

To the Graduate Council:

I am submitting herewith a dissertation written by Abhijeet Sundarrao Dhakane entitled “Understanding the Switching Dynamics in Memristor Materials using Large-scale Simulations and Deep Learning Methods.” I have examined the final paper copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Data Science and Engineering.

Panchapakesan Ganesh, Major Professor

We have read this dissertation
and recommend its acceptance:

Bobby Sumpter

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David Mandrus

Jan-Michael Carrillo

Rama Vasudevan

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Accepted for the Council:

Dixie L. Thompson

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(Original signatures are on file with official student records.)

Understanding the Switching Dynamics in Memristor Materials using Large-scale Simulations and Deep Learning Methods

A Dissertation Presented for the
Doctor of Philosophy
Degree

The University of Tennessee, Knoxville

Abhijeet Sundarrao Dhakane

May 2025

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To my beloved parents and my teachers, mentors who made me to here.

Abstract

The discovery of multifunctional properties such as ferroelectricity in hexagonal nitride and oxide materials has sparked renewed interest in wurtzite materials, given their compatibility with CMOS integration and tunable optical and piezoelectric properties. However, the origin of ferroelectricity and its switching mechanism under electric fields remain poorly understood, posing challenges for designing and improving low-power microelectronic devices based on these materials. Similarly, in ferroelectrics like BaTiO_3 , polar domain walls at the nanoscale show promise for memory devices, but their structure and dynamics, particularly in defective materials, are not well characterized. In this work, we address these gaps by performing largescale simulations to investigate both the field-induced switching in wurtzite-ZnO and the nanoscale domain-wall dynamics in pristine and defective BaTiO_3 . Using reactive force fields of BaTiO_3 and a graph dynamical neural network approach, we capture atomistic switching mechanisms, extract energy barriers, and reveal the role of defects such as oxygen vacancies in slowing dipole relaxation and influencing domain-wall dynamics on the hysteretic behavior [Dhakane et al. \(2023\)](#). In addition, we analyzed ferroelectric switching trajectories in ZnO with/without Mg-dopants and identified the key switching mechanism in good agreement with recent experimental results [Calderon et al. \(2023\)](#); [Dhakane et al. \(2025\)](#). Furthermore, large-scale simulations revealed a new design principle on how to lower the coercive fields in wurtzite ferroelectrics, that will revolutionize their adoption in making low-power microelectronic devices. More generally, we show the power of combining large-scale simulations and data analytics, including deep learning techniques to provide a new paradigm of ‘*dynamics-by-design*’ for discovering novel functional materials. In addition to field-induced switching, advantage of this paradigm in controlling out-of-equilibrium

processes such as material synthesis will also be discussed in the outlook section of this thesis.

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Chapter 1

Introduction

1.1 Background and Motivation

Modern electronics faces an increasing demand for energy-efficient figure 1.1, low-power operation as device scaling approaches fundamental atomic limits. Power density and energy consumption have become critical concerns from portable devices to data centers Andrae and Edler (2015); Sorrell (2014). The scaling of dynamic power in CMOS logic goes as the square of the supply voltage, CV^2 . Hence reducing operating voltage is a direct way to curb power dissipation Scott and Paz de Araujo (1989); Íñiguez et al. (2019). However, conventional silicon transistors cannot easily operate below a certain voltage due to the thermionic limit on subthreshold slope (approximately 60 mV/decade at room temperature). This “*Boltzmann tyranny*” fundamentally restricts the reduction of switching voltage and thus the energy per logic operation in standard FETs Salahuddin and Datta (2008).

In response, research efforts are exploring novel materials and device physics to break these limits and achieve ultralow-voltage electronics. One promising avenue is the integration of ferroelectric materials, which exhibit unique electrical properties that can be harnessed for low-power device operation., Ferroelectrics are especially attractive because they can retain polarization states without power (i.e. non-volatility) and potentially provide internal voltage amplification i.e. via negative capacitance, offering new strategies to reduce power consumption in electronic circuits Salahuddin and Datta (2008); Li and Toriumi (2020).

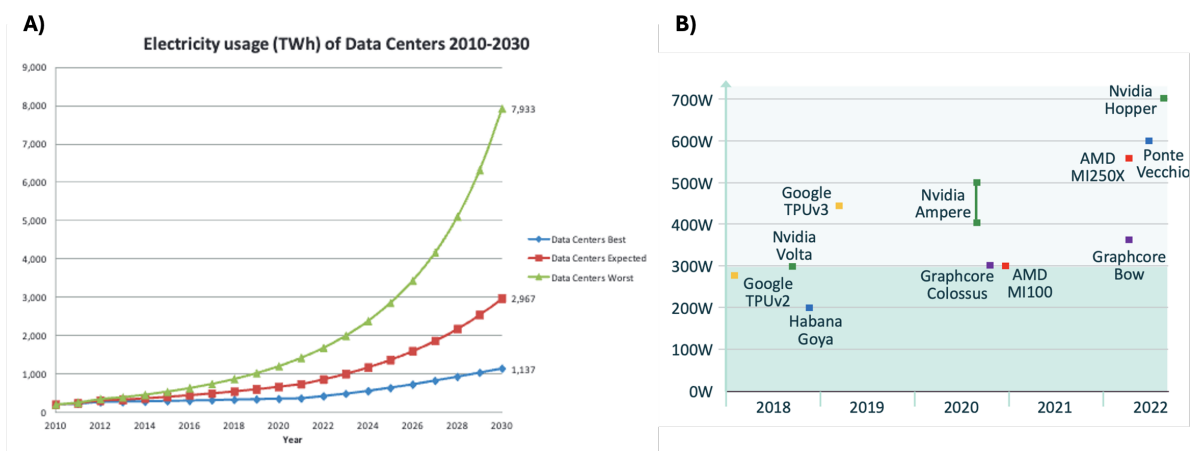


Figure 1.1: (A) This plot shows the projected energy demand for the data centers over the next 10 years. Andrae and Edler (2015) (B) Shows the typical energy consumption in the modern GPUs

Ferroelectric materials have long been studied in materials science and electrical engineering, but their relevance has recently surged with the industry’s push toward green and sustainable technologies. Also widescale adoption of AI/ML powered applications in mainstream which highly relied on the power heavy GPUs so far is a big driver for new innovations in ferroelectric materials. The ability of a ferroelectric to switch its internal polarization with very little energy input opens a pathway to highly energy-efficient electronic devices, addressing the pervasive need for minimizing power usage in modern information technology [Khan et al. \(2020\)](#); [Luo et al. \(2022\)](#). Indeed, ferroelectrics are viewed as promising candidates for next-generation low-power devices owing to their spontaneous electric polarization that can serve as an internal state variable, switched without continuous current flow.

In addition to conventional computing architectures, emerging neuromorphic computing paradigm promises significant gains in low-power electronics that are much faster in various operations. Neuromorphic is based on emulating brain-like computing, where the memory and compute are co-located, thereby avoiding the von Neumann bottleneck limiting speed and power in current computing architectures. Memristors – i.e. devices that have significant tunable resistance and thus shows hysteresis (a.k.a non-linearity) but can be switched fast by external fields – are ideal for such neuromorphic computing paradigm [Luo et al. \(2022\)](#); [Kim and Lee \(2019\)](#). Ferroelectrics, due to their non-volatile nature, and ease of switching with external electric-fields between the different non-volatile polarization states, are one of the front runners for memristors devices.

Indeed, driven by the growing demands for miniaturization and energy efficiency in nanoelectronics, researchers are striving to further reduce the operating voltages of ferroelectric-based memristor devices. The motivation is clear: if one can harness ferroelectricity to operate transistors and memory elements such as memristor at lower voltages (on the order of a few hundred millivolts or less) while maintaining functionality, it would significantly reduce energy per operation and heat generation. Such progress would be transformative for ultra-dense computing systems, battery-powered applications, and IoT sensors, enabling longer battery life and lower cooling requirements. In this context, ferroelectric materials and devices form a critical research domain at the intersection of

materials science and electronic engineering, offering a pathway toward the ultralow-voltage operation that future of microelectronics Wang et al. (2025).

Ferroelectric Materials

Ferroelectric materials are a class of crystalline solids that exhibit a spontaneous electric polarization which can be reversed by an external electric field Kao (2004); Damjanovic (1998); Valasek (1921) . In other words, they possess built-in electric dipoles even in the absence of an applied field, and these dipoles can be reoriented between at least two stable polarization states Figure 1.2. This behavior gives rise to a characteristic polarization–electric field hysteresis loop, analogous to the hysteresis in ferromagnets, and is the hallmark of ferroelectricity. Importantly, the two stable polarization states in a ferroelectric can represent binary logic states (e.g. “0” and “1”) without the need for power to maintain them, making ferroelectrics inherently nonvolatile.

Traditional ferroelectric compounds are typically oxides with specific crystal structures that lack inversion symmetry (allowing a polar axis). For example, perovskite-structure oxides such as barium titanate (BaTiO_3) Ziebińska et al. (2008) and lead zirconate titanate (PZT) Jaffe et al. (1954) were among the first widely studied ferroelectrics, known for their sizable polarization and well-defined Curie temperatures. Layered perovskite structures like strontium bismuth tantalate (SBT), an Aurivillius phase, also exhibit ferroelectricity and have been noted for their fatigue endurance and low leakage Petrovic and Bobic (2018), making them attractive for memory applications.

In addition to inorganic oxides, certain polymer materials (e.g. poly(vinylidene fluoride), PVDF) are ferroelectric; these tend to have lower polarization but offer mechanical flexibility. Thus, the landscape of ferroelectric materials is diverse, ranging from ceramic crystals to organic polymers, each with a balance of properties (polarization strength, coercive field, dielectric loss, mechanical robustness) relevant to different applications Lovinger (1983).

A major breakthrough in the past decade was the discovery of ferroelectricity in doped hafnium oxide (HfO_2) thin films. Unlike perovskites, pure HfO_2 adopts a centrosymmetric fluorite structure; however, appropriate doping (e.g. Si, Y, Al, Zr) and optimized atomic-layer deposition can stabilize a non-centrosymmetric orthorhombic phase exhibiting robust

ferroelectric polarization [Böscke et al. \(2011\)](#). First reported in 2011, this ferroelectric HfO_2 (and its solid solutions such as $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$, HZO) combines ultrathin film operation (thickness ~ 10 nm) and low switching voltages (1–2 V) with direct CMOS process compatibility, owing to its use as a high- κ gate dielectric in standard transistor fabrication [Lee et al. \(2020\)](#).

In parallel, wurtzite-structure materials—such as Mg-doped ZnO ($\text{Zn}_{1-x}\text{Mg}_x\text{O}$), scandium-doped aluminum nitride ($\text{Al}_{1-x}\text{Sc}_x\text{N}$), and aluminum-boron nitride (AlBN)—have emerged as ferroelectric candidates [Ferri et al. \(2021\)](#); [Moriwake et al. \(2014\)](#); [Calderon et al. \(2023\)](#). These nitrides and oxides leverage the intrinsic polar axis of the wurtzite lattice to achieve switchable polarization. For example, AlScN films with Sc concentrations of 30–40% exhibit remanent polarization comparable to classical ferroelectrics, and ZnMgO alloys can display ferroelectric-like hysteresis under high applied fields [Casamento et al. \(2023\)](#). However, their practical implementation faces challenges: notably higher coercive voltages (often $> 5\text{V}$ in ultrathin films), elevated leakage currents, phase instability or fatigue under cycling, and compositional inhomogeneity. Moreover, integration into CMOS flows remains under development, as these materials typically require specialized epitaxy (e.g. MOCVD or sputtering) on Si substrates with stringent lattice-matching and thermal-budget constraints. But they offer significant high power densities compared to Hafnia.

Nevertheless, the demonstration of ferroelectricity in both doped HfO_2 and wurtzite oxides/nitrides has significantly broadened the palette of CMOS-compatible ferroelectrics [Schönweger et al. \(2023\)](#). Ongoing efforts in chemical doping, interface engineering, and deposition process optimization aim to lower switching voltages and improve reliability, bringing these materials closer to practical ultralow-voltage memory and logic applications.

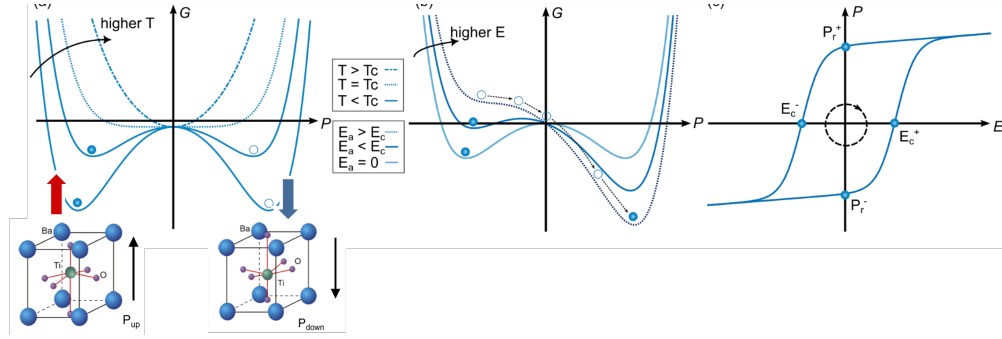


Figure 1.2: This figure shows the typical ferroelectric double-well free energy landscape and unit cell representation of the BaTiO₃ for the ‘up’ and ‘down’ polarization state [Athle and Borg \(2024\)](#).

From a materials science perspective, advanced characterization techniques—such as piezoresponse force microscopy (PFM) [Kelley et al. \(2020\)](#), synchrotron X-ray diffraction [Hadjimichael et al. \(2018\)](#), and in situ transmission electron microscopy (TEM) [Mun et al. \(2024\)](#)—have allowed direct observation of ferroelectric domain structures and switching mechanisms at the nanometer scale. These studies have revealed nontrivial polar topologies, including flux-closure domain patterns and ferroelectric vortices, in thin films. In certain layered ferroelectrics like SBT, topological vortex–antivortex pairs of polarization have been observed, indicating complex nanoscale structures that influence switching dynamics and stability [Ivry et al. \(2010\)](#); [Sánchez-Santolino et al. \(2024\)](#).

Advanced synthesis methods (molecular beam epitaxy, atomic layer deposition, pulsed laser deposition, etc.) now enable growth of high-quality ferroelectric films and heterostructures with atomic precision. Strain engineering and superlattice layering can further enhance ferroelectric properties by tuning the crystal lattice; for example, epitaxial strain can induce ferroelectricity in materials that are otherwise non-ferroelectric in bulk.

These advances in materials discovery, characterization, and engineering directly support the quest for ultralow-voltage operation. Strategies such as thickness scaling, chemical doping and defect engineering, interface design, and strain engineering have all been shown to reduce the coercive field and switching voltage in ferroelectric [Wang et al. \(2020\)](#); [Janolin \(2009\)](#). By combining these approaches—particularly in hafnia-based ferroelectrics—researchers have pushed experimental switching voltages ever lower, moving toward seamless integration with standard low-voltage (< 1 V) CMOS circuits. This progress promises transformative gains in energy efficiency for future electronic and memory devices. But much work still remains in addressing practical challenges as detailed below, specifically in conventional oxides as well as wurtzite-class of materials.

1.1.1 Ferroelectric Devices and Applications in Electronics

The unique properties of ferroelectric materials (namely, switchable and nonvolatile polarization) have led to a variety of device applications, both realized and proposed. Perhaps the most established application is in nonvolatile memory. Ferroelectric random-access memory (FeRAM or FRAM) uses a ferroelectric capacitor as the storage element: binary

data is stored in the polarization orientation (up or down) of a small ferroelectric film sandwiched between electrodes. Reading and writing involve applying voltage pulses to switch or sense the polarization state. FeRAM technology was first explored in the 1950s and 1960s conceptually [Buck \(1952\)](#); [Ramtron International Corporation \(2024\)](#), and it saw commercial realization in the 1990s. Early FeRAM devices often used PZT or SBT thin-film capacitors integrated with transistor circuits. Companies like Fujitsu and Ramtron successfully produced FeRAM chips (e.g., a 256kb FeRAM by Ramtron, or later 2Mb FeRAMs by Fujitsu) that offered fast write speed and lower write energy compared to Flash memory [Ramtron International Corporation \(2024\)](#); [Fujitsu Limited \(2024\)](#) . In these memories, the ferroelectric’s nonvolatility means data can be retained for long periods without power. Moreover, ferroelectric writes do not require the high voltages or currents that Flash memory does, giving FeRAM an energy advantage [Sharma et al. \(2017\)](#). However, traditional FeRAM had challenges too: the need for a relatively large switching voltage (often $>3\text{V}$ in older PZT-based FeRAMs), limited density due to capacitor size, and issues like fatigue (polarization degradation after many cycles) which constrained its widespread adoption. Nonetheless, FeRAM finds niche use in applications needing ultra-low-power writes and radiation hardness (e.g., some microcontrollers and smart cards include FeRAM). The continual improvement of ferroelectric materials (especially the introduction of HfO-based ferroelectrics) is now addressing some of these issues by enabling ferroelectric memories that operate at lower voltages and smaller geometries [Wang et al. \(2025\)](#).

Beyond simple capacitors, ferroelectric field-effect transistors (FeFETs) have gained intense interest. An FeFET is essentially a MOSFET where the gate dielectric is replaced (or augmented) by a ferroelectric layer [Khan et al. \(2020\)](#); [Luk’yanchuk et al. \(2022\)](#). When a ferroelectric is used as the gate insulator, the transistor’s threshold voltage can be modulated by the remnant polarization of the ferroelectric. This means the FeFET can act as a nonvolatile memory transistor: the channel can be in a high or low threshold state depending on the polarization, which remains even when the power is off. The concept of the FeFET was first proposed many decades ago (with J. Moll and D. Buck and others discussing it in the 1950s) and a patent by I. M. Ross in 1957 , but making a practical FeFET was historically difficult [Buck \(1952\)](#). Early attempts in the 1980s (for example, experiments

reported in 1988) suffered from ferroelectric degradation and interface problems (e.g., the ferroelectric would depolarize due to charge trapping at the semiconductor interface). The resurgence of FeFET research today is largely thanks to ferroelectric HfO: since HfO can be made ferroelectric and is inherently compatible with silicon, it became feasible to integrate a ferroelectric gate into advanced transistors. In recent years, prototype FeFETs using HfO-based ferroelectrics have been demonstrated with significant improvements in endurance and retention, and with operating voltages closer to logic levels (around 1–2 V) [Scott and Paz de Araujo \(1989\)](#); [Alcala et al. \(2022\)](#).

Perhaps the most exciting application of ferroelectrics in logic devices is the concept of the negative capacitance field-effect transistor (NC-FET) [Salahuddin and Datta \(2008\)](#). This concept, first proposed in the late 2000s, leverages an intriguing aspect of ferroelectric physics: in a certain regime of its polarization–electric field curve, a ferroelectric can exhibit an effective negative differential capacitance [Salahuddin and Datta \(2008\)](#). If a ferroelectric layer is carefully incorporated into the gate stack of a transistor, it can amplify the gate voltage internally, lowering the subthreshold swing of the transistor below the fundamental 60 mV/dec limit [McGuire et al. \(2017\)](#). In essence, the ferroelectric’s polarization reversal process can give back energy and boost the surface potential in the channel for a given input voltage, acting as an active dielectric. The NC-FET architecture typically involves a ferroelectric layer either directly on the semiconductor (metal-ferroelectric-semiconductor, MFS structure) or in conjunction with a dielectric buffer (MFIS structure) to stabilize the operation. The theoretical foundation comes from the Landau theory of ferroelectrics: the double-well free energy profile of a ferroelectric as a function of polarization leads to an S-shaped polarization–electric field relation, implying a region where the incremental capacitance (dQ/dV) is negative [Khan et al. \(2020\)](#). By coupling this ferroelectric capacitor to the transistor gate, the overall capacitance seen by the channel can be reduced in such a way that the transistor’s body factor <1 , and thus a smaller gate voltage swing produces the same effect on the channel as a larger swing would in a normal device. This translates to a steeper subthreshold slope (potentially $<60\text{mV/decade}$) and allows for lower supply voltage operation for the same on-current.

In the last few years, there have been experimental demonstrations of NC-FETs that validate this principle. Notably, ferroelectric HfO-based capacitors have been used to achieve sub-60 mV/decade switching in transistors at room temperature . For example, one study showed a MoS 2D transistor with a hafnia ferroelectric gate achieving an average subthreshold swing of 8 mV/dec over four decades of current (minimum 6 mV/dec), far below the normal thermal limit [Si et al. \(2018\)](#); [McGuire et al. \(2017\)](#). Silicon-based transistors with ferroelectric HZO have also achieved steep swings and demonstrated internal voltage amplification, confirming the NC effect . These results, while sometimes accompanied by hysteresis or device variability, prove that negative capacitance is a real and exploitable phenomenon. The implications for logic circuits are significant: an NC-FET could operate at, say, 0.3–0.5 V supply voltage yet deliver performance (switching speed, drive current) comparable to a regular transistor at 0.7–1.0 V, drastically cutting power consumption. Logic circuits built from such transistors would dissipate far less energy per operation, enabling more operations per joule – a key metric for everything from mobile processors to large-scale cloud computing. Researchers are also investigating ferroelectric steep-slope devices in combination with novel channel materials (like 2D semiconductors and III-V heterostructures) to further reduce power. Another emerging device concept is the ferroelectric tunnel junction (FTJ), where a nanometer-thin ferroelectric barrier modulates quantum tunneling current, forming a memory bit or a programmable resistor for neuromorphic computing – this also benefits from low voltage operation since tunneling currents are extremely sensitive to voltage changes [Wen and Wu \(2020\)](#); [Sharma et al. \(2023\)](#).

In summary, ferroelectric devices span a range of applications: nonvolatile memories (FeRAM, FeFET), steep-slope logic transistors (NC-FET), non-linear hysteresis loops, and even multifunctional components (piezoelectric sensors, energy harvesters, etc., since many ferroelectrics are also piezoelectric). Their common thread is leveraging the ferroelectrics internal polarization as a state variable or as a means to augment circuit behavior, which can be particularly advantageous for reducing power consumption and adopting new paradigm in electronic systems, such as making memristive devices for neuromorphic computing architectures.

1.1.2 Challenges and Technological Significance

While ferroelectric materials and devices offer exciting opportunities, there remain significant challenges to be addressed before their full promise is realized in ultralow-power electronics. On the materials side, one longstanding challenge is ferroelectric fatigue—the gradual reduction of switchable polarization with repeated switching cycles. Traditional perovskite ferroelectrics (like PZT) could lose a substantial fraction of their polarization after 10^5 – 10^8 cycles, which is problematic for memory devices that require endurance [Namsar et al. \(2014\)](#). Advances such as fatigue-resistant compositions (e.g. SBT was chosen for FeRAM partly for its improved endurance) and new mechanisms (the recently reported interlayer sliding ferroelectricity in 2D materials is one approach to eliminate fatigue) are actively mitigating this issue. Hafnia-based ferroelectrics also show different fatigue behavior—some doped HfO_2 films exhibit a “wake-up” effect (polarization increases over initial cycles) followed by eventual fatigue. Understanding and controlling these phenomena is crucial for reliable device operation over billions of cycles [Cheng et al. \(2022\)](#); [Bian et al. \(2024\)](#). Similar challenges remain in Wurtzite based ferroelectrics as well, which form the core of this thesis.

Another challenge is retention: ferroelectric materials can gradually depolarize over time due to charge injection, thermal activation, or depolarizing fields, which could lead to loss of the stored state (bit flips in memory or drift in transistor threshold). Ensuring long retention times (on the order of years) at reduced coercive voltages often requires careful interface engineering to minimize charge trapping and imprint fields that bias the polarization. This is an active area of research, especially for FeFET memory devices where the gate stack involves interfaces between ferroelectric, dielectric, and semiconductor [Pan and Ma \(2011\)](#); [Tian et al. \(2019\)](#).

From a device integration perspective, scaling ferroelectric devices to nanometer dimensions while maintaining their performance is challenging. Ferroelectric properties can be size-dependent; extremely small ferroelectric capacitors might become reluctant to switch or have unstable domain configurations. For instance, there is typically a critical thickness below which a ferroelectric thin film becomes non-ferroelectric due to depolarization fields. Researchers have made great progress—ferroelectric HfO_2 can be as thin as ~ 5 nm and

still switch, which is a testament to how far scaling has come—but pushing to even thinner dimensions or smaller lateral feature sizes may introduce variability. There is also the matter of variability and uniformity in large arrays of devices: fabrication inconsistencies could lead to distribution in coercive voltages or charges. In a memory array or logic circuit, such variations need to be controlled to ensure uniform behavior. This ties back to materials processing—deposition methods for ferroelectric films must achieve uniform thickness and composition across wafers, and ferroelectric phase purity (especially for hafnia which can also form non-ferroelectric phases) must be maintained [Park et al. \(2023\)](#); [Gradauskaite et al. \(2023\)](#).

Another set of challenges is associated with the integration into CMOS technology. Although HfO_2 is CMOS-friendly in principle, the introduction of a ferroelectric layer in the gate stack of a transistor can interact with other elements (for example, the channel doping profile or source/drain fields) in complex ways. Reliability qualifications like bias temperature instability (BTI), hot-carrier effects, etc., need to be re-evaluated for transistors with ferroelectric gates [Crespo-Yepes et al. \(2022\)](#). Furthermore, the thermal budgets of CMOS processes can sometimes conflict with ferroelectric phase stability (hafnia’s ferroelectric phase can be sensitive to annealing conditions). Thus, process integration know-how must be developed to include ferroelectrics in a production environment. *Most importantly, role of heterogeneities, such as defects and dopants on the stability and switching dynamics of ferroelectrics needs to be fully understood.*

On the circuit and system level, one has to consider how to leverage ferroelectric devices most effectively. For instance, NC-FETs might achieve low-voltage switching, but if they introduce even a minor hysteresis, how will that affect logic gate design or clocking schemes? Conversely, if they are hysteresis-free, how close can one approach the theoretical energy limit (Landauer’s limit) for computation? Landauer’s principle sets a fundamental lower bound on energy dissipation per bit operation ($kT \ln 2$), and while ferroelectric NC devices do not break thermodynamics, they can help approach such fundamental limits by reducing the overhead energy dissipated above the minimum required [Cao and Banerjee \(2020\)](#).

The technological significance of overcoming these challenges is immense: successfully integrating ferroelectrics could redefine the energy efficiency of computing. Information

processing could see a paradigm shift where nonvolatility and ultralow voltage are intrinsic properties of the computing elements, not afterthought add-ons.

In summary, ferroelectric materials and devices stand at the forefront of research aimed at pushing electronics into a new low-power regime. The motivations are clear—from the needs of battery-powered portable electronics to the operational costs of large-scale computing infrastructure, energy efficiency is paramount. Ferroelectrics bring an unusual and highly desirable toolkit: they can store data without power, switch with potentially very low energies, and even perform electronic functions (like voltage amplification via negative capacitance) that were previously not possible with conventional materials. Significant challenges in material science (fatigue, retention, scaling) and device engineering (stability of negative capacitance, variability, integration) are active areas of investigation. The field has seen rapid progress, with state-of-the-art strategies lowering operating voltages and new material discoveries continually emerging. The technological significance of this research is underscored by its potential impact: enabling future information technologies that consume orders of magnitude less power than today. As Wang et al. note, the ultimate aim is to facilitate energy-efficient applications of ferroelectric materials and devices in future information technologies. Achieving ultralow-voltage operation with ferroelectrics could herald a new era of electronics, where the marriage of novel materials and devices meets the global challenge of sustainable, low-power computing. *A critical understanding at the atomistic level of the role of defects and dopants, and how they influence switching dynamics, pathways and timescales under external fields is crucial to overcome these challenges.*

1.1.3 Molecular Dynamics Simulations in Materials Science

Molecular dynamics (MD) simulations have become a cornerstone in materials science for investigating atomic-scale phenomena over finite time scales. By numerically integrating the equations of motion for particles, MD provides detailed insight into temperature-dependent structural evolution, defect dynamics, and phase transitions that are often inaccessible experimentally. One of the key advantages of MD is its ability to bridge length and time scales – enabling the study of nanoscale processes (on the order of nanometers and nanoseconds or longer) that link atomistic mechanisms to macroscopic material behavior. For example,

ferroelectric materials exhibit phenomena such as polarization switching and domain wall motion that occur over tens of nanometers and on nanosecond timescales . First-principles approaches like density functional theory (DFT), while highly accurate for static calculations, are typically limited to small system sizes ($\sim$ a few nanometers) and very short times (< 100 ps) due to their high computational cost . This makes it impractical for DFT alone to capture long-range domain interactions, hysteresis loop formation, or slow defect migration. In contrast, classical MD simulations can reach the length and time scales required to observe complete ferroelectric switching cycles, domain nucleation/propagation, and defect diffusion.

In the realm of materials design, MD thus plays a significant role: it allows researchers to explore the dynamical response of materials (e.g. under applied fields or stress), test the influence of temperature or microstructural factors, and generate statistical ensembles that bridge to continuum models. Such capabilities are critical for ferroelectric materials, where switching kinetics and thermal effects dictate device performance. However, the reliability of MD outcomes depends on the quality of the interatomic force fields employed. Traditional empirical potentials (e.g. Lennard-Jones, Buckingham, or shell-model potentials for ferroelectrics) can simulate large systems quickly, but they often impose fixed bond topologies or assume constant charge distribution. These simple potentials lack the ability to model chemical bond breaking/formation or dynamic charge polarization, limiting their transferability when chemical environments change (as occurs with defects, surfaces, or phase transitions).

Reactive force fields have emerged to overcome these limitations by incorporating more complex functional forms that can adapt to changing bonding situations. In particular, the ReaxFF (reactive force field) formalism has proven to be a powerful approach for large-scale MD simulations that require chemical fidelity [Goddard III et al. \(2002\)](#). ReaxFF was first introduced by van Duin as a general bond-order-based potential with dynamic charge equilibration, enabling the simulation of bond breaking and formation in an MD framework [Akbarian et al. \(2019\)](#). Since then, ReaxFF has been applied to a wide range of materials and chemistries – from hydrocarbons and combustion reactions to metal oxides and interfaces – demonstrating its versatility in modeling reactive processes at scales far beyond the reach of quantum methods [Van Duin et al. \(2001\)](#); [Srinivasan et al. \(2015\)](#).

1.1.4 ReaxFF Formalism and Comparison to Other Methods

ReaxFF is built upon the concept of a continuously updating bond order, which allows it to smoothly interpolate between bonded and non-bonded atomic interactions as atoms approach or separate. Unlike fixed-topology force fields, ReaxFF does not require predefined bonds – instead, bond orders are computed on-the-fly based on interatomic distances, and the potential energy is adjusted accordingly. Additionally, ReaxFF employs a charge equilibration scheme (such as the Electronegativity Equalization Method, EEM) that assigns partial charges to atoms dynamically, responding to changes in local chemistry [Goddard III et al. \(2002\)](#). This means ReaxFF can capture the polarization of the electron density in different environments, an essential feature for simulating ferroelectric behavior where ionic charges shift during polarization switching. Overall, the formalism enables chemical reactivity in MD: bonds can break and form, and atoms can change oxidation states or coordination environments during the simulation. This is a marked improvement over traditional empirical ferroelectric potentials (like the shell model), which often treat polarization via an ad hoc core-shell separation and cannot handle changes in bonding or chemistry.

The strengths of ReaxFF relative to other modeling approaches can be summarized as follows. Compared to ab initio methods such as DFT, ReaxFF offers orders-of-magnitude lower computational cost, allowing simulations of much larger systems (tens of thousands of atoms) over longer timescales (nanoseconds to beyond) . Crucially, phenomena like ferroelectric hysteresis loops, temperature-dependent phase transitions, and domain wall motions become tractable in ReaxFF-based MD, whereas these require prohibitively large supercells or long simulation times that are beyond DFT’s reach . While DFT is often regarded as the gold standard for accuracy and transferability in studying ferroelectric materials’ electronic structure , its scale limitations mean that it cannot easily explore the dynamical aspects of polarization switching or the collective behavior of defects and domains. ReaxFF, by being parametrized against DFT data, attempts to retain quantum-level accuracy for energies and forces in a computationally efficient classical form.

Compared to conventional empirical potentials, ReaxFF provides far greater flexibility. Standard interatomic potentials for perovskite oxides (e.g. BaTiO_3) might require fixed formal charges (Ti^{4+} , O^{2-} , etc.) and predefined interaction parameters that work only for one phase or composition [Akbarian et al. \(2019\)](#). In contrast, ReaxFF’s charge equilibration allows simulation of mixed-valence states and charge transfer processes. This is particularly important for ferroelectrics, where the presence of defects (such as oxygen vacancies) or surfaces can lead to local charge imbalances. ReaxFF natively handles such situations by redistributing charges in response to the local environment, whereas a fixed-charge potential cannot. Moreover, ReaxFF has been designed to be transferable across different bonding environments: the same force field can often describe multiple phases of a material or even interactions at heterogeneous interfaces . For example, a single ReaxFF parameter set can potentially model a ferroelectric oxide and its surface or interface with electrodes, without re-fitting for each local configuration. This extendability to multi material interfaces is a noted advantage of ReaxFF [Sepehrinezhad et al. \(2024\)](#). Additionally, the ability to handle bond breaking means that processes like defect formation, diffusion, and chemical reactions (e.g. surface redox events or decomposition) can be simulated in tandem with mechanical or electrical loading. Traditional ferroelectric potentials, by contrast, would have to treat such events by introducing explicit new species or switching potential models mid-simulation, which is cumbersome or infeasible.

Another emerging alternative for atomistic simulations is the use of machine-learned interatomic potentials (MLIPs) [Batzner et al. \(2022\)](#); [Batatia et al. \(2022\)](#); [Liu and Mo \(2024\)](#); [Klawohn et al. \(2023\)](#). These potentials (based on frameworks like neural networks or Gaussian processes) are trained on extensive datasets of DFT calculations to reproduce the potential energy surface of materials with high fidelity. Indeed, recent advances have shown that MLIPs can achieve near DFT-level accuracy for complex materials, including ferroelectrics, given sufficient training data . However, MLIPs also face challenges: the training process is computationally intensive and requires a carefully curated database that spans all relevant configurations . Moreover, ML models can struggle with extrapolation, meaning unusual defect configurations or chemistries not seen in training might be handled poorly. In contrast, ReaxFF, while not as systematically improvable as MLIPs, encodes

physical chemistry insights in its functional form and typically requires a more modest training set (often using key DFT data for structures and reaction pathways). ReaxFF parameters can be iteratively optimized to reproduce quantum-mechanical results for a given material, as was done in the studies discussed below, and once fitted, the force field can be used widely without retraining.

In summary, ReaxFF occupies a useful middle ground: it is more chemically realistic than simple empirical potentials (due to its reactive and polarizable nature) and more scalable than first-principles methods, all while providing a degree of accuracy that has been validated against quantum calculations and experiments in many cases.

In the remaining chapters of this thesis, we will combine large-scale MD simulations using ReaxFF of heterogeneous ferroelectrics – such as oxygen-deficient BaTiO_3 and chemically-doped wurtzite like ZnO ferroelectrics – with machine-learning based data-analytics to gain unparalleled insights into the role of defects and dopants on ferroelectric switching dynamics, pathways and timescales. **Chapter-2** will detail the simulations and results for BaTiO_3 and will also introduce the graph-based neural network approach we have developed for obtaining these insights for perovskite oxides. **Chapter-3** will detail the simulations and results for field induced switching in wurtzite type doped ZnO with extensions of the graph representation of crystal structures to any ferroelectric material, such as wurtzite. **Chapter-4** will finally provide future outlook of how our approaches can be extended to go from atoms-to-devices for ferroelectric memristors, and also applied to other out-of-equilibrium processes such as material synthesis.

Chapter 2

A Graph Dynamical Neural Network Approach for Decoding Dynamical States in Ferroelectrics

A version of this chapter was originally submitted to Carbon Trends by Abhijeet Dhakane, Dr. Tian Xie, Dr. Dundar Yilmaz, Dr. Adri van Duin, Dr. Bobby G. Sumpter and Dr. P. Ganesh:

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Abstract

Ferroelectric materials such as BaTiO_3 show tremendous potential for emerging advances in memory devices, particular neuromorphic type devices. High density of memory can be obtained by stabilizing polar domain walls at the nanoscale, regions of discontinuity between the well-defined polarization order parameter, but little is known about what controls their structure and dynamics in real nanoscale materials. Indeed, chiral polar domain walls have been observed in heterogeneous ferroelectrics, such as oxygen-deficient BaTiO_3 , but very little is known about how such polar-domains walls interact with defects. Indeed, a critical understanding of how dynamics of domain-walls depend on point-defects is crucial to create engineered ferroelectric memory devices. We perform large-scale simulations of nanoscale domain-wall dynamics in pristine and defective BaTiO_3 using reactive force-field developed by us earlier (PHYS. CHEM. CHEM. PHYS., 2019, 21, 18240-18249), and capture their dynamical dependence on point defects using a graph dynamical neural-network approach, which we adapted to interrogate solids with well-defined order-parameters, and implemented using Pytorch based libraries. Our machine learning (ML) approach goes beyond the traditional post-processing methods to capture both spatial and temporal heterogeneities of large-scale molecular dynamics simulations of complex defective ferroelectric oxide materials. We crucially find that isolated oxygen vacancies introduce very localized spatial regions (~ 1 -2 unit-cell in length) that show slow dipole relaxation due to formation of defect-dipoles, and that these defect-dipoles in turn slow the intrinsic dynamics of domain walls. Further, the roughness of domain walls, also influenced by vacancies, introduce dynamic heterogeneity along the domain-wall [Zhang et al. \(2020\)](#). As such we find a novel mechanism by

which quenched disorder due to defects introduce dynamic heterogeneity thereby influencing response to external fields (particularly time varying fields) in a ferroelectric. Our study also emphasizes the need for creating digital twins of dynamical quantities to achieve autonomous *in operando* control of nanoscale switching.

2.1 Introduction

The recent surge in applications related to AI and big data analytics have pushed the limits of the traditional Si-based memory devices and demands more reliable non-volatile memory devices [Chanthbouala et al. \(2012b\)](#); [Chen \(2016\)](#); [Sharma et al. \(2017\)](#). Additionally, there is an increasing need to co-locate memory and processing units to minimize the von Neumann bottleneck for information transfer [Sangwan and Hersam \(2020\)](#); [Sung et al. \(2018\)](#); [Chen et al. \(2022\)](#). Such computing paradigms that mimic the functioning of the human brain is now called "neuromorphic computing" [Sangwan and Hersam \(2020\)](#); [Sung et al. \(2018\)](#). Non-volatile switching such as those in ferroelectric (FE) materials are front runners for building appropriate neuromorphic devices. A major challenge lies in speeding up ferroelectric switching at low power, particularly when the devices are made smaller than 150 nm, in existing microelectronic devices [Jiang et al. \(2022\)](#). The challenge in miniaturizing ferroelectric based neuromorphic materials lies in reducing leakage current, while achieving non-linear response to external stimuli when the device is made to switch. Switching is achieved because the spontaneous electric polarization which characterizes the memory state of the material system can be modified by an applied external electric-field. Typically, domains with well defined polarization form, with boundaries between domains, that are called domain walls. So, under an applied voltage the domain wall moves, changing the total polarization state, and hence giving rise to a hysteretic response [Dasgupta et al. \(2018\)](#); [Saremi et al. \(2018\)](#); [Jo et al. \(2009\)](#); [Chanthbouala et al. \(2012a\)](#).

Real materials are defective. Defects such as oxygen-vacancies are known to cause local defect dipoles. While initially it was determined that domain-wall motion is not affected by the presence of point-defects, recent studies have shown that at the nanoscale, physical heterogeneities, such as point- or extended-defects can affect domain wall motion and hence nucleation of domains, thereby leading to phenomena such as wake-up [Pešić et al. \(2016\)](#); [Kashir et al. \(2021\)](#); [Kelley et al. \(2022\)](#); [Lee et al. \(2021\)](#). Point defects (and their clusters) have also been shown to form topological polar domains or relaxor-like glassy dynamic heterogeneous behavior [Kircher et al. \(1998\)](#). To engineer ferroelectric devices with well defined memory states, and high non-linear switching between those states, it is imperative

to understand how the dynamics of domain-walls depend on such atomic heterogeneities, such as point-defects, yet this understanding is lacking.

While dynamic measurements of ferroelectrics or other neuromorphic materials during switching is now becoming possible [Prosandeev et al. \(2021\)](#); [Kelley et al. \(2022\)](#); [Du et al. \(2019\)](#); [Rapin et al. \(2021\)](#), the timescales that can be probed experimentally still remains too large. THz spectroscopy is a viable mode to explore *ps* relaxation processes, and find a rich array of metastable topological structures under intense pulses [Prosandeev et al. \(2021\)](#), but do not offer much control over switching. While atoms vibrate in *ps* timescales, motion of domain walls that lead to switching of polarization occur over *ns* timescales. As such to understand nanoscale switching, and eventually control it in a deterministic manner, we need to create digital twins of nanoscale dynamics, interlinked between atomistic and phase-field simulations. This interlinking will at the least require automated coarse-graining approaches of the atomistic simulations that naturally lead to identifying dynamically disparate regions. While modeling and simulation techniques do provide a natural route to explore the nanoscale *ps* to *ns* dynamics, treatment of defects, their interaction with local dipole-moment and even their diffusion, will require a reactive force-field that can describe charge-reorganization due to missing atoms. Conventional force-fields such as shell model, bond-valance model and effective Hamiltonian model fail to capture both ferroelectricity and their coupling to defects, particularly charged-defects [Nishimatsu et al. \(2008\)](#); [Tinte et al. \(1999\)](#); [Khatib et al. \(1989\)](#); [Wang et al. \(2016\)](#); [Qi et al. \(2016\)](#); [Elangovan et al. \(2021\)](#). In this light, we have recently developed a reactive force-field approach that is able to describe switching of ferroelectrics under external stimuli, even in the presence of different types of defects [Akbarian et al. \(2019\)](#). In the present work we used large scale molecular dynamics (MD) simulations ($\sim 80,000$ atoms) with reactive force-field, to understand the nature and dynamics of domain-walls and how they are influenced by defects for the classic BaTiO_3 (BTO) ferroelectric. Our approach is a step towards constructing interlinked multi-scale simulation capabilities to create digital twins of switching in heterogeneous nanoscale materials.

As a first step, we want to understand how different the equilibrium dynamics of bulk ferroelectric regions is compared to that of domain-walls. Secondly, we would like to understand if there is dynamic heterogeneity in the presence of point-defects, and how this

might impact the stability and control of domain wall motion. Knowledge of the relaxation dynamics of the different regions of a defective ferroelectric would further allow us to control FE switching using time-dependent fields.

We determine regions of barium titanate oxide (BTO) with similar dynamics by adapting the recently introduced neural-network approach called Graph Dynamical Network [Xie et al. \(2019\)](#). Our adaptation extends this method, formerly used to study alloys and ion-conducting materials, to identify phase-transitions in ferroelectrics. In particular, the local polarization is used as a feature vector, and the global dynamics is encoded in a Koopman Matrix using graph-dynamical neural networks to construct Markov state models (MSM), projected onto polarization states which enables showing differing collective dynamics.

We find that large ferroelectric regions that are related to each other by discrete symmetries (e.g. up and down regions in a tetragonal phase) show similar dynamics. We also find that domain-walls between such symmetry-related ferroelectric domains show dynamics that are an order-of-magnitude faster than the bulk dynamics. Interestingly, the regions of the domain-wall that have high curvature (or other structural heterogeneities) seem to show dynamics slower by an order-of-magnitude from the average domain-wall relaxation, indicative of dynamic heterogeneity within the domain-wall. These findings open the door for controlling ferroelectric switching by coupling them to ac fields with specific frequencies that resonantly activate specific parts of the domain wall. It also sets the stage for engineering nano- and micro-scale structures to (specifically) precisely control switching dynamics in ferroelectrics, for low-power and high-memory neuromorphic device applications. Further, our approach also effectively allows us to identify collective variables that can coarse-grain atomic dynamics to construct efficient mesoscale dynamical models [Liu et al. \(2019\)](#); [Gu et al. \(2022\)](#); [Yang et al. \(2017\)](#).

The methods section below details the combined reactive force-field MD and graph-dynamical neural-network approach that we have taken to construct the Koopman matrix, as well as our new scalable implementation of the approach using the PyTorch based libraries [Paszke et al. \(2019\)](#); [Fey and Lenssen \(2019\)](#); [Falcon and The PyTorch Lightning team \(2019\)](#) which scales to thousands of GPU-nodes. Results and discussions sections detail the findings of applying the neural-network method to analyse the dynamics and their interpretation. We

end with the conclusion section summarizing the main conclusion from this study and its implications for controlling FE switching in neuromorphic devices.

2.2 Methods

2.2.1 MD simulation

We perform large scale reactive molecular dynamics (MD) simulations using the LAMMPS code [Plimpton \(1995\)](#) with ReaxFF force-field. ReaxFF is a bond-order force-field that can be used to model a variety of complex systems such as polymer, metal oxides/hydrides/carbide systems [Li et al. \(2021\)](#); [Raju et al. \(2015\)](#); [Ganesh et al. \(2011\)](#). We model supercells of BTO with 77600 atoms in a slab geometry, with dimensions of 161.6 Å and 80.8 Å in the periodic x- and y-directions. The slab thickness along the z-direction is 120.8 Å including a 12 Å vacuum at top and bottom of the supercell to mimic the free-standing nature of the thin film. The initial state of the system was constructed with dipoles aligned up/down in the upper/lower halves of the slab. MD simulations were performed with a timestep of 0.25 *fs*, and charges were self-consistently calculated using the charge-equilibration method [Rappe and Goddard III \(1991\)](#).

The production level equilibrium runs were preceded by initially ramping the system up to 120K at ambient pressure over 37.5 *ps* using a Berendsen barostat and thermostat and additionally performing an NPT simulation at 120K for 25 *ps*, where the equilibrium fluctuations were seen in energy, temperature and structural parameters. Production level runs were performed in an NVT ensemble using a Berendsen thermostat at 120K for an additional 694 *ps*. Atomic positions along with atomic charges were recorded every 1 *fs*. All graph-neural /adremnetworks network described below were trained on this data to eventually construct a Markov state model.

The local polarization were calculated using the positions and charges at each timestep using the following relation [Akbarian et al. \(2019\)](#).

$$P_u = \frac{1}{V_u} \left(Z_{Ti}^* \cdot r_{Ti,i}(t) + \frac{1}{8} \cdot Z_{Ba}^* \cdot \sum_{i=1}^8 r_{Ba,i}(t) + \frac{1}{2} \cdot Z_O^* \cdot \sum_{i=1}^6 r_{O,i}(t) \right) \quad (2.1)$$

where P_u is a polarization of the unit cell. V_u is the volume of the unit cell, Z_{Ba}^* , Z_{Ti}^* , Z_O^* are the charges and $r_{Ba,i}(t)$, $r_{Ti}(t)$, $r_{O,i}(t)$ are the positions of the Ba, Ti and O at each timestep.

2.2.2 Markov state models

Molecular dynamic trajectories are the solutions of Newton’s equations evolved over time in a potential energy function. These are integrable equations written as a discrete timestep process as shown in Eq. 3.2 .

$$y_{t+\tau} = F(y_t) \quad (2.2)$$

F encodes the exact dynamics, which may have both linear and non-linear components. According to Koopman’s theorem, this can be exactly described by a Markovian process i.e., where the (configuration) state of the system at time $t + \tau$ is only dependent on the current state, with t being the time step, and knowledge of the lag-time τ . Such Markov state models (MSMs) are justified for any physical processes, either deterministic or stochastic, since the dynamics of this physical system is intrinsically Markovian. Lack of any memory terms also makes it easier to analyze and interpret these models. Existence of MSMs allows us to linearize Newton’s equations for deterministic systems as

$$\chi(y_{t+\tau}) \approx K^T \chi(y_t) \quad (2.3)$$

χ is a transformation that needs to be discovered, which linearizes this equation, with K being the Koopman matrix. The equation is exact for infinite time-series. The goal is to determine χ and τ where this equation holds true for a given MD trajectory, and also thereby determine the Koopman matrix. The Koopman matrix contains the transition probabilities to go from one Markov state χ to another, and hence also their relaxation-times. Since these states themselves are not steady states, they are hence referred to as *dynamical* states. We apply the variational approach to Markov processes (VAMP) [Mardt et al. \(2018\)](#) scheme to build the MSMs, and represent our system using graph neural network. The approach is detailed below.

2.2.3 Graph Dynamical Network

A scheme to featurize atomic positions and chemical identities using crystal graph convolutional neural-network (CGCNN) and determine the embeddings of χ as well as the transition probabilities entering K using the VAMP scheme was recently introduced by Tian Xie *et al* Xie et al. (2019). This so-called Graph dynamical networks (GDyNets) was successfully employed to coarse-grain glassy and ionic-conducting materials for determining both the representations as well as the relaxation-time of the states that transition into one another. However, the existing framework is not immediately able to capture Landau type phase-transitions characterized by an order-parameter that breaks certain symmetries, necessary to describe ferroelectric phase-transitions. Further, the existing implementation of the neural-network approach was not applicable to millions of atoms that are necessary to model domain-walls because it was limited by scalability to multi-node-core. In this work we extended the existing GDyNet framework Xie et al. (2019) to allow featurizing polarization, and perform implementation using PyTorch based libraries allowing scalable neural-network implementation for constructing MSMs on hybrid CPU/GPU architectures.

Our workflow and network architecture is shown in figure 2.1. For each atomic snapshot generated along an MD trajectory, its graph representation has nodes at atoms. In addition to representing the positions and identities of chemical species from each snapshot of our MD trajectory in a graph neural-network (GNN), we also add the local dipole moment, a 3D vector P_x, P_y, P_z , for individual unit cells, centered on the Ti atoms, as an additional node feature in the neural network. This way, polarization dynamics can be directly learned when constructing the MSM via the VAMP-scheme. Distances between neighboring atoms form the edges of the graphs. So, the graph $G = (v_{(i,j)}, r_{ij}, P_i)$, where, v_i is the center node (source) and v_j (target) are the M nearest neighbors. r_{ij} is the distance between v_i, v_j , with these distances expanded using a Gaussian kernel as shown in the equation 2.4. In this work the graph was made by connecting 4 nearest neighbors within a 4 Å radius. Further, no symmetrization was performed for the graph representation – so for example UP and DOWN polarization in the tetragonal phases will be treated as separate entities. This is important to

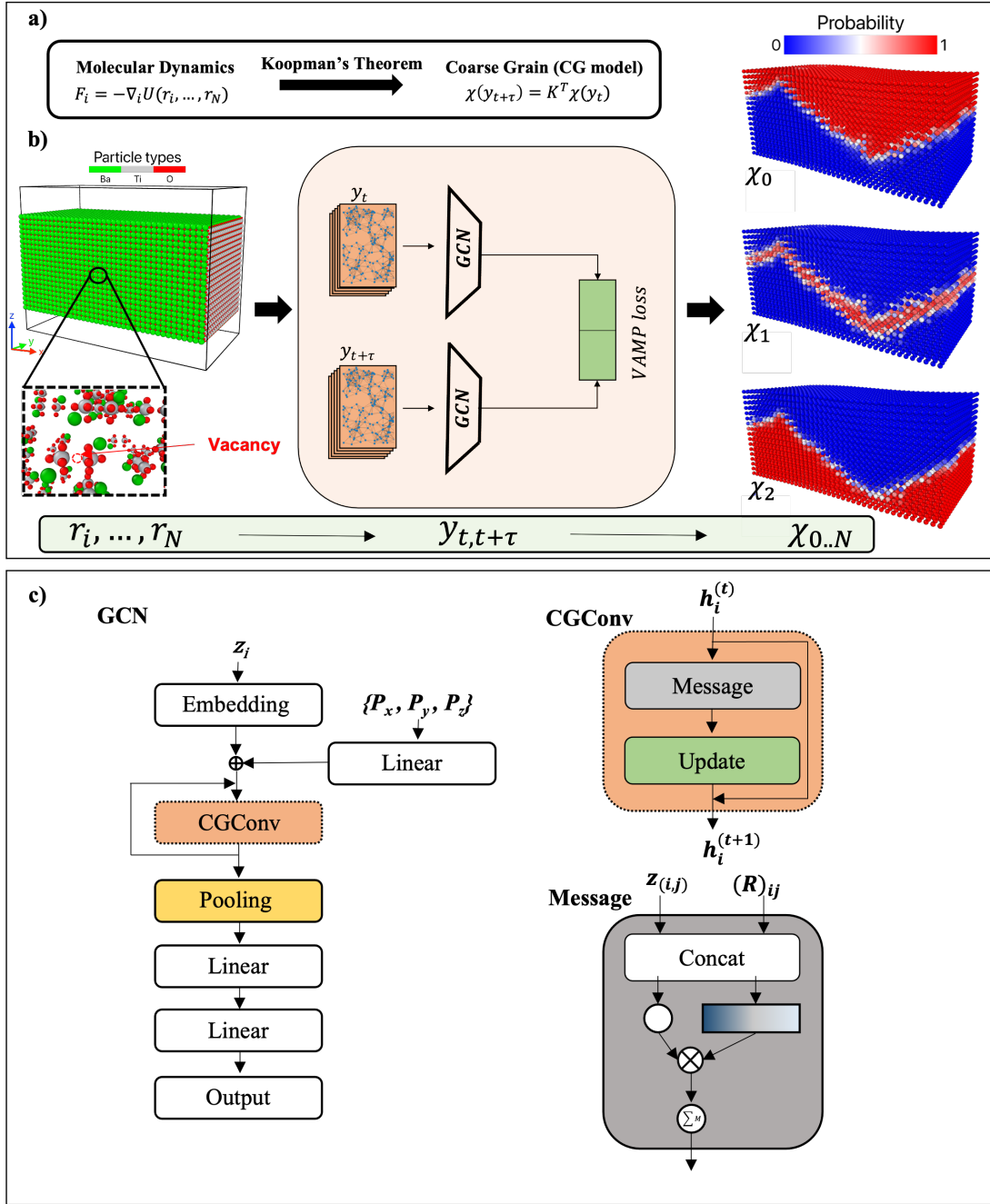


Figure 2.1: Briefly describes the GDyNet-ferro workflow: (a) shows the mapping of Newton’s equation into a coarse grained Markov State Model (MSM) via the Koopman’s theorem; (b) shows the various steps schematically – left panel shows a molecular dynamic snapshot, middle panel shows the time-lagged autoencoder where we input the graph representations of the MD trajectory and use Graph Convolutional Networks (GCNs) along with the VAMP [Mardt et al. \(2018\)](#) loss to obtain the dynamic representations of the states as shown in the right panel; (c) shows the architecture of Graph convolutional network (GCN) used in the time-lagged autoencoder.

study how these UP and DOWN domains are relatively impacted in the presence of domain walls and/or defects.

$$\mathbf{R}_{(ij)} = \exp \left(- \left(r_{(ij)} - \mu_t \right)^2 / \sigma^2 \right) \quad (2.4)$$

In our PyTorch based implementation, we retained most of the architecture as implemented in the original implementation [Xie et al. \(2019\)](#). We used the PyTorch Geometric library to implement the graph convolutional neural network for scalability and speed-up. Our modified GDyNet implementation here onward called *GDyNet – ferro*, consists of an extra layer as shown in the architecture diagram in Fig. 2.1 (c), i.e., the linear layer with no activation which takes the 3D local polarization vector. This layer is then added to the embedding layer formed originally by chemical identities of the species. The embedding layer consists of random weights initiated into a fixed length of vector for each atom type $z_{(i)}$. The final output is derived by passing the sum of the embedding and polarization layer $h_i^{(t)}$ into the CGconv layer. The CGConv layer is explained in [Xie et al. \(2019\)](#), includes the message passing, attention, and average pooling operations. The indices with source and target $v_{(i,j)}$, and their distance expanded with a Gaussian Kernel R_{ij} along with the embedding from previous layer $h_i^{(t)}$ are fed into the concatenate (Concat) layer. The concatenate layer expands (stacks into a single vector) the information gathered from these three inputs into a single vector having embedding of the source and target along with the distance vector as shown below.

$$z_{(ij)}^{(t)} \rightarrow h_i^{(t)}[v_i] \bigoplus h_i^{(t)}[v_j] \bigoplus R_{ij} \quad (2.5)$$

Attention and average pooling are used with the following sets of equations 2.6 and 2.7, where *relu* is a non-linear activation function.

$$\alpha_{ij} = \exp \left(z_{(ij)}^{(t)} \right) / \sum_j \exp \left(z_{(ij)}^{(t)} \right) \quad (2.6)$$

$$h_i^{(t+1)}[v_i] = h_i^{(t)}[v_i] + \sum_j \alpha_{ij} \cdot \text{relu} \left[h_i^{(t)}[v_i] \bigoplus h_i^{(t)}[v_j] \bigoplus R_{ij} \right] \quad (2.7)$$

The concatenate layer is used to compute the attention coefficient α_{ij} , and the fixed length vector with a similar length of *embedding* vector defined initially. The attention coefficient and fixed length vector were then multiplied and averaged, by performing these operations source embeddings learn the relations in the local proximities by reweighting the strength i.e., attention of the M neighbors (target) around the source node.

By performing the CGConv operation K times, source atom embedding $h_i^{(t)}[v_i]$ learn the surrounding information of K^{th} neighbors. Atom embedding with updated information $h_i^{(t+1)}$ at the end of CGConv, are selectively pooled for the atom indices of interest i.e., Ti-atoms in our case. This subset of $h_i^{(t+1)}$ are passed through a shared two-layer fully connected network. Using the softmax function in the final linear layer, a probability is extracted into a pre-defined matrix vector.

A graph from molecular trajectory constructed by the above approach is fed into two parallel networks, with individual snapshots going into these networks differing by a lag time τ . The output vector from each network is optimized by maximizing the VAMP-2 score and minimizing the VAMP loss [Mardt et al. \(2018\)](#); [Xie et al. \(2019\)](#), to evaluate the consistency between the two-parallel networks at lag time τ . This is the VAMP-scheme to constructing the MSM.

$$\text{Loss} = -VAMP(v'_{([l],t)}, v'_{([l],t+\tau)}) \quad (2.8)$$

For a given τ the mapping χ and corresponding Koopman matrix K were obtained. By analyzing the relaxation time-scale as a function of lag time τ , a τ_{msm} was chosen such that the Koopman matrix captures dynamics slower than this value [Mardt et al. \(2018\)](#); [Xie et al. \(2019\)](#). To see the validity of the mapping for our choice of τ_{msm} , the Chapman-Kolmogorov (CK) test was performed as shown below in equation 2.9.

$$K(n\tau) = K^{n(\tau)}, n = 1, 2, \dots \quad (2.9)$$

To summarize the methods, the above approach allows us to construct an MSM with a neural-network representation of the coarse-grained Markovian states that transition between each other over the course of the MD simulation with a characteristic relaxation-time larger

than τ (a hyperparameter) and transition probabilities that determine the relaxation-times given by the K matrix. The regions (or cluster or atoms) comprising these states hence can change their identity over time, thereby capturing the underlying dynamics.

To discover the regions with similar dynamics, and their relaxation times using this approach, we performed equilibrium MD for pristine and defective tetragonal BTO system at 120K in a slab geometry. Data was written at a rate of $\Delta T = 25 \text{ fs}$ for $\Delta T_{total} \sim 665 \text{ ps}$. We used the first 302.25 *ps* data for training the network and the next 60.45 *ps* data for validation. Testing was performed on the remaining 302.25 *ps* data.

2.2.4 K-Means Clustering

While dynamical states, as mentioned above, are clusters of atoms that reproduce the underlying dynamics, clusters of atoms on static snapshots can also be computed, where clustering is performed based on direction of polarization in a given snapshot. Such clusters can be obtained by unsupervised algorithms on static snapshots such as K-means clustering. K-means can be used to group or partition data into clusters based on similarities between data points on a static snapshot, which can again be represented by a graph with node features containing positions, identity of atoms and the local polarization. K-means clustering also known as Lloyd’s algorithm [Lloyd \(1982\)](#), partitions the data into a predefined number of clusters, where each cluster is represented by its centroid (the mean of all the points in the cluster). The algorithm iteratively assigns each data point to the closest centroid, and then recalculates the centroids based on the points that are assigned to them. This process is repeated until the centroids stop moving or the assignments of points to clusters stop changing. K-means clustering has been actively used to identify spatial parts of the conformations in protein dynamics [Xu et al. \(2023\)](#); [Bijral et al. \(2022\)](#). Since the spatial parts of the ferroelectric materials such as domains are well defined we applied the K-means algorithm on a single static snapshot of the local polarization, to identify the spatial features of the ferroelectric material. Our goal is to identify how the Markovian states that describe the underlying dynamics differ from clusters constructed from static snapshots of polarization, as one might obtain from a transmission electron microscopy (TEM) experiment.

2.3 Results and Discussion

2.3.1 Equilibrium dynamics of a 180-degree ferroelectric domain wall in pristine tetragonal BTO

We begin to study the dynamics of an equilibrated pristine BTO system in a slab geometry (see Methods) from a 665 *ps* MD trajectory. Given the tetragonal phase of BTO, it mainly has a sizable z-component (P_z). The P_z component of the polarization of one representative snapshot is shown in figure 2.2, with the up(red)/down(blue) domains clearly seen in the figure, and a domain wall with significant roughness. The planar averaged line-profiles of the polarization are also plotted, which shows that the domain wall to be Ising-Neel type, albeit with a large roughness associated with it. The shape of the domain wall resembles that of a sawtooth-like pattern, seen in earlier effective Hamiltonian based Monte Carlo simulations as well as experiments in PbTiO_3 and BiFeO_3 [Zhang et al. \(2020\)](#). The line profile also indicates that it takes ~ 7 -8 u.c.'s from the center of the DW to reach bulk-like polarization. The domain wall is a larger perturbation to the system than the ferroelectric surface itself, where effects of screening lead to dipole rearrangements, but in a significantly narrow range of distance. In the remainder of the manuscript we ignore the surface effects and focus on the dynamics of the bulk vs domain-wall, with and without defects.

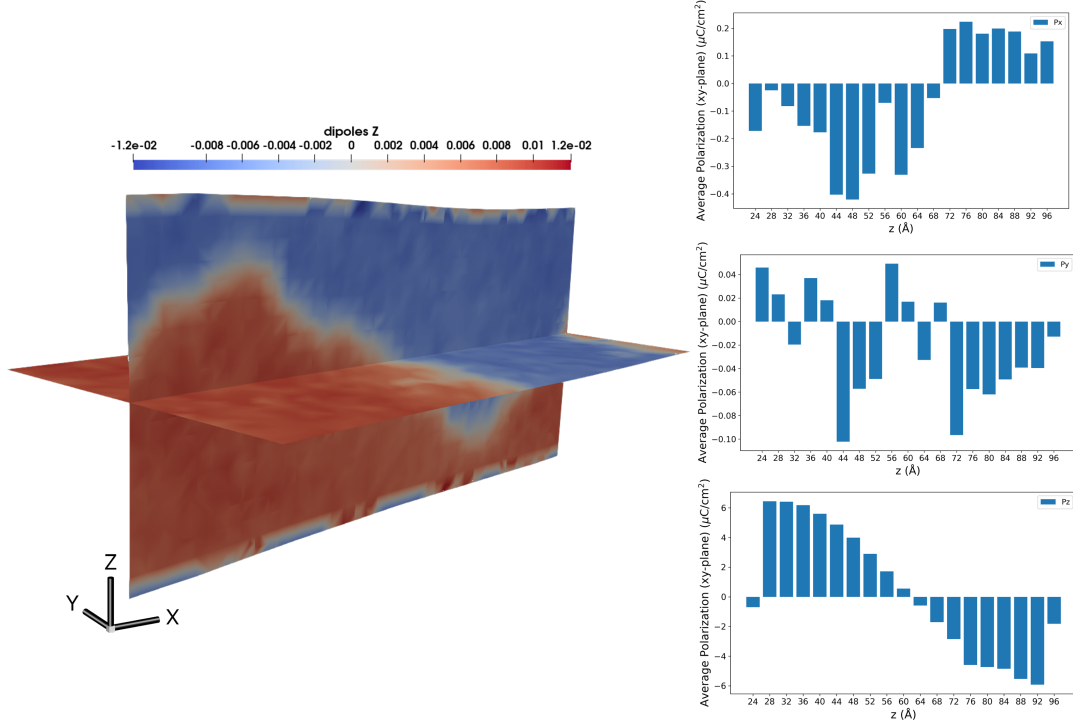


Figure 2.2: For our pristine BTO slab simulation, (left panel) shows a plot of the polarization component P_z along two orthogonal planes in our simulation box and (right panel) shows the line profile of individual polarization components averaged along the z -direction (x-y plane).

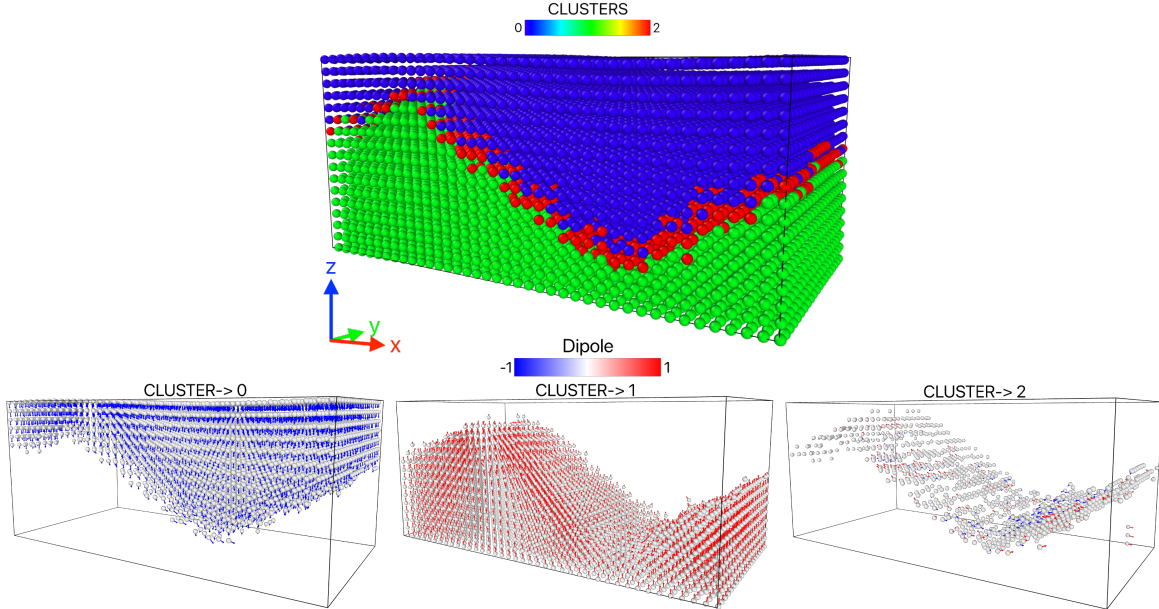


Figure 2.3: K-Means clustering analysis on a single snapshot of local polarization of the pristine slab with three clusters (i.e. $K=3$), along with individual representations of these polarization clusters.

By applying K-Means clustering algorithm we were able to identify the spatial feature of the ferroelectric material. Since from figure 2.2, it is inferred that there will be three distinct features existing in the pristine slab, domain up/down and domain wall. Setting hyperparameters for n cluster to be 3, K-Means exactly partitioned three clusters with distinct labels as shown in figure 2.3. For more clarity, the polarization of individually extracted clusters are plotted separately in figure 2.3. Note that the domain wall has components of polarization in all directions, consistent with being an Ising-Neel type domain wall.

To see how the domain-wall dynamics compares with that of the bulk, we apply the *GDyNet – ferro* framework to the same MD trajectory. We expect at least three different dynamical regions or states – one each corresponding to the up/down domains, and one at the domain wall. Indeed, our three state *GDyNet – ferro* model is able to distinguish these three main features of the BTO domain wall slab as shown in figure 2.4 (a). The relaxation time remain above the chosen lag time, up to 300 *ps*, and is flat beyond lag time of 150 *ps*, suggesting an average Markovian dynamics as shown in figure 2.4 (e). Using $\tau_{msm} = 150$ *ps* we performed the CK test and obtain the eigenvectors of the Koopman matrix, as shown in figure 2.4 (d,c), respectively. Compared to the bulk-like up/down states, the domain wall state shows faster equilibrium fluctuations with a non-zero transition probability to the up/down domains. Eigenvector decomposition at particular lag time, provides information about the dynamic relevance of the individual state with other states i.e. transition probability with other states. The transition primarily occurs reversibly between high-low eigenvector states. The relaxation times of these states calculated from the eigenvalues of the Koopman matrix at given τ_{msm} , are indicated in figure 2.4 (c). We find that the domain wall has a relaxation time ~ 400 *ps*. This corresponds to a frequency of ~ 2.5 *GHz*, suggesting that fields banded with this frequency can efficiently drive domain wall motion. Indeed, while resonance is expected in this frequency, the DW should show motion even at frequencies below and up to this Salje et al. (2013). 2.5 *GHz* falls in the low to mid-band 5G spectrum range of radio frequencies.

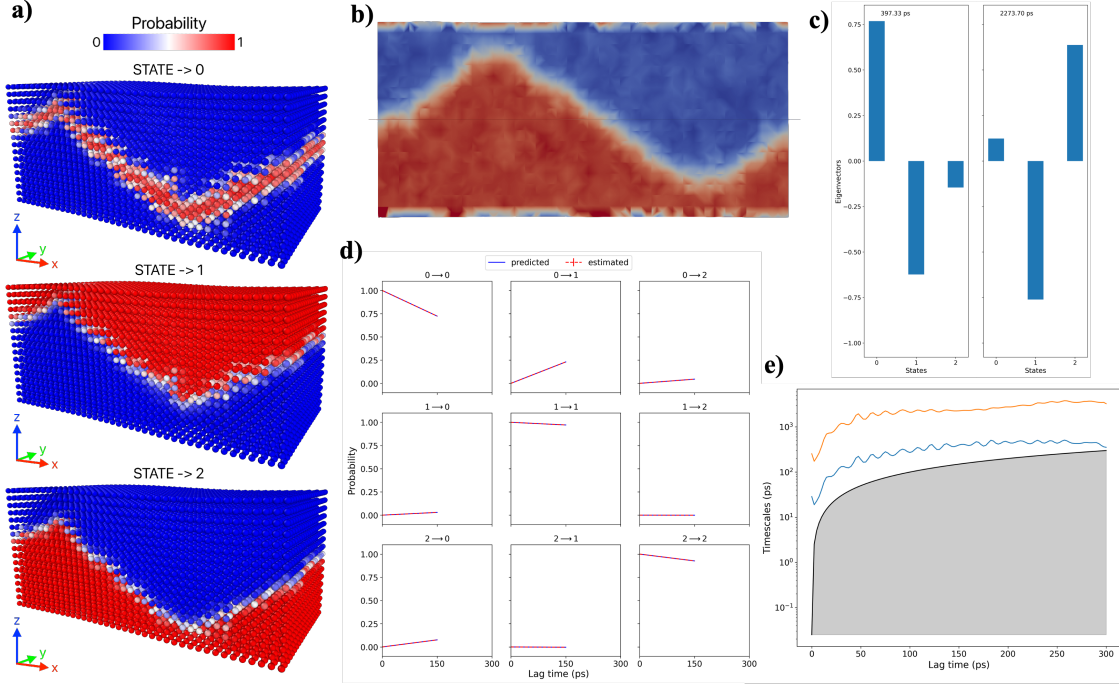


Figure 2.4: a) Representations of the three different dynamic states obtained from GDyNet-ferro projected on the titanium atoms. Red (blue) color indicate regions of high (low) probabilities for each state. b) Shows plot of the z-component of the local polarization centered on Ti atoms for a 2D slice in the x-z plane of our simulation box. c) Plot shows the eigenvectors of the Koopman matrix and relaxation times calculated from the corresponding eigenvalues. The Koopman matrix is computed for a Markov process incorporating dynamics slower than $\tau_{msm} = 150ps$. (d) Long-time dynamics estimated by the Markov process compared with the predicted dynamics from the underlying MD simulation using the CK-test. e) Relaxation timescales obtained from Koopman models as a function of lag time (black line is where relaxation time scales equals to the lag time).

2.3.2 Equilibrium dynamics of a 180-degree ferroelectric domain wall in 1% oxygen vacancy tetragonal BTO

Now that we have established the relaxation time of the domain wall for the pristine BTO, we look at effects of vacancies. So, we similarly performed equilibration simulation for the BTO system with 1% randomly distributed oxygen vacancy at 120K for 665 *ps*. The polarization of the slab is now shown in figure 2.5. Given the negligible y-component (P_y) of the polarization, we find that the domain wall is again an Ising-Neel type. Unlike the pristine slab, the defective slab does not have a symmetric polarization profile about the domain-wall (DW). It again takes ~ 7 u.c.'s to reach the bulk-like value, which is 11% diminished as compared to pristine slab. We also see that the roughness of the DW has significantly increased. This is consistent with experimental findings which show that with oxygen vacancies DW roughness is higher [Paruch et al. \(2005\)](#); [Guyonnet et al. \(2012\)](#); [Zhang et al. \(2020\)](#) . Interestingly, polarization forms around the oxygen vacancy-site – i.e., the defect-dipoles, and they seem to be opposite to the direction of the bulk-like polarization, both for the up and down domains. Formation of defect-dipoles signifies condensation of a soft-mode with different symmetry than the surrounding bulk-like polarization state. As such, we intuitively expect the defect-dipoles to show different dynamics than the remaining bulk-like region, but it is not clear how large of a region around these defect-dipoles will show different dynamics compared to the bulk, and what if any will their effect be on the domain wall dynamics.

We first tried to isolate how many static polarization clusters form using K-Means clustering, and compare with a similar analysis above made for the pristine slab. As seen in figure 2.6, we find that more than three distinct clusters exist in the defective slab. In addition to domains up/down and the domain wall region, additional clusters are seen. While it appears that these are likely regions with non-tetragonal polarization values, clustered about their value of direction, the significance is not immediately clear. Also, the domain wall is much broader with sharp curvatures in the middle of the slab which is not present in the pristine slab, again with features that have little interpretability. As such, clustering on a static snapshot, as might be obtained from static microscopy data [Schmitt et al. \(2021\)](#);

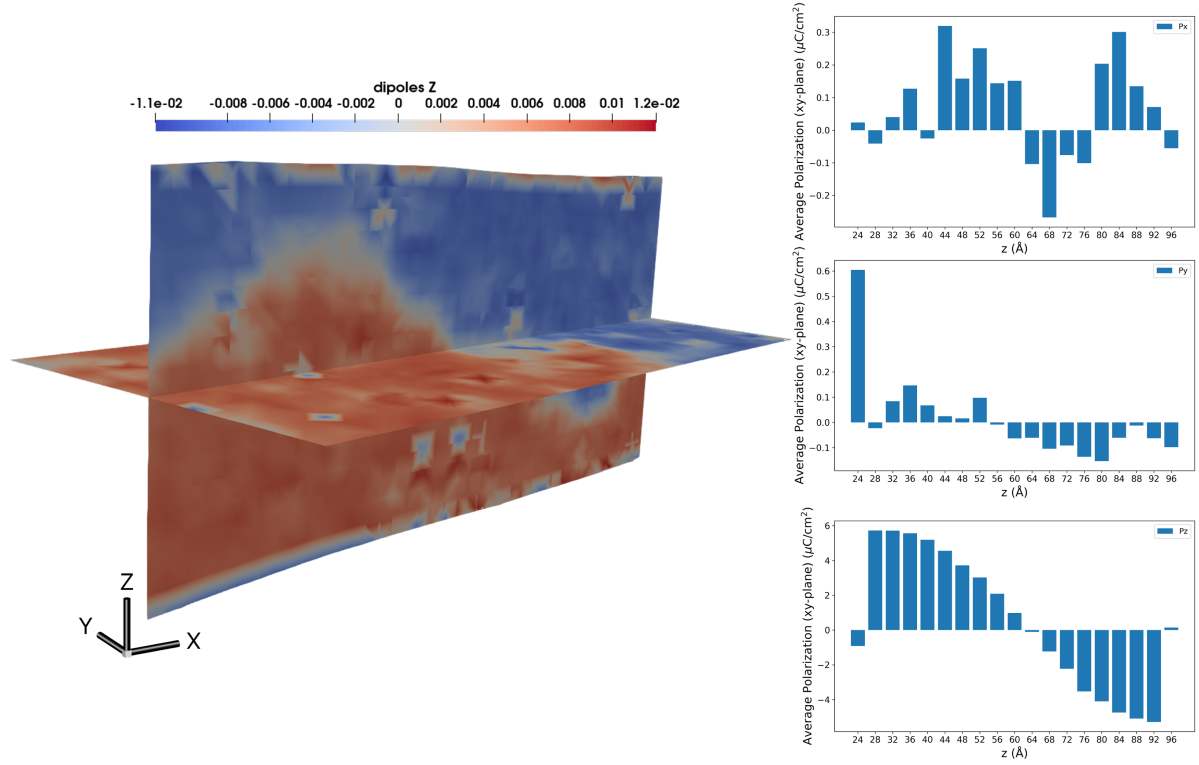


Figure 2.5: For our BTO slab simulation with 1% oxygen vacancy, (left panel) shows a plot of the polarization component P_z along two orthogonal planes in our simulation box and (right panel) shows the line profile of individual polarization components averaged along the z -direction (x-y plane).

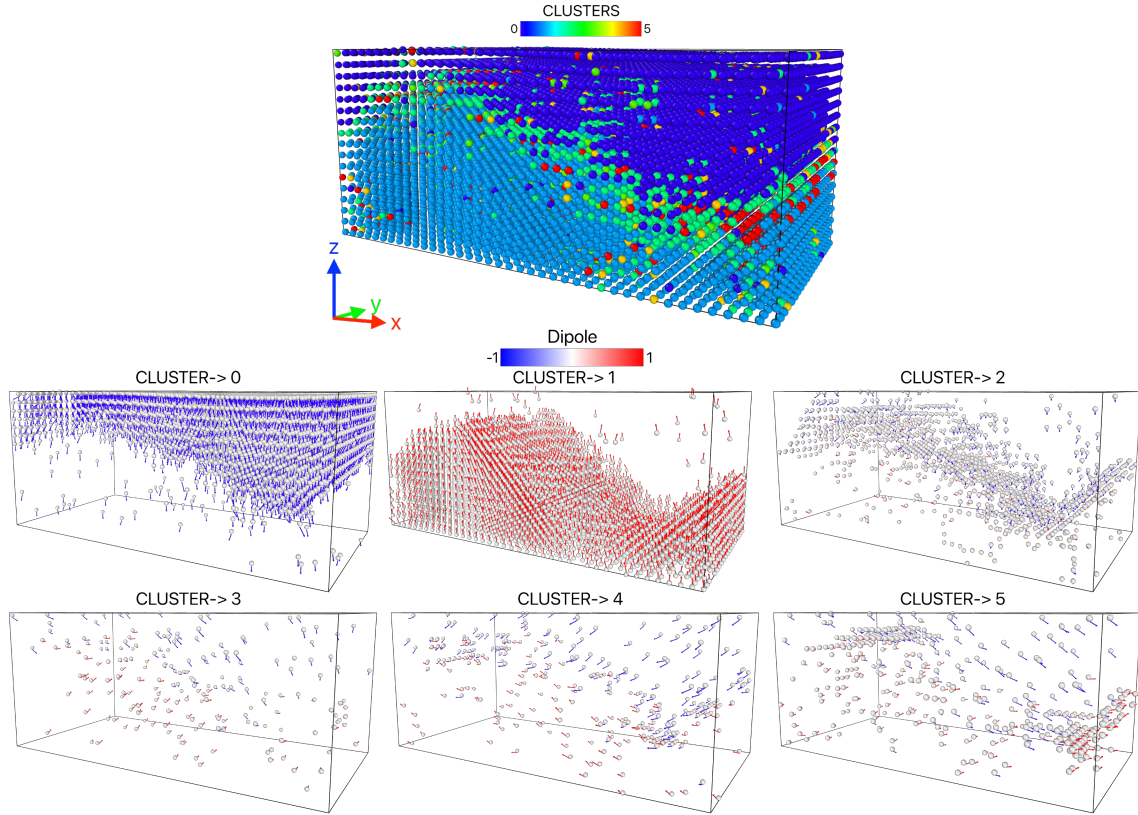


Figure 2.6: K-Means clustering analysis on a single snapshot of local polarization of the BTO slab of 1% oxygen vacancy with six clusters, along with individual representations of these polarization clusters.

Li et al. (2018) might drastically limit our understanding of how dynamical regions form in a heterogeneous ferroelectric material.

Since we have access to the full dynamics in our simulations, we can answer this question by applying our *GDyNet – ferro* approach. To identify additional dynamical states due to defects, we trained a Markov model for up to six states. As expected, *GDyNet – ferro* was able to distinguish the three main features i.e., the bulk up/down (state-5 and state-1) and the domain wall state (state-2) as shown in the figure 2.8 (a), which look similar to the pristine case, except that the domain wall is much more rougher. But in addition, this approach was also able to identify states involving oxygen defects, that show drastically different dynamics. Results from the CK-test as well as the eigenvector plots obtained from diagonalizing the Koopman matrix and corresponding relaxation times are shown in figure 2.8 (b,c). We find that the domain wall now has a larger relaxation time ~ 600 ps as compared to the pristine case (corresponding to ~ 33 % slower dynamics in the presence of defects). This corresponds to a resonant frequency of ~ 1.67 GHz, lower than that of pristine BTO domain wall. This suggests that the DW motion is slower in the defective BTO system than in the pristine. Note that structurally, defects present near the equilibrium DW position, will likely interact with this defect-free DW state. Figure 2.8 shows the polarization vector plot for the six states with different dynamics. While state-1 and state-5 correspond to the bulk-like down/up polarization, state-2 is largely the domain wall. The other three states seem to be related to defect dipoles that are distinct from each other. State-0 is composed of pairs of crisscrossing dipole moments with their z-component (P_z) pointing *along* the surrounding bulk-like polar region. State-3 and state-4 are essentially defect dipoles pointing down, but embedded in the up or down domains, respectively. Interestingly, the immediate neighboring dipoles of the defect dipole is significantly more dynamic than itself. This is consistent with the observation that all of these defect-dipole states have considerably longer relaxation times, compared to the DW state, consistent with them being a very localized distortion resulting from the condensation of a soft-mode.

Projecting these defect dipole states now on atomic indices, we can look at the exact local atomistic origin of these soft-mode states. From inspection, the three different defect dipole states identified by *GDynet – ferro* Dhakane (2025) correspond to the three symmetrically

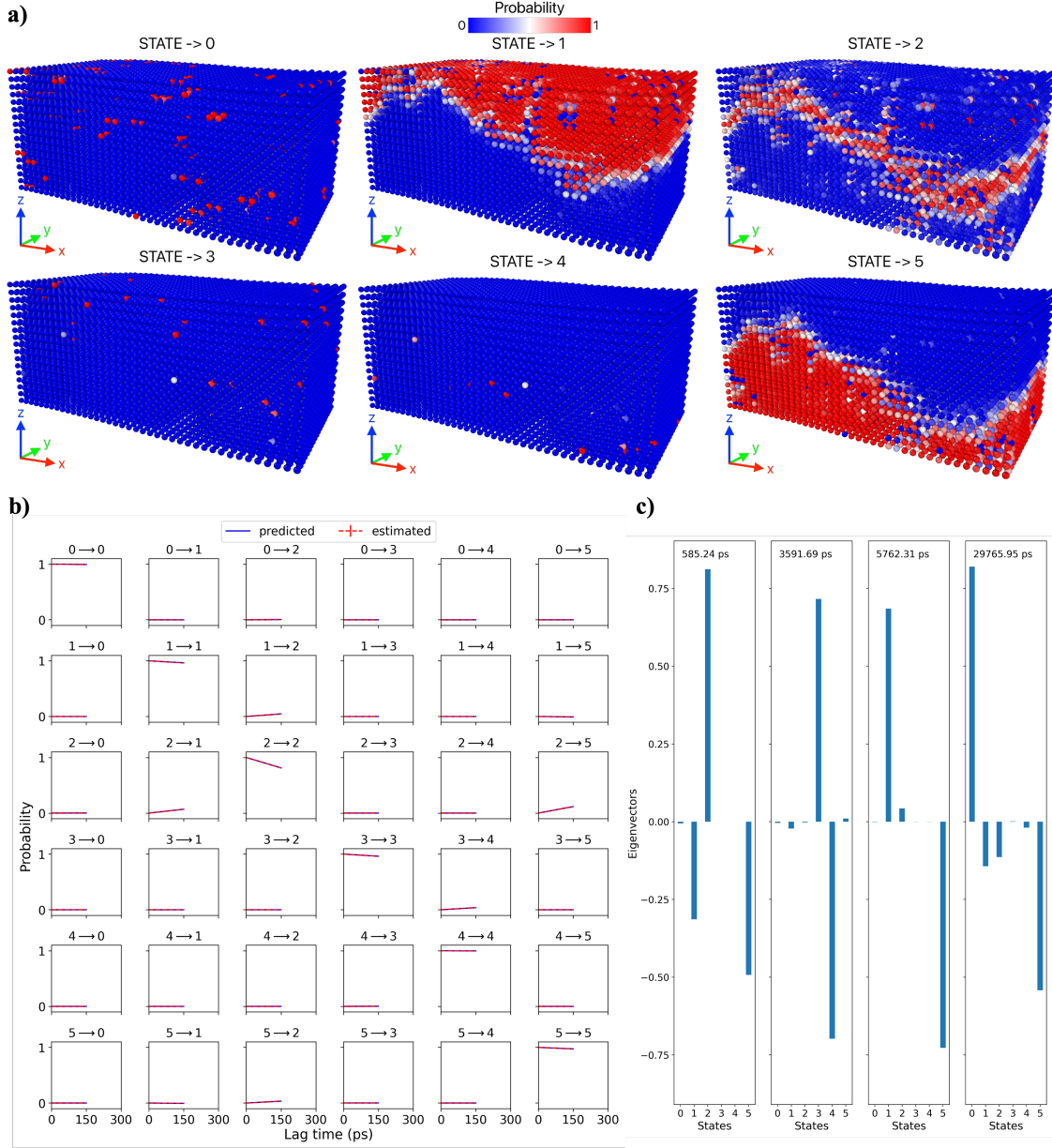


Figure 2.7: a) Representations of the six different dynamic states obtained from GDyNet-ferro projected on the titanium atoms. Red (blue) color indicate regions of high (low) probabilities for each state. (b) Long-time dynamics estimated by the Markov process compared with the predicted dynamics from the underlying MD simulation using the CK-test. (c) Plot shows the eigenvectors of the Koopman matrix and relaxation time calculated from the corresponding eigenvalues. The Koopman matrix is computed for a Markov process incorporating transitions slower than $\tau_{msm} = 150ps$. (d) Shows the state projected polarization vectors.

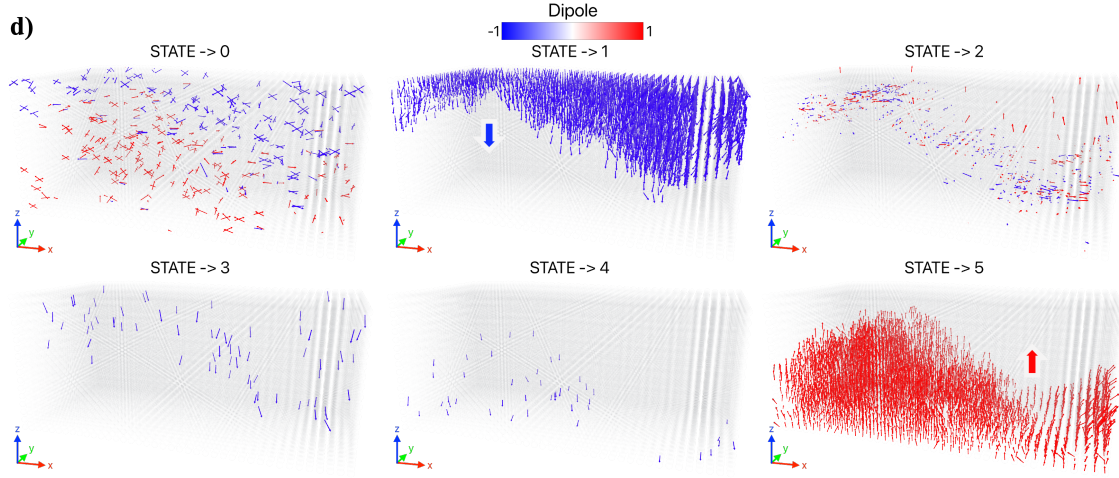


Figure 2.8: 2.7 Continued

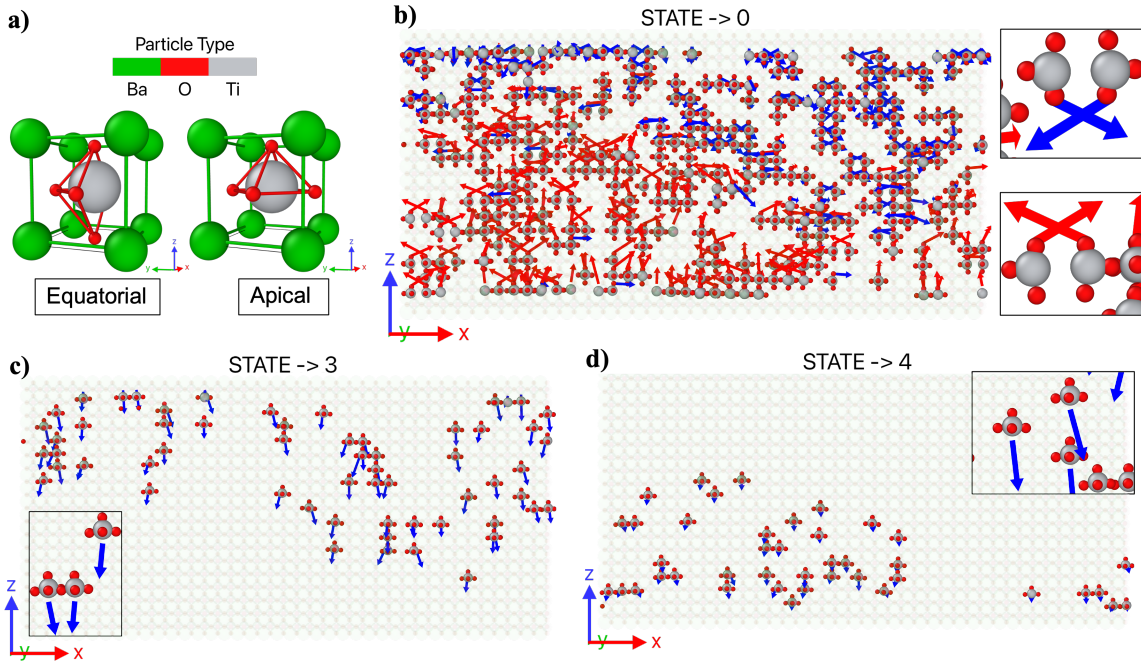


Figure 2.9: (a) Shows the equatorial and apical oxygen vacancies; (b,c, and d) overlays the local atomistic neighborhood around defect states 0,3 and 4 with local defect polarization shown as arrows.

inequivalent soft phonon modes around an oxygen vacancy. In interest of BTO, there are two distinct types of oxygen vacancies according to the location of missing oxygen in single unit cell of BTO, as shown in figure 2.9 (a) *equatorial* oxygen vacancy formed if oxygen is missing in the equatorial plane while for *apical* if oxygen missing on axial plane. From the model, states with *equatorial* oxygen vacancies have a different polarization shown in figure 2.9 (b). Interestingly, these state have a net ‘z’ component of the polarization that points along the direction of the bulk-like polarization around them. The dynamics of these defect-states is very localized but depends on their surroundings. Similarly, states with Ti-atoms with *apical* oxygen vacancies have polarization pointing down, and form two dynamical states – one corresponding to defects in the bulk-like up-domain (state-3) shown in figure 2.9 (c) and the other in the bulk-like down-domain (state-4). This suggests that while the defect-state polarization has a strong dependence on the surrounding bulk-like polarization direction, their dynamics is very slow. For example, transitions from the *apical* oxygen vacancy state to the bulk-like states occurs over nanosecond time-scales figure 2.8 (c). The disparate timescales of localized defect-dipoles and the domain wall further suggests that defect-dipoles may not be able to pin a moving DW, but can perhaps alter their dynamics as well as the effective field felt by them due to the net down defect-polarization, corresponding to a net down-electric field. This should invariably give rise to an asymmetric hysteresis loop, both in the quasistatic fields, as well as in fields oscillating at the *GHz* regime, with the degree of asymmetry controlled by the frequency of the driving field.

2.4 Conclusion

We have extracted the atomic representation as well as the relaxation times of domain walls in pristine as well as defective BaTiO_3 by building a Markov state model for MD trajectories. To do this, we modified the recently introduced GDyNet approach to build a Markov state model that can describe Landau-type phase-transitions such as in a ferroelectric solid, and also implemented it using Pytorch based libraries. We found that relaxation times of domain walls in BaTiO_3 are much shorter than the bulk-like region and are ~ 400 *ps*. This time increases to ~ 600 *ps* in the presence of even $\sim 1\%$ oxygen vacancies. We noted no change in the width of the domain wall due to defects. Oxygen vacancies introduce spatially localized states, with a single unit-cell extent, that have very slow dipolar relaxation times compared to the domain walls, and hence cannot necessarily pin a moving domain wall. Nevertheless, vacancies can change the domain wall dynamics, particularly their roughness. Domain wall regions with different curvature show differing dynamics, suggesting a novel mechanism by which quenched disorder due to defects introduce dynamic heterogeneity thereby influencing response to external fields (particularly time varying fields) in a ferroelectric. These findings open the door for controlling ferroelectric switching by coupling them to ac fields with specific frequencies that resonantly activate specific parts of the domain wall.

Chapter 3

Understanding Switching in Hexagonal Ferroelectrics by Combining Large-scale Reactive MD and Experiments

A version of this chapter is in preparation for submission to a scientific journal by **Abhijeet Dhakane**, Kyle Kelley, Bobby Sumpter, Adri van Duin, and P. Ganesh.

Abstract

The recent discovery of ferroelectric properties in hexagonal nitride and oxide materials has generated renewed interest for wurtzite structured materials, especially due to their existing complementary metal-oxide semiconductor compatibility. Ferroelectric wurtzite's, including $\text{Al}_{1-x}\text{B}_x\text{N}$ and $\text{Zn}_{1-x}\text{Mg}_x\text{O}$, show high durability, excellent breakdown strength, and tunable piezoelectric properties by doping. However, their typically high coercive fields pose significant barriers to integration into current microelectronics. Furthermore, the origin of ferroelectricity and the corresponding switching mechanisms under electric fields remain poorly understood, making the design and improvement of hexagonal ferroelectrics particularly challenging. Here, we performed large-scale simulations ($> 60\text{K}$ atoms) of field-induced switching in wurtzite-ZnO using reactive force-fields. By analyzing the trajectory along the hysteresis loop using novel data analytics approaches, we capture the atomistic switching dynamics during polarization reversal finding a '2-stage' switching process. We further reveal the origin of high coercive fields in these materials, and systematically analyze the strain and charge effects of doping hexagonal ferroelectrics such as ZnO using Mg like dopants and unearth a design principle to drastically reduce the coercive fields. These results provide a fundamental understanding of polarization reversal in $\text{Zn}_{1-x}\text{Mg}_x\text{O}$, and in turn lead to new methodologies for reducing the coercive field in wurtzite ferroelectrics.

3.1 Introduction

The recent discovery of ferroelectric wurtzite structures, including $\text{Al}_{1-x}\text{B}_x\text{N}$ and $\text{Zn}_{1-x}\text{Mg}_x\text{O}$, have sparked significant interest due to their compatibility with complementary metal-oxide semiconductor (CMOS) technology and their ability to be synthesized at back-end-of-line-compatible temperatures, making them promising candidates for future microelectronic applications [Liu et al. \(2021a,b\)](#); [Pradhan et al. \(2024\)](#). Moreover, wurtzite ferroelectrics have exceptional properties including direct bandgaps, strong bonding, and largely tunable lattice parameters making them technologically relevant for photonic and electronic applications [Zu et al. \(2023\)](#). Importantly, the strongly bonded polar wurtzite unit cell provides large polarizations that are insensitive to external stimuli, beneficial for high temperature and harsh environment applications. However, for low energy applications, the coercive field, or energy needed to switch the polarization, is too high and often near the breakdown strength of the material. Recent advances in doping wurtzite structured AlN and ZnO with Sc/B and Mg, respectively, have resulted in the emergence of ferroelectricity, i.e. polarization reversal (a.k.a switching), with promising fatigue and ‘wake-up’ characteristics. Yet, a comprehensive understanding of polarization reversal dynamics - specifically the atomistic mechanisms of domain nucleation and growth - remains limited, presenting an urgent need for deeper insights to optimize these materials.

The polarization reversal in wurtzite structures requires a coordinated displacement of metal ions traversing the (0001) basal plane through systematic tetrahedra inversion along the c-axis. [Baksa et al. \(2024\)](#) showed there is a local strain effect, which leads to the formation of the growth site for the growth of the wurtzite domains near the surface. Scanning transmission electron microscopy (STEM) experiments at different stages of switching seemed to show that a small filament-like transient state – called the inversion boundary – formed between the up and the down wurtzite phase in the thin films during switching [Calderon et al. \(2023\)](#). But it was not clear how these inversion boundaries formed, what their correlation length was, and the mechanism by which the entire wurtzite ferroelectric switched via this process. Indeed, there is a wealth of experimental evidence that has already confirmed the remarkable properties of these materials and their potential

use in future memory, neuromorphic, and storage devices. However, there is a limited understanding of these materials in the atomistic level i.e. the origin of the ferroelectricity. While the recent STEM experiment is a significant step forward in this direction, there are fundamental limitations on the spatiotemporal resolutions in experimental measurements that limits identification of these important switching characteristics. In turn, this further limits the determination of the origin of the characteristic properties such as coercive field, remnant polarization, etc. of these materials. To engineer the material for targeted applications, understanding these properties will be a crucial step. One must understand the switching dynamics at the atomistic scale capturing all relevant correlations that determine the domains and switching pathways.

Atomistic simulations can bridge this gap in understanding. For example, [Lee et al. \(2024\)](#) showed the first-principle based energy landscape highlighting the various intermediate metastable states with non-polar structural arrangement exist in the Wurtzite switching. Major contribution in this states are contributed by the more electro-negative cations in the $\text{Al}_{1-x}\text{Sc}_x\text{N}$ such as Sc facilitate lowering the switching barrier. This suggests that certain dopants might lower the switching barrier, but a clear rationale of why this would happen and how it would influence the filamentary switching observed in STEM is lacking. [Behrendt et al. \(2024\)](#) developed the machine learning based force-field (MLFF) for AlN reproduces DFT-level energies, forces, and phonon spectra at a fraction of the cost, enabling molecular-dynamics simulations of systems orders of magnitude larger than practical with DFT. With this model they captured long-range phenomena—such as frequency-dependent dielectric response and the behavior of multiple ferroelectric domains—and accurately describe different phases and domain walls. However, they could not reproduce the field dependent switching mechanism as reported in the [Calderon et al. \(2023\)](#) STEM experiments, which showed the formation of the lamellar filamentary boundaries that grow from the surface. These investigations motivate a detailed in-depth investigation of the switching mechanisms in wurtzite ferroelectrics using predictive large-scale molecular dynamics simulations.

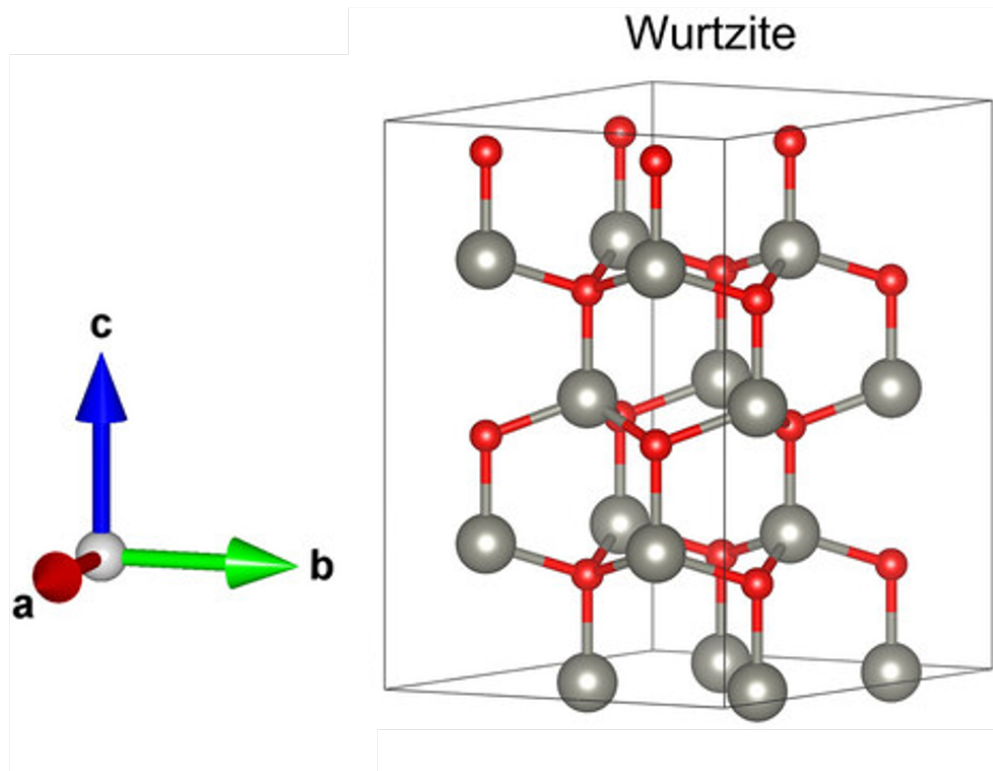


Figure 3.1: This figure shows a representative structure of the Wurtzite ZnO [Han et al. \(2023\)](#)

Recent advances in reactive force-fields – that can capture bond breaking and formation – allow thousands of atom simulations under external electric fields and finite temperatures. These force-fields are fit to ab initio energies and as such have similar ab initio accuracies. In this work, we have simulated small- and large-scale simulations of ZnO and with various % of Mg doping – investigating systematically effects of strain and charge-doping. We also included random as well as layered doping and unraveled the switching dynamics under an electric field using a reactive force field. Based on the various simulations we not only revealed the origin of coercive fields in hexagonal ferroelectrics, but also took a ‘*dynamics-by-design*’ strategy and unearthed a design principle to significantly reduce the coercive field in these materials, thereby solving the major bottleneck for use of these materials in low-power applications.

3.2 Methods

3.2.1 MD Simulation

Large-scale molecular dynamics simulations of pristine ZnO were performed in LAMMPS [Thompson et al. \(2022\)](#) using the ReaxFF reactive force field [Sepehrinezhad et al. \(2024\)](#). A ZnO supercell of dimensions $9 \times 9 \times 8$ nm (approximately 55 552 atoms) was constructed, with an additional vacuum layer along the z -axis to eliminate spurious periodic interactions and mimic a freestanding thin film. All runs employed a time step of 0.25 fs.

The system was equilibrated at 100K by first ramping from 0 to 100K over 50 000 steps (12.5ps) under the Berendsen barostat and thermostat, and then by a further 50 000 steps (12.5ps) of constant-temperature relaxation with the Berendsen thermostat. During this equilibration phase, all atomic charges were held fixed as point charges; no charge-equilibration procedure was applied thereafter. Nominal fluctuations in the total energy confirmed that the system had reached equilibrium.

A sawtooth electric field was then applied along the z -direction, stepping in increments of 2 MV/cm over the range -40 to $+40$ MV/cm. Configurations were dumped every 1 fs. From these trajectories, the total polarization was computed as follows:

$$P_{total} = \sum Z_{Zn} \cdot r_{Zn} + \sum Z_O \cdot r_O + \sum Z_{Mg} \cdot r_{Mg} \quad (3.1)$$

and the local polarization P_u for each ZnMgO unit cell, the relative displacement vectors from the central Zn/Mg atom to its four nearest O atoms were used to determine the geometric center, and the resulting dipole vector was assigned to the Zn/Mg site.

$$P_u = \sum_{i=1}^4 \Delta r [Zn/Mg - O_i] \quad (3.2)$$

For each field, the global polarization was calculated by averaging P_{total} over the trajectory for the given electric field.

3.2.2 Extending Graph Neural Network to Arbitrary Materials and Order Parameters

The graph dynamical neural network approach in the previous chapter laid out the principles behind constructing a Markov state model from MD simulations for a perovskite ferroelectric oxide. For wurtzite materials, the structure is quite different. Further, unlike perovskite, where the central metal-atom always has six bonded oxygen atoms, wurtzite has four near neighbor oxygens, with the index of the fourth neighbor changing when the polarity switches. In addition, switching in wurtzite leads to non-wurtzite like structures – such as the inversion boundary – as mentioned above, unlike perovskite ferroelectrics that always have the same perovskite-like co-ordination during switching. As such, our graph neural network representation of the structure needs to be generalized to capture these additional changes during the field induced phase-transition. Most notably, in materials where we do not know how to compute the order-parameter – i.e. which distortions we should include to compute the order-parameter such as the total polarization - can further limit applicability of our graph dynamical neural network. We hence generalize the graph representation to automatically detect the order parameter that is relevant to describe the dynamical states AND construct the MSM for these states.

There are several local representations in the literature for representing structures. But not all of them are ideal for our problem. Equivariant neural-networks have become popular for representing structures for building ML models. Unfortunately, since we would like to distinguish every possible direction of the order-parameter, which maybe equivariant locally, but globally break symmetry, this representation is not suitable for our purpose. Similarly, local order parameters such as SOAP and its generalization, ACE, have been used quite successfully in ML models for material property prediction. The idea is to expand the local density around an atom in terms of combinations of radial and angular basis functions. While smooth overlap of atomic positions (SOAP) [Bartók et al. \(2013\)](#) or atomic cluster expansion (ACE) [Batatia et al. \(2022\)](#) is capable of capturing the local order-parameter, their enumeration is computationally too expensive to be readily applicable in our neural-network model where $> 100\text{K}$ atoms are present in MD simulations, with millions of snapshots. Given our variational auto-encoder is a time-lagged encoder, the representations are found to be impractical for analyzing large-scale MD simulations. We find inspiration from these local crystal representations, and identify a scalable representation that can (a) represent charges and distortions that give rise to order-parameters contributing to the total-polarization and (b) generalize to cases outside perovskite, such as wurtzite type ferroelectrics and (c) are easy to compute and store for downstream learning of dynamics from long trajectories of large MD simulations.

3.2.3 Spherical Harmonics

Spherical harmonics are a set of orthogonal functions defined on the surface of a sphere, forming a complete basis for representing functions on spherical domains.

$$\mathcal{Y}^l : \mathbb{R}^3 \rightarrow \mathbb{R}^{2l+1}$$

They are particularly useful in physics and engineering for solving problems with spherical symmetry, such as quantum mechanics and electromagnetism. This representation becomes particularly valuable when studying materials exhibiting symmetry breaking, such as ferroelectrics. In these materials, the spontaneous polarization leads to a deviation from

perfect symmetry. By leveraging spherical harmonics within GNNs, one can capture and analyze these subtle symmetry-breaking phenomena. Spherical harmonics are part of equivariant neural networks as well and as shown by [Smidt \(2018\)](#) they can capture static properties of the ferroelectric materials. We adapt spherical harmonics based graph representations and show that it works for both static as well as phase-transitions where non-ideal transient structures form during switching.

3.2.4 BaTiO₃

Barium titanate oxide (BaTiO₃) is a classical ferroelectric material that exhibits characteristic ferroelectric behavior, notably the presence of a ferroelectric hysteresis loop upon the application of an external electric field. This behavior arises from the displacement of the titanium ion within the oxygen octahedron, leading to a spontaneous polarization that can be reoriented by an external field.

To analyze and quantify the local structural distortions associated with ferroelectricity in BaTiO₃, one can employ the spherical harmonics representation of the relative vectors between the titanium atom and the surrounding oxygen atoms. This approach utilizes the spherical harmonics basis functions, denoted as $\mathcal{Y}^l$, which map a point in three-dimensional space to a $(2l + 1)$ -dimensional real vector space: By projecting the local atomic configurations onto these basis functions, one obtains a set of descriptors that capture the angular distribution of the local environment.

As shown in figure [3.2](#), summing the spherical harmonics components across the respective angular degrees yields distinct fingerprints of the local structural states. Notably, the odd-order spherical harmonics (i.e., those with odd l values) are sensitive to the directionality of the polarization and can distinguish between the ‘up’ and ‘down’ polarization states in BaTiO₃. In contrast, the even-order spherical harmonics are invariant under inversion and thus cannot differentiate between these two states. This property makes the odd-order spherical harmonics particularly suitable as order parameters for identifying and characterizing symmetry-breaking phenomena in ferroelectric materials. They are also good representations forming the structural fingerprints to include in the GNN based graph

dynamical neural networks described in the earlier chapter, and replace the computed polarization vector as a node feature.

3.2.5 Wurtzite- ZnO

Zinc oxide (ZnO) crystallizes in the wurtzite structure, characterized by a non-centrosymmetric hexagonal lattice. Each zinc atom is tetrahedrally coordinated by four oxygen atoms, forming a polar structure along the $[0001]$ direction. This polarity gives rise to two distinct orientations: the ‘up’ and ‘down’ states, corresponding to the direction of the spontaneous polarization. Unlike perovskites, the index of the fourth neighbor changes. Further, during phase-transition, non-wurtzite like structures form, such as the inversion domain boundary.

To capture and differentiate these polar states at the atomic level, we employ spherical harmonics as a mathematical tool to represent the local atomic environments. Specifically, we consider the relative position vectors from a central zinc atom to its four neighboring oxygen atoms. To capture the more detailed structural changes in Wurtzite ferroelectrics compared to BaTiO_3 , while at the same time keeping a tractable computational overhead, we utilize spherical harmonics of degree $l = 6$ to ensure a detailed representation of the local geometry. Unlike in perovskites, an even value is able to distinguish ‘up’ and ‘down’ states figure 3.3. By summing the spherical harmonics components corresponding to each Zn–O bond, we obtain a composite descriptor that encapsulates the angular distribution of the local environment.

Furthermore, this methodology proves effective in identifying inversion domain boundaries (IDBs) within ZnO. IDBs are planar defects where the direction of polarization inverts, leading to a transition between ‘up’ and ‘down’ domains. By mapping the spatial variation of the spherical harmonics descriptors across a region containing an IDB, we can pinpoint the location of the boundary and monitor its movement. As illustrated in figure 3.4, the transition in the descriptors corresponds to the shift from one polarization state to the other, with the IDB’s progression indicated by the orange arrow. The blue/red square denotes the ‘up’/‘down’ domain, while the thin black arrow highlights the transformation pathway of the IDB.

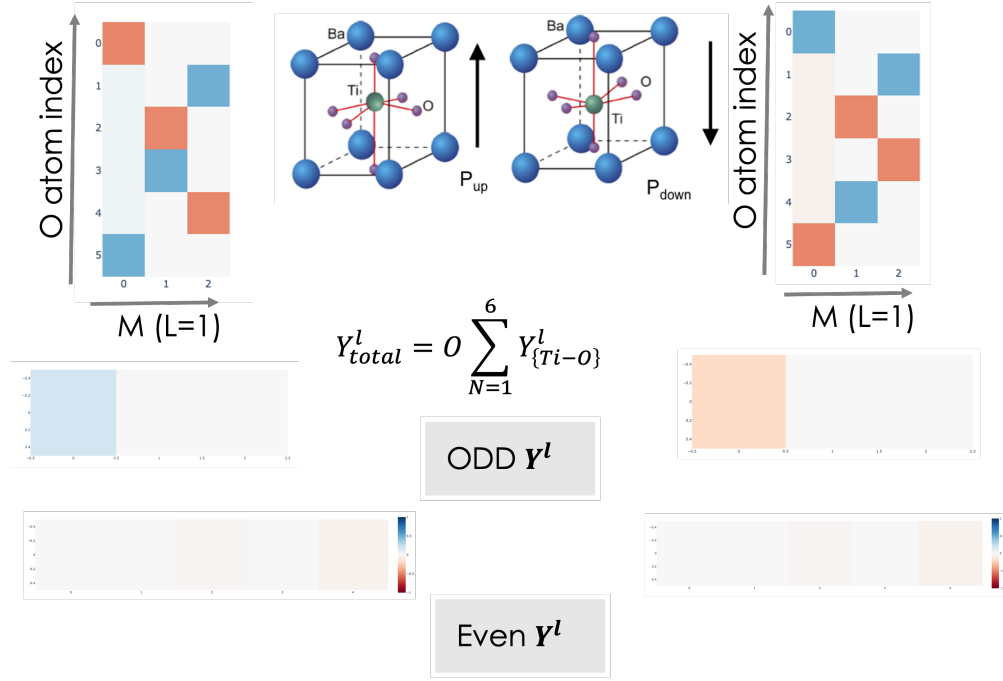


Figure 3.2: Illustration of the spherical harmonics (YLM) representation of the local environment in BaTiO₃. The summed quantity over the nearest oxygen atoms of a given Ti with an odd-value of l capture the asymmetry associated with the ‘up’ and ‘down’ polarization states, while the even-order components remain symmetric.

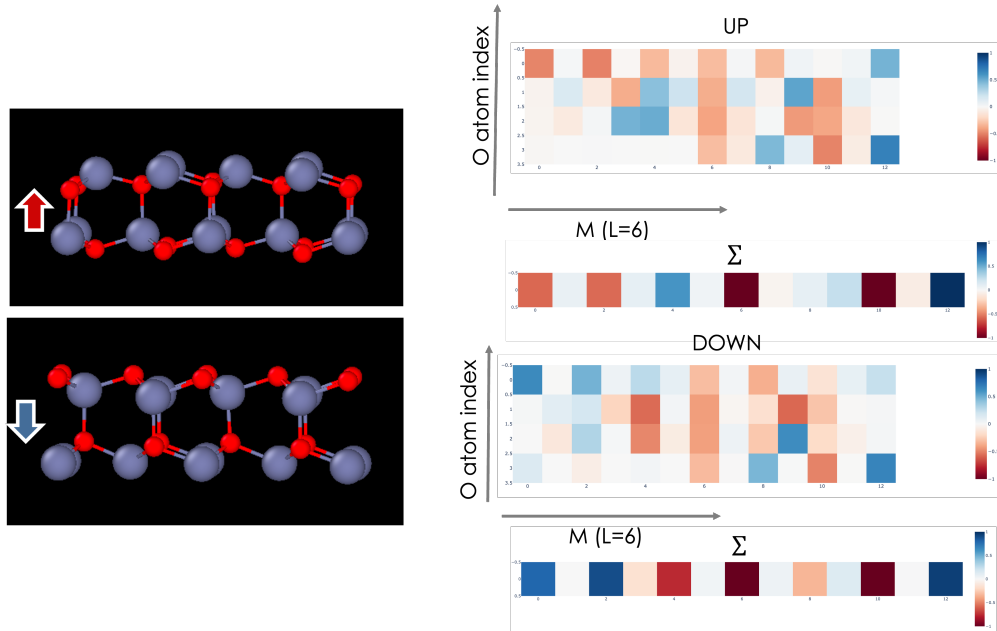


Figure 3.3: Visualization of the spherical harmonics (YLM) representation for the local environment around Zn atoms in wurtzite ZnO. The odd-degree components highlight the differences between the ‘up’ and ‘down’ polarization states.

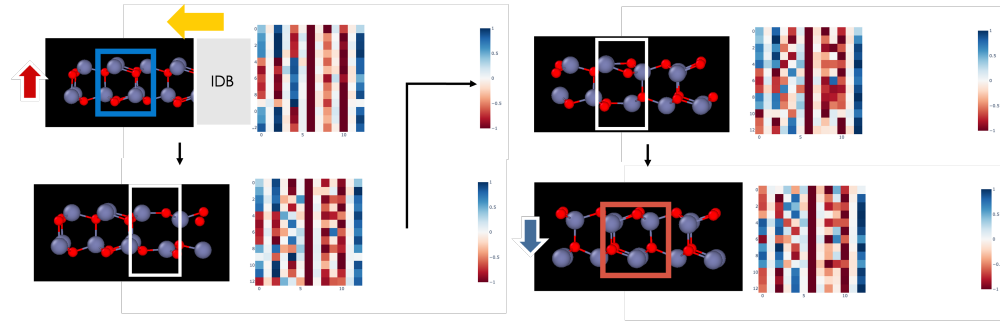


Figure 3.4: Detection of an inversion domain boundary (IDB) in wurtzite ZnO using spherical harmonics descriptors. The change in the descriptors across the region signifies the presence and movement of the IDB.

In summary, the application of spherical harmonics provides a robust framework for characterizing local structural environments in wurtzite ZnO. This approach enables the differentiation of polar states and the detection of intermediate non-wurtzite like bonded structures, such as inversion domain boundaries, offering a scalable compact representation to develop graph dynamical neural networks that can extract valuable insights into the material’s ferroelectric properties and domain dynamics from large-scale MD simulations.

3.3 Results and Discussion

3.3.1 Pristine ZnO

We begin by analyzing the pristine ZnO thin film, where no doping is present, using the simulation protocol outlined in the Methods section. Figure 3.5(A) presents the resulting hysteresis loop, characteristic of ferroelectric materials under electric-field switching, exhibiting a remanent polarization of approximately $36 \mu\text{C}/\text{cm}^2$, a saturation polarization of about $46 \mu\text{C}/\text{cm}^2$, and a coercive field of around $15 \text{ MV}/\text{cm}$. The inset of figure 3.5(A) shows representative structural configurations at different fields, revealing that the wurtzite phase initially maintains a single polarity at high positive and negative fields. As the field is reversed, an inversion boundary appears, separating the ‘UP’ and ‘DOWN’ wurtzite domains. The inversion boundary has similar atomic arrangement as well as width to the one observed in the STEM experiment, as mentioned above. To visualize the switching dynamics more clearly, a surface mesh was created around the inversion boundary, masking the wurtzite phase.

Representative snapshots of the hysteresis loop (numbered 1–6) in figure 3.5(B) illustrate the filamentary growth originating from both surfaces along the z -direction, with faster progression of the filament along the field direction. Once these filaments meet the opposite surface, they form columnar structures (figure 3.5(B-3)), which then expand laterally in the xy -plane until the entire wurtzite film switches polarity. This suggests a two-step switching process, hitherto unknown in the literature. The incubation time for the system to go from filamentary switching to lateral switching leads to a ‘bump’ in the hysteresis loop. Recent

experiments have indeed observed such a bump in the hysteresis loop, but we for the first time reveal the atomistic dynamics that give rise to this [Yang et al. \(2024\)](#).

To get a picture of the local polarization during this filament formation at the atomic scale, we calculated the local polarization vector for each ZnO unit cell, as shown in figure 3.5(C). Wurtzite-like regions are not shown (appearing as white background) in these plots, which show the different stages of the filament formation. At the onset of switching (~ -5 MV/cm), a prominent polarization vector (colored blue) propagates from the top surface to the bottom surface. This blue-vector region of local polarization forms the core of the filament, and has the inversion boundary structure shown in the inset of figure 3.5(A). The magnitude of the local polarization (i.e. blue-vector) is largest at the head of the filament. A closer examination of the inversion boundary in figure 3.5(C) reveals a chiral core-shell arrangement, where the core adopts an anti-polar orientation (blue-vector) with a tilted opposing polarization (red-vector) in the shell. Presence of these opposing polarization reduces the overall polarization of the filament, thereby reducing the total energy of the system. We are not aware of any other material where such a core-shell type switching has been reported so-far in the bulk, but nanostructured 2D materials have shown core-shell type skyrmionic states, or even bubble-domains during switching. This remains a key prediction of our large-scale simulations, and as we show below reveals the origin of the large coercive field in hexagonal ferroelectrics. For further discussions of the filamentary switching, we will refer to the large polarization at the head of a filament core (i.e. the largest blue-vector) $\mathbf{P}_{\text{fil-head}}$ and the opposing polarization (i.e. the red-vectors) that screen this anti-polar state $\mathbf{P}_{\text{screening}}$. Most importantly, we hypothesize that the large polarization at the filamentary-head leads to the large coercive field for switching ZnO and similar hexagonal ferroelectrics.

Overall, the switching proceeds in two steps: lamellar filamentary growth of the inversion boundary which leads to small domain switching, followed by lateral (in-plane) expansion of the switched domain when a critical number of such domains have been formed. Figure 3.6 (A) further reveals a clear thickness dependence in wurtzite films: both the 7nm and 10nm samples exhibit the characteristic two-step switching behavior seen in the pristine systems. Notably, the 7 nm film initially have a cubic phase—as evidenced by its near-zero remanent polarization at zero applied field—rather than the wurtzite structure. Upon application of

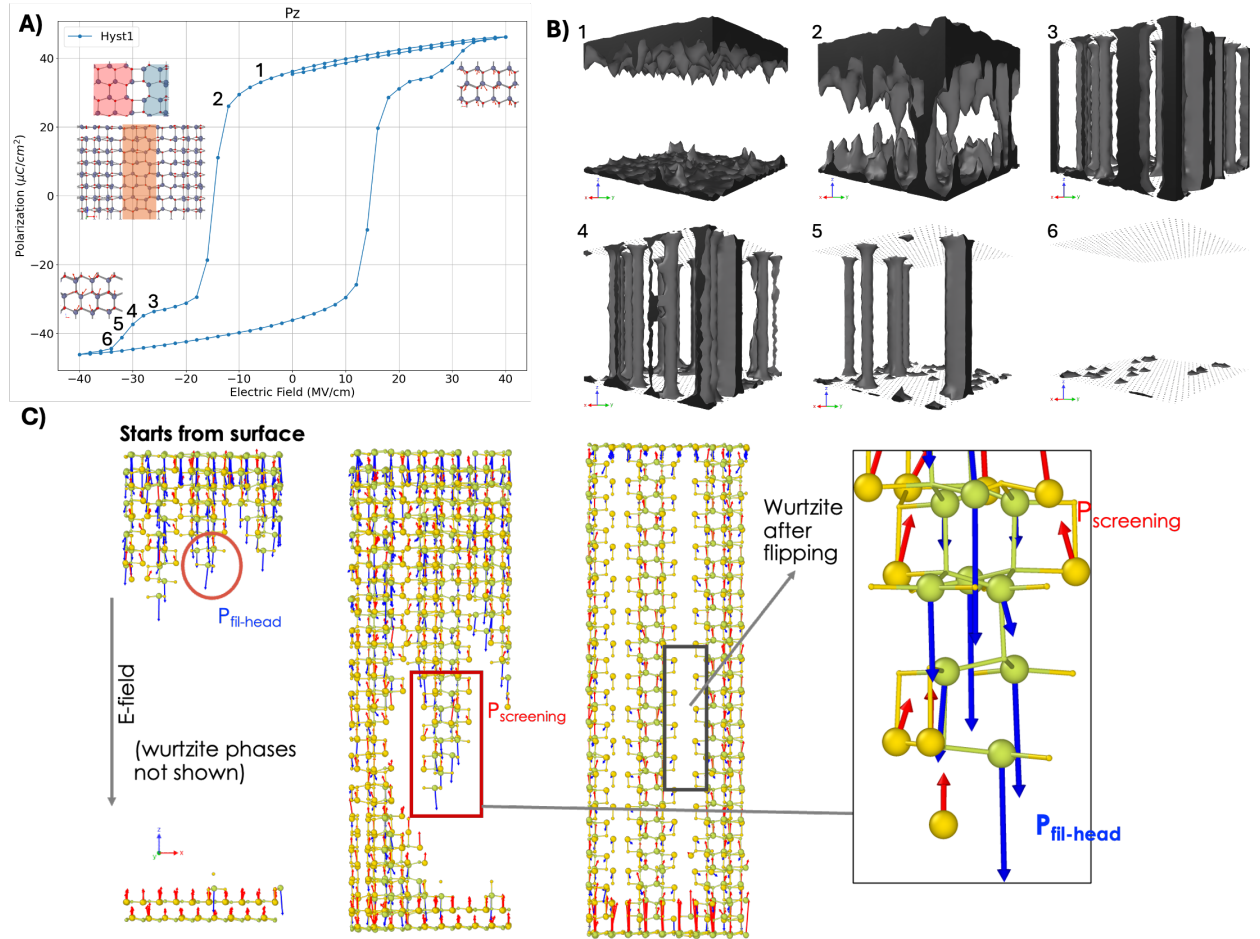


Figure 3.5: (A) Hysteresis loop and inset structural snapshots. (B) Domain evolution snapshots 1–6 (with 3 showing columnar structures). (C) Snapshots of the local polarization during the different stages of the filamentary growth of inversion domain boundaries. We clearly see a core-shell filament, with large polarization in the core and opposing polarization in the shell ($P_{\text{screening}}$) that screens this large polarization at the core. The head of the filamentary core has the largest polarization, helping it to punch through the wurtzite phase under an applied field. We label it as $P_{\text{fil-head}}$.

the sawtooth electric field, this cubic phase converts to wurtzite, and the film remains in the wurtzite phase through subsequent polarity reversal. These observations demonstrate the robustness of Reax force field and its ability to accurately capture the phase-to-phase transitions within the wurtzite energy landscape.

3.3.2 Hypothesis and rationale for lowering the coercive field

As discussed above, we hypothesize that the large polarization at the filamentary-head (i.e. $\mathbf{P}_{\text{fil-head}}$) leads to the large coercive field for switching ZnO and similar hexagonal ferroelectrics. Lowering $\mathbf{P}_{\text{fil-head}}$ would hence lower the coercive field. We put forth three rationale strategies for lowering it using extrinsic dopants:

1. *Dopant charge-effect:* Given that $\nabla \cdot \mathbf{P}_{\text{fil-head}} = \text{dopant-charge}$, increasing the charge on a dopant atom should help suppress $\mathbf{P}_{\text{fil-head}}$.
2. *Dopant strain-effect:* Given that for a dopant with radii different from Zn, the local polarization in the filament head would change as $\sim \mathbf{P}_{\text{fil-head}} = \mathbf{P}_{\text{fil-head}} \frac{\text{Zn_radii}}{\text{dopant_radii}}$, a dopant with a larger radii would effectively lower this polarization.
3. *Dopant polarizability-effect:* One could in principle also increase the $\mathbf{P}_{\text{screening}}$ by choosing dopants with high atomic polarizability α compared to zing. In this case dopant $\mathbf{P}_{\text{screening}} = \alpha_{\text{dopant}} E$, and help with effectively reducing the total polarization, and hence the energy cost for switching.

Our critical understanding of the atomistic switching process has thus resulted in three different rationale approaches to lower the coercive fields. In large-scale MD simulations, it is easy to test the charge and strain effects. We show in the next few subsections the individual and combined effects of strain and charge on the hysteresis loop of the bulk doped ZnO. For sake of simplicity, we choose Mg-atom as the dopant in our MD simulations as we explore the effect of strain and charge effects.

3.3.3 Dopant strain-effect in Mg doped ZnO

Mg dopants have a slight amount of strain compared to Zn owing to its different atomic radii. Experimentally, coercive field was shown to be low when $\sim 37\%$ Mg dopants were substituted

in place of Zn in ZnO. In order to examine how Mg doping influences the ferroelectric switching behavior of ZnO, a 37% Mg concentration was introduced into the ZnO supercell, with the Mg atoms randomly distributed throughout. We considered the doped Mg to have the same charge as Zn, as such exploring only its strain effect. The resulting hysteresis loop, shown in figure 3.7(A), exhibits slightly reduced remanent ($\sim 30 \mu\text{C}/\text{cm}^2$) and saturation ($\sim 42 \mu\text{C}/\text{cm}^2$) polarizations compared to the pristine system, along with a minimal increase in the coercive field. Notably, the two-step switching characteristic of the undoped film is absent in the Mg-doped material. The slight increase is consistent with Mg possessing a slightly smaller radii compared to Zn. We expect the screening polarization ($\mathbf{P}_{\text{screening}}$) on Mg to be hence lowered, thereby resulting in larger $\mathbf{P}_{\text{fil-head}}$ on an average. Mg doping also introduces significant disorder which further changes the two-step switching process.

Figure 3.7(B) illustrates the evolution of the inversion boundary for representative points [1–6] on the hysteresis loop (figure 3.7(A)), with the wurtzite phase masked to highlight only the boundary. At the onset of switching, lamellar filaments initiate from both surfaces and grow more rapidly in the direction of the applied field—similar to the pristine system. However, Mg doping induces additional disorder: the interfaces become rougher, and small nucleation centers appear within the bulk. As the electric field increases, the filaments meet the opposite surface and spread laterally, yet they do so without forming the metastable phase observed in the undoped film. This is largely because the individual filaments do not form a pristine column all at the same time due to Mg-disorder, and this asynchronous filament formation leads to an asynchronous two-step switching process that is smeared out by this disorder effect.

Figure 3.7(C) [1–6] presents atomistic snapshots, including the local polarization vectors at each representative point on the hysteresis loop. Early in the process (figure 3.7(C)[1]), most of the domain exhibits an “UP” polarization. As the field reverses, inversion boundaries emerge between UP and DOWN regions, and near the coercive field, the majority of the wurtzite switches polarity. Overall, Mg doping introduces local strain that fosters rapid switching centers absent in the pristine system. This results in a more disordered asynchronous two-step switching process that replaces the clear synchronous two-step mechanism seen in undoped ZnO. Increasing the Mg concentration further amplifies this

disordered behavior, ultimately suppressing the pure lamellar growth mode characteristic of the pristine film.

Recent experiments on ferroelectric wurtzite $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films have demonstrated clear hysteresis over a broad Mg range (8%–55%) [Spurling et al. \(2025\)](#). An oxygen/ozone sputter-deposition process reduces electronic defects, ensuring sufficient insulation resistance for clear loops. While the remanent polarization shows only modest composition dependence, the coercive field initially decreases with increasing Mg (likely due to structural softening) and then rises above $\sim 13\%$ (attributed to heightened crystallographic disorder), producing a non-linear trend. The most resistive films lie within the 25%–38% Mg window, and a uniform Mg distribution is confirmed across the samples. Moreover, ferroelectric hysteresis remains observable in films as thin as 66 nm, even in the Mg-rich regime.

Figure 3.8 (A) and (B) presents hysteresis loops for doping concentrations of 18.75%, 31.25% and 37% Mg doped system in 7 nm and 10 nm thick supercells respectively, revealing the non-linear trend in the coercive field that aligns with these experimental observations. This behavior underscores the interplay between structural softening at lower Mg contents and increased crystallographic disorder at higher concentrations, consistent with recent experimental reports. Nevertheless, importantly we have discovered that doping imparts strain, and dopants with smaller strain can lead to slightly larger coercive field due to a higher screening polarization.

3.3.4 Dopant charge-effect in Mg doped ZnO

Earlier first-principles investigations have shown that Mg doping in ZnO induces charge disproportionation, which in turn alters the local charges on Zn/Mg/O. To isolate and quantify the charge effects we performed molecular-dynamics simulations exploring this pure charge effect here, whereby 37% of the Zn sites were assigned an effective point charge of 1.37 e (as reported in previous density-functional studies for Mg-dopants), while the remaining Zn atoms carried a unit charge of 1 e and all oxygen atoms were assigned charges such that the supercell remained overall neutral.

As seen in figure 3.9 the coercive field in the pure charge effect is approximately ~ 12 MV/cm, significantly reduced by ~ 3 MV/cm compared to the pristine case. There is

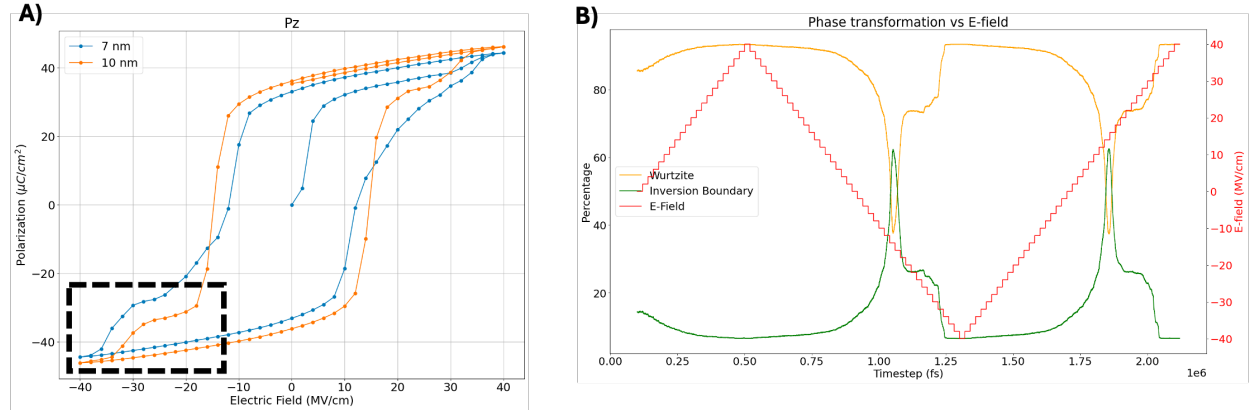


Figure 3.6: (A) Hysteresis loop of the pristine ZnO with 7nm and 10 nm thickness. (B) Evolution of the Wurtzite and inversion domain boundary phases during the sawtooth electric field switching.

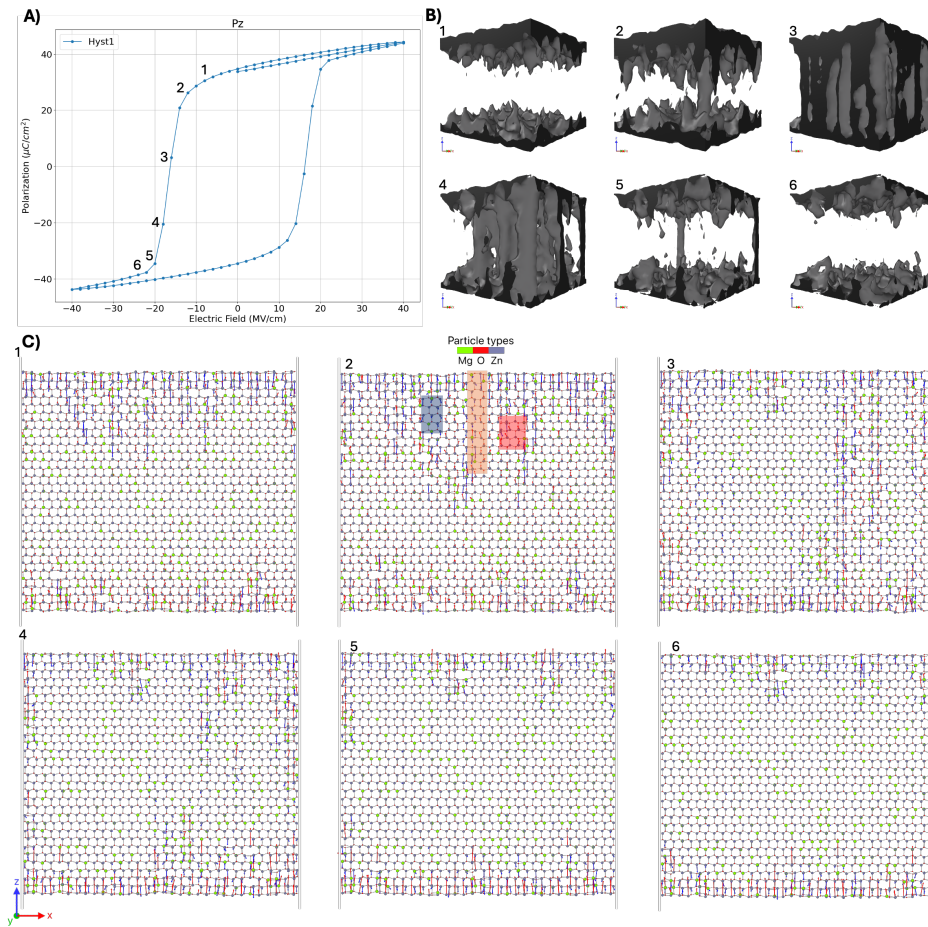


Figure 3.7: (A) Hysteresis loop of 37% Mg doped system including only the strain-effect from Mg. (B) Domain evolution snapshots (1–6) from the hysteresis loop. (C) Atomic snapshot at respective (1-6) along the hysteresis loop

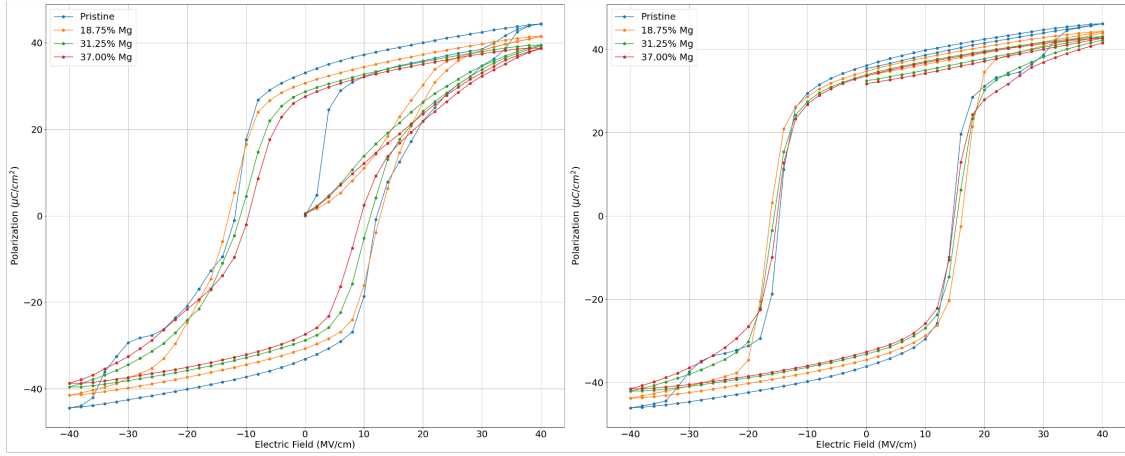


Figure 3.8: Hysteresis loop of pristine, 18.75%, 31.25% and 37% Mg doped system including only the strain-effect from Mg of (A) 7 nm thick (B) 10 nm thick supercell.

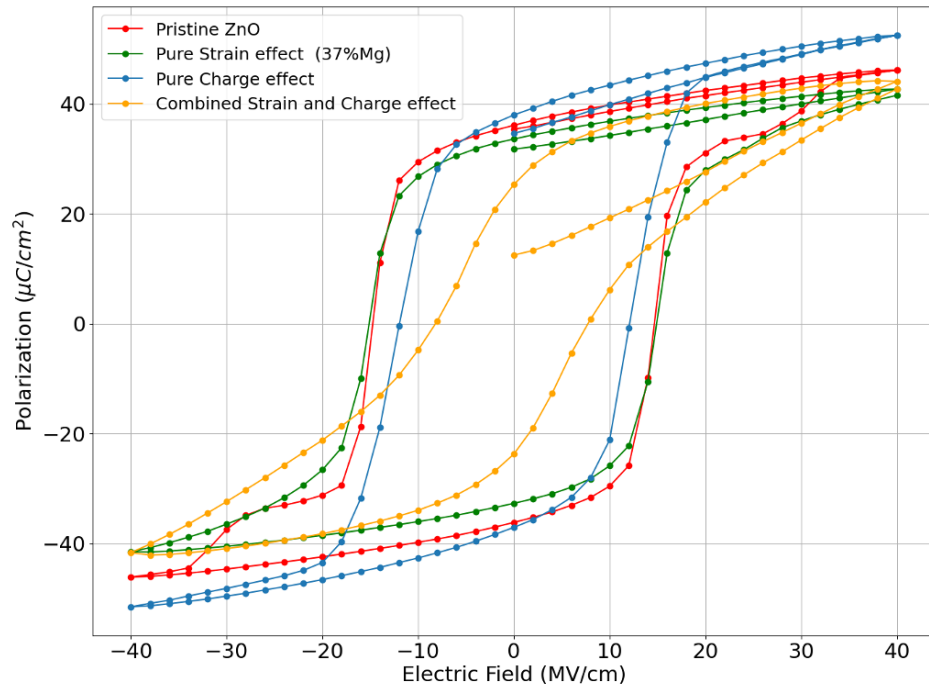


Figure 3.9: Hysteresis loops comparing pristine ZnO, pure charge-effect, pure strain-effect and combined charge and strain effect due to Mg dopants. All doping is performed at the same 37%.

no chemical disorder in this model system because all metal atoms have Zn, and hence the hysteresis loop is still quite squarish. As argued earlier, presence of dopant charges should in principle lead to screening the $\mathbf{P}_{\text{fil-head}}$, thereby reducing the coercive field. To investigate the local atomic polarization during switching we plot the average up (blue) and down (red) polarization during the hysteretic switching process as shown in figure 3.10. Figure 3.10(A) shows the high value of $\mathbf{P}_{\text{fil-head}}$ as we saw earlier. Compared to the pristine case, as shown in Figure 3.10(B) $\mathbf{P}_{\text{fil-head}}$ for the dopant charge-effect case is significantly lowered by about 50%. In contrast, $\mathbf{P}_{\text{screening}}$ hardly changes. This observation from the analysis we have presented here clearly proves our fundamental hypothesis – the coercive field is directly proportional to the magnitude of $\mathbf{P}_{\text{fil-head}}$ and that adding dopant charges will lead to lower $\mathbf{P}_{\text{fil-head}}$ resulting in a lower coercive field. We have hence not only discovered the origin of high coercive fields in hexagonal ferroelectrics, such as ZnO but also rationally come up with a design strategy by looking at the dynamics of ferroelectric switching on how to lower the coercive field. We further extend this ‘*dynamics-by-design*’ approach to investigate the combined strain and charge effect.

3.3.5 Combined dopant charge and strain effect

We have seen above that while strain from dopants introduces disordered switching, it is the charge on the dopants that significantly screens the large polarization in the filamentary-head, thereby lowering the coercive field. To explore the combined effects of how charged dopants that are randomly distributed in the lattice inducing disordered strain, we introduced 37% Mg dopants at the same sites as the charged Zn sites above, and with identical point-charge assignments as in the charge-only model, thereby incorporating both the electrostatic and lattice-strain effects of Mg substitution. Interestingly, as shown in figure 3.9, we find that the coercive field drops even further to $\sim 8 \text{ MV/cm}$, the lowest among all cases explored and nearly $\sim 50\%$ of the value in the pristine ZnO case. Further, due to disorder, the loop assumes a highly sloped shape indicative of an order-disorder dominated switching mechanism. In both doped models, the two-step switching characteristic of the undoped system disappears completely, and we mainly see asynchronous switching with small filamentary-head polarization.

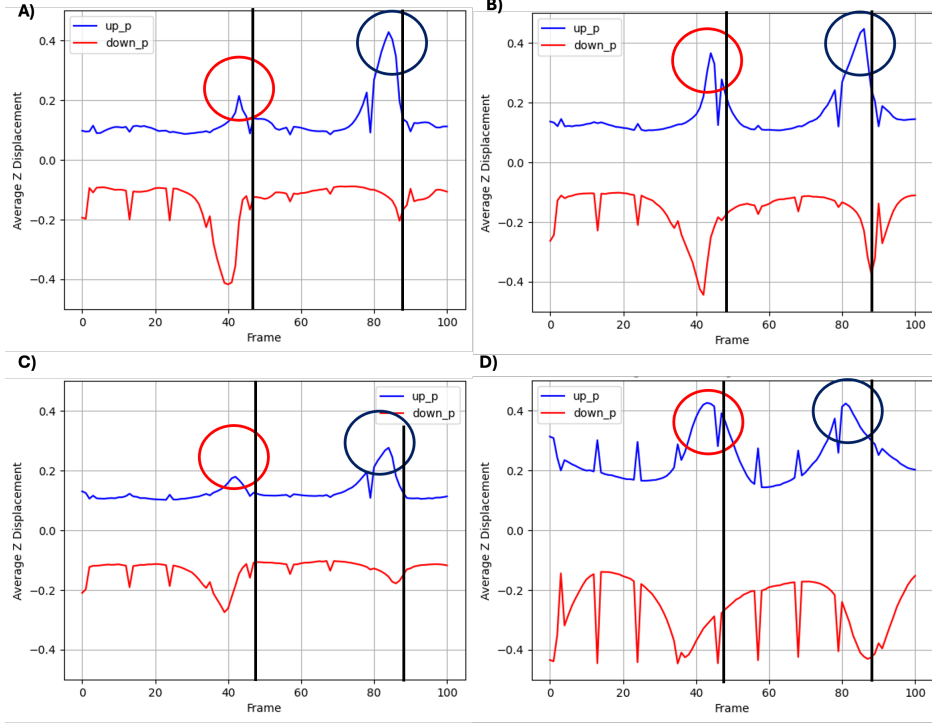


Figure 3.10: Average Z-direction displacement of local dipoles over simulation frames for different ZnO-based configurations during electric field-driven switching. Each subplot corresponds to the four cases: (A) pristine ZnO, (B) pure strain-effect, (C) pure charge-effect and (D) combined charge and strain effect. The black circle indicates the highest value of $\mathbf{P}_{\text{fil-head}}$ in the filamentary core during the field induced hysteresis, while the red circle indicates the corresponding $\mathbf{P}_{\text{screening}}$ in the filamentary shell region. The solid black lines show the position of the coercive field. We also interestingly see that the screening polarization reaches a maximum after the filamentary core has reached its maximum, and helps suppress the polarization at the filament head.

As shown in figure 3.10 (D), this drop in coercive field is largely due to a relative decrease in the $\mathbf{P}_{\text{fil-head}}$ compared to the $\mathbf{P}_{\text{screening}}$. The picture is much more complicated in the combined case but nevertheless support our hypothesis that a lower filamentary head polarization compared to the screening polarization should result in a lower coercive field.

3.3.6 Layered dopants to reduce switching time

While adding charge dopants or combining them with larger strained dopants seem to lower the coercive field, the 1D filamentary nature of switching implies that unless the filament reaches from one surface to another, it cannot induce the complete switching of the ferroelectric film. This naturally limits the switching time. Recent experiments [Skidmore et al. \(2025\)](#) show that heterostructured ZnO/ZnMgO can be grown with high precision. We hypothesize that such heterostructures might further lead to concurrent filamentary switching from the different buried interfaces involved and lead to faster switching dynamics due to the smaller distance that each filament needs to propagate before the film switches completely in polarity.

To prove this hypothesis, we investigated a layered dopant configuration in which a 3–6-atomic-layer region was selectively doped with Mg, creating a planar defect within the ZnO supercell and resulting supercell resembles the heterostructure ZnO/ZnMgO/ZnO. In addition to that the charge and strain effects were also explored by assigning different charges as reported on the Zn and Mg atoms. In the presence of both charge and strain, the resulting hysteresis loop (figure 3.11(E)) shows a moderate reduction in both remanent and saturation polarization compared to the case with pure strain effect from Mg doping (figure 3.11(D), as well as a decrease in the coercive field. We further see that the dopant layer acts as an intermediate growth center for the filamentary growth, thereby supporting our hypothesis for achieving faster switching in heterostructured films.

Figure 3.11 (B) and (C) show the corresponding local polarization vectors at each field point (plotted as frames) for the pure strain case and the combined charge and strain case, respectively. In the case of the pure strain, $\mathbf{P}_{\text{fil-head}}$ is still significantly high, but is much reduced when charges are added to the dopants. As expected, the coercive fields as seen in the hysteresis loops from figure 3.11 (D) and (E) are much reduced when charged dopants

are present. Further, switching via filamentary formation is now seen from the ZnO/ZnMgO interface, absent in the case without charged dopants. This suggests that the design principle of reducing $\mathbf{P}_{\text{fil-head}}$ by adding charged dopants observed in our uniformly doped ZnO films extends to these heterostructured films as well. But given the nucleation of filaments at the ZnO/ZnMgO interface they now need to travel shorter distances, thereby significantly accelerating the switching times. Hence we proved that heterostructured films of ZnO with charge-doped ZnO will be ideal for a low-power fast memristor application.

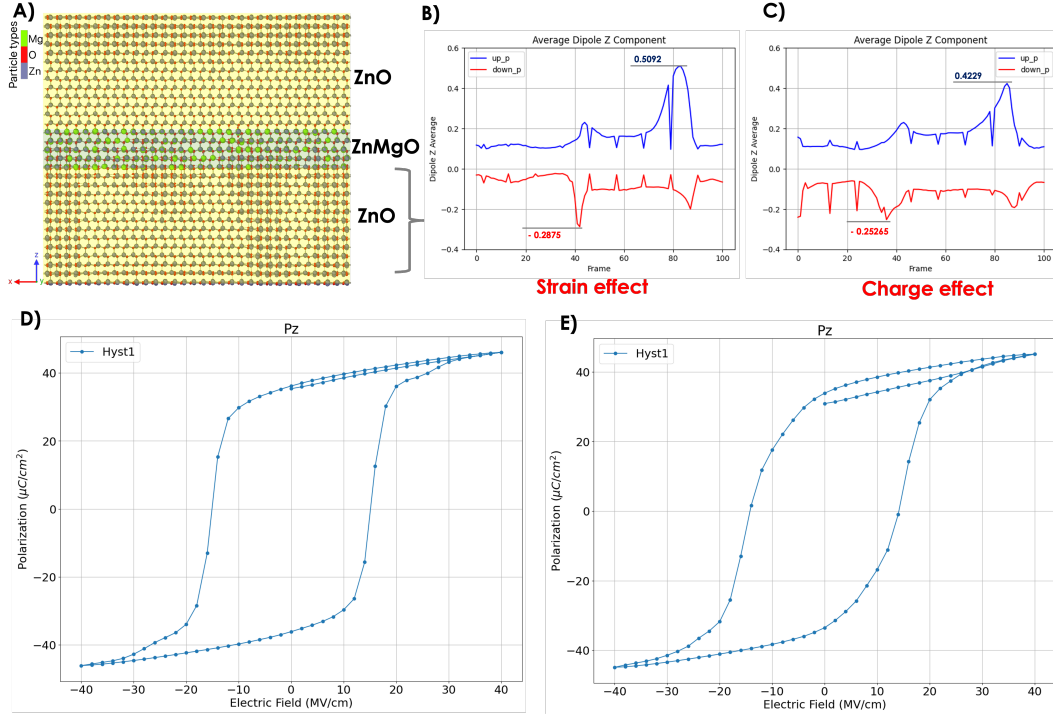


Figure 3.11: (A) Schematic illustration of the heterostructure configuration with layered Mg doping. Charge disproportionation due to Mg leads to variable charges on Zn and Mg throughout the slab, while a pure strain effect assumes same charge on Mg and Zn atoms. (B) Variation in the average local polarization for the respective ‘up’ and ‘down’ polarization states in the bottom ZnO layer for the case of pure strain-effect. (C) Variation in the average local polarization for the respective ‘up’ and ‘down’ polarization states in the bottom ZnO layer in the presence of combined charge and strain effect. We see nucleation and growth of filamentary regions even at the ZnO/ZnMgO interfaces when charge effect is present, suggesting that heterostructuring can reduce the length traversed by these filaments, accelerating the switching time when ZnO is doped with charged dopants. A lower value of the $\mathbf{P}_{\text{fil-head}}$ is again seen due to the presence of charged Mg dopants, which as we showed will result in a lower coercive field compared to pristine ZnO (or the case with pure strain effect). (D) Shows the hysteresis of the heterostructure when only pure strain effects are present (E) Shows the hysteresis of the heterostructure when combined charge and strain effects are present.

3.4 Conclusion

To conclude, we have used large-scale reactive MD simulations and advanced data-analytics to systematically unveil the detailed switching mechanism in the CMOS compatible wurtzite ferroelectrics, such as ZnO. We discovered a 2-step switching process via formation of 1D filamentary structures called inversion boundaries. We further showed that the filaments that propagate have a core-shell structure, with a large polarization in the filament core and small opposing polarization in the filament shell. We hypothesized how the coercive field might be related to the large polarization in the head of the filamentary core, and via a dynamics-by-design approach rationally proved that charged dopants should lower this filament-head polarization and thereby the coercive fields. We further demonstrated that heterostructured ZnO/doped-ZnO superstructures offer a viable way of achieving nanoscale hexagonal ferroelectric capacitors that can not only switch at significantly lower coercive fields than pristine ZnO, but also switch much faster due to multiple nucleation sites at the buried dopant interfaces. Our studies solve a major outstanding challenge in the ferroelectrics community of understanding ferroelectric switching in the CMOS compatible hexagonal ferroelectrics, explaining its high coercive fields, and proposing a rationale approach of designing new materials with significantly lower coercive fields that also switches much faster than current materials. We expect this work to revolutionize the future of low-power electronics.

Chapter 4

Outlook

The research presented in this dissertation has established foundational insights into the atomic scale switching in large-scale molecular dynamics simulations of classical ferroelectric material BaTiO_3 and the emerging hexagonal oxides such as wurtzite ferroelectric material ZnO . This research also provides a deeper understanding of various cases such as inclusion of oxygen vacancies and their implication on the dynamics of ferroelectric domain-walls. Additionally effects of charge, strain and heterostructuring due to inclusion of dopants were also discussed for the wurtzite materials. These insights obtained from the large-scale molecular dynamics simulations at a high degree of spatiotemporal resolution resolve outstanding questions from existing experimental observations. Building upon this atomistic work, we can enhance our knowledge of non-equilibrium dynamics pertaining to domain switching at the device level. This can be achieved by performing larger length and time scale Kinetic Monte Carlo simulations, ultimately facilitating advancements in theoretical as well as practical understandings of these technologically important materials in the presence of heterogeneities. In this outlook, I briefly outline key directions and promising areas for subsequent research efforts to go from atoms-to-devices in ferroelectric based electronic devices, specifically probing out-of-equilibrium dynamics. I also discuss parallels of investigating out-of-equilibrium dynamics in ferroelectric switching and materials-synthesis, and opportunities of applying the combined atomistic, machine-learning and kinetic monte carlo methods to studies of material synthesis.

4.1 Extending Atomistic Simulations to Long-Timescales

Continued advances in simulation techniques are poised to bridge the gap between atomistic ferroelectric simulations and real device timescales. A key frontier is the development of kinetic Monte Carlo (KMC) [Yang et al. \(2017\)](#) frameworks that leverage data-driven insights to access microsecond-to-second dynamics, which remain inaccessible via brute-force molecular dynamics. While molecular dynamics (MD) simulations using high-fidelity potentials (e.g., ReaxFF) can now capture picosecond-to-nanosecond switching events in large ferroelectric models, the stochastic nucleation and growth processes underlying polarization reversal typically unfold over substantially longer timescales.

KMC simulations provide a natural path forward: by coarse-graining the system into discrete states and associated transition events with calculated rates, one can efficiently simulate rare events and long-time behavior. The principal challenge is obtaining accurate transition probabilities or rates for these complex ferroelectric processes. Emerging machine learning approaches offer a promising solution to this challenge. Recent studies demonstrate that reduced-order KMC models can be learned directly from MD trajectories by extracting the essential state-to-state dynamics [Dhakane et al. \(2023\)](#); [Mardt et al. \(2018\)](#); [Xie et al. \(2019\)](#), as described in this thesis.

In the context of ferroelectrics, deriving KMC transition rates from Koopman operator analyses or Markov state models (MSMs) constructed from MD data is particularly promising. The Koopman framework, for instance, can identify slow eigenmodes of polarization dynamics, correlating with metastable domain configurations and transition pathways, thereby providing a quantitative foundation for simulating long-term evolution. Similarly, graph dynamical neural networks have emerged as powerful tools for characterizing complex dynamical state spaces. [Dhakane et al. \(2023\)](#) employed graph neural networks to automatically identify distinct dynamical regimes within BaTiO₃ domain wall simulations, elucidating how local defect environments influence transition kinetics.

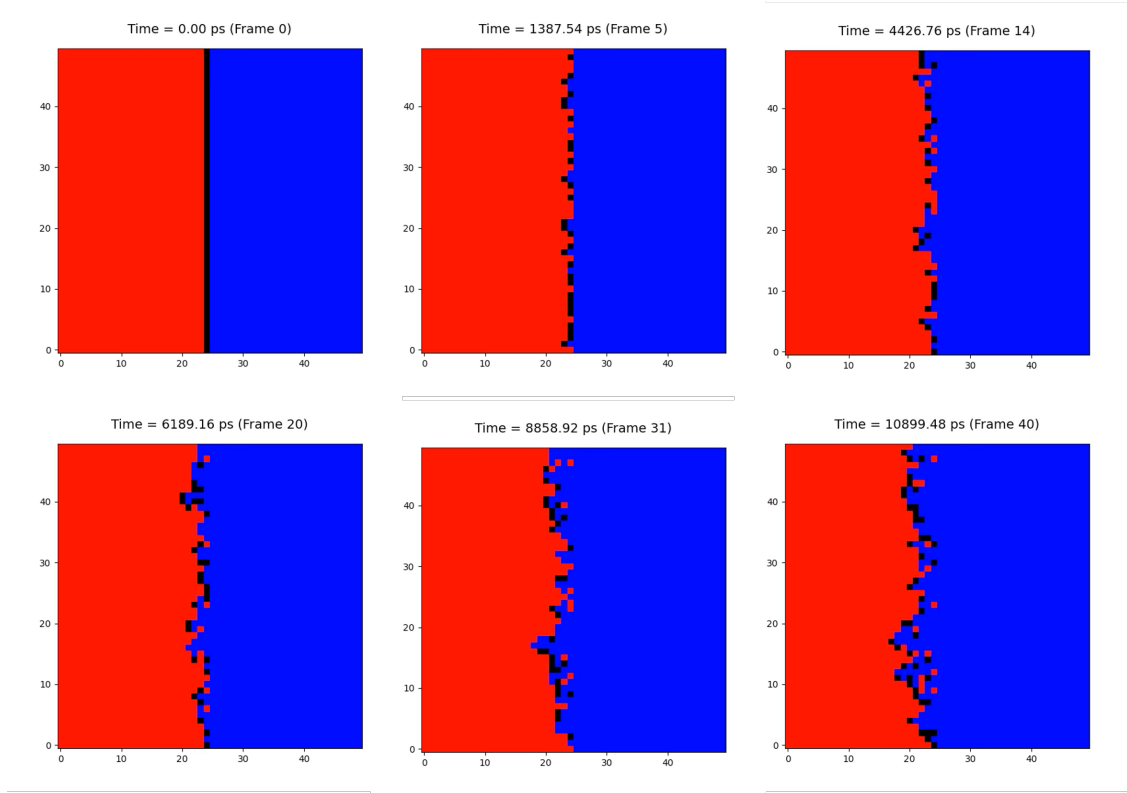


Figure 4.1: This figure shows the domain evaluation in kinetic Monte Carlo simulation using relaxation timescales obtained via graph dynamical network for the pristine BaTiO_3 , where blue and red color represents are the up and down domains while black color represent the domain wall.

Building upon these methods, a KMC simulation engine informed by machine learning could be constructed. The neural network or Koopman-based analysis would yield a network of potential polarization states (such as domain configurations or defect arrangements) along with corresponding transition probabilities. Such a data-driven KMC approach would enable ferroelectric simulations to realistically access microsecond timescales and beyond, allowing statistically rigorous investigations into phenomena like domain wall roughness, creep, fatigue, and aging. even in the presence of different types of heterogeneities, such as point-defects, doping or grain-boundaries.

We employed the KMC simulation using JAX [Schoenholz and Cubuk \(2020\)](#) with the Koopman matrix obtained from the MSMs. Results shows the long -term dynamics obtained from the KMC simulation on the 2D grid for the pristine system of the BaTiO₃. Following figure 4.1 shows the domain evaluation over the time of the and the snapshots of the KMC simulation. We see roughening of the domain wall over time, with critical length-scales comparable to what is seen in experiments [Paruch et al. \(2005\)](#). In principle, this can be extended to include electric-fields, using Koopman matrices we have extracted for field-dependent switching in Chapter-2.

4.2 Material Synthesis

As the frontiers of computational materials science continue to advance, the ability to simulate, understand, and ultimately control dynamical transformations in functional materials has grown considerably. In ferroelectrics, much progress has been made in capturing atomic-scale polarization switching and domain wall dynamics. At the same time, materials synthesis—long guided by thermodynamics and intuition—is beginning to benefit from predictive simulations that link external stimuli to structural evolution. What emerges from these parallel developments is a compelling opportunity to unify the physics of field-driven switching with that of material formation and transformation under thermochemical control. This outlook explores the conceptual, mechanistic, and methodological common ground between ferroelectric switching and materials synthesis (4.2). By highlighting their shared dependence on external conditions, energy landscapes, phase stability, and engineered

outcomes, we set the stage for a new paradigm of ‘*dynamics-by-design*.’ Here, simulation tools not only reveal how materials respond to their environments but also offer pathways to direct and optimize those responses toward desired functionalities—whether in memory devices or synthesized phases.

4.2.1 Structural Reconfiguration Under External Stimuli

A central theme unifying ferroelectric switching and material synthesis is structural reconfiguration driven by external stimuli. In ferroelectric and ferromagnetic systems, domain reorientation—manifested as polarization or magnetization switching—occurs in response to external electric or magnetic fields, respectively. Similarly, material synthesis processes such as chemical vapor deposition (CVD) or hydrothermal methods rely on precisely controlled temperature, pressure, and chemical environments to drive atomic or molecular rearrangements, enabling the formation of desired structures or phases. Both processes fundamentally represent transitions between stable or metastable states triggered and guided by carefully controlled external conditions.

4.2.2 Critical Role of Energy Landscapes

Understanding and navigating the energy landscapes is crucial in both ferroelectric switching and material synthesis. Ferroelectric switching involves overcoming energy barriers separating different polarization states. These barriers can be modulated by external factors such as temperature, electric field strength, or doping concentration. Likewise, the synthesis of new materials, whether crystalline or amorphous, necessitates surmounting energetic thresholds associated with nucleation, phase transitions, and growth processes. Thus, achieving a target ferroelectric state with a pre-defined polarization domain or forming a new synthesized phase relies on precise control over how and under what conditions these energy barriers are traversed. This commonality underscores the importance of quantifying energy landscapes to strategically manipulate and optimize outcomes in both domains.

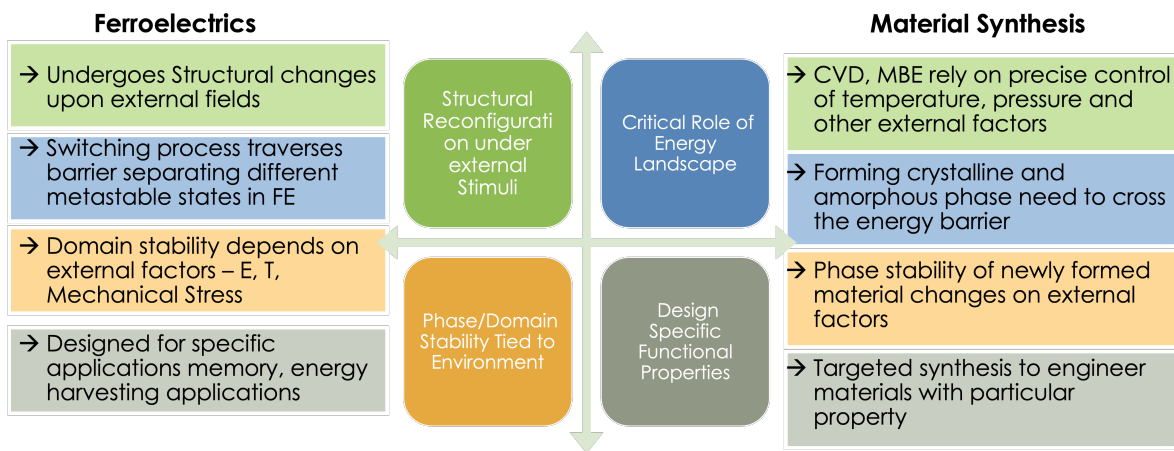


Figure 4.2: This figure provide an overview of the commonality in the ferroelectric switching.

4.2.3 Phase and Domain Stability Tied to Environmental Conditions

Stability in ferroelectric domains and synthesized materials alike is intimately linked to environmental conditions. For ferroelectrics, domain configurations depend critically on external parameters such as electric field intensity, mechanical stress, and temperature; even slight modifications can induce transitions across stability thresholds, altering domain orientation or polarization direction. In material synthesis, similar environmental sensitivities exist: subtle variations in precursor concentration, temperature gradients, or pressure conditions can result in significantly different final phases or microstructures. Recognizing these parallels emphasizes the need for rigorous control and predictive modeling to maintain desired configurations or to deliberately induce controlled transformations.

4.2.4 Design for Specific Functional Properties

Another compelling parallel between ferroelectric switching and material synthesis is the intentional design for targeted functional properties. Ferroelectric and multiferroic devices are engineered to leverage controllable polarization or magnetization switching mechanisms, essential for applications in sensors, non-volatile memory, and energy harvesting technologies. Correspondingly, synthesis methodologies aim at producing materials with specific, optimized attributes such as enhanced conductivity, magnetism, or catalytic activity. Both fields embody the concept of "engineering" the microstructural and atomic-level arrangements of materials to achieve particular functional outcomes, be it efficiently switchable domains in a ferroelectric device or a novel synthesized phase with superior or desired performance characteristics.

Hence, all techniques we have developed in this thesis for ferroelectrics can be applied to obtain unprecedented insights into material-synthesis, a direction of research that presents an unparalleled opportunity for the discovery of new synthesis science, in the future.

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Vita

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During his master's program, Abhijeet interned at Oak Ridge National Laboratory, where he conducted molecular dynamics simulations to investigate electron-beam interactions with the amorphous Si-Ge interface and dopant dynamics in CMOS materials. This internship ignited his interest in computational materials research, particularly in ferroelectrics, deep learning and advanced simulation techniques.

Abhijeet is currently pursuing a PhD in Data Science and Engineering through a joint program at the Bredesen Center, a collaboration between the University of Tennessee Knoxville and Oak Ridge National Laboratory. His research interests lie at the intersection of computational materials science and artificial intelligence/machine learning (AI/ML), with a focus on using advanced simulations and deep learning methods to better understand complex material behaviors.