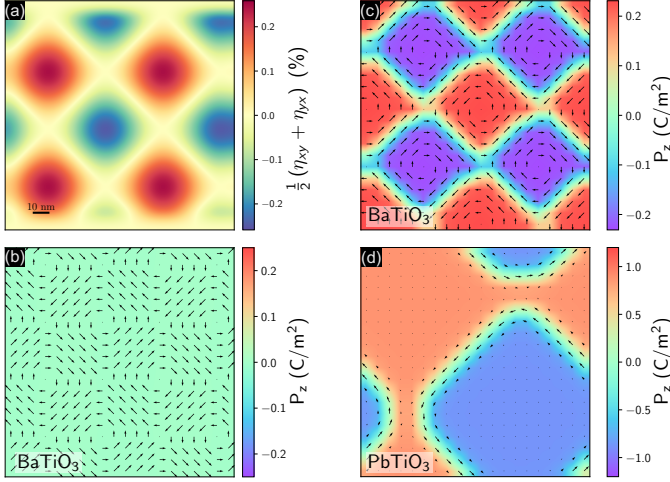


Figure 6.10: Stabilization of different topological defects by combining longitudinal and transversal acoustic phonons from the $\Gamma - X$ branch of the $Pm\bar{3}m$ phase of (a-c) BaTiO₃ and (d) PbTiO₃. (a) Local initial in-plane shear strain, and (b) in-plane polarization after relaxation in BaTiO₃ by the pumping of transversal APEX along x and y with periodicities of $q = 1/10$ u.c.⁻¹. (c) Polarization pattern after relaxation in BaTiO₃ displaying a meron-antimeron lattice when transversal APEX of periodicity $q' = 1/10$ u.c.⁻¹ are imposed on top of the in-plane distortion. For visualization purposes, the pattern has been shifted by 3 u.c. along the $[110]$ direction relative to (a) and (b). (d) Polarization pattern after relaxation in PbTiO₃ displaying skyrmion as a result of transverse APEX with periodicities of $q = 1/20$ u.c.⁻¹. Arrows indicate the direction of the in-plane components of the polarization while color maps reflect the out-of-plane component.

For instance, using a combination of longitudinal phonons from the $\Gamma - X$ branch, an alternating pattern of positive and negative η_{xy} shear strains, defined as $\frac{1}{2} \left(\frac{\partial u_y}{\partial x} + \frac{\partial u_x}{\partial y} \right)$, can be induced in bulk BaTiO₃ where u_x and u_y are the atomic displacements in the x - and y -directions with respect to the undistorted cell respectively. Interestingly, this initial structure resembles the experimentally observed 2D ferroelectric vortex pattern in twisted BaTiO₃ freestanding layers [301], as shown in Figure 6.10 (a). Therefore, pumping this combination of longitudinal APEX subsequently gives rise, after relaxation, to an in-plane polar texture similar to that observed in twisted bilayers, as evidenced in Figure 6.10 (b). The aforementioned modes can be combined with a transverse APEX similar to the ones discussed previously for the PbTiO₃ case and create a non-zero η_{xz} and η_{yz} shear strain map. This induces the development of an out of plane component of the polarization on top of the in-plane components that leads to the formation of a meron/anti-meron lattice. This phase is similar to those already observed in PbTiO₃/SrTiO₃ freestanding layers [314] or chiral magnets [315]; however, this constitutes, to the best of the author's knowledge, the

first prediction of a meron/anti-meron lattice in BaTiO_3 . Following a similar spirit of combining APEX, more complex phases can also be stabilized in PbTiO_3 . As shown previously, alternating positive and negative η_{xz} and η_{yz} strains can create ferroelectric domain walls. These ferroelectric domain walls have been demonstrated to be the key ingredient in nucleating polar skyrmions equivalent from the one studied in Section 5.1.2. By combining the transverse APEX that leads to ferroelectric domain walls along the x -axis with the mode that leads to ferroelectric domain walls along the y -axis, the creation of a polar skyrmion is naturally achieved, as shown in Figure 6.10 (c). As demonstrated by the previous examples, fine-tuning of the polarization texture can be achieved in various ferroelectric materials by combining several APEX. The discussed method not only proves effective in stabilizing previously reported polarization textures but also predicts novel configurations. Furthermore, the method is deterministic, allowing the resulting polarization pattern to be anticipated a priori after selecting the appropriate modes.

6.2.3 Dynamical control of polar patterns

Until now, the focus has been placed solely on the stabilization of various polar patterns. However, unlike conventional methods where mechanical boundary conditions are solely fixed by growth conditions, the flexoelectric response to acoustic waves is dynamical [311], enabling real-time manipulation of polar textures by activating APEX.

This section provides a concrete example in demonstrating that the method enables dynamical control of the orientation of the ferroelectric domains in PbTiO_3 . Previous studies have shown that the orientation of the domains exhibits a stochastic Vogel-Fulcher-type behavior [316].

Relying on the specific conductive properties of domain walls [317], a deterministic control of this orientation might so reveal crucial for designing novel nanoelectronic devices such as transistors [318].

To achieve precise control over the orientation of the ferroelectric domains, a two-step process is employed. Initially, a transverse APEX with a periodicity of $q_1 = 1/10 \text{ u.c.}^{-1}$ is

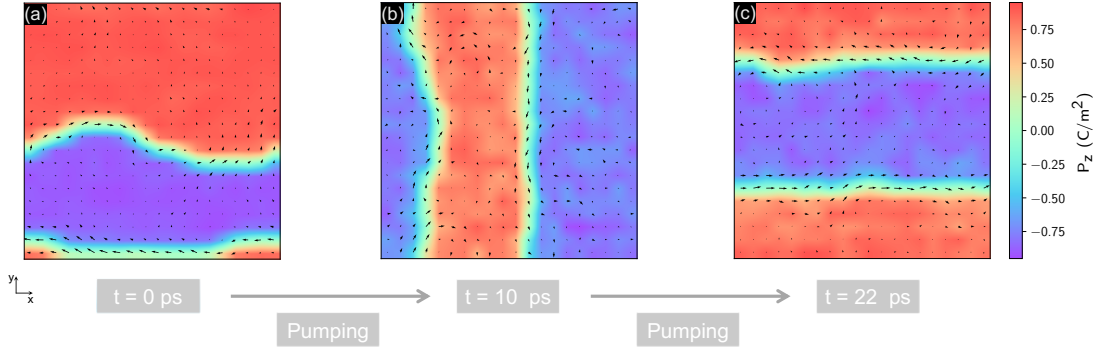


Figure 6.11: Dynamical tuning of domain orientation in PbTiO_3 by APEX as described in the text. Snapshots of molecular dynamics simulation at (a) 0 ps showing a domain along the x -direction, (b) 10 ps showing a domain along the y -direction after the application of the acoustic phonons and (c) 22 ps showing the reversal to a x -oriented domain driven by the phonon pumping. Arrows indicate the in-plane components of the polarization whereas the color map represents the out of plane polarization.

pumped. The strain gradient associated with this periodicity, of approximately $6.1 \times 10^7 \text{ m}^{-1}$, has been shown to be sufficient to reorient the domains with a moderate phonon amplitude of $12 \text{ \AA}$. This corresponds to a maximal lead displacement of $0.17 \text{ \AA}$ compared to the cubic phase that does not break the stability of the crystal. Subsequently, APEX with the desired periodicity, specifically $q_2 = 1/20 \text{ u.c.}^{-1}$ in this instance, are pumped. This dynamical approach underscores the potential of this method for fine-tuning polar textures in advanced material applications. As illustrated in Figure 6.11 (a), the simulation is initialized with the ferroelectric domains oriented along the x -direction. Then, q_1 is pumped eight times at intervals of 0.36 ps , propagating along the x -direction. Note that, as shown in Figure 6.9, these acoustic phonons along the x -direction would favour the y -orientation of the domains. Afterwards, q_2 is pumped four times at intervals of 0.36 ps , again propagating along the x -direction. Finally, the system is allowed to evolve over a period of 7 ps and as shown in Figure 6.11 (b) the domain orientation is flipped. To revert again the domain orientation and transit back to an x -oriented domains (see Figure 6.11 (c)), the same procedure is applied but now with the wave propagating along the y -direction.

As demonstrated here, the orientation switching of the domains can occur even at relatively low temperatures where the domains are typically expected to be static [316]. This suggests that effective tuning of the polar phase by means of APEX could be achieved at room temperature, making it a

promising candidate for new electronic applications. Moreover, this example serves as a proof of concept, indicating that this dynamical control approach could be extended to other phenomena, thereby offering new opportunities for the control of polar patterns.

6.3 Summary

This chapter presented two complementary approaches for the dynamical manipulation of polar textures in bulk ferroelectric perovskites, both relying on spatially modulated excitations rather than static homogeneous boundary conditions.

The first approach, based on inhomogeneous and time-dependent electric fields, was shown to enable precise and reversible control over a broad range of polarization configurations in PbTiO_3 and BaTiO_3 . Through the appropriate choice of field geometry, amplitude, and periodicity, stripe domain structures, skyrmion lattices, vortex/antivortex lattices, and individual skyrmion defects were stabilized deterministically. In rhombohedral BaTiO_3 , it was further demonstrated that skyrmions and antiskyrmions can be nucleated and switched between each other in a controlled manner, providing a concrete experimental pathway for their realization. The dynamical study of domain-wall motion under time-dependent fields revealed features consistent with creep dynamics, an asymmetric response delay at the onset of motion, and an intrinsic upper bound on the domain-wall propagation speed.

The second approach, based on *APEX*, exploited the strong flexoelectric coupling in ferroelectric perovskites. It was shown that pumping a single transverse acoustic mode generates well-defined strain gradients that deterministically nucleate ferroelectric domain walls, with domain size and location tunable through the choice of q -point and phonon amplitude. By combining multiple *APEX*, a richer variety of polar textures was accessed, including in-plane vortex patterns, meron/anti-meron lattices in BaTiO_3 , and skyrmion defects in PbTiO_3 . The dynamical character of the flexoelectric response was further exploited to demonstrate real-time switching of the ferroelectric domain orientation in PbTiO_3 ,

even at temperatures where domains are typically expected to be static.

Taken together, these results establish spatially modulated excitations as a powerful and versatile tool for the in situ engineering of polar topologies, opening new perspectives for the design of nanoelectronic devices based on the controlled manipulation of ferroelectric domain structures.

Ferroelectricity and synthetic antiferroelectricity in CaTiO_3

7

CaTiO_3 occupies a peculiar place among perovskite oxides. In its bulk ground state, it adopts the nonpolar orthorhombic $Pbnm$ structure, characterized by oxygen octahedra rotations, and is, strictly speaking, neither ferroelectric nor antiferroelectric: macroscopically, it behaves as an ordinary dielectric, with a polarization that varies linearly with the applied electric field. Yet it does not sit far from polar order. The low-temperature increase of its dielectric constant has long led to its description as an incipient ferroelectric [224, 230], and a genuine spontaneous polarization can indeed be induced by tensile epitaxial strain or by chemical substitution [220, 225, 319–322]. CaTiO_3 is therefore best understood as a compound poised close to a ferroelectric instability, whose latent polar character can be revealed by appropriate external control.

This proximity to polar order also raises the question of its relation to antiferroelectricity. In this respect, the comparison with PbZrO_3 , the prototypical antiferroelectric perovskite, is instructive: the two compounds have remarkably close Goldschmidt tolerance factors, yet PbZrO_3 is a well-established antiferroelectric while CaTiO_3 is not [232]. This contrast shows that the tolerance factor alone does not determine antiferroelectric behavior, and that CaTiO_3 , despite not being antiferroelectric, lies close enough in configuration space for the question of its potential antiferroelectric character to be a meaningful one.

This chapter examines the ferroelectric and antiferroelectric potential of CaTiO_3 from this standpoint. The first part focuses on bulk CaTiO_3 and on the metastable polar $R3c$ phase: its connection to the $Pbnm$ ground state through the minimum energy path, its thermal stability, and the conditions under which an electric field could stabilize it, thereby probing whether bulk CaTiO_3 can be regarded as ferroelectric or antiferroelectric. The second part turns to epitaxial CaTiO_3 films grown on differently oriented NdGaO_3 substrates, and shows, through a combination of experimental and theoretical approaches, that epitaxial strain can tune the energy landscape associated with different orientation of the polarization and ultimately enable a deterministic *first-order*

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- 12. Phys. Rev. B 112 (22), 224103
- 15. arXiv:2603.27590

polarization process, an electric analogue of the first-order magnetization process known in magnetism [323, 324], giving rise to the associated double hysteresis loops. This second part stems from a close collaboration with experimentalists, in particular Lukas Korosec, from the group of Jean-Marc Triscone, and Marios Hadjimichael: the experimental results, which are essential to the conclusions and inseparable from the theoretical analysis, were obtained by our collaborators, while the contribution of the author concerns the theoretical and computational part. The complete list of contributors is given in the corresponding publication [231].

7.1 Finite-temperature properties and the hidden ferroelectric $R3c$ phase

As seen in Section 4.3.5, although the polar $R3c$ phase has a higher energy than the $Pbnm$ ground state, it is free of lattice instabilities (see Figure 4.33 (b)), so that it corresponds to a local minimum on the potential energy surface and has the potential to be stabilized at low temperatures. Consistently, this polar $R3c$ phase has been experimentally stabilized in CaTiO_3 films grown on (111)-oriented LaAlO_3 substrates at room temperature [325]. The second-principles CaTiO_3 model presented in Section 4.3.5 successfully captures this metastable $R3c$ phase, providing an opportunity to further investigate its intrinsic properties in bulk. The focus is therefore placed on the metastability of the $R3c$ phase in bulk CaTiO_3 and on the conditions under which it can be stabilized under an external electric field, with the aim of probing the potential ferroelectric or antiferroelectric nature of bulk CaTiO_3 .

7.1.1 Minimum energy path connecting $Pbnm$ and $R3c$ phases

First, the minimum energy path connecting the $Pbnm$ ($a^-a^-c^+$) and $R3c$ ($a^-a^-a^-$) phases is explored using the NEB method. Although these two phases exhibit different oxygen octahedra rotation patterns, they share a common rotation component, $a^-a^-c^0$. To construct the initial path, the atomic displacements contained in the common rotation component are first aligned and then a linear interpolation is performed.

The NEB calculations is repeated on supercells of different sizes.

The calculation on $2 \times 2 \times 2$ supercells (with respect to the five-atoms perovskite unit cell) converged to a path that exhibits one energy barrier, as illustrated in Figure 7.1 (a). Along this path, from *Pbnm* to R3c, the octahedra rotations around the pseudocubic [001] direction (denoted as “*c*-rotations”) gradually change from in-phase to antiphase, i.e., the rotation direction of every second layer of oxygen octahedra is flipped. The energy barrier of the NEB path is 40.3 meV/f.u. from the *Pbnm* side and 14.0 meV/f.u. from the R3c side.

On supercells larger than $2 \times 2 \times 2$, an interesting observation is that the calculations converge to NEB paths with multiple energy barriers. Specifically, two energy barriers are observed on the NEB path calculated using $4 \times 4 \times 4$ supercells, three barriers for $6 \times 6 \times 6$ supercells, and so on, with N barriers expected for $2N \times 2N \times 2N$ supercells, as illustrated in Figure 7.1 (a). A close inspection of the structural changes along the NEB paths reveals that each of the energy barriers corresponds to the flipping of one layer of octahedra rotations in the simulation supercell. In the $2 \times 2 \times 2$ supercell, there is only one layer of octahedra rotation flipped during the change of *c*-rotations from in-phase to antiphase, resulting in one single energy barrier; whereas in larger supercells, more layers of octahedra are allowed to flip independently, and therefore the calculations result in multiple energy barriers. The multiple energy barriers in larger supercells indicate that along the minimum energy path from *Pbnm* to R3c, different layers of octahedra are flipped one-by-one.

Another interesting observation from the NEB calculations is the decreasing trend of the energy barrier with the increase of the supercell size (Figure 7.1 (a)), which seems to imply a paradox: as the supercell size becomes infinitely large, the barrier for the transition from R3c to *Pbnm* will tend to be infinitely small. This could lead to the suspicion that the R3c phase might not be able to remain stable on a macroscopic scale, as even a small perturbation could destabilize R3c in favor of *Pbnm*, which seems to contradict the fact that the R3c phase is dynamically stable and does not show lattice instability at 0 K. To resolve this paradox, the localized nature of the layer-by-layer flipping of oxygen octahedra rotations along the NEB path must be considered, and the way of computing the energy need to be changed. It should be noted

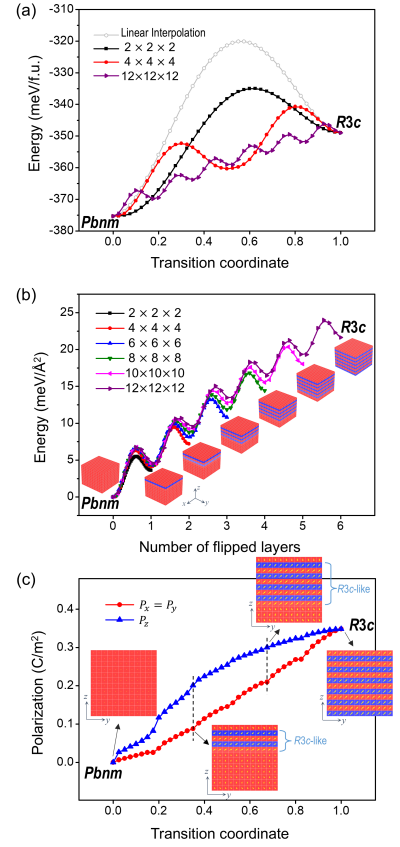


Figure 7.1: Minimum energy path connecting the *Pbnm* and R3c phases calculated using the NEB method on supercells of different sizes. (a) Energy normalized over the size of the entire simulation system (energy per formula unit) and plotted against the transition coordinate. (b) Energy normalized by cross-sectional area and plotted against the number of flipped layers of octahedra rotations. The inset cubes in (b) depict the evolution of oxygen octahedra rotations around the pseudocubic [001] axis, characterized by ϕ_z as defined by Eq. (4.4), along the NEB path for $12 \times 12 \times 12$ supercells. (c) Evolution of polarization components P_x ($= P_y$), and P_z along the NEB path for $12 \times 12 \times 12$ supercells. The insets in (c) show the cell-by-cell polarization map of the *Pbnm*, R3c, and two representative intermediate states, with arrows representing the polarization component within the *yz* plane and the background colored squares indicating the oxygen octahedra rotations, characterized by ϕ_z . The cell-by-cell polarization was calculated based on B-site-centered 5-atom pseudocubic perovskite unit cells.

that each time one layer of octahedra rotations flips, the energy cost is concentrated locally on that flipping layer, rather than being distributed throughout the entire system. From this view, instead of normalizing the energy over the size of the entire system (energy per formula unit), a more appropriate way to represent the energy is to normalize with respect to the cross-sectional area perpendicular to the oxygen octahedra rotation axis.

In Figure 7.1 (b), the energy normalized with respect to the cross-sectional area is plotted against the number of flipped layers of the octahedra rotations. It can be seen that the energy barrier for flipping one layer is approximately the same in the calculations performed on supercells of different sizes. In this representation, the energy barrier is not expected to decrease toward zero when extrapolating the size of the system to macroscopic scale. Therefore, the calculations reveal that the minimum energy path connecting the $Pbnm$ and $R3c$ phases consists of consecutive flips of the c -rotations, and emphasize the localized nature of the layer-by-layer flips along the path.

Interestingly, going from the nonpolar $Pbnm$ phase to polar $R3c$ phase, the layer-by-layer flipping of oxygen octahedra rotation is also accompanied with a gradual development of the polarization. Figure 7.1 (c) shows the evolution of the polarization components P_x , P_y , and P_z along the NEB path, all of which increase as the system goes from $Pbnm$ to $R3c$. A closer examination of the cell-by-cell polarization (insets in Figure 7.1 (c)) reveals that the development of polarization is spatially non-uniform. In the intermediate states along the NEB path, in-phase and antiphase c -rotations coexist. In the region with antiphase c -rotations, the cell-by-cell polarization vectors are nearly aligned, locally resembling the $R3c$ structure. By contrast, the region with in-phase c -rotations is similar to the $Pbnm$ phase, but exhibits a finite P_z , which arises from the requirement to maintain polarization continuity with the adjacent $R3c$ -like region. The presence of a non-zero P_z component in this region accounts for the fact that the net polarization P_z exceeds both P_x and P_y . According to the previous discussion, the transition from $Pbnm$ to $R3c$ along the NEB path can also be interpreted as the movement of the interface between these two phases. This interfacial motion is accomplished by the local flipping of the oxygen octahedra rotations and the reorientation of the polarization in the unit cells close to the interface.

These results are consistent with the experimental findings of Ref. [325], where the R3c phase is stabilized in CaTiO₃ films grown on (111)-oriented LaAlO₃ substrates. In that case, the $a^-a^-a^-$ oxygen octahedra rotation pattern of the LaAlO₃ substrate, which matches that of the R3c phase of CaTiO₃, provides the epitaxial boundary conditions that seed and pin the antiphase rotation pattern at the interface, thereby stabilizing the R3c phase against the competing *Pbnm* ground state.

7.1.2 Thermal stability of the R3c phase

Then, assuming that the R3c phase has been induced in some way, its thermal stability is studied by performing second-principles HMC heating simulations in $16 \times 16 \times 16$ supercell. The model-based calculations confirm that the R3c phase, once stabilized, remains stable below a certain finite temperature. Figure 7.2 shows that the R3c phase, characterized by $P_x = P_y = P_z \neq 0$ and $\phi_x^- = \phi_y^- = \phi_z^- \neq 0$, remains stable up to around 300 K, consistent with the experimental stabilization of the R3c phase at room temperature [325]. Between 300 K and 350 K, a transition from the R3c phase to some nonpolar structure occurs, as evidenced by the fact that the polarization abruptly drops to zero (Figure 7.2 (a)). Above 350 K, the oxygen octahedra rotations around two of the pseudocubic axes remain antiphase ($\phi_x^- = \phi_y^- \neq 0$, and $\phi_x^+ = \phi_y^+ = 0$), while the rotations around the third pseudocubic axis change to a complex pattern ($\phi_z^- \neq 0$ and $\phi_z^+ \neq 0$) [326]. As the temperature further increases, both ϕ_z^- and ϕ_z^+ exhibit several jumps (Figure 7.2 (b)). When the temperature reaches around 1200 K, the system goes into the C2/*m* phase, and both ϕ_z^- and ϕ_z^+ become zero. At higher temperatures, the phase transitions are the same as those observed when heating from the *Pbnm* phase in Figure 4.34 from Section 4.3.5.

The evolution of oxygen octahedra rotations and cell-by-cell polarization with temperature is shown in Figure 7.3. It can be seen that the antiphase rotations around the three pseudocubic axes and the uniform polarization are well preserved up to 300 K.

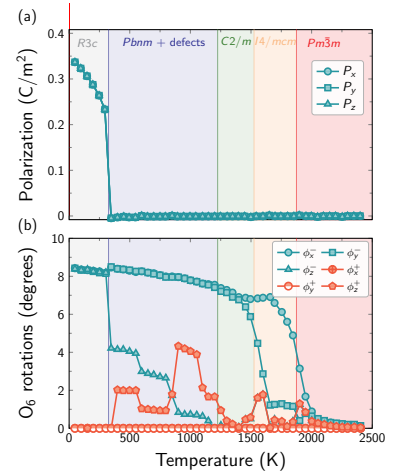


Figure 7.2: Structural phase transitions during the heating process from the R3c phase. (a) Polarization, and (b) oxygen octahedra rotations as functions of temperature. The simulation was performed in $16 \times 16 \times 16$ supercell using the second-principles model of CaTiO₃.

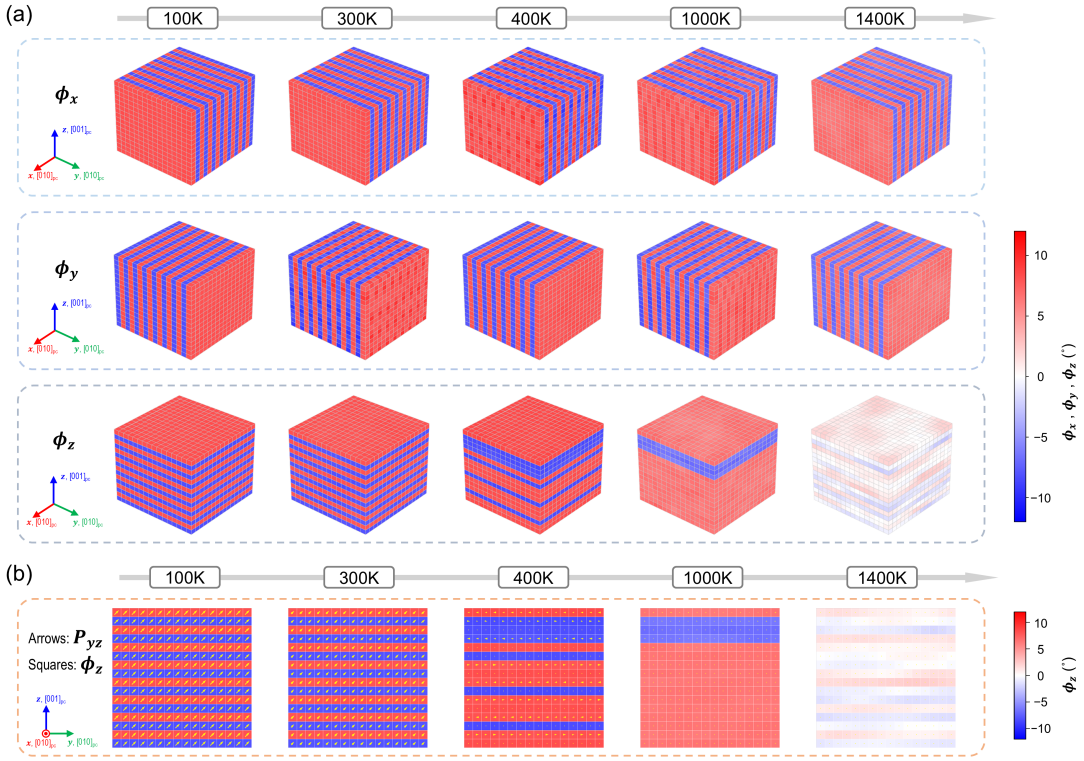


Figure 7.3: Evolution of (a) oxygen octahedra rotations and (b) cell-by-cell polarization during the heating process from the $R3c$ phase. The intensity of the colors in (a) represents the amplitude of ϕ_x , ϕ_y , and ϕ_z defined by Eq. (4.4), with red and blue indicating opposite signs. The arrows in (b) denote the in-plane component of the cell-by-cell polarization component within the yz plane. As $P_x = P_y$ holds at all temperatures, the out-of-plane component P_x is not shown. The background colored squares indicate the oxygen octahedra rotations, characterized by ϕ_z . The cell-by-cell polarization was calculated based on B -site-centered 5-atom pseudocubic perovskite unit cells.

Above this temperature, the oxygen octahedra rotations around the pseudocubic $[001]$ axis, which are characterized by ϕ_z , are neither in-phase nor antiphase, but exhibit some complex patterns. These complex patterns can also be regarded as a defective in-phase pattern, as the planes across which ϕ_z changes its sign can be viewed as defect planes within a matrix with in-phase rotations.

Accordingly, the polarization mostly disappears with small residual polarization remaining close to the defect planes. As the temperature further increases, these defect planes are progressively eliminated, the proportion of in-phase rotations increases, and the polarization disappears. This process occurs through local switching of oxygen octahedra rotations, very similar to what has been observed in the NEB calcula-

tions illustrated in Figure 7.1. In fact, the jumps in ϕ_z^- and ϕ_z^+ correspond to the local switching of oxygen octahedra rotations. Therefore, the results reveal that the thermal destabilization of the R3c phase toward the Pbnm phase does not occur as a direct and global transition, but rather happens progressively in a temperature range through consecutive and localized flipping of oxygen octahedra rotations.

7.1.3 Electric-field induced switching

The remaining question is to which extent the hidden R3c phase could be eventually stabilized in bulk CaTiO₃. Given the reasonably small energy difference between the Pbnm and R3c phases (see Section 4.3.5)* and the large polarization of the latter, it is reasonable to expect that the R3c phase could be stabilized over the Pbnm phase under appropriate electric field.

To confirm this first at 0 K, Figure 7.4 compares the field-dependent energy functional F defined as $F = U - \Omega(\mathbf{E} \cdot \mathbf{P})$ (where U is the internal energy, Ω the unit cell volume, $\mathbf{P}$ the macroscopic polarization vector and $\mathbf{E}$ the homogeneous electric field vector), for the Pbnm and R3c phases as a function of electric field[†]. At zero field, the Pbnm phase exhibits the lowest F , but this is changing for increasing fields. Above 1.7 MV/cm, the R3c phase becomes thermodynamically more favorable, suggesting a tendency for a transition from Pbnm to R3c under sufficiently large electric field. Despite this, the electric field of 1.7 MV/cm is not sufficient to induce the Pbnm-to-R3c transition. A larger field is required to overcome the barrier between the two phases (even 5 MV/cm is not sufficient, the Pbnm phase remains metastable according to Figure 7.5), and the transition would be very difficult at 0 K because there is no assistance from thermal fluctuations.

To directly simulate the electric-field induced Pbnm-to-R3c transition at finite temperature and access polarization-electric field (P - $\mathcal{E}$) hysteresis loops, HMC simulations have been performed while adding the same extra energy term $-\Omega(\mathbf{E} \cdot \mathbf{P})$,

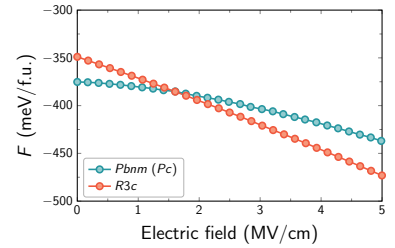


Figure 7.4: Field-dependent energy F of the Pbnm and R3c phases as a function of electric field, calculated from structure relaxations with the electric field applied along pseudocubic [111] direction. Note that the symmetry of the Pbnm phase is lowered to Pc under the applied electric field.

* It is important to notice that, compared to DFT, the MULTIBINIT model tends to overstabilize the R3c phase respect to the Pbnm phase (see Section 4.3.5), so the Pbnm-to-R3c transition fields reported in this section should be seen as a lower bound.

[†] Strictly speaking, F is not the electric enthalpy (which would include an additional $\mathcal{E}^2$ term) but is a proper quantity to minimize to identify the ground state under finite electric field [327]

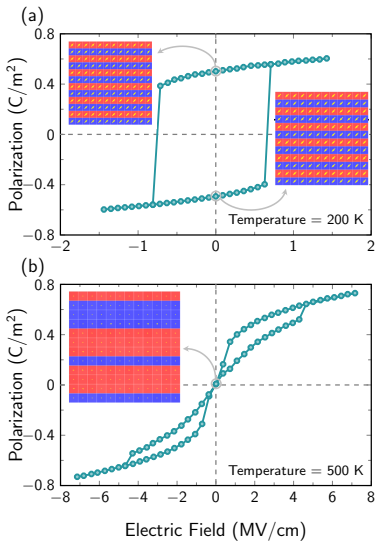


Figure 7.5: Simulated P - E hysteresis loops of CaTiO_3 at (a) 200 K and (b) 500 K. The insets show the cell-by-cell polarization (arrows, representing P_{yz}) and oxygen octahedra rotations (colored squares, representing ϕ_z). The electric field was applied along the pseudocubic $[111]$ direction, and the polarization was projected to the same direction. The simulations were performed in $12 \times 12 \times 12$ supercells using the second-principles model of CaTiO_3 .

as above. This gives rise, in practice, to an extra force on each of the atoms, proportional to the product of the Born effective charge (estimated in the parent cubic phase) and the field. The simulations were performed at two representative temperatures: 200 K, at which the $R3c$ phase is metastable in the absence of electric field, and 500 K, at which the $R3c$ phase becomes dynamically unstable and transforms spontaneously into nonpolar structure in zero field (see [Section 4.3.5](#)).

At 200 K, starting in the metastable $R3c$ phase, the model-based simulations reveal a well-defined single P - E loop with a reasonable coercive field of about 0.75 MV/cm ([Figure 7.5 \(a\)](#)), confirming the switchable character of the polarization and the ferroelectric nature of the $R3c$ phase. This result is consistent with the experimental observation in Ref. [325], where reversible polarization switching was detected by piezoresponse force microscopy in thin films. This suggests that bulk CaTiO_3 could potentially be made ferroelectric. However, starting in the $Pbnm$ phase, the simulations reveal that turning the system into the $R3c$ phase would require a field of 3–5 MV/cm which is beyond the breakdown field of real samples [328]. Since the model tends to overstabilize the $R3c$ phase, the fact that the transition remains inaccessible even under these conditions indicates that such a field-induced transition is unlikely to occur experimentally. Alternatively, cooling CaTiO_3 from 1300 K (in the $C2/m$ phase) under a more reasonable field of 1 MV/cm might help stabilize the ferroelectric $R3c$ phase at low temperature but would certainly remain very challenging experimentally as well.

At 500 K, the finite-field simulations reveal a double P - E hysteresis loop ([Figure 7.5 \(b\)](#)), fingerprint of an antiferroelectric behavior. The vanishing remanent polarization confirms that the polar $R3c$ phase is no longer stable at zero field. Instead, the system adopts a nonpolar structure with complex oxygen octahedra rotation pattern, which can be regarded as $Pbnm$ structure with planar defects. The electric-field induced transition to the $R3c$ phase is first order and identified by an abrupt jump of the polarization and a change in the oxygen octahedra rotation pattern from $a^-a^-c^+$ to $a^-a^-a^-$ ([Figure 7.3](#)). As such, CaTiO_3 could be considered as antiferroelectric in this temperature regime. However, once again, the electric field for the nonpolar-polar transition (around 4.7 MV/cm) clearly exceeds the breakdown field of real samples [328], making such behavior hardly accessible experimentally.

These results are consistent with the fact that, although not a priori impossible, the antiferroelectric-like switching in bulk CaTiO_3 has never been reported experimentally. All this points out that not only the energetic proximity of the polar and non-polar phases but also the energy barrier between them is key in assessing the antiferroelectric behavior of a compound in a given temperature range.

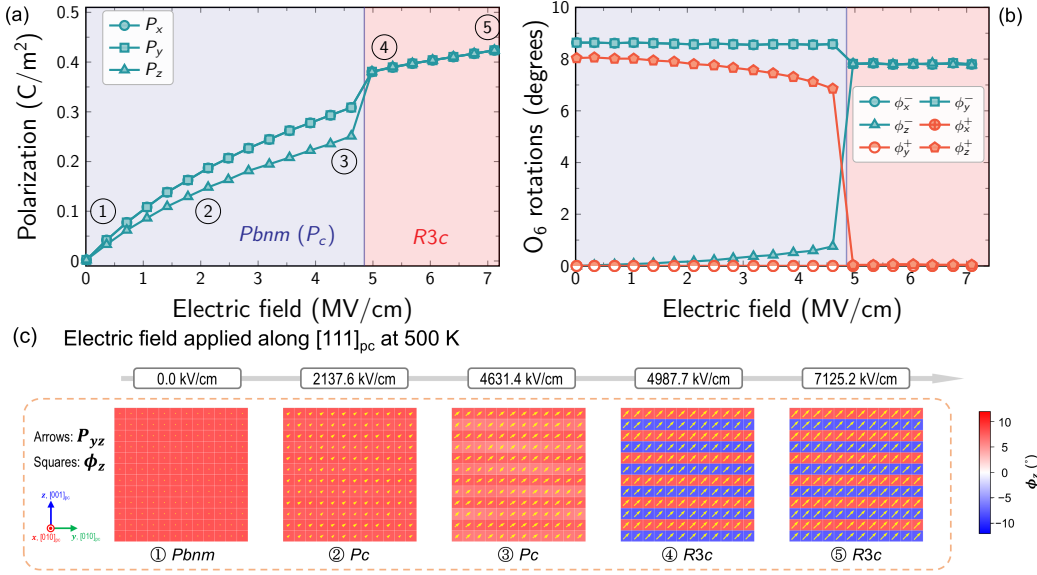


Figure 7.6: Electric-field induced $Pbnm$ -to- $R3c$ phase transition at 500 K with the electric field applied along the pseudocubic $[111]$ direction. (a) Polarization and (b) oxygen octahedra rotation angle as functions of the applied electric field. (c) Cell-by-cell polarization (arrows, representing P_{yz}) and oxygen octahedra rotations (colored squares, representing ϕ_z) during the transition. Note that the symmetry of the $Pbnm$ phase is lowered to Pc under the applied electric field. The simulation was performed in $12 \times 12 \times 12$ supercells using the second-principles model of CaTiO_3 .

7.2 First-order polarization process as an alternative to antiferroelectrics

A modern definition of antiferroelectricity introduced in Chapter 2 characterizes these materials through several criteria, one of which is particularly relevant from an applied perspective: the electric-field-induced switching between antipolar and polar states, responsible for the characteristic double hysteresis loops in the polarization versus electric field

(P - $\mathcal{E}$) curves. This response underlies a broad range of technological applications, including energy storage, electrocaloric cooling, neuromorphic computing, and water purification via piezocatalysis [310, 329–332].

In contrast to antiferromagnetism, which is widespread among magnetic compounds, only a limited number of materials satisfy all the criteria required to be strictly classified as antiferroelectrics. Many more, however, fulfill only part of these criteria while still reproducing some of the associated functional properties, and are therefore referred to as synthetic antiferroelectrics.

Because materials that are intrinsically antiferroelectric in the strict sense are scarce, significant efforts have recently been devoted to designing synthetic antiferroelectric systems that reproduce their functional behavior. Various strategies have been proposed, including the engineering of antipolar-polar transitions in heterostructures [333–336] and interface-induced effects in nanostructures [337, 338]. In many cases, the underlying idea is to tune the depolarizing field so as to slightly destabilize the polar phase relative to the antipolar one, while still allowing the polar state to be recovered under an applied electric field. Among these synthetic antiferroelectrics, the present chapter focuses on those reproducing the field-induced switchability and the associated double hysteresis loop.

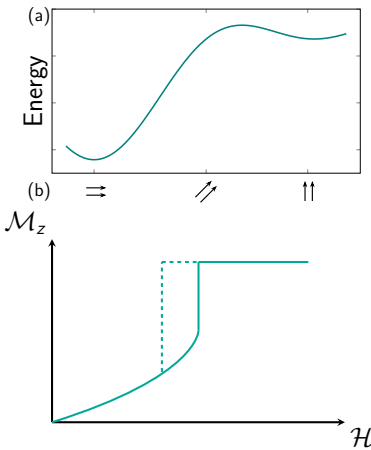


Figure 7.7: Illustration of first order magnetization process. (a) Energy landscape of different orientation of the magnetization. (b) Related $\mathcal{M}$ - $\mathcal{H}$ curves

In magnetic systems, double-hysteresis loops in magnetization versus magnetic field ($\mathcal{M}$ - $\mathcal{H}$) curves are not restricted to antiferromagnets but can also appear as a feature of some ferromagnetic systems showing first-order magnetization process [323, 324]. In such systems, the free energy shows two slightly inequivalent extrema associated with distinct orientations of the magnetization, as illustrated in Figure 7.7 (a). In some cases, the application of an appropriate external magnetic field can reverse the stability of the two inequivalent minima, producing a first-order transition from one state to the other through an abrupt rotation of the magnetization. In the case where this field-induced transition is reversible under removal of the magnetic field, it can give rise to double-hysteresis $\mathcal{M}$ - $\mathcal{H}$ loops, as illustrated in Figure 7.7 (b).

One may wonder whether, by analogy, a similar mechanism could exist in polar materials, leading to a first-order polarization process capable of generating double hysteresis

loops without invoking a conventional antipolar ground state. While a few early studies hinted at such possibilities in liquid crystals, amorphous systems or models inspired by biological systems [339–341], this concept has remained largely unexplored in crystalline ferroelectrics. Demonstrating an electric analogue of the first-order magnetization process would not only broaden the fundamental understanding of polarization switching but also open new opportunities for designing materials with controllable hysteresis and enhanced functional responses.

The way tensile epitaxial strain can induce and stabilize different polar states in CaTiO_3 is first examined. As shown in Section 4.3.5, bulk CaTiO_3 adopts an orthorhombic $Pbnm$ phase which can be seen as a small distortion of the reference cubic perovskite structure: it arises from the condensation of in-phase and anti-phase rotations of the oxygen octahedra according to a pattern ($a^-a^-b^+$) in Glazer notation [21], and further includes secondary antipolar motions of the Ca cations [223] in the plane perpendicular to the in-phase rotation axis of the oxygen octahedra. Previous theoretical [220, 225, 319] and experimental [321, 342] studies have shown that, under epitaxial tensile strain, CaTiO_3 preserves its oxygen octahedra rotation pattern but further develops polarization along different directions and exhibits competing ferroelectric phases. This testifies to a complex and tunable energy landscape and provides an appealing opportunity to explore the possibility of achieving a first-order polarization process.

7.2.1 Epitaxial mechanical constraints

To investigate this phenomenon, high-quality CaTiO_3 thin films have been deposited on $(110)_o$ and $(001)_o$ -oriented NdGaO_3 substrates, with high structural quality and atomically flat surfaces (see Appendix B-Section B.2). The NdGaO_3 substrate adopts the same orthorhombic $Pbnm$ phase as bulk CaTiO_3 . Simple inspection of the lattice parameters (see Appendix B, Table B.1) suggests that, when epitaxially grown on $(110)_o$ and $(001)_o$ NdGaO_3 , CaTiO_3 should keep in each case the same orientation as the substrate to minimize elastic energy. The second-principles calculations support this expectation and show that by imposing only epitaxial strain, the most favorable orientation for the film is that of preserving the orientation of the substrate (see Appendix B, Table B.2).

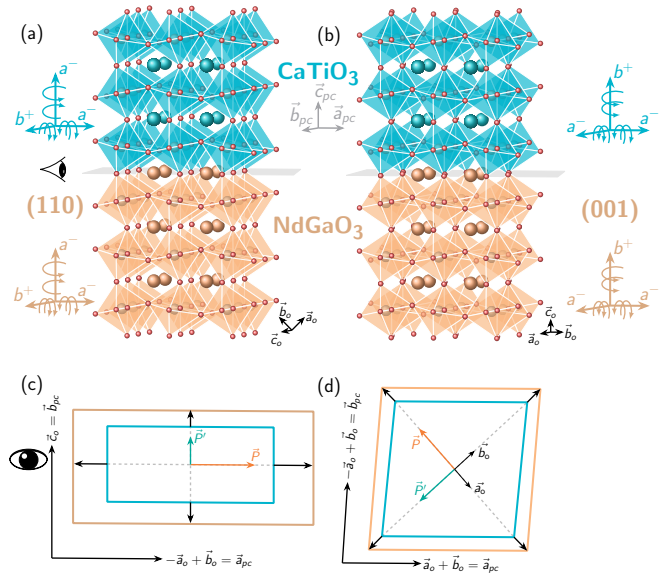


Figure 7.8: Sketch of atomic configuration and oxygen octahedra orientation of CaTiO_3 films grown on (a) NdGaO_3 (110)_o-oriented and (b) (001)_o-oriented. Tensile strain imposed by NdGaO_3 (c) (110)_o-oriented and (d) (001)_o-oriented as well as the resulting dominant polarization orientations

In practice, this additionally preserves the continuity of the pattern of oxygen octahedra rotations across the interface (Figure 7.8), which should further stabilize the orientation. For both orientations, X-ray diffraction confirms that the films are fully strained, twin-free, and inherit the substrate oxygen octahedra rotation pattern across the interface (see Appendix B-Section B.3).

Importantly, although they arise from the same material, the mechanical constraints imposed on the CaTiO_3 film by the NdGaO_3 substrate are significantly different for the two substrate orientations (see Appendix B, Table Table B.2) and should therefore affect the energy landscape differently. The (110)_o substrate applies a rectangular biaxial tensile strain along $\vec{c}_o$ and $\vec{b}_o - \vec{a}_o$, while the (001)_o substrate produces an orthorhombic tensile constraint in the (a_o, b_o) plane. This difference in the degree of strain leads to markedly different behavior for the two orientations of films, as will be shown below.

CaTiO_3 on (110)-oriented NdGaO_3

aTiO_3 films grown on (110)_o are first examined (see Methods). Combined X-ray diffraction, electrical measurements (see Appendix B-Section B.3) and first-principles calculations, demonstrate that this strain state stabilizes a low-symmetry

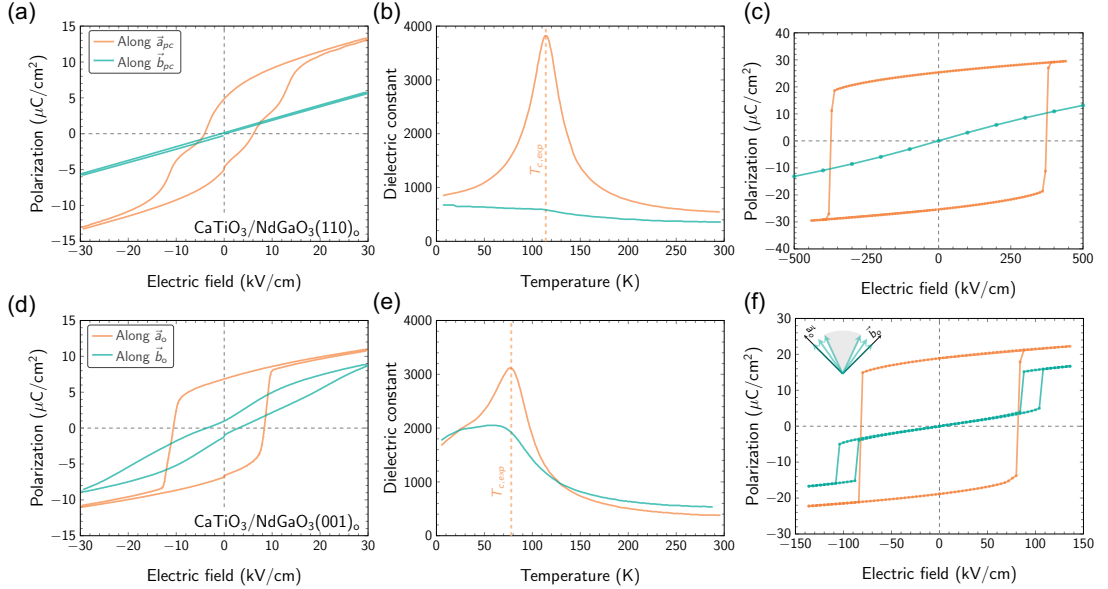


Figure 7.9: Characterisation of the ferroelectric properties of CaTiO_3 films. (a) Experimental polarization versus electric field measurement for a 18.2 nm-thick CaTiO_3 film grown on $\text{NdGaO}_3 (110)_0$ along $\mathbf{a}_{pc}$ and $\mathbf{b}_{pc}$ at $T_{exp} = 4.2$ K in Pm phase. (b) Experimental dielectric constant versus temperature measurement for the same film as panel (a), along $\mathbf{a}_{pc}$ and $\mathbf{b}_{pc}$, showing a characteristic peak at $T_{c,exp} = 110$ K signifying the transition from Pm to $P2_1/m$ phase. (c) Second-principles polarization versus electric field curve for CaTiO_3 strained on $\text{NdGaO}_3 (110)_0$ along $\mathbf{a}_{pc}$ and $\mathbf{b}_{pc}$ at $T_{sim} = 40$ K in Pm phase. (d) Experimental polarization versus electric field measurement for a 17.4 nm-thick CaTiO_3 film deposited on $\text{NdGaO}_3 (001)_0$ along $\mathbf{a}_0$ and $\mathbf{b}_0$ at $T_{exp} = 4.2$ K in Pm phase. (e) Experimental dielectric constant versus temperature measurement for the same film as panel (d), along $\mathbf{a}_0$ and $\mathbf{b}_0$ showing a characteristic peak at $T_{c,exp} = 80$ K signifying the transition from Pm ($P2_1nm$ -like) to $Pbnm$ phase. (f) Second-principles polarization versus electric field curve for CaTiO_3 strained on $\text{NdGaO}_3 (001)_0$ along $\mathbf{a}_0$ and $\mathbf{b}_0$ at $T_{sim} = 40$ K in Pm ($P2_1nm$ -like) phase.

Pm polar phase with an in-plane polarization along $\mathbf{a}_{pc}$ (Figure 7.8(b)), slightly lower in energy than a competing $P2_1$ phase polarized along $\mathbf{b}_{pc}$.

Having resolved the structure, the electrical response of an 18.2 nm thick film along the two orthogonal in-plane axes is examined. Figure 7.9(a) shows that a well-defined ferroelectric hysteresis loop is obtained at 4.2 K when the field is applied along $\mathbf{a}_{pc}$, whereas only a linear dielectric response is observed along $\mathbf{b}_{pc}$. Capacitance–voltage measurements (Appendix B, Figure B.9) and second-principles simulations (Figure 7.9 (c)) further confirm this anisotropic response, demonstrating that CaTiO_3 behaves as a uniaxial ferroelectric under this strain state.

It has to be noted that the ferroelectric hysteresis loop occasionally exhibits a step-like or partially pinched shape (Figure 7.9(a)). Such pinched loops have previously been reported in ferroelectric thin films and ceramics and are often

associated with extrinsic effects, such as defect dipoles or inhomogeneous switching conditions [343–345]. The degree of pinching in the hysteresis loops varies from sample to sample, and depends on their switching history. This suggests that this behavior is not an intrinsic property of CaTiO_3 under this strain state but is most likely associated with extrinsic effects.

The temperature dependence of the dielectric constant along the two orthogonal directions shown in Figure 7.9 (b) further supports the uniaxial ferroelectric behavior: a pronounced peak appears only when the field is applied along the ferroelectric axis $\mathbf{a}_{\text{pc}}$, while the curve remains flat when the field is applied along the orthogonal $\mathbf{b}_{\text{pc}}$ direction (see Appendix B, Figure B.10 and Figure B.11 for frequency-dependent capacitance and loss tangent versus temperature, showing strong anisotropic response along the two orthogonal directions). This further identifies the ferroelectric Curie temperature to $T_{c,\text{exp}} = 115$ K, a value slightly overestimated by the second-principles model ($T_{c,\text{sim}} = 245$ K). Together, these results highlight the strong directional coupling between strain, octahedra rotations, and polarization in such orientation.

CaTiO_3 on (001)-oriented NdGaO_3

Attention is now turned to CaTiO_3 films strained on (001)_o-oriented NdGaO_3 . Below approximately 87 K, synchrotron X-ray diffraction and electrical measurements reveal a symmetry lowering to a polar Pm phase (see Appendix B-Section B.2), in excellent agreement with second-principles calculations which yield a transition temperature of 85 K. The polarization is predominantly oriented along $\mathbf{a}_o$ and show a smaller component along $\mathbf{b}_o$.

First- and second-principles calculations corroborate this picture and further reveal the presence of two nearly degenerate polar Pm phases, separated by only 0.7 meV/f.u. (Figure 7.8(d)). One is polarized primarily along a_o (close to $P2_1nm$), the other along b_o (close to $Pb2_1m$). Their near degeneracy arises from a subtle competition: in the $P2_1nm$ -like state, the main polarization component is perpendicular to the antipolar motions of the Ca cations, whereas it is parallel to them in the $Pb2_1m$ -like state. In what follows, in order to avoid any ambiguity between both Pm phases, the notation $P2_1nm$ and $Pb2_1m$ is adopted, according to the direction of

the main component of their polarization, without changing the generality of the following results.

The electrical and dielectric measurements reveal a marked anisotropy: while a conventional ferroelectric loop is observed when the field is applied along $\mathbf{a}_0$, a double hysteresis loop emerges when the field is applied along $\mathbf{b}_0$ (Figure 7.9 (d–e)). This distinct behavior is reproduced in second-principles simulations (Figure 7.9(f)), which reproduce a simple ferroelectric loop along $\mathbf{a}_0$ and the emergence of a double hysteresis loop when the electric field is applied along $\mathbf{b}_0$.

Temperature-dependent dielectric measurements in Figure 7.9(e) provide an independent manifestation of this duality and anisotropic response, revealing markedly different dielectric signatures depending on the orientation of the applied electric field. This anisotropy is additionally evident from the frequency dependent capacitance and loss tangent (see Appendix B, Figure B.10 and Figure B.11).

The pronounced directional switching observed here is unusual. This behavior evokes features typical of first-order magnetization process, but alternative mechanisms could, in principle, produce such a behavior. In particular, Ref. [336] shows that, in ferroelectric/dielectric superlattices, competition between domain configurations and field-induced reorientation, governed by electrostatic and mechanical boundary conditions, can lead alternatively to single or double hysteresis loops depending on the orientation of the applied electric field.

To assess the origin of this behavior in CaTiO_3 films, a fine sampling of the polarization energy landscape has been performed (Figure 7.10 (a)) and the associated switching pathways are examined. The minimum-energy path connecting the two experimentally accessible polarization states ($P2_1nm$ ground state and $Pb2_1m$ metastable phase) is first computed using second-principles NEB calculations (Figure 7.10 (a,c)). The resulting path reveals a “Mexican hat”-shape energy landscape, which is compatible with a progressive in-plane rotation of the polarization vector between the nearly orthogonal minima, without passing through the paraelectric $Pbnm$ state, when a field is applied along $\mathbf{b}_0$. This polarization rotation is further confirmed by field-driven molecular-dynamics simulations. Finite-temperature simulations under electric

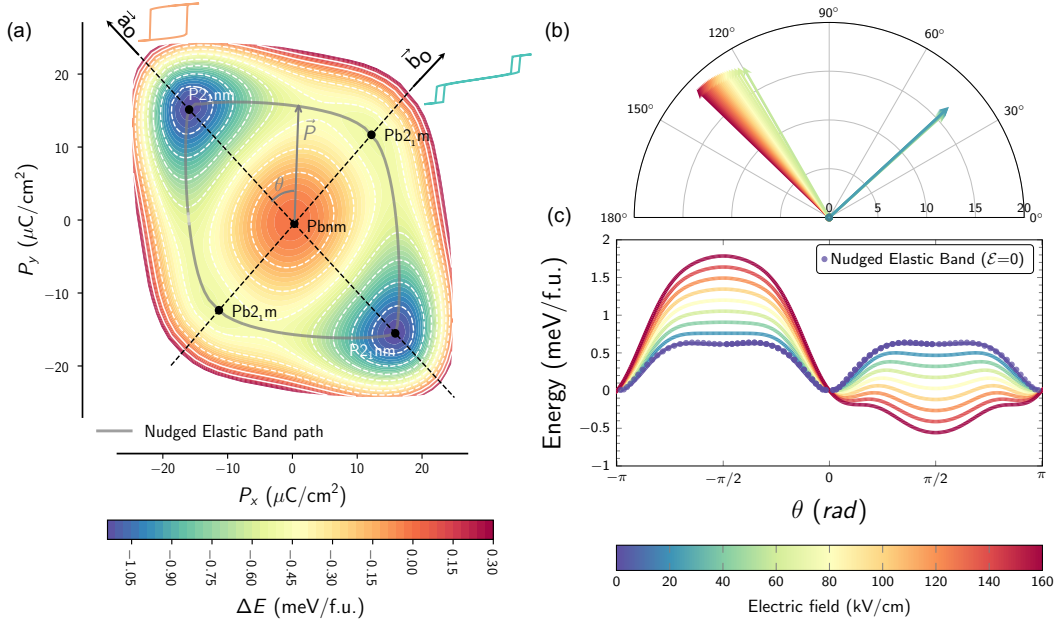


Figure 7.10: (a) Energy landscape of CaTiO_3 strained on NdGaO_3 (001)₀, shown as a function of the pseudo-cubic polarization components P_x and P_y . The grey line marks the lowest-energy path (nudged elastic band) connecting the $P2_{1nm}$ ground state and the $Pb2_{1m}$ metastable phase, defining a polar angle θ that parameterize the polarization rotation along this path. The landscape exhibits a Mexican-hat-like shape (although not perfectly flat). For electric fields applied along $\mathbf{a}_0$ (resp. $\mathbf{b}_0$), the system exhibits single (resp. double) hysteresis loops. (b) Reorientation of the polarization in CaTiO_3 strained on NdGaO_3 (001)₀ under electric field along $\mathbf{b}_0$ at $T_{\text{sim}} = 40$ K (Figure 7.9(d)), highlighting an abrupt jump associated with a first-order transition. (c) Energy along the same minimum-energy path shown in panel (a), plotted as a function of the rotation angle θ , and its evolution under electric field applied along $\mathbf{b}_0$, as fitted with Eq. 7.1.

field applied along $\mathbf{b}_0$ (Figure 7.9(f)) show that the polarization rotates progressively from $\mathbf{a}_0$ to $\mathbf{b}_0$ with increasing field until a critical field is reached, where it abruptly jumps from the $P2_{1nm}$ state to the $Pb2_{1m}$ state, while remaining finite throughout the transition and never passing through zero. The polarization trajectories shown in Figure 7.10(b) provide an alternative representation of the same data, directly visualizing this continuous and almost rigid rotation followed by the sudden jump. Together, these results establish that the observed double hysteresis loop is associated with a discontinuous reorientation of the polarization between two ferroelectric states of distinct orientations that are close in energy and separated by a small energy barrier. By analogy with magnetism, the term *first-order polarization process* is introduced here.

7.2.2 Origin of first-order polarization process

The experimental and theoretical results consistently establish that CaTiO_3 films grown on NdGaO_3 (001)_o substrates exhibit either conventional ferroelectric switching or double hysteresis loops, depending on the orientation of the applied electric field. This directional duality arises from a first-order polarization process, an analogue of first-order magnetization process in magnetic systems. This interpretation is supported by a one-to-one correspondence between the key characteristics of first-order magnetization process and the observations in CaTiO_3 .

The foundation of this analogy lies in an underlying energy landscape prone to polarization rotation. The calculations reveal two nearly degenerate, yet non-equivalent, Pm minima (close to $P2_1nm$ and $Pb2_1m$) associated with nearly perpendicular polarization orientations and separated by a small energy barrier.

Extending the analogy to a more quantitative level, the polarization energy landscape can be described within a phenomenological framework using a mathematical formalism directly analogous to that employed for first-order magnetization process. To capture the NEB energy profile U along the minimum-energy path (Figure 7.10 (a)) in a compact form, it is assumed that U depends only on the orientation θ – with respect to $\mathbf{a}_o$ – of the spontaneous polarization of amplitude P_s , taken to be constant, and $U(\theta)$ is fitted using a minimal angular expansion:

$$U(\theta) = U_0 + K_1 \sin^2 \theta + K_2 \sin^4 \theta + K_3 \sin^6 \theta \quad (7.1)$$

This fit (Table 7.1) perfectly reproduces both the relative depth of the two minima and the barrier separating them (Figure 7.10 (b)), providing a concise representation of the anisotropy governing polarization rotation.

Assuming a constant polarization amplitude P_s , the coupling to an external electric field $\mathcal{E}$ along $\mathbf{b}_o$ is introduced through the field-dependent energy $F(\theta) = U(\theta) - \mathcal{E}P_s \sin \theta$. Within this phenomenological framework, the application of an external electric field progressively tilts the energy landscape, leading to a field-induced interchange of stability between the two competing minima at $\mathcal{E} \sim 140$ kV/cm at 0 K, in good agreement with the coercive field obtained from second-principles molecular dynamics simulations. This agreement

Table 7.1: Values of U_0 and anisotropy constant K_1 , K_2 , K_3 (meV/f.u.) and P_s ($\mu\text{C}/\text{cm}^2$) for CaTiO_3 strained on NdGaO_3 (110)_o and NdGaO_3 (001)_o

Terms	NdGaO_3 (110) _o	NdGaO_3 (001) _o
U_0	0.0	0.0
K_1	9.56	2.11
K_2	-11.48	-2.33
K_3	3.76	0.83
P_s	27	21

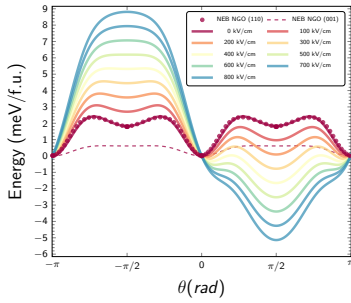


Figure 7.11: Energy versus angle θ obtained by fitting Eq. (7.1) in the case of CaTiO_3 strained on NdGaO_3 $(110)_0$ for different applied field. Dots correspond to the second-principles NEB energies in zero field.

confirms that, at the phenomenological level, the double hysteresis loop is governed by an abrupt and reversible reorientation of the polarization vector that is directly analogous to the magnetization reversal characteristic of a first-order magnetization process.

This unified framework also explains the absence of double hysteresis loops in films grown on $(110)_0$ substrates. Second-principles NEB calculations reveal a substantially higher energy barrier between the competing polarization states (P_{21} and P_m), approximately four times larger than in the $(001)_0$ case (see Figure 7.11). Within the same parametrization, this increased barrier translates into a predicted coercive field exceeding 500 kV/cm at 0 K, well above the dielectric breakdown threshold of CaTiO_3 thin films. As a result, the practically accessible electric fields cannot induce a transition toward the competing polarization states, and only robust uniaxial ferroelectric switching is experimentally observed in this orientation. Such in-plane uniaxial ferroelectrics in thin-films offer a simplified polarization landscape and can be advantageous for applications requiring directional control, such as non-volatile memories, electro-optical modulators and in-plane tunnel junctions [346–349].

These contrasting cases suggest concrete guidelines for realizing first-order polarization processes in ferroelectrics: (i) selecting materials with intrinsic structural anisotropies that differentiate polarization orientations, such as ferroelastic or antipolar distortions; (ii) using epitaxial boundary conditions to tune the relative stability of the resulting ferroelectric states toward near degeneracy without suppressing their polar character; and (iii) ensuring that the barriers separating these states remain moderate, so that polarization reorientation can be driven reversibly by experimentally accessible electric fields. From this perspective, a broad class of strained ferroelastic and antipolar materials emerges as promising candidates for first-order polarization processes [22].

CaTiO_3 provides a concrete realization of these guidelines. The oxygen-octahedra rotation pattern, inherent to its orthorhombic structure, introduces a built-in anisotropy between different polarization directions, while epitaxial strain acts as an external and tunable control parameter that can selectively enhance or partially compensate this intrinsic anisotropy depending on its magnitude and symmetry [225]. The resulting balance stabilizes multiple ferroelectric states

of comparable energy while maintaining moderate barriers between them, thereby enabling a first-order polarization reorientation under moderate applied electric fields.

Viewed from this perspective, the first-order polarization process identified here does not rely on an exotic switching pathway, but instead on a well-established mechanism in ferroelectrics, namely polarization rotation. Polarization rotation is indeed not unusual in ferroelectric perovskites and has been extensively studied in connection with giant piezoelectric responses [350]. In those systems, the rotation of the polarization vector under an electric field is the key mechanism enabling ultrahigh electromechanical coupling, but it typically requires very large fields to overcome substantial intrinsic energy barriers [351, 352]. In contrast, the strain-engineered energy landscape considered here brings competing ferroelectric minima into close energetic proximity, enabling a field-induced polarization reorientation at much lower, experimentally accessible fields. As a result, polarization rotation manifests not as a smooth response, but as a first-order switching process, giving rise to double hysteresis loops.

The discovery of a first-order polarization process immediately raises the question of its technological relevance, since the coexistence of distinct switching modes can be harnessed in practical functionalities. Importantly, the first-order polarization process is not only an alternative to antiferroelectricity. The ability to toggle between ferroelectric-like and antiferroelectric-like responses depending on the orientation of the applied field within the same system is particularly appealing for neuromorphic computing, where ferroelectric switching underlies convolutional neural networks, while antiferroelectric-like behavior can emulate spiking neural networks—two complementary elements for hybrid neuromorphic architectures [331]. Moreover, the duality of the dielectric response extends beyond polarization switching. Indeed, in magnetic systems, first-order magnetization process is often accompanied by magnetocaloric effects [353, 354] of opposite sign depending on the orientation of the applied field; by analogy, first-order polarization process is expected to couple to similar electrocaloric behaviors. Consistent with this picture, and using the formalism introduced in Section 2.2.2, opposite signs of the electrocaloric temperature change are predicted from the second-principles model depending on field orientation: $\Delta T < 0$ when the electric

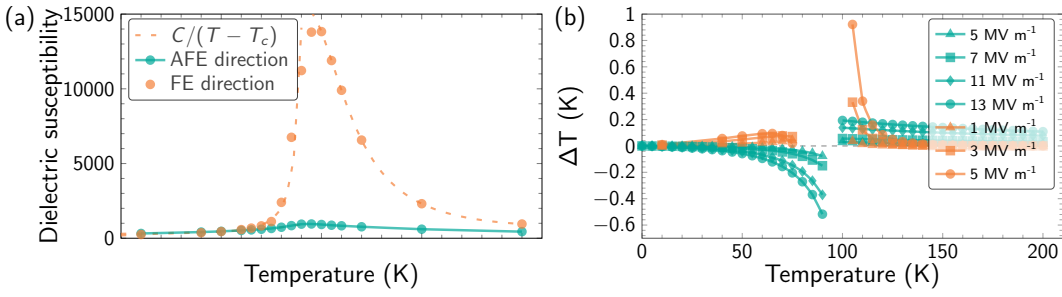


Figure 7.12: (a) Dielectric susceptibility as a function of temperature. (b) Change in temperature under different electric field condition.

field is applied perpendicular to the polarization, with an efficiency in the same range as conventional antiferroelectrics ($\Delta T/\Delta \mathcal{E}^2 = -3 \times 10^{-5} \text{ K cm}^2 \text{ kV}^{-2}$) [355, 356]. On the contrary, $\Delta T > 0$ when the electric field is parallel to the polarization as shown in Figure 7.12 (b) ($\Delta T/\Delta \mathcal{E} = 0.02 \text{ K cm kV}^{-1}$). This mirrors the behavior of first-order magnetization process. It further reinforces the close analogy between first-order magnetization process and first-order polarization process and highlights strained CaTiO_3 as a promising platform for multifunctional applications.

7.3 Summary

This chapter examined the ferroelectric and antiferroelectric potential of CaTiO_3 from two complementary perspectives, combining second-principles simulations with experimental measurements.

The first part focused on the metastable polar $R3c$ phase of bulk CaTiO_3 . The minimum energy path connecting the $Pbnm$ ground state and the $R3c$ phase was explored using second-principles NEB calculations on supercells of increasing size. A layer-by-layer flipping mechanism of the oxygen octahedra rotations was identified along this path, with an energy cost that is localized at the flipping layer and remains finite in the thermodynamic limit. Finite-temperature simulations further showed that the $R3c$ phase is stabilized below approximately 300 K, where it behaves as a genuine ferroelectric, while the $Pbnm$ phase with defects is recovered above this temperature. The response to an applied electric

field was also investigated, revealing that the field must overcome a substantial barrier to drive the system from the $Pbnm$ ground state toward the $R3c$ phase, so that the system does not exhibit the characteristic double hysteresis loops of antiferroelectrics. Bulk CaTiO_3 is therefore confirmed to be neither ferroelectric nor antiferroelectric, but an incipient ferroelectric with a metastable polar phase accessible under appropriate conditions.

The second part turned to epitaxially strained CaTiO_3 films grown on differently oriented NdGaO_3 substrates. It was shown that the substrate orientation acts as a decisive control parameter: films grown on $(110)_o$ -oriented substrates exhibit robust uniaxial ferroelectric behavior, while films grown on $(001)_o$ -oriented substrates develop two nearly degenerate polar Pm phases with nearly orthogonal polarization orientations and a Mexican-hat energy landscape. Under these conditions, the dielectric response becomes strongly anisotropic: a conventional ferroelectric hysteresis loop is observed when the field is applied along $\mathbf{a}_o$, while a double hysteresis loop emerges along $\mathbf{b}_o$. Through a combination of second-principles NEB calculations and finite-temperature molecular dynamics simulations, this behavior was attributed to a discontinuous reorientation of the polarization vector between two nearly degenerate ferroelectric states, driven by a field-induced interchange of their stability. By direct analogy with the first-order magnetization process in magnetic systems, this mechanism is introduced here as a *first-order polarization process*.

The phenomenological framework developed for the first-order magnetization process was extended to the present context, providing a compact parametrization of the energy landscape that quantitatively reproduces both the energy barrier between competing states and the coercive field obtained from molecular dynamics simulations. This framework also accounts for the absence of double hysteresis loops in films grown on $(110)_o$ substrates, where the substantially larger barrier between competing polarization states requires fields well beyond the dielectric breakdown threshold. Concrete guidelines were proposed for realizing first-order polarization processes in other ferroelectric systems, identifying strained ferroelastic and antipolar materials as a broad class of promising candidates. Finally, the electrocaloric signatures of the first-order polarization process were examined, revealing opposite signs of the electrocaloric temperature

change depending on the orientation of the applied field, in direct analogy with the magnetocaloric effect accompanying first-order magnetization process in magnetic systems.

Lattice dynamics across the structural phase transition in YNiO_3

8

The rare-earth nickelates RNiO_3 constitute a paradigmatic family of perovskite oxides exhibiting, upon cooling, a sharp metal-insulator transition (MIT) concurrent with a structural phase transition from the orthorhombic $Pbnm$ phase to the monoclinic $P2_1/n$ ground state. The structural signature of this transition is the appearance of a breathing distortion of the NiO_6 octahedra, which breaks the equivalence between Ni sites and is intimately linked to the opening of the electronic gap. The physical origin of this transition was elucidated by Mercy and co-workers [234], who demonstrated from first-principles calculations that the breathing distortion Q_B (Figure 8.1) does not arise spontaneously but is instead structurally triggered by the oxygen octahedra rotation modes R_5^- and M_2^+ already present in the $Pbnm$ phase. Through a biquadratic coupling of the form $\propto Q_B^2 Q_i^2$ ($i = M_2^+, R_5^-$), these rotations progressively renormalize the curvature of the breathing mode energy well, driving it from a stable single-well to an unstable double-well configuration at the transition temperature T_{MI} . A Landau model built on this triggered mechanism was shown to quantitatively account for the experimentally observed evolution of T_{MI} across the nickelate series. As shown in Figure 8.2, this behavior is correctly reproduced by the MLIP model introduced in Section 4.3.6.

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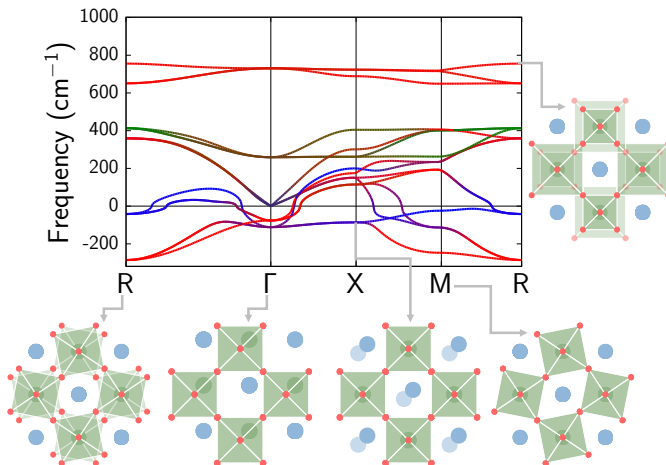


Figure 8.1: Phonon dispersion curve of YNiO_3 in cubic $Pm\bar{3}m$ phase. The unstable modes at Γ , X , M and R are respectively associated with polar modes, anti-polar motion, in-phase oxygen octahedra rotation and out-of-phase oxygen octahedra rotation. The Breathing mode is the highest frequency mode at R .

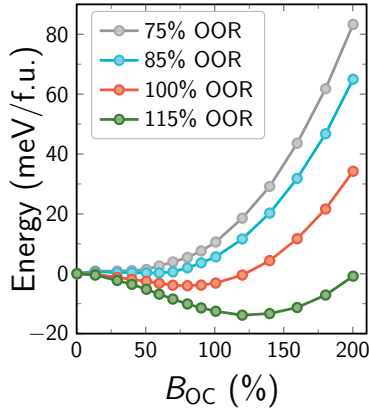


Figure 8.2: Energy as a function of the breathing distortion amplitude Q_B for fixed oxygen octahedra rotation (OOR) amplitudes ranging from 75% to 115% of the ground-state value. The progressive destabilization of the breathing mode energy well with increasing rotation amplitude.

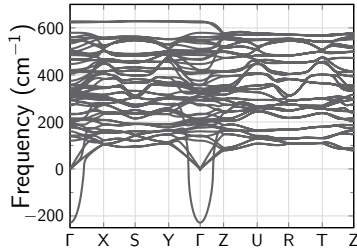


Figure 8.3: Phonon dispersion curve of $Pbnm$ phase in YNiO_3 from DFPT.

Two aspects of this picture are worth noting. First, the Landau model of Mercy and co-workers [234] is constructed around the hypothetical cubic $Pm\bar{3}m$ reference structure, which is never directly observed experimentally, as YNiO_3 melts before reaching this phase [357]. Second, and more fundamentally, the triggered mechanism rests on the progressive softening of the breathing mode as the oxygen octahedra rotations develop: in the cubic reference, the breathing distortion corresponds to the highest-frequency phonon at the R point of the Brillouin zone (Figure 8.1), yet it must evolve into the most unstable mode at the transition. This softening is a central prediction of the triggered mechanism, but to date no experimental evidence of it has been reported. This is not surprising given the considerable experimental challenge involved: the phonon spectrum of the $Pbnm$ phase is dense, and identifying a single mode that softens from the top of the phonon spectrum down to an instability (Figure 8.3) at the transition requires an exceptional spectroscopic sensitivity and a reliable assignment of the mode character across the full temperature range.

The MLIP model presented in Section 4.3.6, combined with the TDEP approach, provides a direct means to address this question. By computing the phonon dispersion curves of YNiO_3 as a function of temperature, the evolution of the breathing mode frequency can be tracked continuously from well above T_M down to the transition, allowing a quantitative test of the picture proposed by Mercy and co-workers [234] and, ultimately, a guide for future experimental detection of this softening.

8.1 Structural phase transition

The finite-temperature structural properties of YNiO_3 are first investigated by characterizing the $Pbnm$ -to- $P2_1/n$ phase transition and establishing the temperature scale over which the model operates, before turning to the lattice dynamics and phonon softening in the following sections.

Finite-temperature properties are investigated by means of molecular dynamics simulations performed with the LAMMPS software [358] using the developed interatomic potential. NPT simulations are carried out on a $16 \times 16 \times 16$

supercell of the five-atom cubic unit cell, spanning temperatures from 1 K to 1000 K at intermediate steps. A timestep of 1 fs is employed throughout. At each temperature, the system is first equilibrated for 50 ps, after which the simulation is continued for a further 50 ps for analysis. The trajectories are analyzed using the AGATE software [144].

The structural phase transition between the $Pbnm$ and $P2_1/n$ phases is monitored through two order parameters: the amplitude of the breathing distortion Q_B , normalized to its value at $T = 0$ K, and the monoclinic angle β . In the orthorhombic $Pbnm$ phase, $\beta = 90$ by symmetry, while a deviation from 90 signals the onset of the monoclinic $P2_1/n$ phase. Both quantities are reported as a function of the reduced temperature T/T_c in Figure 8.4.

Both order parameters vanish continuously at T_c , consistent with a second-order character of the $Pbnm$ -to- $P2_1/n$ structural phase transition. The breathing distortion amplitude decreases smoothly upon heating and goes to zero at T_c , while the monoclinic angle β returns to 90 at the same temperature, confirming that the two structural signatures of the $P2_1/n$ phase disappear simultaneously at the transition. The transition temperature obtained from the simulations is $T_c \approx 120$ K, which underestimates the experimental value of approximately 600 K [359]. This underestimation is likely related to the choice of the LDA+ U functional used to generate the training data, as a similar study on SmNiO_3 using DEEPMD reported a significantly better agreement with experiment when employing a GGA-PBESol+ U functional instead [360].

The evolution of the dominant structural modes across the transition is examined in Figure 8.5. The amplitudes of the R_5^- oxygen octahedra rotation mode and the M_2^+ in-phase rotation mode are tracked as a function of the reduced temperature T/T_c , and their distributions at two representative temperatures, $1.15 T_c$ and $7.25 T_c$, are reported as histograms. Strikingly, the amplitudes of both rotation modes remain essentially constant across the entire temperature range investigated, from T_c up to $7 T_c$. The R_5^- mode shows no significant variation, while the M_2^+ amplitude changes by less than 3% between $1.15 T_c$ and $7.25 T_c$, with their distributions showing no appreciable shift between these two temperatures. This implies that the structural conditions required for the breathing distortion to develop are already fully established well above

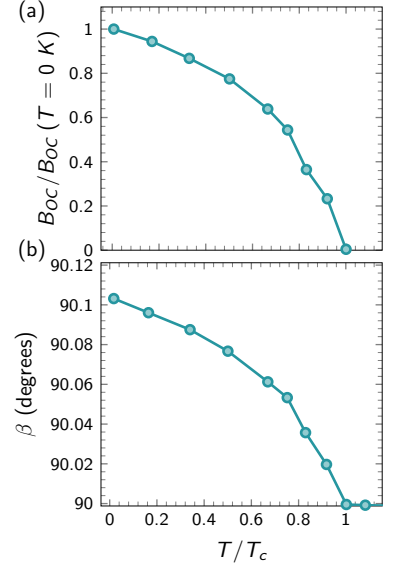


Figure 8.4: Temperature dependence of (a) the breathing distortion amplitude Q_B , normalized to its $T = 0$ K value, and (b) the monoclinic angle β , as a function of the reduced temperature T/T_c . Both quantities vanish continuously at T_c , consistent with a second-order structural phase transition.

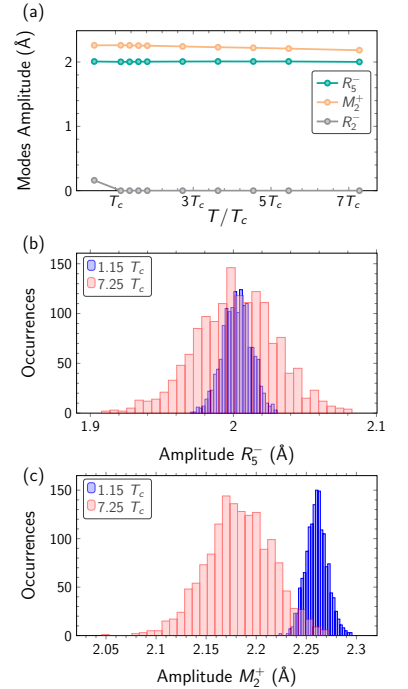


Figure 8.5: (a) Temperature dependence of the amplitudes of the R_5^- , M_2^+ , and R_2^- distortion modes as a function of the reduced temperature T/T_c in YNiO_3 . Distributions of the (b) R_5^- and (c) M_2^+ mode amplitudes (Å) at $1.15 T_c$ and $7.25 T_c$.

T_c , and persist essentially unchanged up to temperatures several times larger than T_c . This behavior stands in sharp contrast with the picture of Mercy and co-workers [234], in which the progressive development of the oxygen octahedra rotations upon cooling is the driving force of the triggered mechanism. In the present simulations, the rotations are already fully developed at all temperatures investigated and do not vary appreciably across the transition, demonstrating that the thermal triggering of the breathing distortion cannot be attributed solely to a temperature-driven growth of the rotation amplitudes.

8.1.1 Temperature-dependent phonon softening

Temperature-dependent phonon dispersions in the $Pbnm$ phase are computed using the TDEP software package [179], which extracts effective interatomic force constants from molecular dynamics trajectories at finite temperature. At each temperature, the dynamical matrix is obtained from a 1280-atom supercell, with interactions truncated at a cutoff radius of 7 Å. The phonon dispersions are then computed from the resulting temperature-dependent force constants.

The analysis focuses on the Γ -point modes of the $Pbnm$ phase whose symmetry is compatible with the $P2_1/n$ ground state, as these are the only candidates to drive the structural phase transition. In $Pbnm$ settings, the two relevant irreducible representations are Γ^{2+} and Γ^{3+} , which can be expressed as combinations of cubic modes as $\Gamma^{2+} = R_3^- \oplus R_5^- \oplus X_3^- \oplus M_5^+$ and $\Gamma^{3+} = R_2^- \oplus R_3^- \oplus R_4^- \oplus M_5^+$ [361], where R_2^- corresponds to the breathing mode. To track the evolution of the breathing character across temperature, the distortion patterns of the $P2_1/n$ ground state are projected onto each Γ^{3+} mode, and the resulting overlap is encoded as the size of each data point in Figure 8.6.

As illustrated in Figure 8.6, all Γ^{3+} modes maintain approximately constant frequencies across the temperature range investigated, except for one. At high temperatures, the breathing character is delocalized across several Γ^{3+} modes with frequencies above 300 cm^{-1} , reflecting strong hybridization between modes of compatible symmetry. As the temperature decreases toward T_c , these contributions progressively concentrate into a single mode that acquires a dominant breathing character. This mode softens continuously down to

65 cm^{-1} at $1.15 T_c$. Close to T_c , ω^2 evolves linearly with temperature, consistent with the soft-mode theory of Cochran [25], as shown in the inset of Figure 8.6. At higher temperatures, the departure from this linear behavior reflects the strong mode hybridization that prevents the identification of a single soft mode.

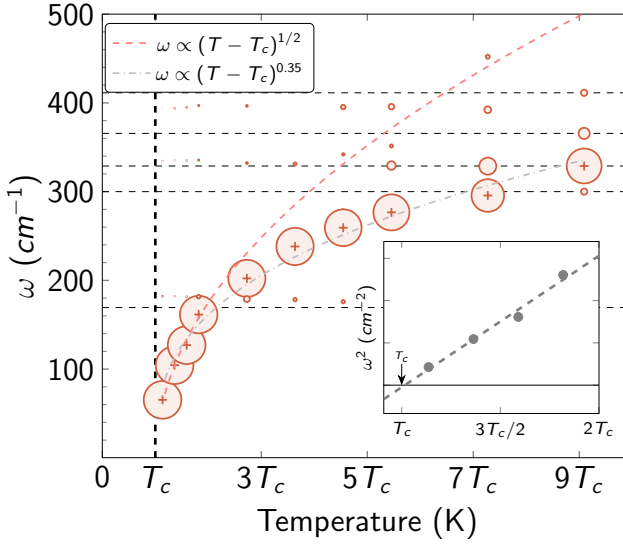


Figure 8.6: Temperature dependence of the Γ^{3+} mode frequencies in the $Pbnm$ phase of YNiO_3 , computed from **TDEP** calculations. The size of each point encodes the overlap with the breathing distortion of the $P2_1/n$ ground state. The mode carrying the dominant breathing character softens continuously upon cooling, from above 300 cm^{-1} at high temperature down to 65 cm^{-1} at T_c . Inset: ω^2 as a function of temperature close to T_c , compared with the soft-mode prediction $\omega \propto (T - T_c)^{1/2}$ and a fit with exponent 0.35.

The phonon spectral functions at $7.25 T_c$ and $1.6 T_c$ are compared in Figure 8.7. At high temperature, the breathing mode is hybridized with several other modes of compatible symmetry across a broad frequency range, making its individual identification impossible. As the temperature approaches T_c , the mode softens and acquires a dominant breathing character, as established in Figure 8.6. However, even at $1.6 T_c$, the mode exhibits a significant spectral broadening at the Γ point, indicative of a reduced phonon lifetime arising from enhanced anharmonic interactions near the transition. These two compounding effects, mode hybridization at high temperature and spectral broadening near T_c , provide a theoretical rationale for the absence of experimental observation of this softening to date, and constitute a concrete prediction for future experiments.

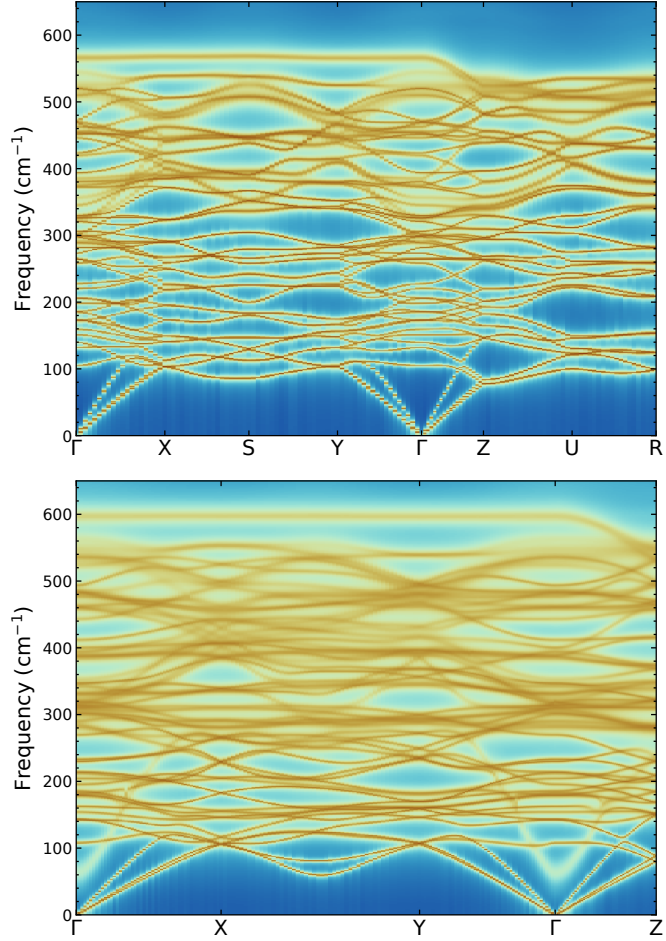


Figure 8.7: Phonon spectral functions of YNiO_3 in the $Pbnm$ phase computed from TDEP at (left) $7.25 T_c$ and (right) $1.6 T_c$. At high temperature, the breathing mode is delocalized across several modes of compatible symmetry and cannot be individually identified. At $1.6 T_c$, the mode has softened and become identifiable at the Γ point, but its significant spectral broadening reflects a reduced phonon lifetime, rendering its experimental detection challenging.

Furthermore, the softening is spatially confined to the immediate vicinity of the Γ point, and is only observable within a narrow temperature window above T_c , where the mode has softened sufficiently to be distinguished from the remaining Γ^{3+} modes while retaining enough spectral weight to be detectable. This places stringent requirements on the momentum and energy resolution of any experimental probe.

8.1.2 Origin of the delayed condensation of the breathing mode

Although the triggered mechanism is correctly reproduced at 0 K and the breathing mode is observed to soften upon

heating toward T_c , the question of why the breathing distortion does not condense at temperatures well above T_c , despite the oxygen octahedra rotations being fully developed, remains to be addressed. To investigate this, the energy cost of condensing the breathing distortion is evaluated both on the average structure and on instantaneous snapshots extracted from the molecular dynamics trajectories at approximately $1.8 T_c$. As shown in Figure 8.8, condensing the breathing distortion on top of the average structure yields a double-well energy profile, consistent with the triggered mechanism of Mercy and co-workers [234]: the oxygen octahedra rotations present in the average structure are sufficient to destabilize the breathing mode. By contrast, when the breathing distortion is condensed on top of individual MD snapshots, the energy profile is positive for the vast majority of configurations, meaning that the breathing distortion costs energy. The average curvature over all snapshots is positive, confirming that the breathing mode is effectively stabilized by the instantaneous fluctuations of the lattice.

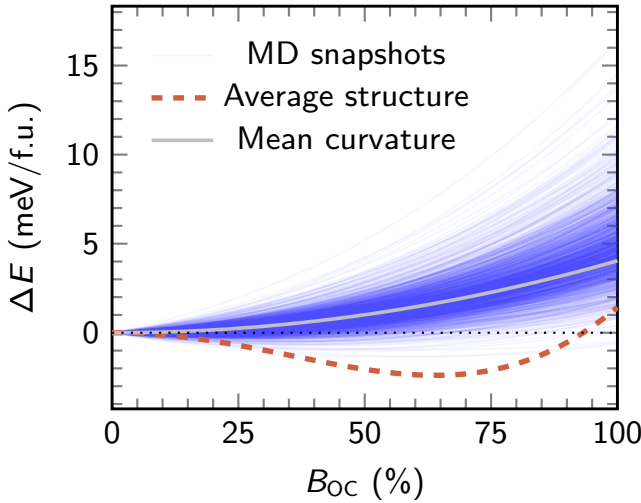


Figure 8.8: Energy as a function of the breathing distortion amplitude B_{OC} at $\approx 1.8 T_c$. The dashed line corresponds to the condensation of the breathing distortion on top of the average structure, yielding a double-well profile. The blue lines correspond to individual molecular dynamics snapshots, for which the breathing distortion costs energy in the vast majority of cases, resulting in a positive average curvature.

These results reveal that the picture of Mercy and co-workers [234] is correct but incomplete. The oxygen octahedra rotations are indeed a necessary condition for the appearance of the breathing distortion, as demonstrated by the double-well profile of the average structure. However, the instantaneous fluctuations of the other phonon modes, absent from the static Landau model of Mercy and co-workers [234], effectively oppose the condensation of the breathing distortion and delay

its appearance to lower temperatures. The structural phase transition is therefore not driven by the progressive growth of the oxygen octahedra rotations, which remain essentially constant in amplitude across the entire temperature range as shown in Figure 8.5, but rather by the progressive reduction of these competing fluctuations as the temperature decreases toward T_c .

8.2 Conclusion

In this chapter, the finite-temperature structural properties of YNiO_3 have been investigated by means of a MLIP potential trained on DFT+ U calculations. The model correctly reproduces the structural phase transition from the $Pbnm$ metallic phase to the $P2_1/n$ insulating ground state, as well as the triggered mechanism identified by Mercy and co-workers [234] at 0 K.

Three main results emerge from this study. First, despite the oxygen octahedra rotations being fully developed at all temperatures investigated and remaining essentially constant across the transition, the breathing distortion does not condense until T_c . This contrasts with the static picture of Mercy and co-workers [234], in which the progressive growth of the rotations is the driving force of the transition. Second, the breathing mode is nonetheless observed to soften continuously upon cooling toward T_c , in fair agreement with the soft-mode theory of Cochran [25], confirming that the triggered mechanism leaves a clear fingerprint in the finite-temperature lattice dynamics. Third, the delayed condensation of the breathing mode is attributed to the instantaneous fluctuations of the other phonon modes, which effectively stabilize the breathing distortion at finite temperature and are absent from the static Landau model of Mercy and co-workers [234].

Taken together, these results provide a more complete picture of the structural phase transition in YNiO_3 , and constitute concrete predictions for experiments seeking to detect the phonon softening associated with the metal-insulator transition.

When this thesis began, fully atomistic second-principles models parametrized on first-principles calculations were rare, and the few that existed were typically not available to the broader community [120, 121]. The landscape has since changed dramatically. The rapid development of machine-learning interatomic potentials, combined with the maturation of open-source second-principles frameworks [122, 127, 128, 132], has made it possible to construct accurate effective models for complex materials with relative ease. This thesis has contributed to this shift by adopting a systematic, transparent, and open approach: every model constructed here has been validated through a three-step procedure and made publicly available with a documented validation passport, enabling reproducibility and reuse by the community.

The models developed in Chapter 4 for BaTiO_3 , PbTiO_3 , SrTiO_3 , BaHfO_3 , CaTiO_3 , PbZrO_3 and YNiO_3 [143, 195, 212, 230] have demonstrated that second-principles approaches can achieve quantitative agreement with density functional theory while enabling simulations at the scales required to study finite-temperature phenomena and complex textures. The role of long-range dipolar interactions [362], often assumed to be essential for modeling polar materials, was investigated using second-principles models. The results showed that short-range effective interactions can capture most bulk properties of ferroelectrics with surprising accuracy, even in the absence of explicit long-range dipolar interactions, helping to explain the success of MLIP approaches, which typically rely on local descriptors, for such materials. The study also identified specific artifacts that arise when long-range contributions are neglected, providing guidance on the contexts in which their explicit treatment remains necessary.

The study of polar textures in ferroelectric materials, addressed in Chapter 5, has revealed a richer phenomenology than was appreciated at the outset of this work [195, 216]. Polar skyrmions and related topological structures, initially regarded with some skepticism as theoretical constructs, have gradually been established as genuine physical features of these materials through both simulation and experiment. The work presented here has contributed to this broader

effort by identifying stable polar textures in bulk and heterostructures geometries and characterizing their properties. The identification of Bloch components in domain walls, reported in collaboration with experimental groups, challenged the prevailing understanding of domain wall structure in $\text{PbTiO}_3/\text{SrTiO}_3$ heterostructures [185]. While the prediction of new topological phases in polar materials through numerical simulations has become somewhat routine in recent years, translating these discoveries into experimentally accessible and controllable phenomena remains an open challenge. The emphasis in this thesis has therefore been placed on their dynamical manipulation and experimental feasibility, keeping in mind the constraints and opportunities of real laboratory conditions. Along these lines, the work presented in Chapter 6 demonstrated that both acoustic phonon excitations and inhomogeneous electric fields can be used to controllably displace, nucleate, and switch complex polar textures [208, 209, 216]. These results offer theoretical guidance toward the possible integration of polar textures in devices, should their technological relevance eventually be established. Temperature gradients, mechanical stress, optical excitations, and combinations of multiple stimuli applied simultaneously remain largely unexplored avenues in this direction, and the experimental feasibility of many of these protocols suggests that this will be a fruitful area of collaboration between theory and experiment in the coming years.

The study of CaTiO_3 , presented in Chapter 7, led to two distinct findings. First, the metastable polar $R3c$ phase was shown to be a genuine local minimum on the potential energy surface, separated from the $Pbnm$ ground state by a layer-by-layer flipping mechanism of the oxygen octahedra rotations. Finite-temperature simulations established that, once induced, the $R3c$ phase remains stable up to approximately 300 K and exhibits switchable ferroelectric polarization, while the large energy barrier between the two phases renders a direct field-induced $Pbnm$ -to- $R3c$ transition experimentally inaccessible in bulk [230]. Second, epitaxial CaTiO_3 films grown on $(001)_o$ -oriented NdGaO_3 substrates were found to host two nearly degenerate polar Pm phases with nearly perpendicular polarization orientations, giving rise to double hysteresis loops under an electric field applied along $\mathbf{b}_o$. This behavior, confirmed by both experiment and second-principles simulations, was identified as a first-order polarization process, an electric analogue of the first-order magnetization

process known in magnetic systems, and proposed as a new route to obtain double hysteresis loops without invoking a conventional antipolar ground state [231].

The investigation of YNiO_3 in Chapter 8 revisited the triggered mechanism proposed by Mercy and co-workers [234] for the structural phase transition and identified a critical missing piece: the instantaneous fluctuations of phonon modes at finite temperature, absent from the static Landau model, effectively stabilize the breathing distortion well above the transition temperature. The predicted softening of the breathing mode as the temperature decreases toward T_c constitutes a concrete, testable prediction for future experiments.

Across these diverse materials and phenomena, a common thread emerges: the interplay between structure, dynamics, and temperature is central to understanding the behavior of perovskite oxides, and effective models that bridge the accuracy of first-principles calculations with the scales required by experiment are now mature enough to provide genuine insight. The field has moved from proof of concept to systematic application, and the open availability of validated models will, it is hoped, accelerate further progress.

The natural next step in the development of these effective models is the explicit reintroduction of electronic and spin degrees of freedom. While these are implicitly present in the models constructed here through their parametrization on density functional theory, they are integrated out and not treated as dynamical variables. This prevents the investigation of phenomena such as charge localization and polaron formation, spin dynamics under external perturbations, charge doping, or electronic excitations that would require time-dependent density functional theory. Recent work [363–365] has begun to address this challenge by coupling lattice dynamics with explicit treatment of electronic degrees of freedom.

The successful integration of these approaches would open an entirely new landscape of phenomena accessible to large-scale simulation. In the context of YNiO_3 , for instance, such a framework would enable the real-time simulation of the metal-to-insulator transition, and in particular the direct observation of the feedback between the electronic degrees of freedom and the lattice, *i.e.*, whether the electronic redistribution accompanying the transition exerts forces on the atoms that in turn modify the structural dynamics. Beyond

bulk transitions, this would also allow one to address the electronic character of non-trivial polar structures: domain walls and topological textures, which have been shown here to be dynamically displaceable, could in principle become charged under appropriate conditions. The ability to move such charged domain walls with external fields would then amount to a controlled displacement of electronic charges, opening prospects for domain-wall-based nanoelectronic functionalities.

Beyond the prototypical perovskites studied in this thesis, the application of second-principles frameworks to less-explored layered oxide families, Ruddlesden-Popper phases, Aurivillius compounds, and Dion-Jacobson structures, is an emerging field where the expertise developed here can be directly applied [366]. These materials exhibit rich structural and electronic phase diagrams that remain largely unexplored at finite temperature and at the scales required to study domain structures and interfaces.

Finally, the study of chirality in crystals [367], which faces many of the same computational challenges as the polar textures investigated here, represents another natural direction for the methods developed in this work. Whether chirality constitutes a genuine ferroic order parameter remains an open question, and settling this issue would naturally call for the same tools developed here: large-scale finite-temperature simulations capable of capturing the formation, stability, and dynamics of non-trivial chiral textures. Should chirality prove to be a ferroic order parameter, the investigation of chiral domain walls, topological chiral structures, and their response to external fields would follow as a direct extension of the work presented in this thesis. More broadly, the methods, models, and physical understanding developed throughout this work are not tied to the specific materials studied here. They represent a general framework for investigating the interplay between structure, order, and dynamics in complex oxides, one that is now sufficiently mature to be turned toward the next generation of open questions in the field.

APPENDIX

Computation of stress

A

This chapter subsection provides a detailed derivation of the stress expressions and discusses their practical implementation. These expressions were independently rederived, reimplemented, and systematically tested within the present thesis. Starting from Eq. (3.31), the reduced coordinate of atom κ in unit cell l can be expressed as

$$R'_{l\kappa\alpha} = \left[(\delta_{\alpha\beta} + \eta_{\alpha\beta}) A_{\alpha\beta}^0 \right]^{-1} R_{l\kappa\alpha}, \quad (\text{A.1})$$

where $A_{\alpha\beta}^0$ denotes the matrix elements that define the elemental unit cell of the reference structure.

In order to compute the stress corresponding to a given atomic configuration $(\boldsymbol{\eta}, \{\mathbf{u}_{l\kappa}\})$, we consider infinitesimal perturbations $\delta\boldsymbol{\eta}$ and $\delta\{\mathbf{u}_{l\kappa}\}$ applied to this configuration under the constraint that the reduced atomic coordinates remain fixed. This condition reads

$$\begin{aligned} & \left[(\delta_{\alpha\beta} + \eta_{\alpha\beta}) A_{\alpha\beta}^0 \right]^{-1} \sum_{\beta=1}^3 (\delta_{\alpha\beta} + \eta_{\alpha\beta}) R_{l\kappa\beta}^0 + u_{l\kappa\alpha} \\ &= \left[(\delta_{\alpha\beta} + \eta_{\alpha\beta} + \delta\eta_{\alpha\beta}) A_{\alpha\beta}^0 \right]^{-1} \sum_{\beta=1}^3 (\delta_{\alpha\beta} + \eta_{\alpha\beta} + \delta\eta_{\alpha\beta}) R_{l\kappa\beta}^0 + u_{l\kappa\alpha} + \delta u_{l\kappa\alpha}, \end{aligned} \quad (\text{A.2})$$

from which one obtains the variation of the atomic displacements induced by the strain,

$$\delta u_{l\kappa\alpha} = \delta\eta_{\alpha\beta} (\delta_{\beta\gamma} + \eta_{\beta\gamma})^{-1} u_{l\kappa\gamma}. \quad (\text{A.3})$$

An additional subtlety arises from the fact that the stresses reported in density-functional theory are computed with respect to the *currently distorted structure*, rather than the reference structure used in the second-principles formalism. In our approach, the strain of the distorted structure is defined as

$$\eta_{\alpha\beta}^{SP} = \frac{A'_{\alpha\beta} - \delta_{\alpha\beta} A_{\alpha\beta}^0}{A_{\alpha\beta}^0}, \quad (\text{A.4})$$

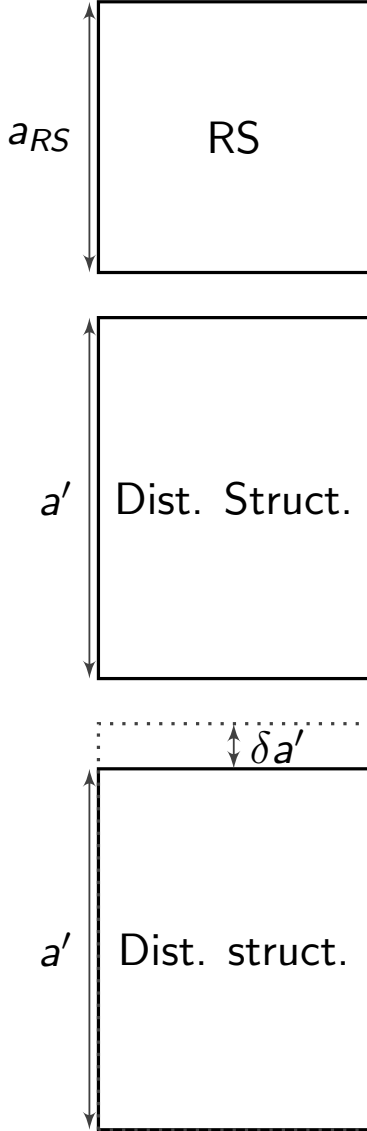


Figure A.1: Sketch of the difference of definition of strain between first- and second-principles

In contrast, the strain entering the DFT definition of the stress is

$$\eta_{\alpha\beta}^{DFT} = \frac{(A'_{\alpha\beta} + \delta A'_{\alpha\beta}) - A'_{\alpha\beta}}{A'_{\alpha\beta}} = \frac{\delta A'_{\alpha\beta}}{A'_{\alpha\beta}}. \quad (\text{A.5})$$

whereas the strain associated with the configuration used to compute the DFT stress is expressed within the second-principles framework is

$$\frac{(A'_{\alpha\beta} + \delta A'_{\alpha\beta}) - \delta_{\alpha\beta} A^0_{\alpha\beta}}{A^0_{\alpha\beta}}. \quad (\text{A.6})$$

We can rewrite Eq. (A.6) in terms of η^{DFT} ,

$$\frac{(A'_{\alpha\beta} + \delta A'_{\alpha\beta}) - \delta_{\alpha\beta} A^0_{\alpha\beta}}{A^0_{\alpha\beta}} = \frac{(A'_{\alpha\beta} + \delta A'_{\alpha\beta}) - \frac{\delta_{\alpha\beta} A'_{\alpha\beta}}{(\delta_{\alpha\beta} + \eta_{\alpha\beta}^{SP})}}{\frac{A'_{\alpha\beta}}{(\delta_{\alpha\beta} + \eta_{\alpha\beta}^{SP})}} \quad (\text{A.7})$$

$$= \frac{(\delta_{\alpha\beta} + \eta_{\alpha\beta}^{SP})(A'_{\alpha\beta} + \delta A'_{\alpha\beta}) - \delta_{\alpha\beta} A'_{\alpha\beta}}{A'_{\alpha\beta}} \quad (\text{A.8})$$

$$= \eta_{\alpha\beta}^{SP} + (\delta_{\alpha\beta} + \eta_{\alpha\beta}^{SP}) \eta_{\alpha\beta}^{DFT} \quad (\text{A.9})$$

the configuration used to evaluate the stress in **DFT** is a function of the second-principles strain η^{DFT} , and this difference in definition must be explicitly taken into account to reproduce DFT stresses within the present framework.

Taking all the above aspects into account, the stress can be written as

$$\begin{aligned} \sigma_a &= \frac{1}{V} \left. \frac{\partial E}{\partial \eta_a^{DFT}} \right|_{\mathbf{u}, \eta} \\ &= \frac{1}{V} \left. \frac{\partial E}{\partial \eta_a^{SP}} \frac{\partial \eta_a^{SP}}{\partial \eta_a^{DFT}} \right|_{\mathbf{u}, \eta} \\ &= \frac{1}{V} \left(\frac{\partial E}{\partial \eta_a^{SP}} + \sum_{l\kappa\alpha} \frac{\partial E}{\partial u_{l\kappa\alpha}} \frac{\partial u_{l\kappa\alpha}}{\partial \eta_a^{SP}} \right) \left. \frac{\partial \eta_a^{SP}}{\partial \eta_a^{DFT}} \right|_{\mathbf{u}, \eta^{SP}, \eta_a^{DFT}=0}. \end{aligned} \quad (\text{A.10})$$

The the above expression, V is the volume of the configuration on which we are evaluating the stress, $\partial E / \partial \eta_a^{SP}$ and $\partial E / \partial u_{l\kappa\alpha}$ can be easily from the potential, $\partial u_{l\kappa\alpha} / \partial \eta_a^{SP}$ can be obtained from Eq. (A.3) and $\partial \eta_a^{SP} / \partial \eta_a^{DFT}$ can be obtained from Eq. (A.7).

Figure 3.14 shows the effect of the last factor of Eq. A.10

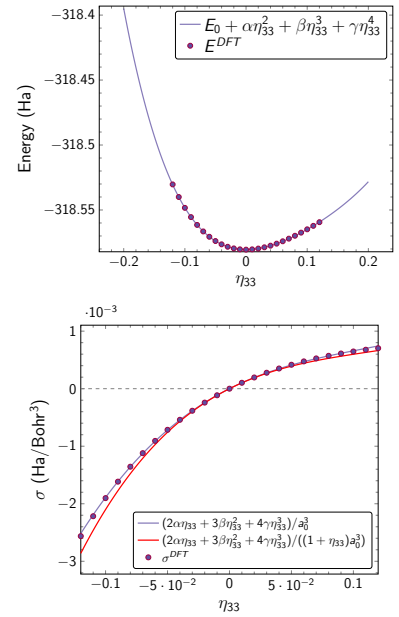


Figure A.2: (top) Fit of DFT energy using a Taylor expansion of the energy with respect to η_{33} and (bottom) calculated stress with and without the correction introduced in MULTIBINIT

First-order polarization process as an alternative to antiferroelectrics

B

B.1 Lattice parameters and strain

	a (Å)	b (Å)	c (Å)	a _{pc} (Å)	b _{pc} (Å)	c _{pc} (Å)	γ (°)
CTO _{DFT}	5.343	5.429	7.595	3.8085	3.8085	3.7975	89.085
CTO _{exp}	5.382	5.443	7.642	3.8275	3.8275	3.8210	89.354
NGO _{001,DFT}	5.393	5.530	7.686	3.8620	3.8620	3.8430	88.5628
NGO _{001,exp}	5.428	5.498	7.710	3.8630	3.8630	3.8550	89.2659

Table B.1: Experimental and first-principles cell parameters of CaTiO₃ and NdGaO₃

Case	CTO axis a _{pc} ,NGO(001)	CTO axis b _{pc} ,NGO(001)	η ₁ (%)	η ₂ (%)	η ₃ (%)	η ₄ (%)	η ₅ (%)	η ₆ (%)	Δ E (meV / f.u.)
1	a _{pc}	b _{pc}	+0.93	+0.93	–	–	–	+0.32	0.0
2	a _{pc}	c _{pc}	+0.93	–	+1.09	–	+2.58	–	+14.96
	CTO axis a _{pc} ,NGO(110)	CTO axis c _{pc} ,NGO(110)							
1	a _{pc}	b _{pc}	+0.93	+0.72	–	–	–	+2.58	+15.90
2	a _{pc}	c _{pc}	+0.93	–	+0.89	–	0.0	–	0.0
3	c _{pc}	a _{pc}	+1.09	–	+0.72	–	0.0	–	+0.21

Table B.2: In-plane epitaxial strain of CaTiO₃ (CTO_{exp}) grown coherently on NdGaO₃ (NGO_{exp}) for different crystallographic alignments (*i.e.* for distinct orientations between both compounds of a_{pc}, b_{pc}, c_{pc} as defined in Table B.1) and the second-principles energy difference in the centrosymmetric phase.

B.2 Atomic force microscopy topography

Atomic force microscopy characterisation of the surface morphology of CaTiO₃ films deposited on (110)_o-oriented NdGaO₃ (Figure B.1 (a)), as well as the films deposited on (001)_o-oriented NdGaO₃ (Figure B.1 (b)) shows atomically smooth surfaces with surface roughness which is less than one unit cell.

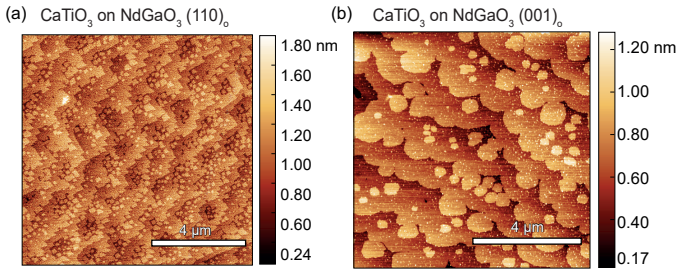


Figure B.1: Atomic force microscopy characterisation of the CaTiO₃ thin films, showing smooth surfaces. Multiple samples from each orientation have been studied, however a representative scan of each orientation is shown. (a) CaTiO₃ thin film on NdGaO₃ (110)_o, showing a mean square roughness of 0.26 nm. (b) CaTiO₃ thin film on NdGaO₃ (001)_o, showing a mean square roughness of 0.18 nm.

B.3 Space group determination

For CaTiO_3 on NdGaO_3 (110)_o, laboratory X-ray diffraction (XRD) (Figure B.2) shows intense Bragg peaks and well-defined finite-size oscillations, indicative of high-quality growth. Furthermore, laboratory XRD reciprocal-space maps and specular scans of half-order peaks (see Figure B.3 and ??) show that the film is fully strained on the substrate, twin-free, and follows the A-cation antipolar motion of the substrate, which confirms that the rotation pattern of the oxygen octahedra is preserved through the interface. Subsequent electrical measurements (see Figure B.9), these results indicate that this substrate stabilizes a low-symmetry Pm polar phase, with the polarization oriented in-plane along a_{pc} .

For CaTiO_3 on NdGaO_3 (001)_o, laboratory XRD reciprocal maps confirm that CaTiO_3 film is coherently strained on the substrate (Figure B.4). To determine the space group symmetry of the ferroelectric phase, we performed synchrotron X-ray diffraction measurements and searched for peaks appearing at the phase transition temperature. The persistence of the 025_o peak across the phase transition, as shown in Figure B.6(a), confirms that the oxygen octahedral rotations and antipolar motion of the Ca atoms persist in the polar phase. A polarization component along the a axis breaks the b -glide plane symmetry of the non-polar $Pbnm$ space group, which causes 0KL diffraction peaks with odd K to become allowed. Similarly, a polarization component along the b axis breaks the n -glide plane symmetry, implying that H0L peaks with odd $(H+L)$ become allowed. Figures ??(b) and (c) show the appearance of clear 036_o and 056_o diffraction peaks below approximately 87 K, while (d) and (e) reveal the emergence of small 306_o and 560_o peaks at the same temperature. This indicates a single structural phase transition where both glide plane symmetries are broken simultaneously. The polarization develops a larger component along a_o and a smaller component along b_o lowering the symmetry to Pm . The highest space group compatible with the existence of these diffraction peaks is indeed Pm .

These results confirm the predictions from first-principles calculations and validate the symmetry assignments used throughout the study.

B.3.1 Laboratory x-ray diffraction

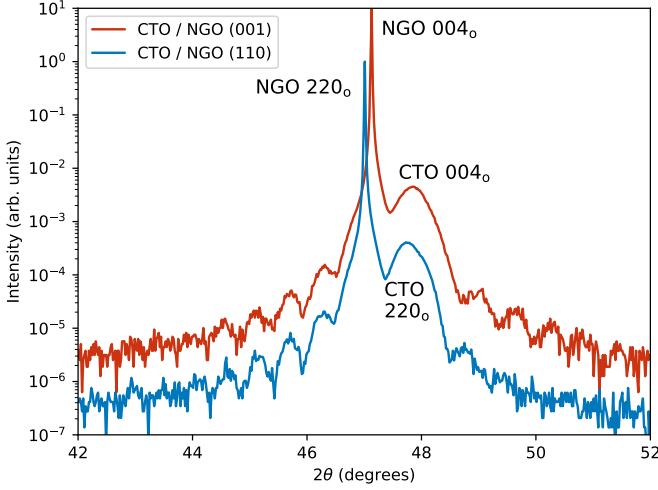


Figure B.2: Symmetric laboratory x-ray diffraction scans, from which out-of-plane lattice constants and film thickness were determined using InteractiveXRD-Fit [InteractiveXRD-Fit]. For CaTiO_3 on NdGaO_3 (001)_o, we obtain $c_o/2 = 3.793 \text{ \AA}$ and a thickness of 17.4 nm. For CaTiO_3 on NdGaO_3 (110)_o, we obtain $|\vec{a}_o + \vec{b}_o|/2 = 3.798 \text{ \AA}$ and a thickness of 18.2 nm.

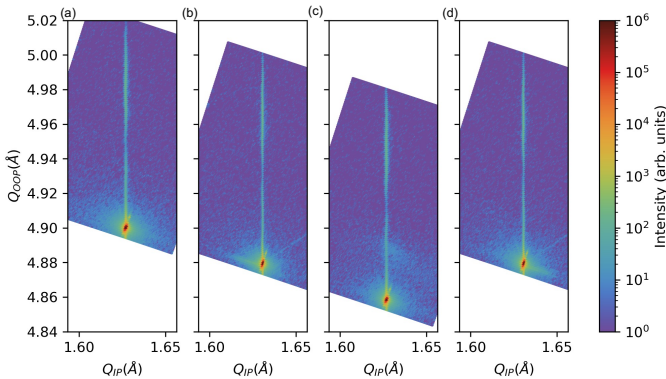


Figure B.3: Reciprocal space maps of CaTiO_3 on NdGaO_3 (110)_o measured around the (a) 240_o , (b) 332_o , (c) 420_o , and (d) $33\bar{2}_o$ diffraction peaks. The perfect alignment of film and substrate peak in Q_{IP} confirms that the film is fully coherently strained to the substrate. A single film peak in each map confirms that this film is twin-free, i.e. there is only a single orientation of the unit cell throughout the film. From the film peak positions, we confirm that CaTiO_3 films on NdGaO_3 (110)_o are monoclinic rather than orthorhombic, as expected for a strained (110)_o-oriented $Pbnm$ -like perovskite film [vailionis2008monoclinic], with lattice constants $a = 5.387 \text{ \AA}$, $b = 5.444 \text{ \AA}$, $c = 7.709 \text{ \AA}$, and the angle $\gamma = 91.02^\circ$.

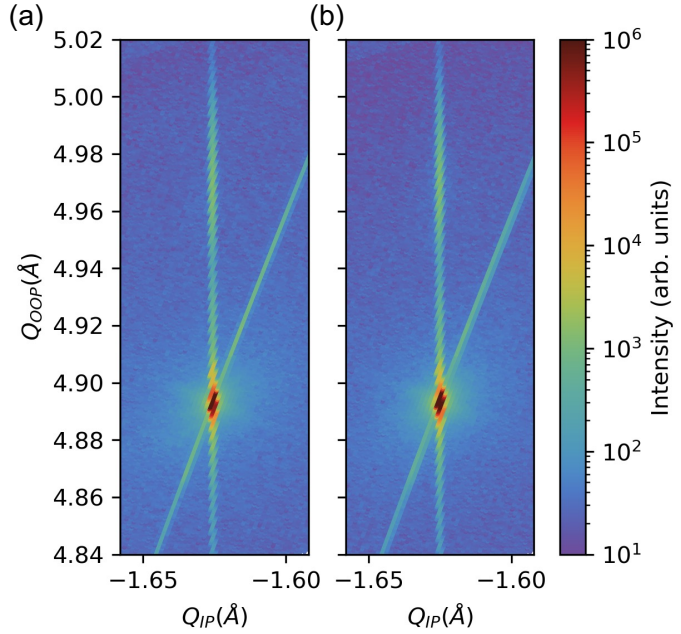


Figure B.4: Reciprocal space maps of CaTiO_3 on $\text{NdGaO}_3 (001)_0$ measured around the (a) 116_0 and (b) $\bar{1}16_0$ diffraction peaks, confirming that the film is fully coherently strained to the substrate. The CaTiO_3 peak positions are consistent with an orthorhombic structure.

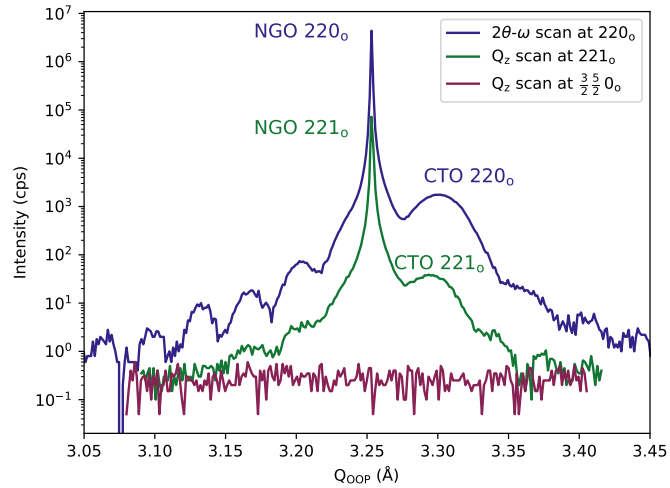


Figure B.5: CaTiO_3 on $\text{NdGaO}_3 (110)_0$: X-ray diffraction peaks confirming the orientation of the c_0 axis is the same in the film and the substrate. The 221_0 diffraction peak is a "half-order" peak arising from the antipolar motion of Ca or Nd cations. If a part of the CaTiO_3 film had its c_0 axis along the perpendicular in-plane direction, its 221_0 diffraction peak would appear at the reciprocal space point corresponding to $\frac{3}{2} \frac{5}{2} 0_0$ of the substrate.

B.3.2 Synchrotron X-ray diffraction

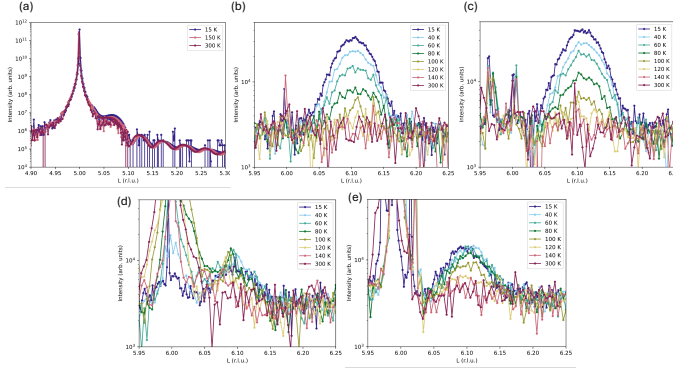
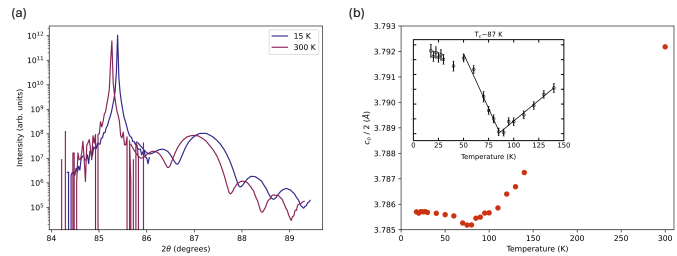


Figure B.6: Q_z -scans of half-order peaks of CaTiO_3 on NdGaO_3 $(001)_0$, measured using synchrotron X-ray diffraction as a function of temperature. (a) 025_0 peak, indicating that both the CaTiO_3 film and NdGaO_3 substrate have the same octahedral tilt pattern. The octahedral rotations and A-cation antipolar motion of CaTiO_3 persist across the phase transition and coexist with the ferroelectric phase. (b) 036_0 , and (c) 056_0 peaks, indicating the broken b glide plane, corresponding to a polarization along the a_0 axis. (d) 306_0 , and (e) 506_0 peaks, indicating the broken n glide plane, corresponding to a polarization along the b_0 axis. The relative intensity of the different peaks indicates that the polarization along the a_0 axis is much larger than that along the b_0 axis.

Figure B.7: Temperature dependence of (a) the specular 008_o reflection of CaTiO_3 on $\text{NdGaO}_3(001)_o$, measured using synchrotron X-ray diffraction. (b) Pseudocubic $c (= c_o/2)$ lattice parameter as a function of temperature, showing that the ferroelectric phase transition is concomitant with a structural transition marked by the anomaly in the out-of-plane lattice constant at approximately 87 K. Inset: etragonality (ratio of film to substrate lattice constants) as a function of temperature showing an anomaly at approximately 87 K.



B.3.3 Electrical measurement

Substrates

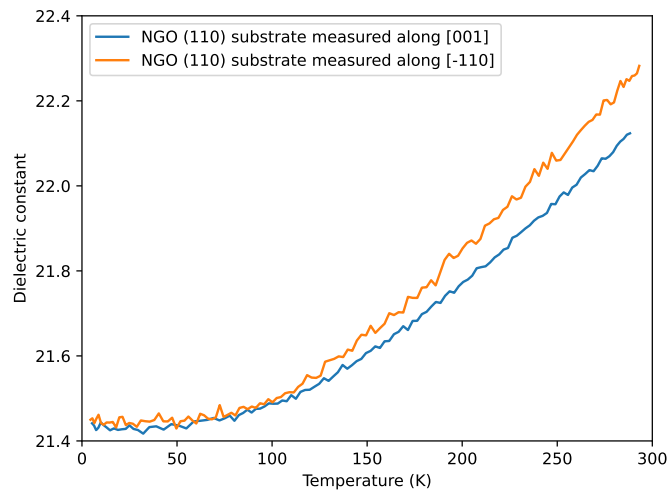


Figure B.8: Temperature dependence of the dielectric constant of a $\text{NdGaO}_3(110)_o$ substrate, measured along the main in-plane directions, $[001]_o$ and $[\bar{1}10]_o$.

CaTiO_3 films

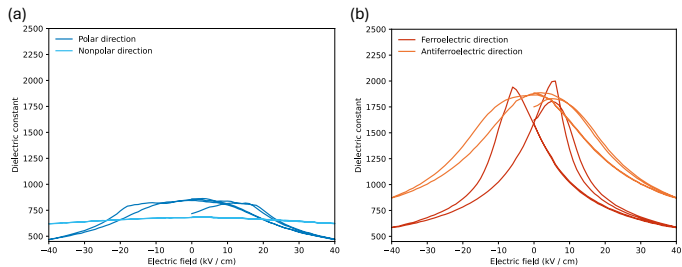


Figure B.9: Capacitance-voltage measurements for (a) CaTiO_3 thin film on $\text{NdGaO}_3(110)_o$ along the polar and non-polar directions, and (b) CaTiO_3 thin film on $\text{NdGaO}_3(001)_o$ along the ferroelectric and antiferroelectric directions. Measurements taken at 4.2 K.

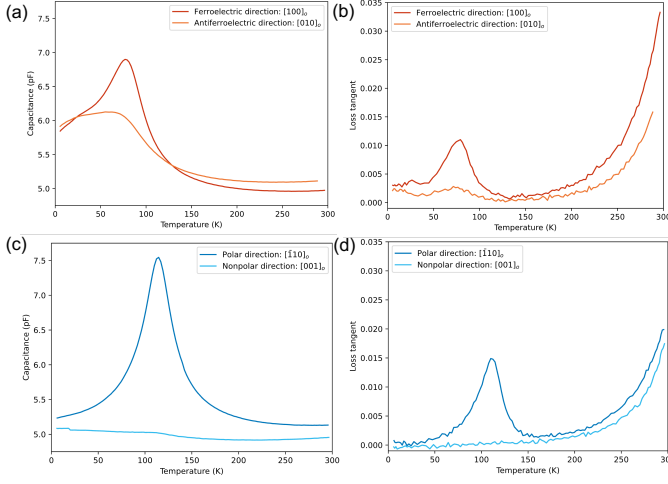


Figure B.10: Raw data for the real part of the capacitance (C') and the loss tangent [$\tan(\delta)$] measured at 1 kHz as a function of temperature for a $\text{CaTiO}_3/\text{NdGaO}_3(001)_0$ structure [(a) and (b)] and a $\text{CaTiO}_3/\text{NdGaO}_3(110)_0$ structure [(c) and (d)]. The ferroelectric phase transition is evidenced by a peak in the loss tangent in all measurements except the one along the non-polar $[001]_0$ direction in the uniaxial ferroelectric $\text{CaTiO}_3/\text{NdGaO}_3(110)_0$.

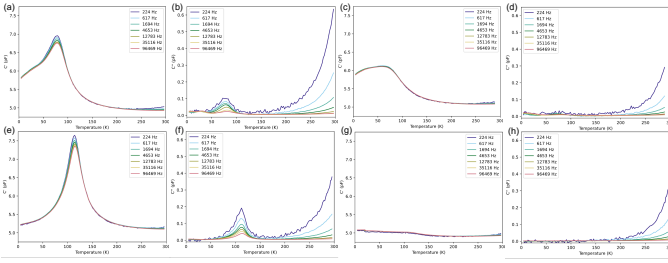


Figure B.11: Real part (C') and complex part (C'') of the measured complex capacitance as a function of temperature at selected frequencies for $\text{CaTiO}_3/\text{NdGaO}_3(001)_0$ measured along a_0 [(a) and (b)] and along b_0 [(c) and (d)], and for $\text{CaTiO}_3/\text{NdGaO}_3(110)_0$ measured along the polar $[\bar{1}10]_0$ direction (e) and (f) and the nonpolar $[001]_0$ direction [(g) and (h)]. The position of the peak associated with the phase transition varies little across multiple decades in frequency, which rules out relaxor-ferroelectric behaviour.

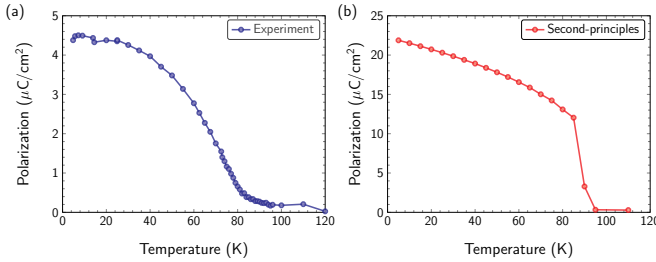


Figure B.12: (a) Experimental and (b) second-principles remanent polarization versus temperature in CaTiO_3 strained on $\text{NdGaO}_3(001)_0$.

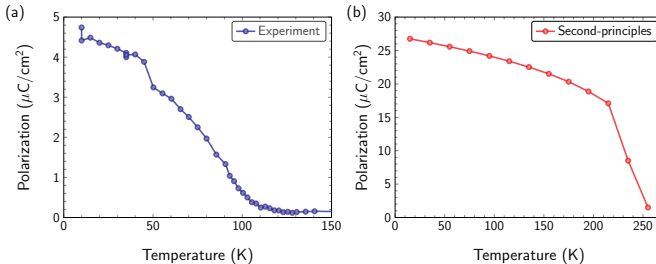


Figure B.13: (a) Experimental and (b) second-principles remanent polarization versus temperature in CaTiO_3 strained on $\text{NdGaO}_3(110)_0$.

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Special Terms

A

APEX Acoustic Phonon EXcitations. 180, 191–198

ASR Acoustic Sum Rule. 66–69

B

BFGS Broyden-Fletcher-Goldfarb-Shanno. 96, 104, 107, 117, 124, 139, 154, 174

D

DD Dipole Dipole. 65, 142

DFPT Density Functional Perturbation Theory. 52, 53, 65, 66, 68, 73, 93, 97–100, 103, 105, 108, 113–115, 117, 118, 122, 123, 125, 126, 129, 132, 140–142, 148

DFT Density Functional Theory. 45, 49, 55, 58, 96, 100, 101, 104, 106–109, 115, 117–119, 123–125, 127, 130–132, 137, 139–141, 148, 152, 156–161, 167, 169, 173, 207, 230, 238, 239

DOS Density Of States. 118

G

GF Goal Function. 73

GGA generalized gradient approximation. 49, 98, 103, 105, 113, 119, 122, 127, 129, 167, 225

H

HMC Hybrid Monte Carlo. 100–102, 106, 109, 111, 116, 118, 126, 132, 205, 207

I

IFC interatomic force constants. 13, 142

L

LDA local density approximation. 48, 119, 137, 157, 173, 225

LO Longitudinal Optical. 20, 142, 144–148

LR Long Range. 65

M

MIT Metal-to-Insulator Transition. 136, 137

MLIP Machine Learning Interatomic Potential. 82, 83, 85, 86, 93, 110, 137, 141, 142, 144, 146–148, 223, 224, 230, 231

N

NEB Nudged Elastic Band. 160, 163, 169, 171, 202–204, 206, 215, 217, 218, 220, 221

O

OOR Oxygen Octahedra Rotation. 224

P

PBEsol Perdew-Burke-Ernzerhof for solids. 98, 103–105, 110, 111, 113, 119, 122, 126, 157, 167, 225

PES Born–Oppenheimer potential energy surface. 45, 65

R

ReaxFF Reactive Force Fields. 57, 58

ReLU Rectified Linear Unit. 84

RPA Random Phase Approximation. 110

RS Reference Structure. 64, 70, 71

S

SATs Symmetry Adapted Terms. 69–73, 76–78, 99, 100, 105, 106, 113, 115, 116, 123, 124, 130, 131

SCF Self Consistent Field. 49, 55

SR Short Range. 65, 142

SSCHA Stochastic Self-Consistent Harmonic Approximation. 111

T

TDEP Temperature Dependent Effective Potential. 87–91, 111, 119, 120, 224, 227, 228

TO Transversal Optical. 20, 142, 144, 146

TS Training Set. 72, 73, 76, 77