

Multi-physics Properties in Topologically Nanostructured Ferroelectrics

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Chapter 1

Introduction

1.1 Multi-physics properties in nanostructured ferroelectrics

Ferroelectric materials such as PbTiO_3 and BaTiO_3 are increasingly being considered as critical components in many advanced technologies, such as nonvolatile random access memory (FeRAM) devices [1,2], sensors, actuators, and transducers in micro(nano)electromechanical systems (MEMS/NEMS) [3,4], due to spontaneous electric polarization and related electromechanical properties including a piezoelectric response and high dielectric constant. Such applications crucially require a fundamental understanding of the ferroelectric domain formation, the susceptibilities and routes to control and manipulate the polarization in the materials, which originate from the interactions between ferroelectric polarization and mechanical and/or electric multi-fields. Ferroelectric materials change from the paraelectric phase to the ferroelectric phase when the temperature is below their Curie temperature, where spontaneous polarization characteristically exists even in the absence of any external field. The phenomenon stems from a change of crystal structure and lattice parameters, i.e., deformation, so that the polarization is intrinsically coupled with mechanical excitation. In addition, the spontaneous polarization is switchable under an applied

external electric field. Therefore, ferroelectric materials interact with both electric and mechanical fields through cross-coupling between ferroelectric polarization and ferroelastic strain, i.e., multi-physics properties in ferroelectric materials.

Recent significant advances in micro- and nanoscale fabrication techniques have obtained nanostructures of ferroelectric materials, such as thin films [5-7], nanowires [8-14], nanodots and nanoislands [15-19]. Ferroelectric nanostructures naturally possess a high surface-to-volume ratio. Recent studies have shown that the screening of a depolarization field in confined ferroelectrics with sizes ranging from several to tens of nanometers is enhanced through the alignment of polarization along the free surfaces [20-22]. The dominant depolarization field results in a formation of closed-flux (vortex) polarization ordering in nanodot [21] or the stripe polarization domains in thin films [23,24], which are entirely distinct from the bulk counterpart. The formation of such polarization patterns result in unusual multi-physics properties in the ferroelectric nanostructures that are highly promising to obtain new functionalities and quite helpful for further improvement ferroelectric devices. Thus, studies on multi-physics properties in ferroelectric nanostructures have aroused a huge attention in recent years. However, research on multi-physics properties of ferroelectrics has still limited to nanostructures with typical and simple shapes, such as thin-films, nanowires, and nanodots.

Beyond such conventional ferroelectric nanostructures, topologically nanostructured ferroelectrics that possess complicated internal shapes and geometries, such as hierarchical nano-metamaterials and nano-porous structures, have recently been achieved [25-27]. Hierarchical nano-metamaterials, which are higher-order nanostructures of ferroelectrics, are regarded as combinations of several basic nano-components, including nanodots, nanowires and thin films, i.e. a bottom-up approach. While nano-porous structures are regarded as sculptured thin films or solids with characterized features in nanoscale, i.e. a top-down approach. Topologically nanostructured ferroelectrics thus emerges as a bridge that connect these two distinct strategies, as illustrated in Fig. 1.1. The diversity and intriguing characteristics of topologically nanostructured ferroelectrics are expected to bring about distinct polarization patterns in comparison with that in the conventional simply shaped nanostructures, resulting in unusual nanostructure-polarization correlation.

Consequently, anomalous multi-physics properties are expected to emerge in the topological nanostructures of ferroelectrics. On the other hand, multi-physics properties of ferroelectrics in basic nano-components from the bottom-up approach have been investigated using *ab initio* (first-principles) density functional theory (DFT) calculations, however, the heavy computational load imposes restrictions on the number of atoms and temperature in a simulation system that make it difficult for further investigation on complicated ferroelectric nanostructures. To avoid this difficulty and provide a complete view on the multi-physics properties in topologically nanostructured ferroelectrics, a distinct strategy from the top-down approach is essential since the recent developed phase field model has successfully applied and provided an unprecedented look at the formation and behavior of polarization in ferroelectric at mesoscopic viewpoint. In this thesis, multi-physics properties of topologically nanostructured ferroelectrics are investigated from a top-down approach using phase field modeling based on the Ginzburg-Landau theory.

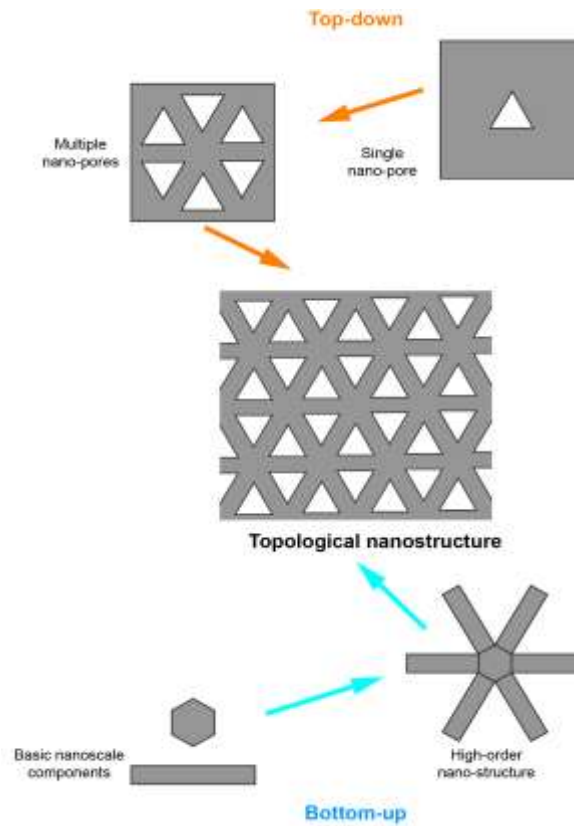


Figure 1.1. Topologies of ferroelectric nanostructures from bottom-up to top-down approaches.

1.2 Multi-physics properties in topologically nanostructured ferroelectrics: towards top-down approach

For systematic understanding, it is necessary to extract structural characteristic from the sizes and shapes to the distribution and connection of pores embed in the topological structures, and study multi-physics properties that intrinsically emerge in the structures. In the present thesis, I firstly start to investigate the multi-physics properties in ferroelectric nanostructure included a single isolated pore. Figure 1.2 shows typical topologies of nanostructures with a single pore embedded inside ferroelectrics, i.e. triangular, square, hexagonal, circle and sharp ellipse nano-porous structures. Due to the structural discontinuity, it has been expected that ferroelectricity in such topological nanostructures response to an external field differently from that of conventional homogeneous counterparts and bulk materials since the mechanical field is favorable to concentrate near the pores, and thus significantly affects the ferroelectricity. In particular, a singularly high stress characteristically concentrates near the tip of a sharp ellipse pore, which are regarded as a crack in realistic circumstance [28-30]. High stress field concentrated at a crack tip may cause polarization switching, thereby changing the local electrical domain structure. The change in local domain structure, in turn, changes the internal electric and internal stress fields near the crack tip due to the cross-coupling between polarization and mechanical field [31-42]; this provides an ideal playground to probe the multi-physics properties. Therefore, it is essentially important to investigate the mechanical behavior of cracks in nanoscale ferroelectric materials, in order to fundamentally understand multi-physics properties of ferroelectric with single and isolated topological nanostructure.

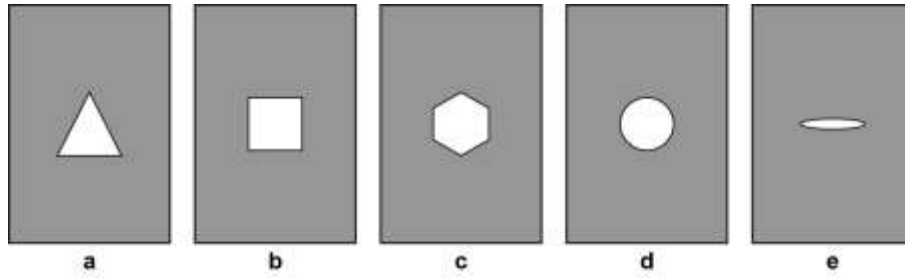


Figure 1.2. Topologies of ferroelectric nanostructures with a single pore: (a) triangular, (b) square, (c) hexagonal, (d) circle and (e) sharp ellipse nano-porous structures.

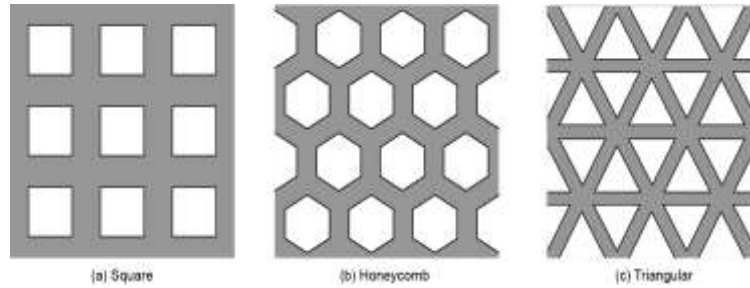


Figure 1.3. Periodic nano-porous ferroelectric structures: (a) Square, (b) Honeycomb and (c) Triangular nanostructures.

To investigate the multi-physics properties in further complicated topological nanostructures, numerous nano-pores are included and arranged periodically in ferroelectric materials. Figure 1.3 shows the common periodic nano-porous ferroelectric structures, of which architectures are belong to a completed set of 2D Archimedean lattices [43]. The appearance of several nano-pores accommodated in topologically nanostructured ferroelectric is predicted to create complex polarization domain patterns due to the mutual interplay among concentration mechanical fields near the pores and significant cross-coupling between ferroelectric polarization and ferroelastic strain. In addition, the structural diversity and intriguing characteristics of periodic nano-porous structures and complex polarization domain patterns would response anomalously to a uniform external field, providing space for a systematic study of the interplay between topological nanostructure and ferroelectricity. Therefore, it is necessary to elucidate the

formation of polarization configuration and probe its multi-physics electromechanical response in the periodic nano-porous ferroelectric nanostructures.

In nano-porous structured ferroelectrics, surfaces, where the discontinuity of electric and mechanical fields occurs and dominates, are considered as interfaces between ferroelectric and vacuum phases. Ferroelectricity may interact with a distinct field at an interface when the vacuum areas in nano-porous structured ferroelectrics are filled by another materials, i.e. nanocomposites (Fig. 1.4), the most important of which is ferromagnetic materials. In ferroelectric/ferromagnetic composites, ferroelectricity can interact with magnetic field that is based on the incorporation of magnetostrictive and piezoelectric effects through interfacial strain mediation, i.e. strain-mediated magnetoelectric effects. Topological nanostructures at the interfaces are thus momentous for multi-physics properties of ferroelectric in nanocomposites. In addition, the magnetoelectric coupling is crucially dependent on domain-level processes. In particular, as the constituent materials approach nanoscale dimensions, the ferroelectric and ferromagnetic domain structures are both altered, bringing about properties distinct from those of their bulk counterparts [20,44]. Therefore, details of simultaneous polarization and magnetization domain structures at the nanometer scale is worth investigating to understand multi-physics properties of ferroelectric/ferromagnetic nanocomposites.

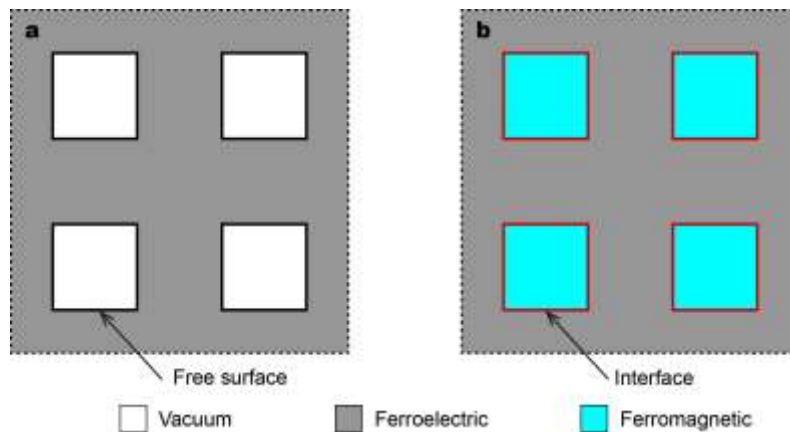


Figure 1.4. Topologically nanostructured ferroelectrics with pores filled by different materials: (a) Vacuum and (b) ferromagnetic (multiferroic nanocomposites).

1.3 Ginzburg-Landau theory based modeling for multi-physics properties

Breakthrough applications of ferroelectric materials require knowledge of both the static structure and the dynamics of field-dependent responses. It is, however, difficult to experimentally observe the dynamics of polarization behavior under external fields or precisely measure the small changes in spontaneous polarization. Advance in phase field modeling based on the Ginzburg-Landau theory now provides an unprecedented look at the temporal and spatial evolution of polarization under external fields. The Ginzburg-Landau theory was proposed on the basis of the fundamental principles of thermodynamics and kinetics to describe the dynamic behavior of ferroelectrics using a polarization vector as an order parameter [45-47]. The polarization vector $\mathbf{P} = (P_1, P_2, P_3)$ is used to describe the free energies of ferroelectric phases in the phase-field model. The total free energy F , of ferroelectric nano-metamaterial is obtained by integrating the total free energy density f , over the entire volume V , of the system [48]:

$$F = \int_V f dV = \int_V (f_{\text{Land}} + f_{\text{grad}} + f_{\text{elas}} + f_{\text{coup}} + f_{\text{elec}}) dV \quad (1)$$

where f_{Land} , f_{grad} , f_{elas} , f_{coup} , and f_{elec} represent the Landau free energy density, gradient energy density, pure elastic energy density, coupling energy density, and electrostatic energy density, respectively. The temporal evolution of a polarization field toward its thermodynamic equilibrium state is driven by a decrease of the total free energy in the ferroelectric system, which is described by the time-dependent Ginzburg-Landau (TDGL) equation:

$$\frac{\partial P_i(r, t)}{\partial t} = -L \frac{\delta F}{\delta P_i(r, t)}, \quad (2)$$

where t denotes time, L is a kinetic coefficient, $r = (x_1, x_2, x_3)$ denotes the spatial vector,

and $\delta F/\delta P_i(\mathbf{r},t)$ denotes the thermodynamic driving force for the evolution of polarization. Phase field modeling based on the Ginzburg-Landau theory has been commonly used to study domain structures in ferroelectric materials, and polarization switching under static electric field and/or mechanical loading [49-52]. In recent years, phase field modeling has been extended for simulations in real-space, which has enabled any ferroelectric structures with arbitrary geometries and boundary conditions to be addressed [53,54]. However, there are few studies focusing on the multi-physics properties of nanostructured ferroelectrics.

Ferroelectric materials, generally, interact with not only electric field, but also with mechanical field. Such mechanical and/or electric multi-fields interactions allow symmetry breaking of the rotationally invariant switching field and cause a variety of complicated instability phenomena in ferroelectric systems, e.g., super switching of in-plane ferroelectric nanodomains in strained thin films [23], labile and ultrafast switching of ferroelastic nanodomains [24], and ferroelectric polarization reversal via successive ferroelastic transitions [55]. The instability in ferroelectric systems, viz., a rapid or catastrophic change in polarization ordering or reversal of the polarization vector with respect to the multi-fields that shift the system to another configuration with lower energy, essentially characterizes the polarization behavior of materials and leads to diverse functionalities or the critical malfunction of devices. Loss of stability in the polarization configuration becomes the general mechanism that underlies a wide variety of macroscopic and microscopic features of considerable importance with respect to the behavior of ferroelectric materials under multi-fields excitations. Therefore, understanding the nature of the instability provides a deep insight into multi-physics properties of ferroelectric materials. Although the phase field model can be used to explore the temporal and spatial evolution of polarization, the absence of theory to describe instability in ferroelectric systems makes it difficult to capture the onset of instability events that occur not only globally but also more often locally. Therefore, a new analytical criterion for instability in ferroelectrics is essential to detect their onset, from local to global events.

1.4 Overview of this thesis

In this study, I investigate the multi-physics properties in topologically nanostructured ferroelectrics under mechanical and/or electric multi-fields from mesoscopic point of view by using phase-field modeling based on the Ginzburg-Landau theory. In addition, a new technique is developed to elucidate nature of various types of instability in arbitrary ferroelectric systems, which is helpful to further study on multi-physics properties in topologically nanostructured ferroelectrics in the future. This thesis is organized as follows.

In chapter 2, the mechanical behavior of cracks in nanoscale ferroelectrics, where a complicated cross-coupling between the polarization and singular stress field occurs, are investigated. The role of cross-coupling between polarization and mechanical field in the behavior of cracks in nanoscale ferroelectrics is also discussed.

In chapter 3, ferroelectricity in periodic nano-porous structures, which are designed based on the architectures of Archimedean lattices, is studied. A closed-relation between topological nanostructure and macroscopic ferroelectric properties is provided and discussed.

In chapter 4, multi-physics of polar and toroidal electromechanical responses in periodic nano-porous ferroelectrics under mechanical excitation are investigated using phase-field modeling based on Ginzburg-Landau theory. I also discuss the effect of the topological nanostructures on the piezoelectric and piezotoroidic properties.

In chapter 5, multi-physics of magnetoelectric coupling in ferroelectric/ferromagnetic nanocomposites is investigated. Discussion on tuning magnetoelectric coupling by designing topological nanostructures embedded in ferroelectric is provided.

In chapter 6, a criterion for instability in continuum ferroelectric system is proposed on the basis of the Ginzburg-Landau theory. The proposed theory is validated by application of the criterion to domain switching and successive ferroelastic transitions in nanostructured ferroelectric.

Finally, conclusion of this thesis is presented in Chapter 7.

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Chapter 2

Unusual toughening in nanoscale ferroelectrics under switching of polarization vortices

2.1 Introduction

Ferroelectric materials are at the heart of many advanced technologies, such as nonvolatile random access memory (FeRAM) devices, sensors, actuators, and transducers in micro(nano)electromechanical systems (MEMS/NEMS) [1-4], due to their large ferroelectricity and related electromechanical properties including a large piezoelectric response and high dielectric constant. However, their inherent brittleness and low fracture toughness often lead to critical failure and malfunction of such devices [5-7] through the propagation of cracks that are typically formed during the growth or production processes [8-12].

The mechanical behavior of cracks in ferroelectric materials is generally complicated due to coherent nonlinear interactions between the mechanical and electric fields [13-15]. The intense stress concentration with the form of a singular field at a crack tip and significant cross-coupling between the ferroelectric spontaneous polarization and mechanical stress/strain induces local polarization switching near the tip [16-27], which often shields (or anti-shields) the crack from applied mechanical loads and thus apparently toughens (or weakens) these ferroelectric materials [17,18,25,27]. Therefore, an understanding of the mechanical behavior of cracks in

ferroelectric materials is of central importance, not only for the reliability of ferroelectric devices, but also with respect to fundamental physics and mechanics. To date, the mechanical behavior of cracks and the polarization switching characteristics have been intensively studied both experimentally and theoretically [16-27], which has mostly elaborated on macroscale ferroelectrics where the cracks are simply assumed to behave in a uniform (monodomain) polarization.

Recent significant advances in manufacturing technology have enabled us to obtain nanostructured ferroelectric materials, such as thin films, nanowires, and nanodots. In such nanoscale ferroelectrics, the charge that appears on a surface due to the termination of electric dipoles generates a counter electric field inside the nanostructures (depolarization field) [4], which destabilizes the normal rectilinear polarization and instead leads to the formation of polarization vortices [28-43]. The clockwise-and-counterclockwise arrangement of polarization vortices that emerges to cover the entire structure of the nanoscale ferroelectric and the spatially continuous rotation of polarization vectors no longer allow us to understand the ferroelectric properties on the basis of conventional domains [40,41]. In addition, the formation of polarization vortices induces a complex internal stress distribution in nanoscale ferroelectrics, which is attributed to the coupling between polarization and stress [43]. Therefore, in the presence of a crack, such a spatially inhomogeneous polarization field of vortices may interact with the singular stress field near the crack tip in a totally different way from that with nearly-homogeneous (single-domain) polarization in macroscale ferroelectrics, and which would further complicate the mechanical behavior of crack. However, the mechanical behavior of cracks in nanoscale ferroelectrics has not yet been clarified.

The Ginzburg-Landau theory was proposed on the basis of the fundamental principles of thermodynamics and kinetics to describe the dynamic behavior of ferroelectrics using a polarization vector as an order parameter [44-50]. Phase field modeling based on the Ginzburg-Landau theory has been commonly used for the study of cracks in ferroelectric materials [51-54] because phase field modeling achieves self-consistency of the electrostatic and elastic interactions, which is essential to describe the electric and mechanical behavior near a crack tip [25,27,51-54]. In recent

years, phase field modeling has been extended for simulation in real-space [51,55-61], which has enables us to address any ferroelectric structures with arbitrary geometries and boundary conditions, and has successfully reproduced the polarization vortices in nanoscale ferroelectrics [40,41]. Therefore, real-space phase-field modeling is suitable and effective for the study of cracks in nanostructured ferroelectrics.

In this chapter, I investigate the mechanical behavior of cracks in nanoscale ferroelectrics, where a complicated coupling between the polarization vortices and singular stress field is expected, using real-space phase-field simulations based on the Ginzburg-Landau theory. I find a dramatically large toughening effect in the nanoscale ferroelectrics. The anomalous toughening is shown to be due to an unusual switching of polarization vortices that is no longer localized near the crack tip, but expands to the entire nanoscale ferroelectrics. I further demonstrate that a strong cross-coupling between polarization and mechanical strain plays a central role in the unusual switching of the polarization vortices.

2.2 Simulation procedure

Fig. 2.1a shows a nanoscale specimen of ferroelectric PbTiO_3 with plate geometry including a single pre-crack at the center. The polarization vortices are typically observed in ferroelectric nanocomponents with sizes ranging from several to tens of nanometers [36,40]; therefore, the dimensions of the nanoscale specimen in the x_1 , x_2 , and x_3 directions were set to 27, 44, and 2 nm, respectively. An impermeable crack with a length of 7 nm is located at the center and goes through in the x_3 direction. Fig. 2.1b shows the details of the mesh partition of the nanoscale specimen for phase-field simulations. The model consists of 3124 brick elements and 6524 nodes. The region near the crack tip, where stress concentration is expected, is treated using a finer mesh with a size of 0.1 nm. Different mesh divisions were carefully tested and the present mesh division was confirmed to be sufficiently fine to describe the mechanical and ferroelectric behavior of a crack. To realize bare free surfaces of the specimen, the electrical boundary conditions on all surfaces are set to be open-circuited, i.e. $\mathbf{D} \cdot \mathbf{n} = 0$,

so that the depolarizing field from the polar surfaces, which is the main source of the polarization vortices in nanocomponents, is explicitly taken into account.

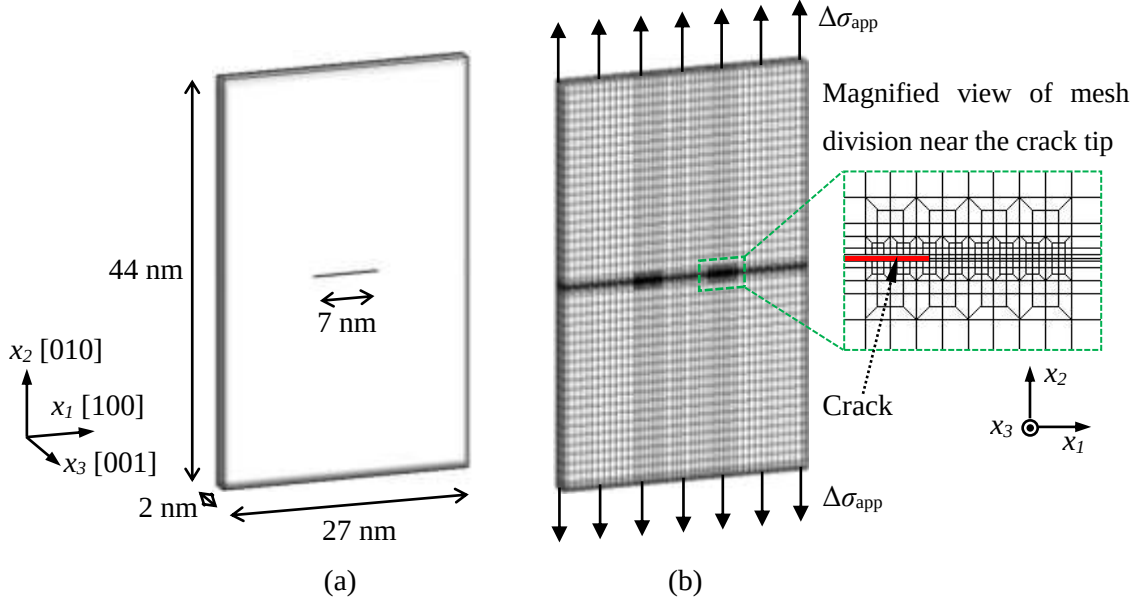


Figure 2.1. (a) Geometry and dimensions of nanoscale ferroelectric specimen with an impermeable crack. The crack is located at the center. (b) Mesh partition and loading conditions for the nanoscale specimen. For tensile tests, a uniform tensile load along the x_2 direction is applied on the top and bottom of the nanoscale specimen.

The nanoscale specimen is quenched from the cubic paraelectric state into the tetragonal ferroelectric state. To obtain the thermodynamic equilibrium state of the nanoscale specimen without an external load, a random polarization perturbation with a small magnitude of 10^{-3} C/m² is applied to each node as an initial state and the time-evolution of polarization $\mathbf{P}$ is simulated by iteratively solving the time-dependent Ginzburg-Landau equation until the change of polarization with time below 1.0×10^{-6} C/m². A backward Euler scheme and Newton iteration method are used for the time integration and nonlinear iteration, respectively, with a normalized time step of $\Delta t^* = 0.02$, where $t^* = t/(\alpha_0 L)$.

The tensile test is performed by application of a small uniform tensile stress $\Delta\sigma_{app}$,

along the x_2 direction on the top and bottom of the specimen step-by-step (as shown in Fig. 2.1b). At each loading step, the thermodynamic equilibrium state is calculated in the same manner as that without external stress.

2.3 Results and discussion

2.3.1 Polarization vortices in a nanoscale specimen

Figs. 2.2a and b show the distributions of spontaneous polarization and internal stress, respectively, in the nanoscale PbTiO_3 specimen at the thermodynamic equilibrium state under no external load. The spontaneous polarization is arranged in a head-to-tail manner and forms circular closed-flux patterns, namely, polarization vortices (as shown in Fig. 2.2a). Two vortices, which consist of counter-clockwise and clockwise vortices, are formed in the nanoscale PbTiO_3 specimen. The characteristics of the polarization vortices obtained here are consistent with those of preceding studies [28-43], which indicates the reliability of present phase-field simulations. Song et al. [43] showed that the formation of polarization vortices induces an internal stress distribution in nanoscale ferroelectrics, I also find the consistent internal stress distribution in the present nanoscale specimen (as shown in Fig. 2.2b). The stress σ_{11} is concentrated near the center of the vortices, while the stress σ_{22} is concentrated not only at the center of vortices, but also in the vicinity of the crack tips.

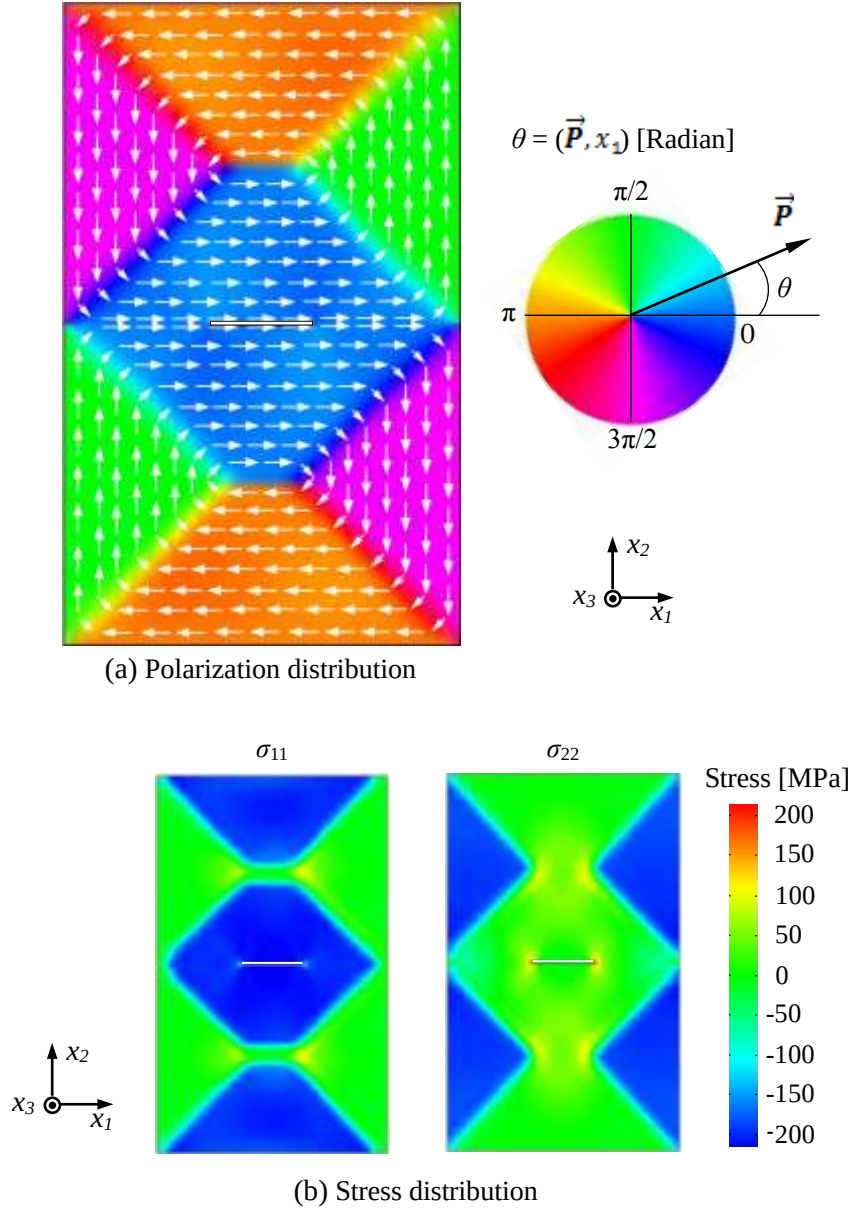


Figure 2.2. Distribution of (a) polarization and (b) stress σ_{11} and σ_{22} in the x_1 - x_2 plane of the nanoscale PbTiO_3 specimen without an external load.

2.3.2 Mechanical behavior of a crack in a nanoscale PbTiO_3 ferroelectric

Fig. 2.3 shows the normal stress σ_{22} as a function of the distance from the crack tip r , along the x_1 direction in the nanoscale PbTiO_3 specimen, where the scales are both logarithmic. The normal stress is intensively concentrated near the crack tip, and forms

a singular field that is inversely proportional to the square root of the distance, $\sigma_{22} = K_I / \sqrt{2\pi r}$, regardless of the applied tensile load levels, as linear elastic fracture mechanics indicates [62]. Here, K_I is the stress intensity factor that represents the intensity of a singular stress field. Fig. 2.4 shows the stress intensity factor K_I , as a function of the applied external load σ_{app} , for the nanoscale PbTiO_3 specimen. The internal stress distribution shown in Fig. 2.2b results in a non-zero K_I value, even in the absence of an external load. K_I increases linearly with the applied tensile load. When the applied tensile load reaches $\sigma_{app} = 40$ MPa, K_I drops dramatically from $0.62 \text{ MPa m}^{-1/2}$ to $0.21 \text{ MPa m}^{-1/2}$, with a drop magnitude of $\Delta K_I = 0.41 \text{ MPa m}^{-1/2}$. This drop of K_I indicates that the concentrated stress near the crack tip is released, and an additional load is required to again increase K_I . The fracture mechanics indicate that the crack becomes mechanically unstable and starts to propagate just when the stress intensity factor reaches a constant fracture toughness of the material; therefore, the dramatic decrease of K_I contributes to an apparent toughening of the crack [25,27].

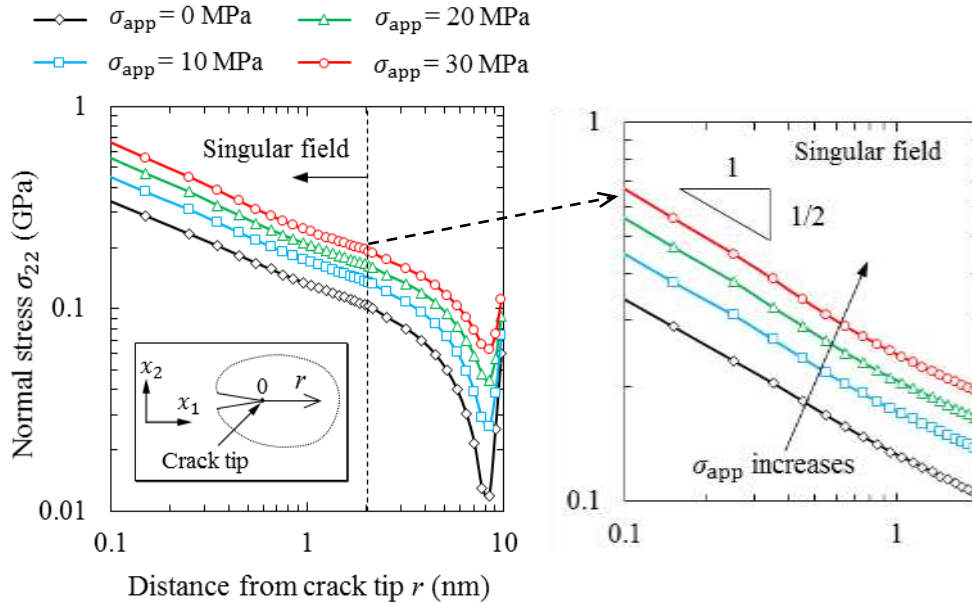


Figure 2.3. Distribution of normal stress along the x_1 direction from the crack tip of the nanoscale PbTiO_3 specimen under various tensile loads of $\sigma_{app} = 0, 10, 20$, and 30 MPa.

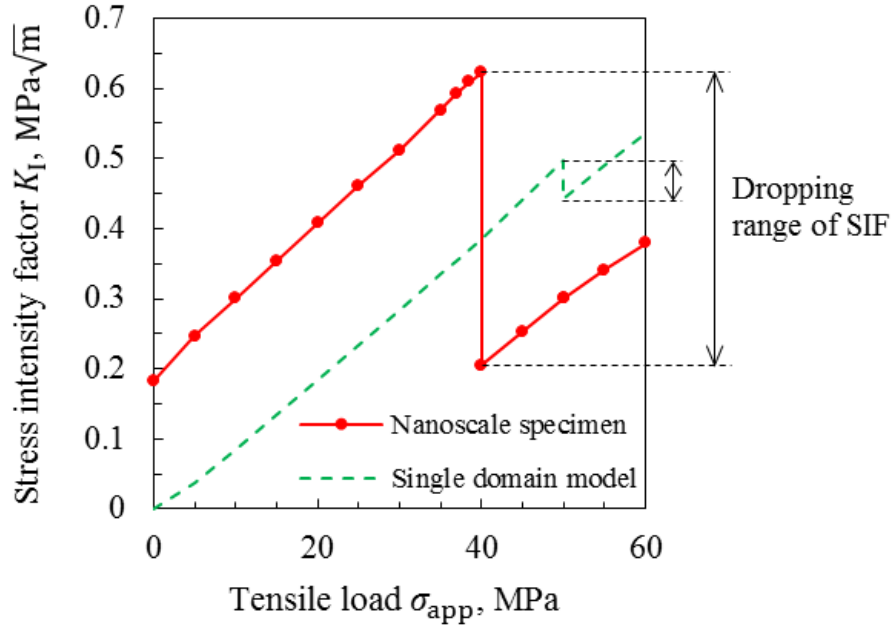


Figure 2.4. Relationship between the tensile load and stress intensity factor for the nanoscale specimen and the single-domain model.

To demonstrate the crucial role of the polarization vortices that appear in the nanoscale PbTiO_3 specimen, the same tensile simulations were additionally performed for a single-domain model of the same shape and size of the specimen by artificially applying a short-circuit electrical boundary condition to the specimen surfaces to neglect the effect of the depolarization field [27,51]. The dashed line in Fig. 2.4 shows that K_I in the single-domain model also increases linearly with the tensile load, and drops at $\sigma_{app} = 50$ MPa. However, the drop magnitude of the single-domain model is $\Delta K_I = 0.06 \text{ MPa}\sqrt{\text{m}}$, which is approximately 7 times smaller than that of the present nanoscale specimen with polarization vortices. This indicates that the polarization vortices release stress more effectively, which results in more dramatic toughening of the crack than the single-domain model. It should be noted here that such a small drop of K_I is similarly observed in a macroscale ferroelectric specimen [27], because the vicinity of crack where the stress is concentrated consists of a single-domain, such as with the present single-domain model. Therefore, the anomalously strong toughening is characteristic of nanoscale ferroelectrics with polarization vortices.

2.3.3 Switching of polarization vortices in nanoscale ferroelectrics

Fig. 2.5a shows the polarization distribution before and after the drop of K_I for the nanoscale PbTiO_3 specimen. The polarization vortices before the drop of K_I remain almost unchanged in comparison with those that appear without an external load. However, the initial 2-vortices state is entirely transformed into a 6-vortices state after the drop of K_I , which indicates that polarization switching occurs. The 6-vortices state is maintained and remains stable even at the higher tensile load. For comparison, the polarization distribution in the single-domain model is shown in Fig. 2.5b. Polarization switching is induced by the tensile load, but the switching zone is highly confined to the vicinity of the crack tip. No substantial change is observed when the tensile load increases. Such localized polarization switching is commonly obtained in macroscale ferroelectric specimens [25-27,51]. Therefore, the entire polarization switching through increase of the polarization vortices is characteristic of nanoscale ferroelectrics.

Figs. 2.6a-f illustrate the temporal evolution of polarization switching in the nanoscale PbTiO_3 specimen under a tensile load of $\sigma_{\text{app}} = 40$ MPa. At the beginning of the evolution ($t^*=0$), the two polarization vortices of the nanoscale specimen are similar to those that appear without an external load, as shown in Fig. 2.6a. However, polarization switching then occurs from the crack tips, as shown in Fig. 2.6b, where the polarization vectors change their orientations towards the vertical direction. The switching zones propagate quickly in the x_2 direction from the crack tips (Fig. 2.6c). The switching zones gradually expand, while the polarization vectors in the switched zones simultaneously adjust their orientations towards the vertical direction (Figs. 2.6c and d). Fig. 2.6d shows that the switching zones divide the vortex structure of the upper part of the nanoscale specimen into three vortices. A similar tendency is observed in the lower part of the nanoscale specimen because of the symmetry. The 6 vortices emerge in the nanoscale specimen when the polarization vectors in the switched zone are parallel or anti-parallel to the x_2 direction (Fig. 2.6e). Finally, the polarization vectors stop changing their orientations, and the evolution then reaches steady-state (Fig. 2.6f). Fig. 2.6 shows that the polarization transformation from the 2-vortices state to the 6-vortices state occurs in the nano-scale specimen as a result of polarization switching induced by mechanical load.

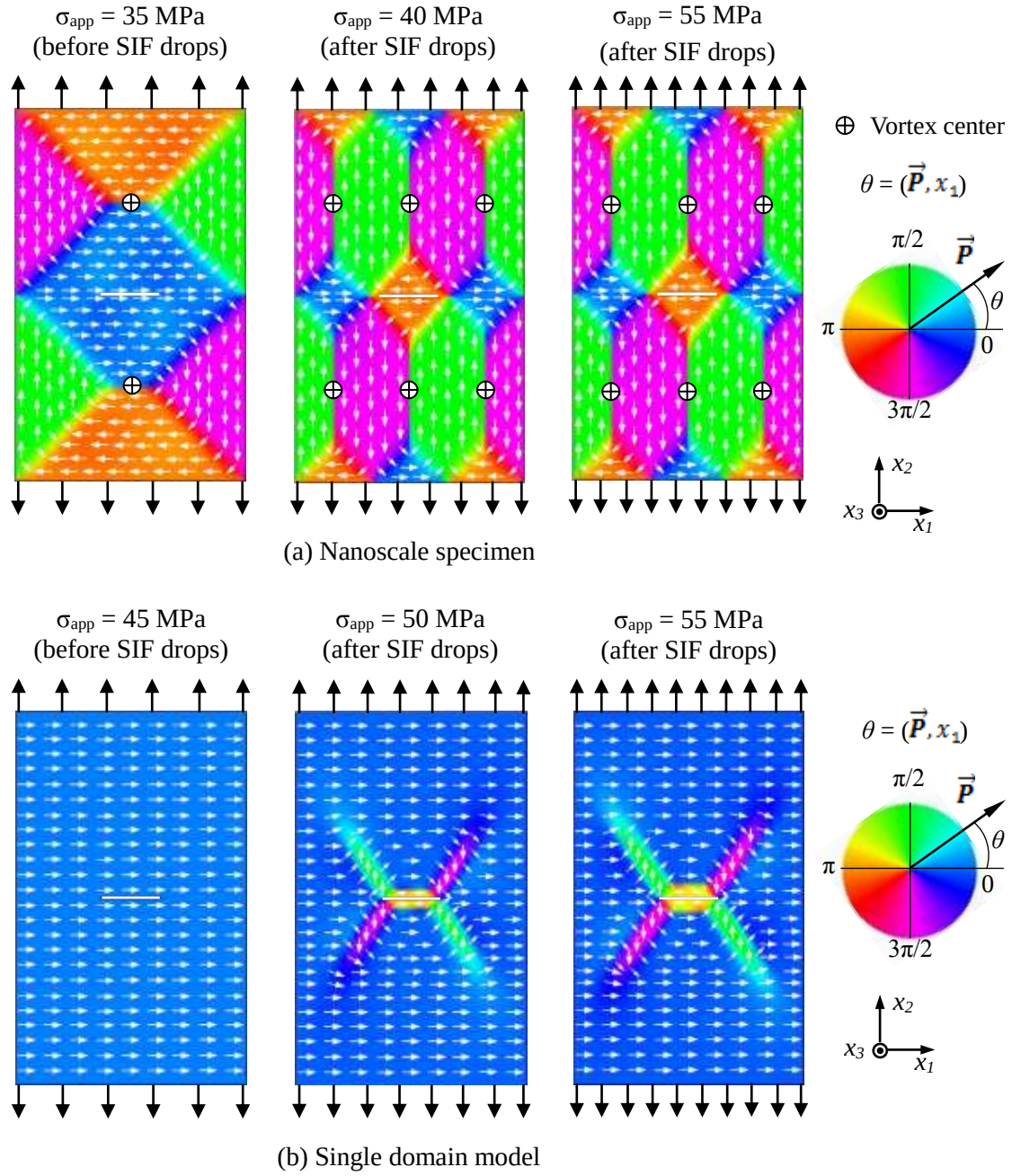


Figure 2.5. Polarization distribution at the thermodynamic equilibrium state before and after the drop of the stress intensity factor (SIF) for (a) the nanoscale specimen, and (b) the single-domain model. The contour indicates the angle between the polarization vector and the x_1 direction.

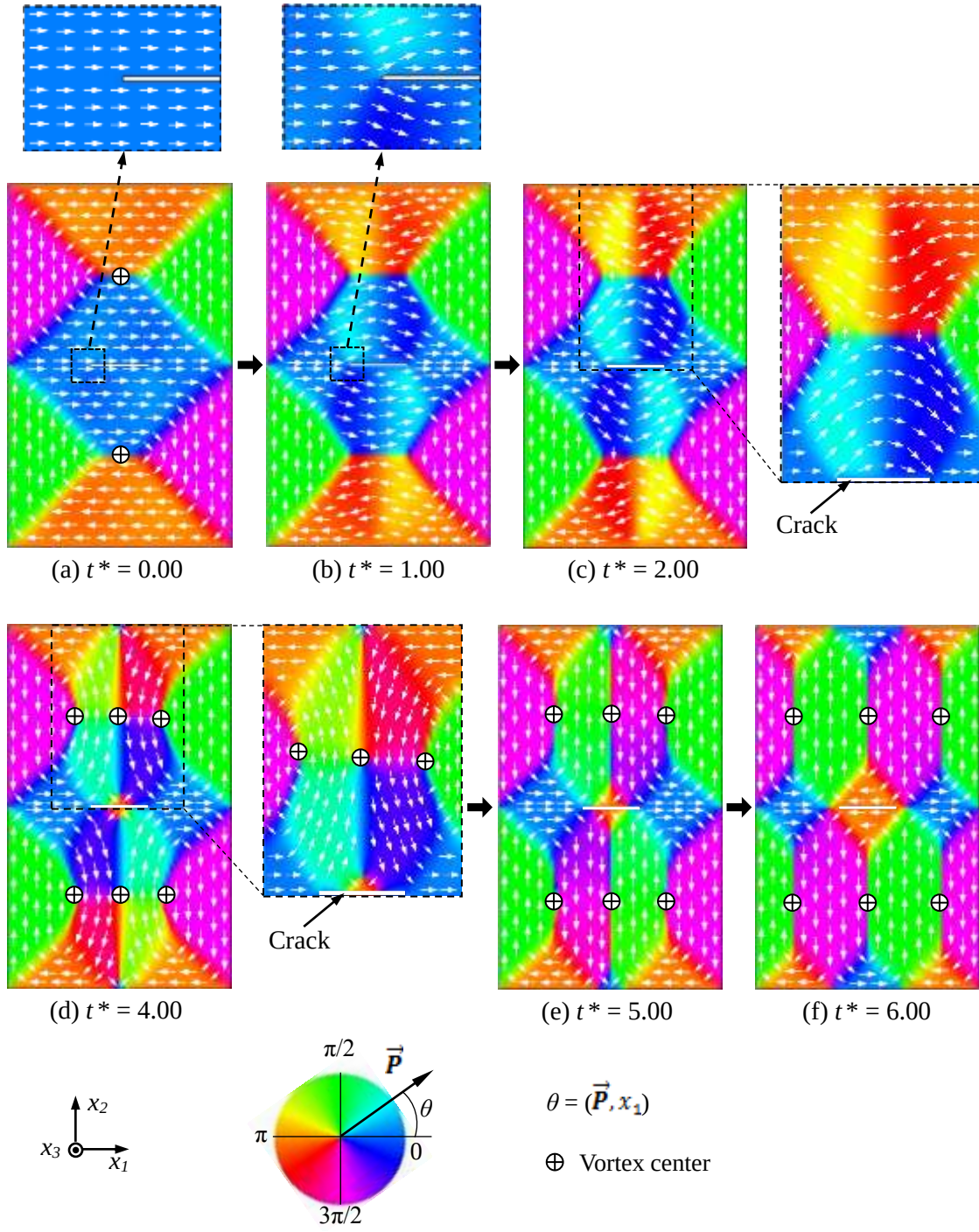


Figure 2.6. Temporal evolution of polarization switching in the nanoscale PbTiO_3 specimen under a tensile load of $\sigma_{\text{app}} = 40$ MPa. The contour indicates the angle between the polarization vector and the x_1 direction.

2.3.4 Energetics in local-to-global switching of polarization vortices

To elucidate the mechanism responsible for the mechanical and ferroelectric behavior in the nanoscale specimen, the evolution of the various energies during the polarization process is discussed by comparison with that in the single-domain model. Let us begin with the single-domain model for clarity.

Fig. 2.7a shows the temporal evolution of the various energy contributions in the single-domain model during the polarization switching process. The total free energy rapidly decreases during $t^* = 0-0.2$, which corresponds to the occurrence of the local domain switching shown in Fig. 2.5b. Fig. 2.7a shows that the gradient, electric, Landau and coupling energies remain constant or increase, while the elastic energy decreases during the evolution. Only the elastic energy contributes to a decrease of the total free energy; therefore, the single-domain system changes to release the strain energy stored by mechanical loading. This is typically observed in macroscale ferroelectrics with cracks [25,63]. The distribution of elastic energy density and the normal stress σ_{22} , are shown in Fig. 2.7b. The highest elastic energy density is initially located only in the vicinity of crack tip due to the stress concentration. It then begins to scatter with the polarization switching, but the strain energy is still confined to a small region near the crack tip. Thus, the polarization switching, which releases the high strain energy, is also confined to the vicinity of crack tip. Fig. 2.7b shows that the normal stress is still highly concentrated near crack tip, although it is redistributed during the switching process due to the coupling between stress and polarization.

Fig. 2.8a shows the temporal evolution of the various energies in the nanoscale specimen during the polarization switching process. The total free energy also decreases during the evolution; however, the magnitude of the decrease is larger than that in the single-domain model. The relatively large decrease of the total free energy is responsible for the entire polarization transformation from the 2-vortices state to the 6-vortices state. By tracing the evolution of the energies, as shown in Fig. 2.8a, only the coupling energy is observed to decrease, which causes a decrease of the total free energy, while the other energy components remain constant or increase. This indicates that the system changes to release the electro-elastic coupling energy in the nanoscale specimen. Therefore, for nanoscale ferroelectrics, it is not elastic energy, but electro-elastic

coupling that is the driving force for the switching of polarization vortices. Fig. 2.8b shows the distributions of the coupling energy density and the normal stress σ_{22} , in the nanoscale specimen during polarization switching. The high coupling energy is not only located near the crack tip, but also distributed almost entirely to the nanoscale specimen. The coupling energy starts to be released from a local site of the crack tip and then expands to the entire specimen. Finally, the coupling energy is almost released not only near the crack tip, but also almost entire nanoscale specimen. The process of coupling energy release corresponds to the switching of polarization vortices shown in Fig. 2.6. Because of the strong coupling between polarization and stress, the stress is similarly redistributed from the crack tip to the entire specimen through the global switching of the polarization vortices (Fig. 2.8b). After the redistribution, the normal stress is dramatically decreased at the crack tip. Such a dramatic decrease of the normal stress causes a considerably large drop of the stress intensity factor in the nanoscale specimen compared with that for the single-domain model and for a macroscale ferroelectric specimen.

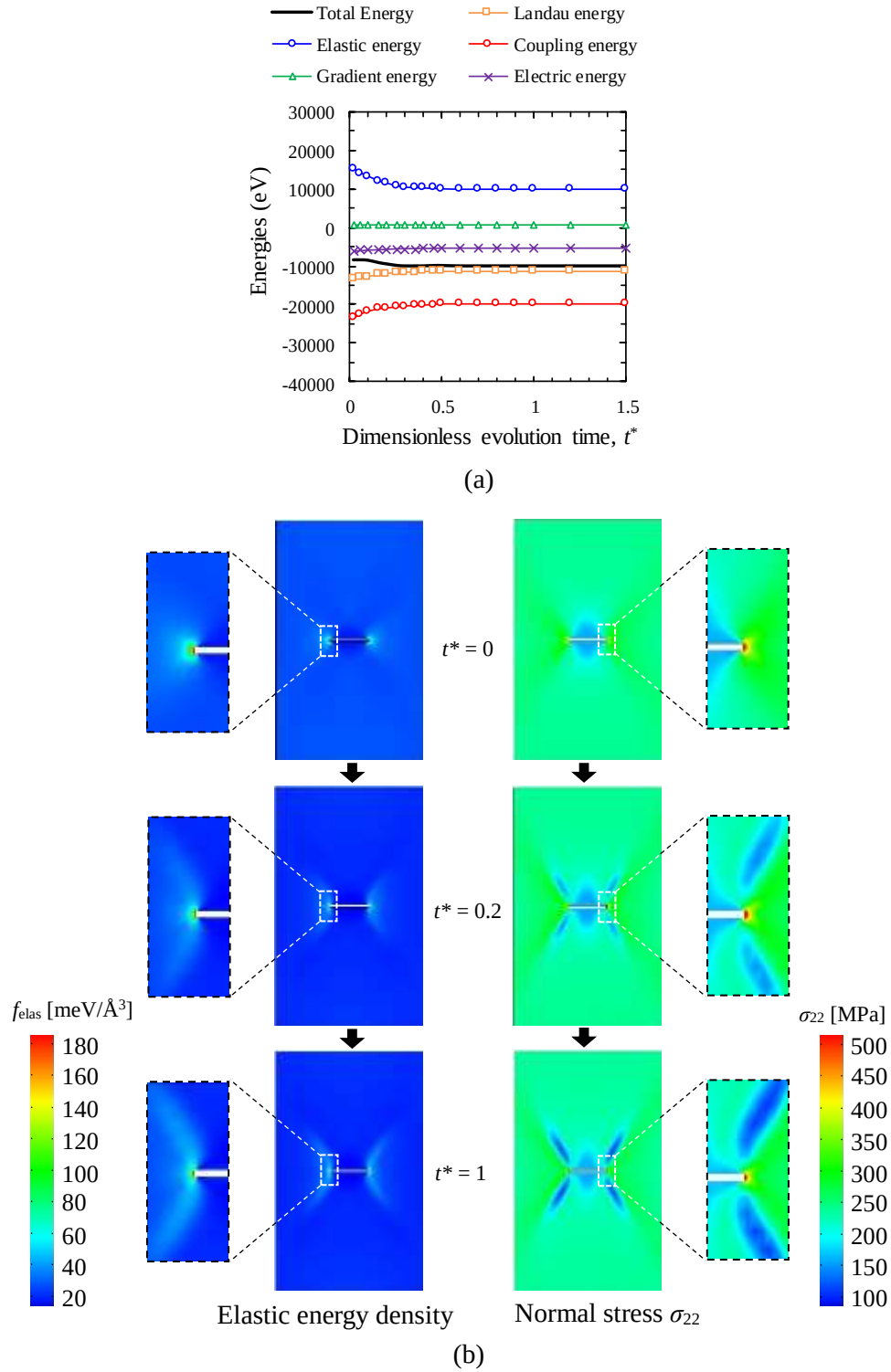
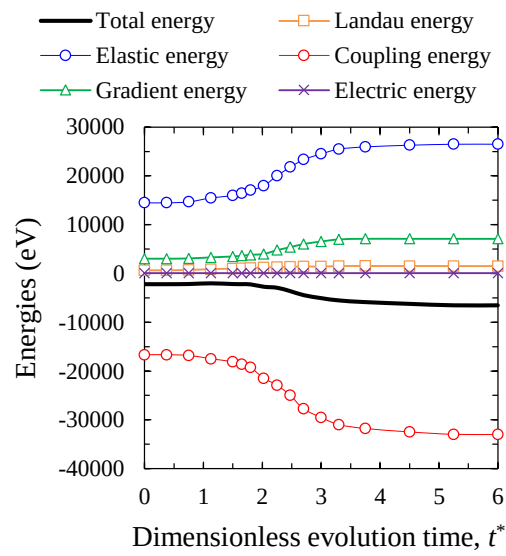
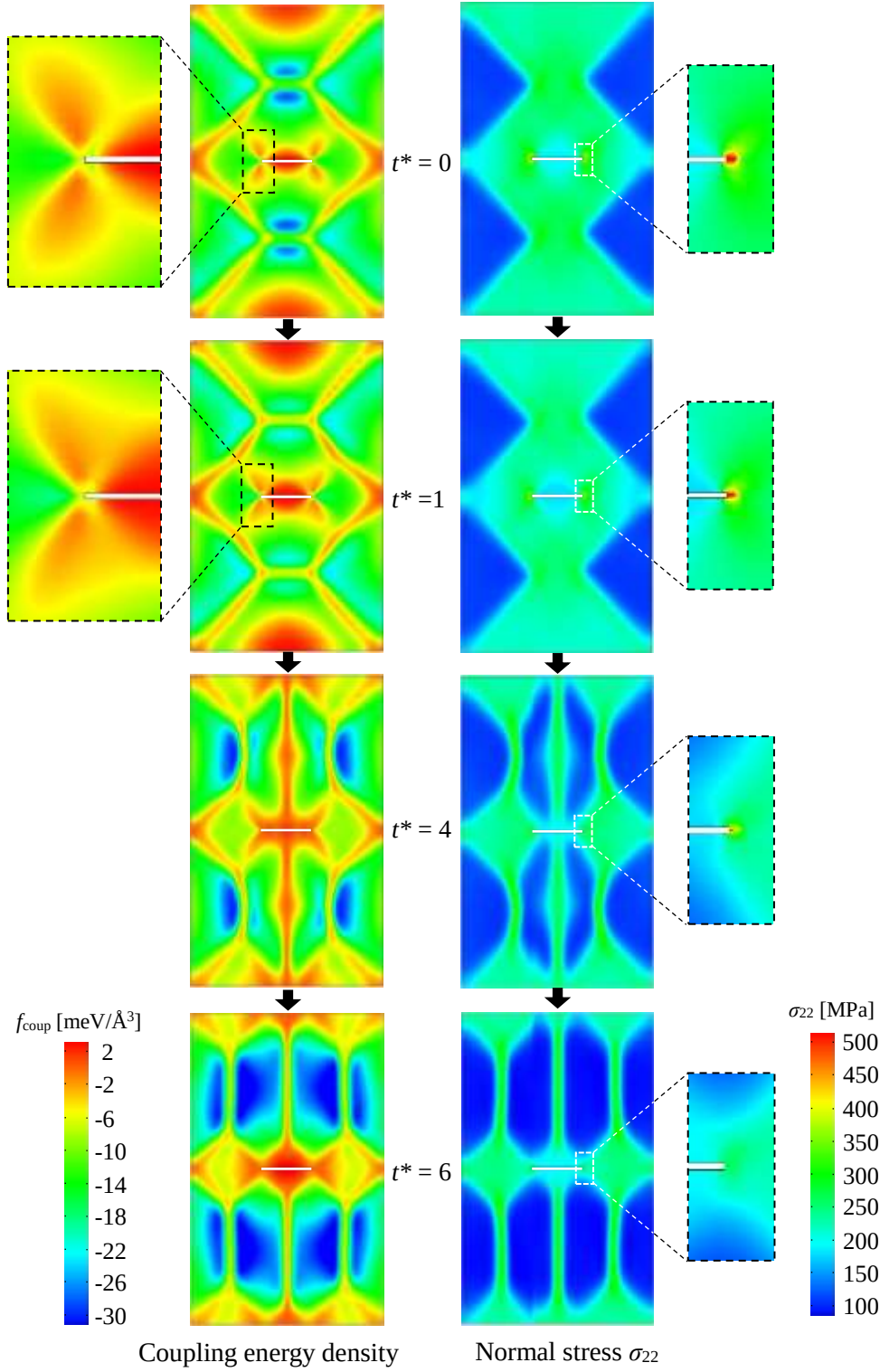


Figure 2.7. Temporal evolution of (a) the various energy contributions, and (b) the elastic energy density and normal stress σ_{22} in the single-domain model during the polarization switching process.



(a)

Figure 2.8. Temporal evolution of (a) the various energy contributions, and (b) the coupling energy density and normal stress σ_{22} in the nanoscale specimen during switching of the polarization vortices.



(b)

Figure 2.8. (continued) Temporal evolution of (a) the various energy contributions, and (b) the coupling energy density and normal stress σ_{22} in the nanoscale specimen during switching of the polarization vortices.

2.4 Conclusion

In this chapter, I have investigated the unusual mechanical behavior of cracks in nanoscale ferroelectrics, where polarization vortices characteristically appear, using real-space phase-field modeling based on the Ginzburg-Landau theory. An anomalously large toughening effect in nanoscale ferroelectrics is revealed due to drastic stress release near the crack tip, which is almost one order of magnitude larger in stress intensity than that observed in macroscale ferroelectric materials. The anomalous toughening is shown to be due to the unusual switching behavior of the polarization vortices in nanoscale ferroelectrics. The polarization switching in nanoscale ferroelectrics is no longer localized near the crack tip, as with macroscale ferroelectrics, but expands to the entire structure through splitting and multiplication of the vortices. I further demonstrate that the unusual switching of polarization vortices is intrinsically induced by strong cross-coupling between the ferroelectric polarization and mechanical strain. The coupling concentrates to the electro-elastic energy, not only in the vicinity of crack tip, but also to each polarization vortex due to its inhomogeneous distribution. Therefore, my finding first sheds light on the crucial role of polarization vortices for the toughness and strength of materials. Engineering the ability of polarization vortices to scatter and release stress concentration opens a new avenue for tailoring the material strength and toughness through ferroelectric microstructures and designing tough and strong ferroelectric nanostructures. Additionally, the present work also paves the way for further studies to systematically probe a crack reaction to the relaxation of the stress near the crack tip accounting the effect of polarization vortices. In particular, the stress relaxation near the crack tip, which is caused by the global switching of polarization vortices, may also result in a gradual closer of the microcrack tip or even healing.

However, more work is needed to produce predictive simulations of the crack reaction in nanoscale ferroelectric material. When the microcrack tip is closed, the mechanical and electrical boundary conditions of crack surfaces completely change. The change would be further complicate the interactions among the ferroelectric microstructure, localized stress and electric fields, and thus many physically realistic crack conditions should be analyzed.

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Chapter 3

Coexistence of hierarchical ferroelectric and ferrotoroidic polarizations in nano-metamaterials

3.1 Introduction

Metamaterials are rapidly emerging at the frontier of science involving physics, material science, engineering and chemistry due to their exotic, tunable and sometimes even unprecedented material properties, which arise from (periodic) arrangements of rationally designed structures rather than from the intrinsic properties of the chemical constituents. Being initially intended to realize negative refraction just over a decade ago [1,2], this deceptively simple but extraordinarily powerful concept then quickly covered a much broader range in the field of electromagnetics or optics, and has allowed the realization of many new and unusual optical properties, such as ultrahigh positive refractive index [3], magnetism at optical frequencies [4], giant circular dichroism [5], subwavelength imaging [6], perfect absorption [7], and enhanced nonlinear optical properties [8]. Beyond electromagnetism, the metamaterials concept has recently been extended to classical mechanics and also to quantum mechanics [9]. Mechanical metamaterials have continued to exhibit fascinating properties, such as ultra-lightweight yet strong and recoverable metamaterials [10], auxetic mechanical metamaterials [11], negative compressibility and negative incremental stiffness metamaterials [12], and an elastomechanical unfeelability cloak [13]. Therefore, further

proposals and developments of new class metamaterials are promising for material science and engineering [14].

One of the high-potential candidates to extend the concept of metamaterials is ferroelectric materials. Ferroelectric materials are at the heart of many advanced technologies, such as nonvolatile random access memory (FeRAM) devices [15,16], sensors, actuators, and transducers in micro(nano)electromechanical systems (MEMS/NEMS) [17,18], due to their large ferroelectricity and related electromechanical properties including a large piezoelectric response and high dielectric constant. As a characteristic of ferroelectric materials, spontaneous polarization and its arrangement (i.e., domain configuration) are crucial for determining the ferroelectric and related piezoelectric and dielectric properties. In particular, as a material approaches nanoscale dimensions, the spontaneous polarization, and thus the domain patterns, is altered due to the high surface-to-volume ratio, bringing about properties distinct from the bulk counterpart [19]. Recent studies have shown that the screening of a depolarization field in confined ferroelectrics with a size of several nanometers is enhanced through the alignment of polarization along the free surfaces, which results in the formation of closed-flux (vortex) polarization ordering, i.e., polarization vortices [20]. The vortex structure in nanoscale ferroelectrics is regarded as a toroidal order, which is distinct from the common homogeneous polarization order. The discovery of the polarization vortex has attracted considerable attention due to its scientific impact as a new class of order parameter in materials and the potential for technological applications including ultrahigh-density data storage as a novel functional device paradigm. Intensive work has thus been conducted to realize and control the vortex structure, and the formation of polarization vortices or domain structures has been demonstrated to be quite sensitive to the geometry of the nanostructures [21]. This implies the availability of an extrinsic method to tune the domain configurations and control the properties of ferroelectrics through the use of rationally designed nano-structures, i.e., the principle of the metamaterials concept. The majority of work to date on nanoscale ferroelectrics has focused on the level of individual elements, where the domain patterns adopt a single order parameter and are somewhat simple. However, to meet the ever increasing demand for further the improvement of ferroelectric devices,

there is a strong requirement to stabilize and control rather complex domain patterns that possess a high possibility to offer novel functionalities. Although complex domain patterns have motivated numerous theoretical and experimental investigations [22-25], they have not yet been commonly observed, and the control of such complex patterns has been elusive. Instead, a combination of several nano-ferroelectric components accommodated in a hierarchical nanostructure is predicted to create complex domain patterns due to the dual advantages of variable length-scale and dimensionality, the nano-size effect, and the interplay between polarization domains accommodated in the constituent nanostructures.

In this chapter, I introduce a concept of ferroelectric nano-metamaterials, and demonstrate through conducting an experiment *in silico* with hierarchically nanostructured ferroelectrics using state-of-the-art real-space phase-field techniques based on the Landau-Devonshire theory. In this concept, the internal shape of hierarchically nanostructured ferroelectrics can be used as an additional degree of freedom to extrinsically tune the domain configurations, and thus the macroscopic properties. This new concept allows a variety of unusual and complex yet controllable domain patterns to emerge in ferroelectric nano-metamaterials. I further explore a key design feature to realize such unusual domain patterns using the parity of junctions that connect constituent nanostructures in the metamaterials.

3.2 Simulation procedure

To illustrate the idea of ferroelectric nano-metamaterials, 11 two-dimensional (2D) nano-specimens of ferroelectric PbTiO_3 are designed based on architectures of a completed set of 2D Archimedean lattices (ALs) (see Fig. 3.1), then a simulation is performed to test the formation of spontaneous polarization in such structures at the room temperature. ALs, first introduced by Kepler in 1619 [26], are defined as edge-to-edge tiling of a plane with regular polygons such that all vertices are of the same type. There are 11 ALs, in which three consist of a specific polygon (Squares, triangles, or hexagons, as shown in Fig. 3.1a-c, respectively), and eight require the

combination of two or more different polygons (Fig. 3.1 d-k), which gives rise to further complicated internal structures. Ubiquitous members of the ALs are the Square, Honeycomb, Triangular, and Kagome lattices, while more exotic lattices are the CaVO, Star, SrCuBO, Bounce, Trellis, Maple-leaf, and SHD lattices [27]. The structural diversity and intriguing characteristics of ALs provide an ideal playground for a systematic study of the interplay between nano-metamaterials structures and ferroelectricity.

Taking into account the strong effect of the depolarization field, the dimensions of all lattices in the specimens are set in a range from several to tens of nanometers. Therefore, the thickness of specimens and the width of the lattices are prepared at 4 and 6 nm, respectively. To access the intrinsic role of the nano-metamaterial structure on the domain configurations, free-standing specimens with the same filling fraction of 30% are investigated. The periodicity is taken in the x_1 and x_2 directions. The specimens consist of a single crystal of ferroelectric PbTiO_3 , where the $[100]$, $[010]$, and $[001]$ axes correspond to the x_1 , x_2 , and x_3 directions, respectively.

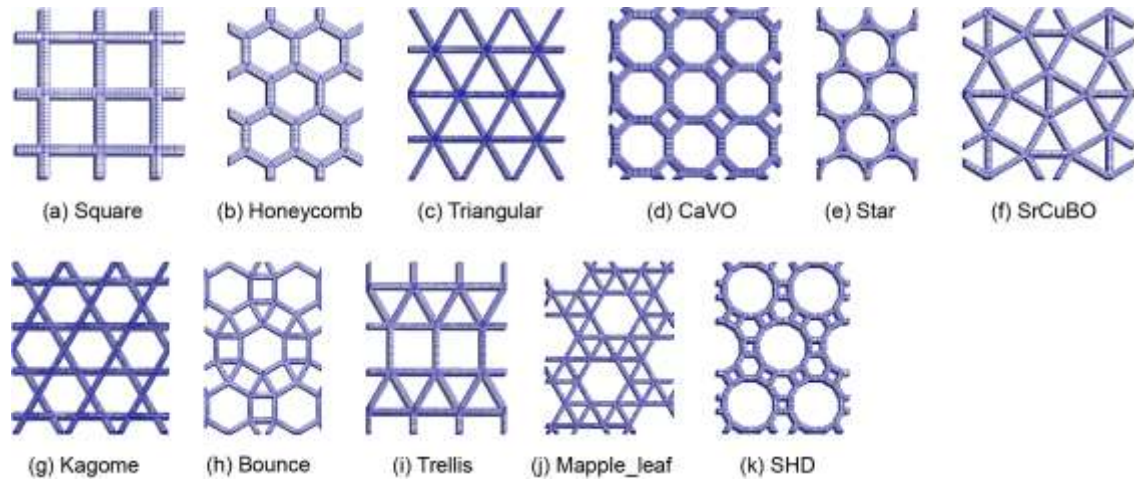


Figure 3.1. Ferroelectric nano-metamaterial specimens with 2D Archimedean lattice structures.

In the present study, the formation of spontaneous polarization in free-standing nano-metamaterials specimens at room temperature is carefully tested using sophisticated real-space phase-field techniques based on the Ginzburg-Landau theory, which explicitly includes the depolarization effect and non-trivial electro-elastic coupling (see Appendix A). To realize bare free surfaces of the specimens, the electrical boundary conditions on all surfaces are set to be open-circuited, i.e., $\mathbf{D} \cdot \mathbf{n} = 0$, so that the depolarizing fields from the polar surfaces are explicitly taken into account. Note that my preliminary analysis showed that there is no difference in polarization domain structures under open-circuited and general electrostatic boundary conditions. The open-circuited boundary condition is employed in consideration of computing resources due to the complex geometry of AL structures. Testing is started by the introduction of an initial state with random fluctuations of polarization around zero, which recognizes the paraelectric state of ferroelectric nano-metamaterials. At room temperature, evolution of the polarization field toward its thermodynamic equilibrium distribution is driven by the decrease of total free energy in the ferroelectric system, which is obtained by numerically solving the time-dependent Ginzburg-Landau equation (see Appendix A). The domain patterns are then stably formed when no significant change in the polarization can be observed. The properties of PbTiO_3 have been described in previous study [28].

3.3 Results

3.3.1 Spontaneous polarization configurations

Fig. 3.2a-c show the spontaneous polarization distribution at the thermodynamic equilibrium state in Square, Honeycomb, and Triangular specimens, respectively. A strong confinement in the x_3 direction of the nano-metamaterials results in purely in-plane polarization, which is consistent with the experimental observations [22,23,24,29,30] and simulated predictions [31,32] for ferroelectric lamellae. The contour color indicates the angle θ between the polarization vector $\mathbf{P}$ and the x_1 direction. Fig. 3.2 shows that the polarizations align along the lattices and thus form a

normal rectilinear domain accommodated in each lattice. Such a single domain configuration causes a decrease in the electrostatic interaction energy through elimination or reduction of the depolarization fields at free surfaces. Thus, the common single domain is an energetically favorable domain configuration that appears in the lattices of nano-metamaterials. Unlike a conventional configurations of random rectilinear domains in bulk ferroelectric materials or regular arrays of stripe domains in ferroelectric thin films, the single domains in the Square, Honeycomb, and Triangular nano-metamaterials connect to each other by gradually rotating the orientation of the local polarization vectors at the lattice junctions to form a continuous flow pattern. Such continuous flow represents novel polarization patterns that are characteristic for the Square, Honeycomb, and Triangular specimens.

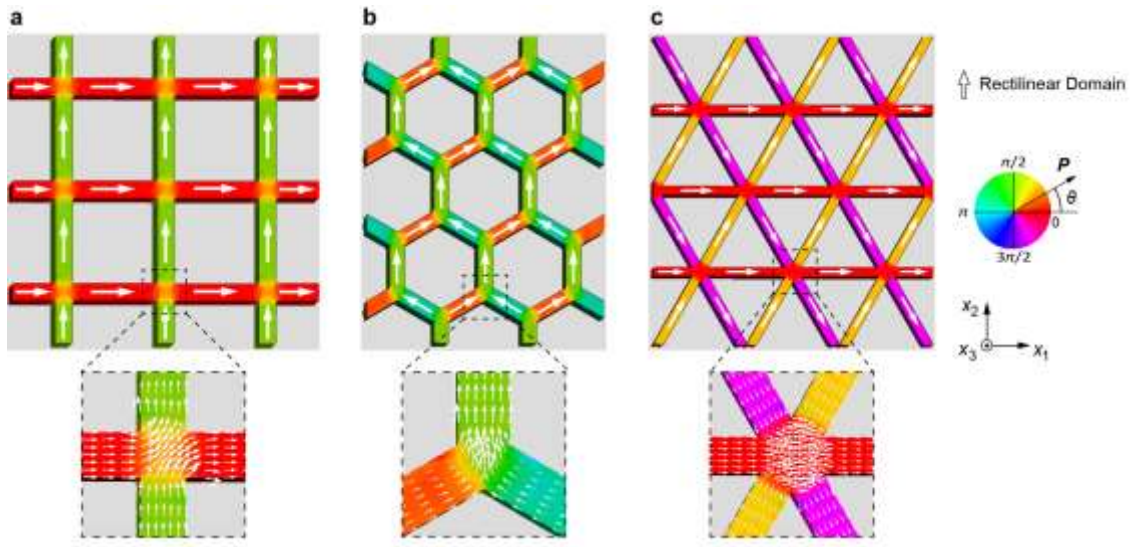


Figure 3.2. Polarization distribution in ferroelectric nano-metamaterials of (a) Square, (b) Honeycomb, and (c) Triangular specimens. The polarization patterns are characterized by the continuous flow of polarization. The contours indicate the angle between the polarization vector P and the $[100]$ direction.

Fig. 3.3a-c depict domain configurations at the thermodynamic equilibrium state in the CaVO, Star, and SrCuBO specimens, respectively. Single domains are also formed in most lattices of the specimens and connect themselves through alteration of the local polarization orientations at the junctions. Besides the rectilinear domains, the polarizations in some lattices terminate the continuous flow and then curl their orientation to form clockwise and/or counter-clockwise microvortices. Such unusual domain configurations with ferrotoroidic polarization due to the strong depolarization field have been recently reported in various isolated ferroelectric nanostructures, such as nanodots [20], nanowires [33], and nanobars [34,35]. The local microvortex is characterized by a toroidal moment, i.e., $g_{micro}^{local} = \frac{1}{V} \int_V (r \times P) dV$ [36], where r is the position vector, V is the ferroelectric volume that the vortex occupies, and P is the spontaneous polarization vector. In the present study, the toroidal moment, g_{micro}^{local} , is determined to be equivalent to $0.154 \text{ e/\AA}$, which is similar to that obtained for a nanodot [37]. This shows that a microvortex in a ferroelectric nano-metamaterial is intrinsically similar to the vortex in a nanodot. On the other hand, the most valuable feature that emerges in the CaVO, Star, and SrCuBO specimens is the coexistence of vortices and rectilinear polarizations, which are characterized by two different order parameters, i.e., ferrotoroidic and ferroelectric order parameters, respectively. The coexistence permits a cross-coupling between two order parameters that appear in the same ferroelectric nanostructure, and makes it possible to tailor the toroidal moments by a homogeneous electric field. As a result of the coexistence, spontaneous polarization forms an unusual pattern with a maze-like polar structure. The coexistence of the ferroelectric and ferrotoroidic domains, and the resulting maze-like polarization pattern are characteristics of the CaVO, Star, and SrCuBO specimens. Since the polarization found a preferred path to continuously connect through the maze-like pattern, this would be particularly useful for next-generation of chirality logic devices [38]. Furthermore, the complexity of the maze-like pattern may bring about an unusual domain switching process, such as multi-step switching process that potentially leads to interesting multi-state devices.

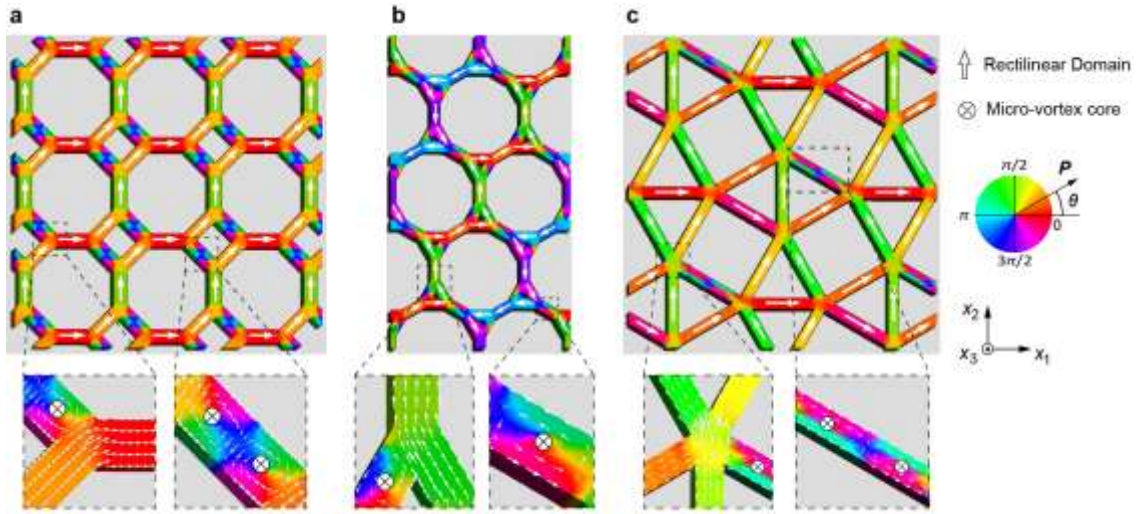


Figure 3.3. Polarization distributions in ferroelectric nano-metamaterials of (a) CaVO, (b) Star, and (c) SrCuBo specimens. The polarization is characterized by the coexistence of rectilinear and microvortex polarizations. The contours indicate the angle between the polarization vector P and the $[100]$ direction.

Fig. 3.4g and h show that the continuous flow pattern of polarization also appears in the Kagome and Bounce specimens at the thermodynamic equilibrium state. However, an intriguing characteristic that is distinct from the continuous flow pattern in the Square, Honeycomb, and Triangular specimens (shown in Fig. 3.2) is a nesting of flux-closure configurations of polarization at the larger mesoscopic scale, which occupies a complete loop of several neighboring single domains, to form a mesovortex. Staggered chirality of alternating clockwise and counter-clockwise mesovortices appear in the Kagome specimen, while necklace-like chains of mesovortices are observed in the Bounce specimen. The mesovortices in the Kagome and Bounce specimens are characteristically different from that observed in isolated nanostructures such as nanodots and nanowires, due to the absence of a physical vortex core, which facilitates elimination of the energetic vortex core. The local toroidal moment of the mesovortex is

defined in a similar manner to that of the microvortex: $g_{meso}^{local} = \frac{1}{V} \int_V (r \times P) dV$, where V is the volume of the ferroelectric media within the mesovortex. The toroidal moment of the mesovortex is determined to be $g_{meso}^{local} = 1.47 \text{ e/\AA}$, which is approximately ten times higher than that for g_{micro}^{local} . Therefore, the mesovortex is distinct from the microvortex not only by the absence of physical vortex core and its size but also by the magnitude of its toroidal moment. The appearance of mesovortices in a continuous flow pattern of polarization such as that characterized for the Kagome and Bounce specimens results in an intriguing and unusual polarization pattern. Additionally, the absence of physical vortex core and large toroidal moment may possess high piezotoroidic effect [39], which is a new kind of electromechanical coupling of strain/stress and toroidal moment, providing a new additional functionality that can be exploited for electromechanical devices.

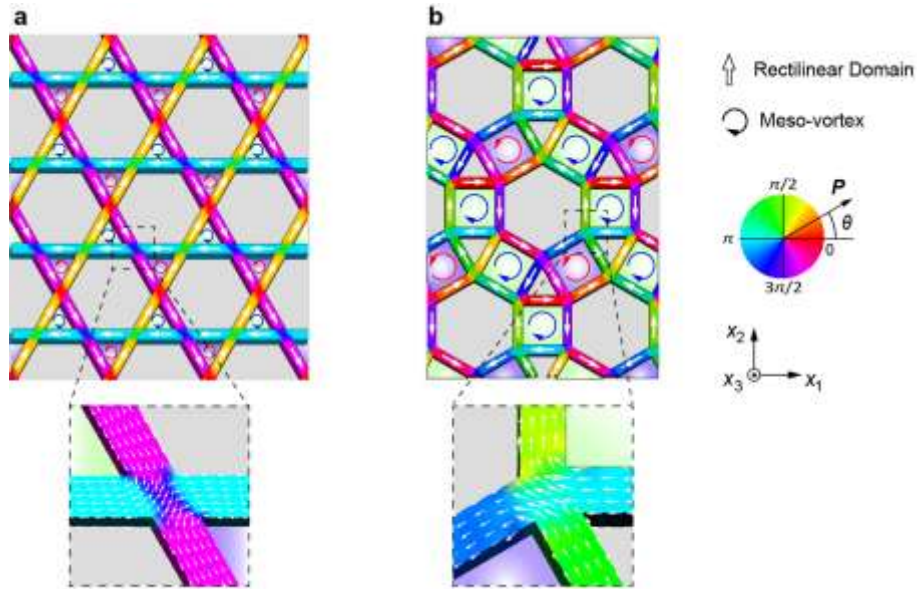


Figure 3.4. Polarization distributions in ferroelectric nano-metamaterials of (a) Kagome and (b) Bounce specimens. The polarization patterns are characterized by mesovortex polarization appearing in a continuous flow configuration. The contours indicate the angle between the polarization vector P and the $[100]$ direction.

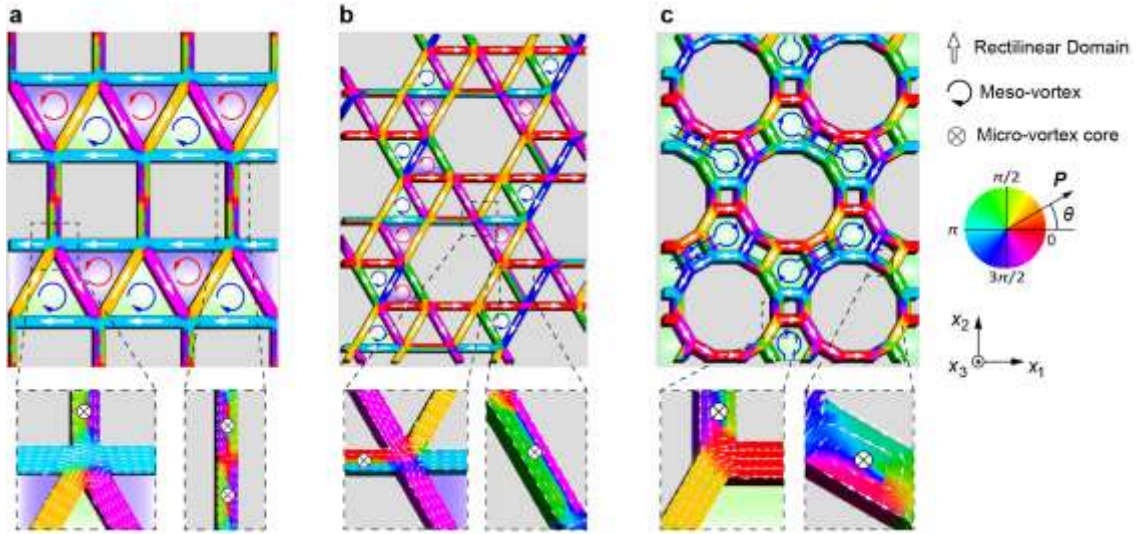


Figure 3.5. Polarization distributions in ferroelectric nano-metamaterials of (a) Trellis, (b) Maple-leaf, and (c) SHD specimens. The polarization patterns are characterized by the coexistence of hierarchical vortex and rectilinear polarizations. The contours indicate the angle between the polarization vector P and the $[100]$ direction.

Fig. 3.5a-c feature striking characteristics in the polarization patterns in the respective Trellis, Maple-leaf, and SHD specimens at the thermodynamic equilibrium state. Here, the polarization vortex occurs simultaneously at two different length scales within the single structure of the nano-metamaterial, thereby exhibiting hierarchical vortices. To the best of my knowledge, such hierarchical vortex patterns are unprecedented for ferroelectric or ferromagnetic vortices. As a result of the coexistence of hierarchical rectilinear, micro- and mesovortex polarizations, unusual and complicated patterns emerge in the Trellis, Maple-leaf and SHD specimens. Pairs of stable clockwise and counter-clockwise mesovortices appear surrounded by rectilinear domains and the microvortices in the Trellis and Maple-leaf specimens. A two-lobe-shaped mesovortex that not only occupies a large area of three adjacent polygons but also traps two micro-vortices inside it emerges in the SHD specimen to exhibit a vortex-in-vortex configuration, which is reminiscent of fractal behavior. The

discovery of the nested dual-scale vortex states coexistent with rectilinear domains establishes a new benchmark in my exploration of complexity in the spontaneous ordering of electrical dipoles, which have the potential to produce unique functionalities and tunability through the coupling of two different order parameters, similar to multiferroics.

The surprising wealth of polarization patterns shown in Fig. 3.2-3.5 is interestingly a consequence of a well texture to form characterized polarization patterns from existing polarization domains, i.e., single domains and polarization vortices, rather than a haphazard combination of them. This suggests that the connectivity of lattices at the junctions is crucial to understand the mechanisms that lead to the formation of unusual polarization patterns in ferroelectric nano-metamaterials. Only one type of junction is structurally permitted for a given AL, which is characterized by the odd-numbered (odd-junction) and even-numbered (even-junction) binding lattices. From an energetic perspective, the polarization in ferroelectric nano-metamaterials would continue to join together with a head-to-tail arrangement due to the long-range electrostatic interaction in order to reduce the electrostatic energy, which drives the connection of the polarization domains in neighboring lattices. A careful observation of the polarization configurations presented in Fig. 3.2-3.5 reveals that a connection preferably involves two single domains that are jointed at the junction to maintain the head-to-tail arrangement (except the Honeycomb specimen, which consists of connections of 3 single domains due to the 3-fold symmetry junction). As a result, a continuous flow pattern of polarization is spontaneously formed in the specimens that consist of even-junctions (Fig. 3.2 and 3.4), where every single domain in the lattices establishes a connection to an adjacent domain. In contrast, the connection of polarization becomes more complex in the specimens with odd-junctions (Fig. 3.3 and 3.5) because the polarization domains have to emulate each other to establish a connection, which leads to the termination of polarization in one lattice. The polarizations in such an uncoupled lattice would no longer be favored with a rectilinear domain, but the orientation would instead curl to produce a vortex domain so that the internal depolarization is reduced, which arises from the termination of continuous flow. Therefore, unlike isolated nanodots or nanobars, the mechanisms that leads to the formation of microvortices in

ferroelectric nano-metamaterials is caused not only by free surface depolarization but also by internal depolarization and elastic interaction. The formation of microvortices in a structure with odd-junctions reveals the underlying reason for the stable coexistence of the rectilinear domains and polarization vortices in ferroelectric nano-metamaterials, which is difficult to achieve in simple isolated ferroelectric nanostructures. Thus, the junctions of lattices in ferroelectric nano-metamaterials are the key design features of my proposed concept.

3.3.2 Macroscopic properties in ferroelectric nano-metamaterials

Given the intriguing features of polarization patterns in ferroelectric nano-metamaterials, I proceed by considering the macroscopic ferroelectric properties to provide a comprehensive picture of the interrelationships between nano-metamaterial structures, polarization patterns, and the global behavior in ferroelectric nano-metamaterials. Table 1 summarizes the average polarization, $|P_{ave}|$, and its orientation, θ , toward the x_1 direction in ferroelectric nano-metamaterials, and the density of vortices (micro- and mesovortices), which is defined by the number of vortices per the number of lattices in the ferroelectric nano-metamaterials. The average polarization at all the sites is determined as $|P_{ave}| = \sqrt{\langle P_1 \rangle^2 + \langle P_2 \rangle^2}$, in which

$$\langle P_i \rangle = \left(\sum_{j=1}^n P_i^j \right) / n, \text{ and } n \text{ is the total number of the nodes of simulated models. } |P_{ave}| \text{ and } \theta,$$

which characterize the global polarization, cover a wide range of magnitudes, depending on the structure of the nano-metamaterial. This indicates that the control of the shape of ferroelectric nano-metamaterials can be used to further tailor the magnitude and direction of global spontaneous polarization. The zero net polarization shown in Table 1 is attributed to the high density of vortices, which is significantly dependent on the structures of the junctions and the shape of the ferroelectric nano-metamaterials. On the other hand, several equivalent states of polarization patterns, which are depicted in Fig. 3.6, can be realized due to the symmetry of the nano-metamaterials structures. The number of states, n , is also listed in Table 1 and its maximum can be achieved as

equivalent to the symmetry order of the nano-metamaterial structure. Thus, control of the ferroelectric nano-metamaterial shape provides a novel way to control the global ferroelectric characteristics, including the magnitude and direction of macroscopic polarization, the density of vortices, and the number of stable states of domain patterns.

Table 1. Structural and global ferroelectric characteristics of ferroelectric nano-metamaterials.

	Structural characteristics		Global ferroelectric characteristics			
	Number of lattices at junction	Structural symmetry order	Average polarization, P_{ave} (C/m ²)	Direction of P_{ave} to the x_1 axis, θ (degree)	Density of vortices	Number of states, n
Square	4	4	0.534	45	0	4
Honeycomb	3	6	0.432	90	0	6
Triangular	6	6	0.481	45	0	6
CaVO	3	4	0	0	2/3	4
Star	3	6	0	0	6/19	3
SrCuBo	5	4	0.407	78	1/10	4
Kagome	4	6	0	0	1/3	2
Bounce	4	6	0	0	1/4	3
Trellis	5	2	0	0	4/5	2
Mapple-leaf	5	6	0.178	72	4/15	6
SHD	3	6	0	0	1/3	6

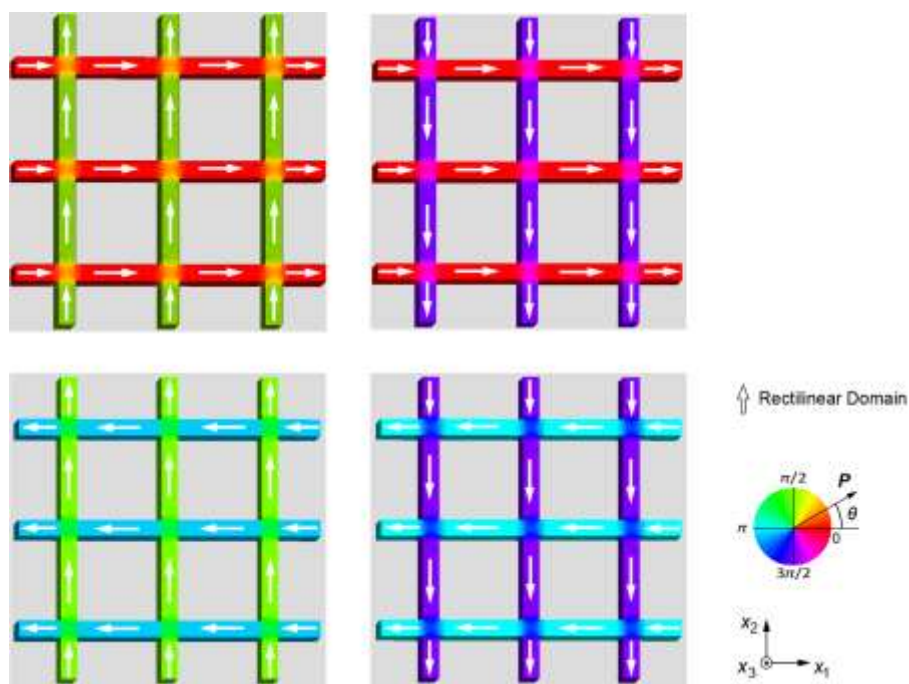


Figure 3.6. (a) 4-equivalent stable states in the Square specimen.

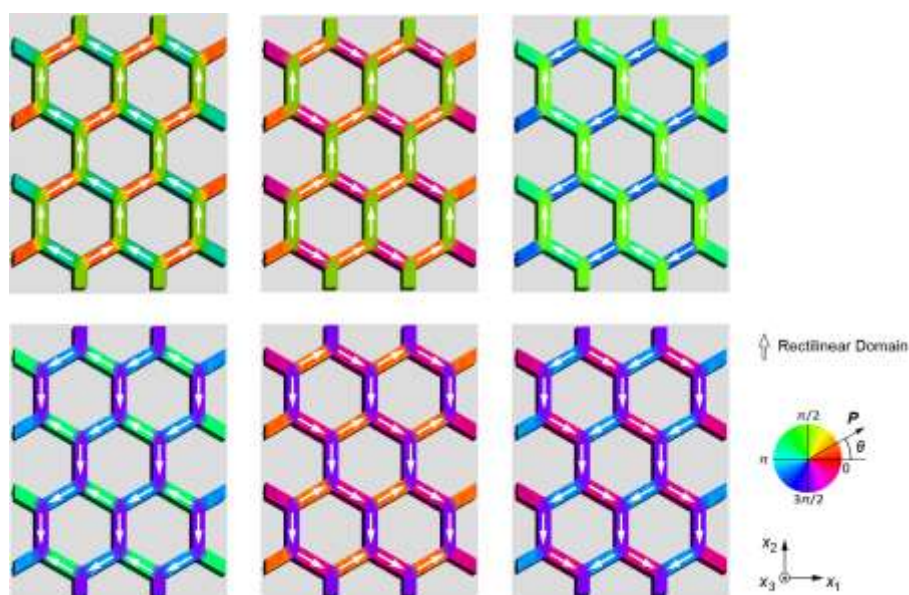


Figure 3.6. (b) 6-equivalent stable states in the Honeycomb specimen.

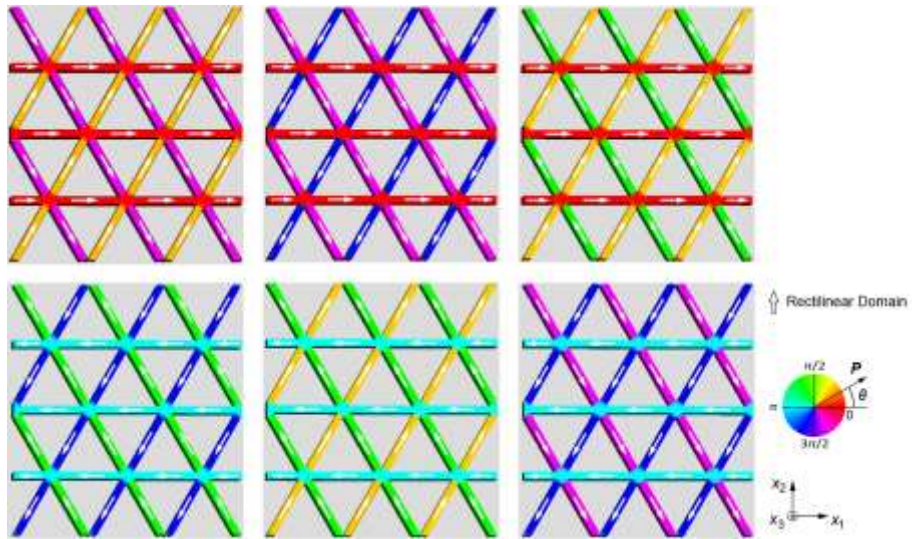


Figure 3.6. (c) 6-equivalent stable states in the Triangular specimen.

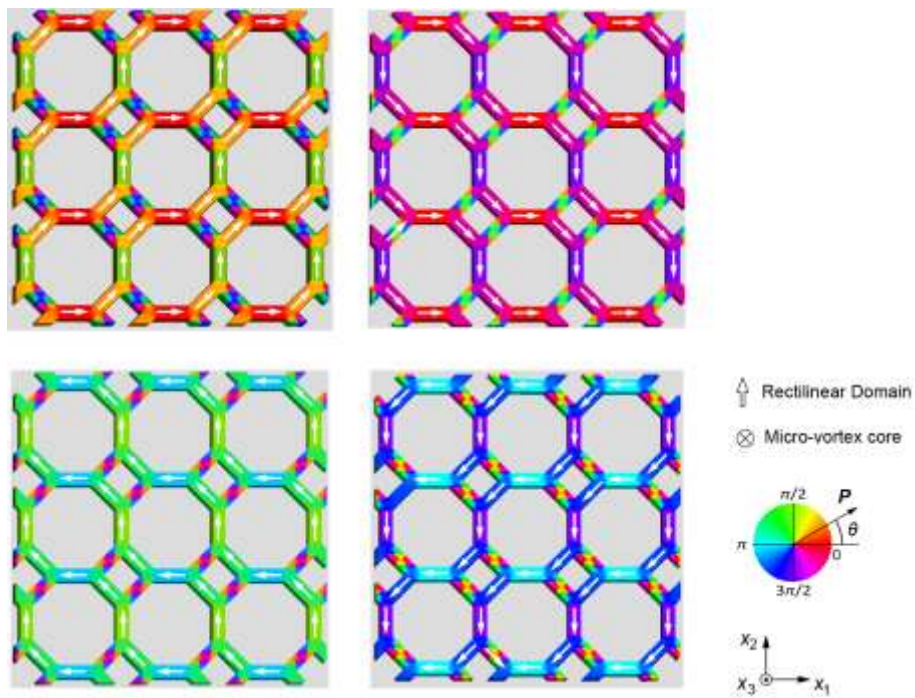


Figure 3.6. (d) 4-equivalent stable states in the CaVO specimen.

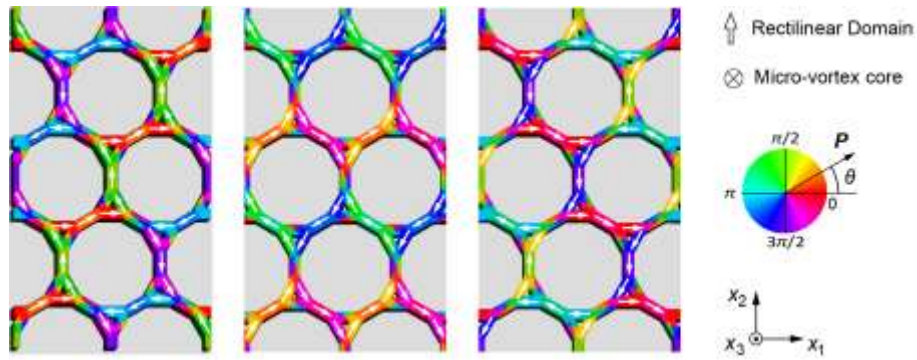


Figure 3.6. (e) 3-equivalent stable states in the Star specimen.

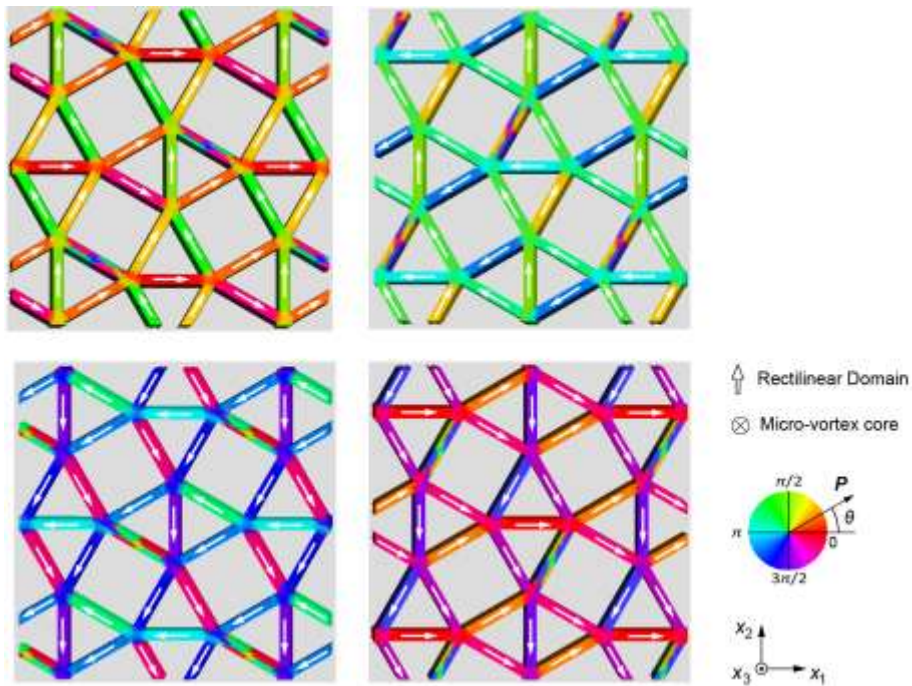


Figure 3.6. (f) 4-equivalent stable states in the SrCuBO specimen.

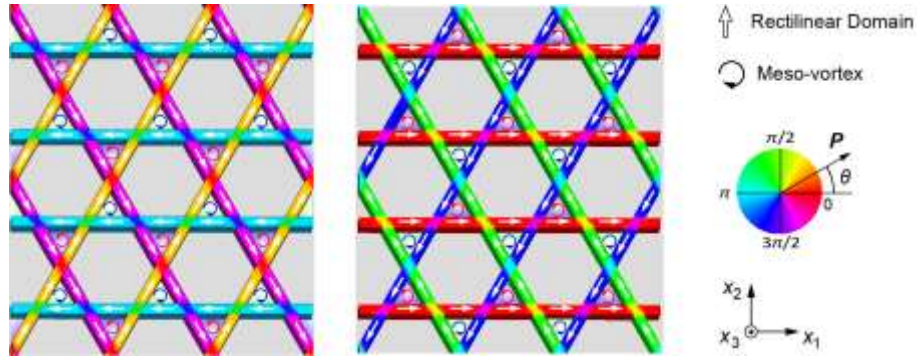


Figure 3.6. (g) 2-equivalent stable states in the Kagome specimen.

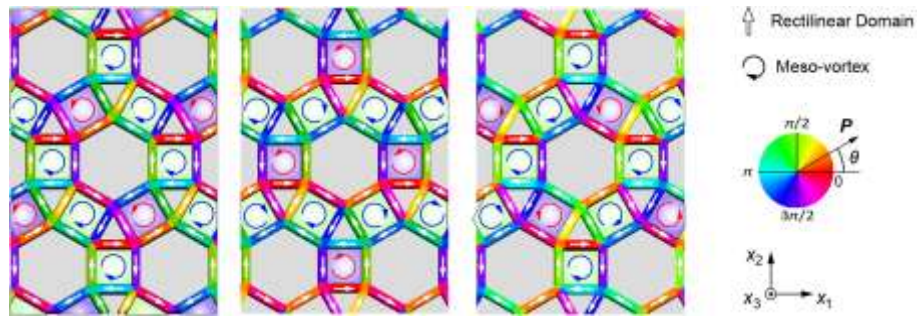


Figure 3.6. (h) 3-equivalent stable states in the Bounce specimen.

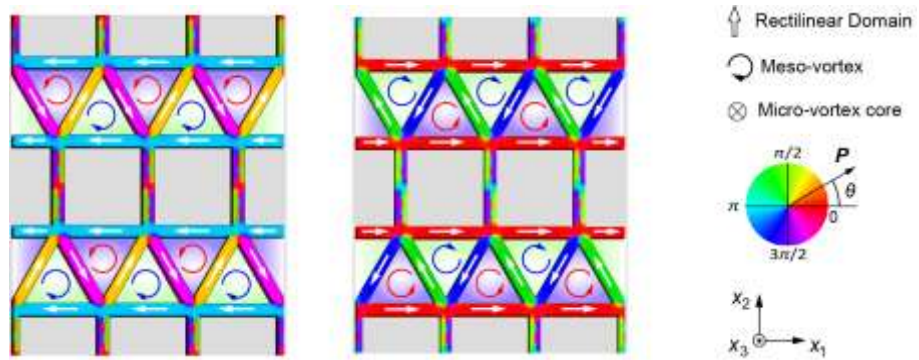


Figure 3.6. (i) 2-equivalent stable states in the Trellis specimen.

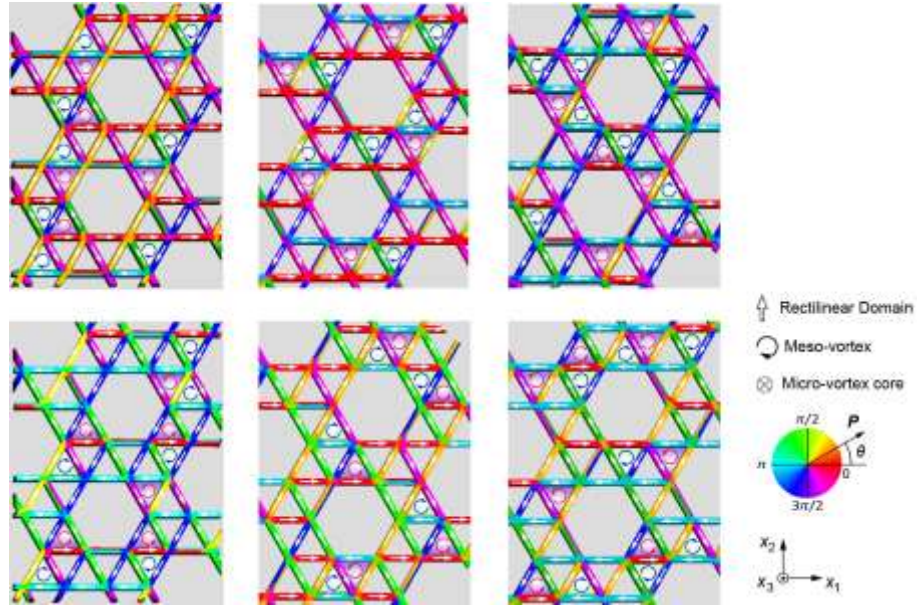


Figure 3.6. (j) 6-equivalent stable states in the Mapple_leaf specimen.

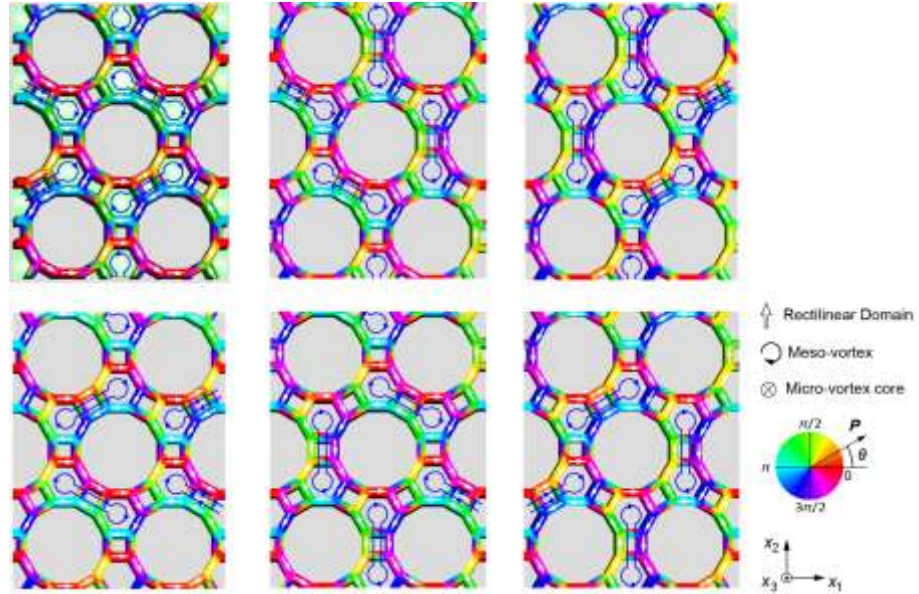


Figure 3.6. (k) 6-equivalent stable states in the SHD specimen.

3.4 Discussion

My proposal of this ferroelectric nano-metamaterials concept provides a fundamentally new way to achieve and manipulate a rich diversity of complex domain patterns. The present results further indicate the possibility to obtain novel functionalities that could be particularly useful for the development of ferroelectric devices. Firstly, the mechanical and electrical responses of ferroelectric nano-metamaterials to a uniform external field would be inhomogeneous due to their diversity of lattice directions and polarization domains. This suggests an alternative strategy to efficiently tailor the piezoelectric properties through deliberate control of the internal shape of the ferroelectric nano-metamaterial, which is distinct from conventional methods such as doping [40], and domain wall engineering [41]. Secondly, the presence of multiple equivalent stable states could realize the possibility to switch from one stable state to another by application of an external electrical field with a particular direction, giving rise to highly tunable ferroelectricity that would be appealing for multistate logic. Thirdly, the presence of mesovortices along with the ability of local polarization switching at lattices suggests that the toroidal moment of mesovortices could be strongly affected and even switched by homogeneous electric fields. The switching of polarization vortices by using the conventional homogeneous electric field suggests an alternative and practical way to control the toroidal moment, which is easier than the recently proposed use of a curled electric field [42]. Finally, the coexistence of ferroelectric and ferrotoroidic domains in ferroelectric nano-metamaterials may give rise to a cross-coupling between two order parameters due to the intrinsic relationship between ferroelectricity and ferrotoroidicity, which would enable control of the chirality of the vortex domain structure by controlling the direction of the adjacent polar domain. The coupling interaction therefore provides an additional degree of freedom in the design of multifunctional devices, and possesses a great potential for unconventional functionalities. Significant advances in micro- and nanoscale fabrication techniques have recently achieved hierarchical nanostructures of ferroelectric materials [43], thereby providing potential for the realization of such design possibilities. However, further research is required to conduct detailed investigation into the possibilities for ferroelectric nano-metamaterials.

3.5 Conclusion

In this chapter, I have proposed a new concept of ferroelectric nano-metamaterials and demonstrated that this new concept enables the discovery of a variety of unusual and complex yet controllable domain patterns, extending our knowledge on the possible domain patterns that can form spontaneously in ferroelectric materials. The coexistence between hierarchical ferroelectric and ferrotoroidic polarizations establishes a new benchmark in my exploration of complexity in the spontaneous ordering of electrical dipoles, facilitating access to the stabilization and control of complex domain structures. Tailoring the domain configuration through control of the ferroelectric nano-metamaterial structure paves a novel way for manipulation of the properties of ferroelectric materials, including not only the macroscopic properties such as macroscopic polarization and piezoelectric response but also ferrotoroidicity and the numbers of stable states of polarization. The present study proposes an entirely new discipline of ferroelectric nano-metamaterials that can be compared to those of electromagnetic metamaterials and mechanical metamaterials, further driving the advance of metamaterials research. The present work opens a rich avenue in the field of metamaterials, which is expected to evolve fruitful ideas to achieve even more fascinating properties of ferroelectric materials. The proposed concept may stimulate future experimentation and simulation efforts to explore and realize novel functionalities in ferroelectric nano-metamaterials. In addition, this new concept can be extended to the other ferroic and multi-ferroic systems.

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Chapter 4

Design of polar and toroidal electromechanical properties by ferroelectric nano-metamaterials

4.1 Introduction

Control of the properties of materials, going beyond the limit that is accessible with naturally existing or chemically synthesized substances, has become a reality with the advent of metamaterials [1,2]. Being introduced just over a decade ago, metamaterials, advanced artificial materials composed of tailored structural building blocks, have triggered significant interest due to numerous remarkable breakthroughs based on the realization of many tunable, extreme, or even unprecedented material properties in electromagnetism or optics [3-9], and recently in mechanics [10-16]. Metamaterials are thus rapidly emerging at the frontier of science involving physics, material science, engineering, and chemistry [17]. This deceptively simple but extraordinarily powerful concept of metamaterials, i.e., tuning material properties by deliberately engineered structures rather than chemical constituents, offers an entirely new route to further enhance the design of material properties at will.

Inspired by the outstanding progress in electromagnetism and mechanical metamaterials, I have previously proposed and demonstrated the concept of ferroelectric nano-metamaterials as a new stream of metamaterial concepts [18]. The proposed concept allows variety of unusual and complex yet controllable domain patterns to be achieved, in which a coexistence between hierarchical ferroelectric and ferrotoroidic polarization occurs, even in a simply branched network composed of connected ferroelectric nanowires. A key design parameter to realize such complex patterns was explored based on the parity of junctions that connect constituent nanostructures, and the formation of characterized polarization patterns in ferroelectric nano-metamaterials was also discussed [18]. As a characteristic of ferroelectric materials, spontaneous polarization and its arrangement (i.e., domain configuration) is crucial to determine the ferroelectric and related piezoelectric and dielectric properties [19-21]. The rich diversity of complex domain patterns that emerge in ferroelectric nano-metamaterials provides an ideal playground to determine not only distinct ferroelectricity, but also related properties, the most important of which is piezoelectricity, which places ferroelectric materials at the heart of many advanced technologies, such as sensors, actuators, and transducers in micro(nano)electromechanical systems (MEMS/NEMS) [22,23]. In addition, the emergence of polarization vortex configuration, which is characterized by a distinct ferrotoroidic order parameter rather than the common polarization order, is quite promising for the realization of unique electromechanical responses to external fields, and gives rise to novel functionalities in ferroelectric nano-metamaterials. Thus, knowledge regarding the electromechanical response of ferroelectric nano-metamaterials is essentially important to satisfy the ever increasing demand for the further improvement of ferroelectric devices. However, a deep understanding of the ferroelectric and/or ferrotoroidic response to external mechanical fields in ferroelectric nano-metamaterials has remained elusive due to the complexity of their non-trivial electro-elastic cross-coupling, which has impeded the application of ferroelectric nano-metamaterials in advanced nano-electromechanical devices.

In this work, polar and toroidal electromechanical responses of ferroelectric nano-metamaterials to mechanical excitation are investigated using a state-of-the-art real-space phase-field model based on Ginzburg-Landau theory. A wide range of

apparent piezoelectric coefficients are obtained, which makes them more available with respect to the control and manipulation of piezoelectricity. In addition, a new effect of piezotoroidicity is introduced to characterize the electromechanical response of the polarization vortex in ferroelectric nano-metamaterials to mechanical strain. I further discuss the effect of the nano-metamaterial internal structure on the tailoring of piezoelectric and piezotoroidic functional properties.

4.2 Simulation procedure

To investigate the electromechanical responses of ferroelectric nano-metamaterials, the internal structures are designed based on the architectures of the 2D Archimedean lattices shown in Fig. 4.1 [24]. Eleven structures compose a complete set of infinite tiles for a plane with regular polygons, which are arranged in such a way that only one vertex type appears in each structure. Although the Archimedean lattices consist of regular simple polygons, the structurally diverse characteristics of the Archimedean lattices provide space for systematic study of the electromechanical activities in ferroelectric nano-metamaterials. All lattices are designed in the range of several to tens of nanometers with a thickness of 3 nm and a lattice width of 6 nm to take into account the strong depolarization effect at the nanoscale. To access the intrinsic effects of the nano-metamaterial structure on the electromechanical responses, all specimens are prepared with the same filling volume fraction of 30%. Specimens are composed of a single crystal of ferroelectric PbTiO_3 , in which the $[100]$, $[010]$, and $[001]$ orientations correspond to the x_1 , x_2 , and x_3 directions, respectively. Periodic boundary conditions are applied in the x_1 and x_2 directions. The electrical boundary conditions on all surfaces are set to be open-circuited, i.e., $\mathbf{D} \cdot \mathbf{n} = 0$, to realize bare surfaces of the specimens.

To obtain the thermodynamic equilibrium polarization distribution in the nano-metamaterial specimens without external strain, a random distribution of polarization with its magnitude around zero is introduced as the initial state, and evolution of the polarization field toward its stable state is numerically simulated by iteratively solving the time-dependent Ginzburg-Landau equation until the change of

polarization becomes insignificant. Three tests, which consist of two uniaxial tensile tests along the x_1 and x_2 directions and one pure shear test, are then performed by application of a corresponding global strain to each specimen, step-by-step with the magnitude up to 2%, to investigate the electromechanical responses of the ferroelectric nano-metamaterials. The thermodynamic equilibrium state of polarization is obtained at each step in the same manner as that in the absence of external strain.

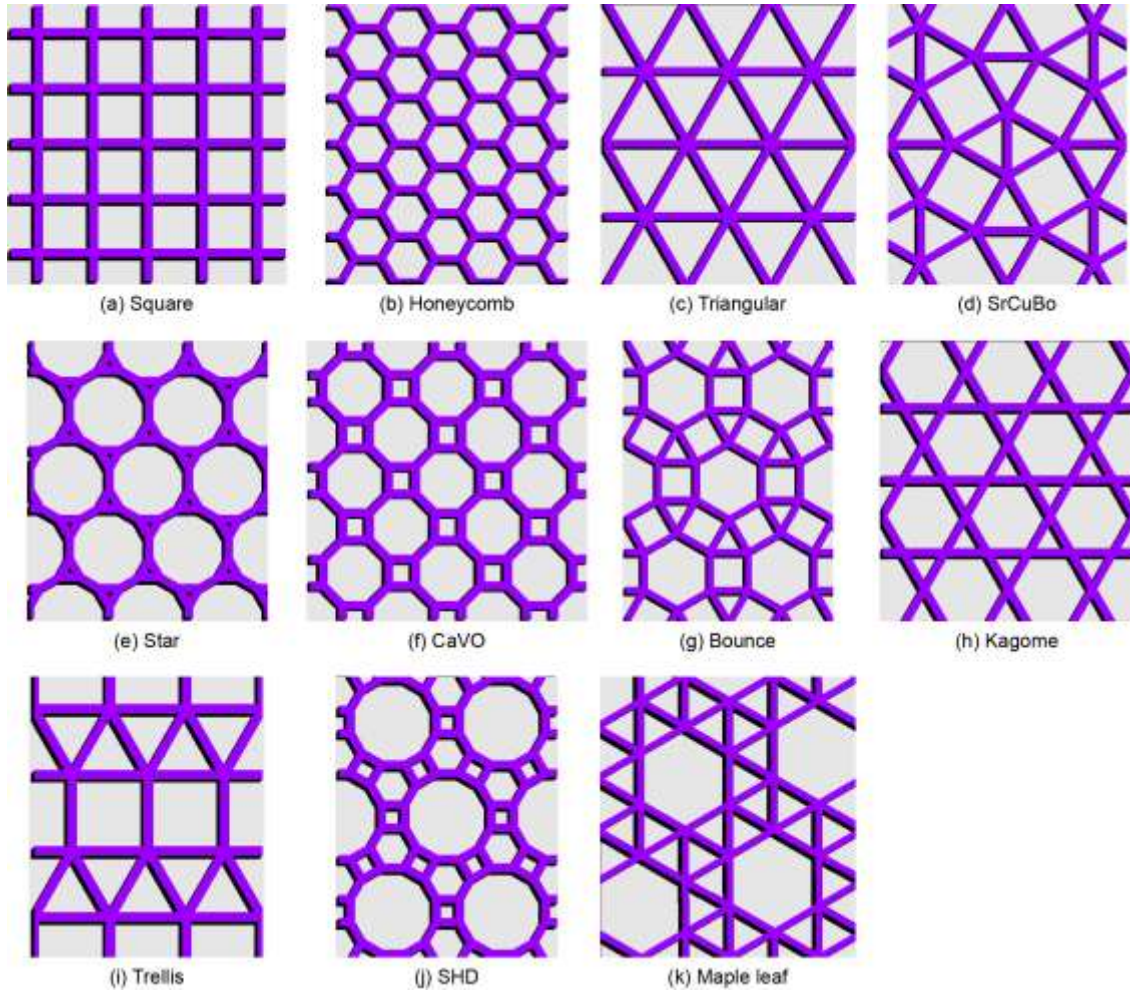


Figure 4.1. Ferroelectric nano-metamaterial specimens with architectures of 2D Archimedean lattices.

4.3 Results and discussion

4.3.1 Spontaneous polarization pattern of ferroelectric nano-metamaterials

Fig. 4.2 shows spontaneous polarization configurations in 11 nano-metamaterial specimens at the thermodynamically equilibrium state in the absence of an external field. The polarization component in the x_3 direction is suppressed due to a large depolarization field that originates from the strong geometrical confinement. The in-plane ferroelectric configuration is consistent with the experimental observations [25-29] and simulated predictions [30,31] for ferroelectric lamellae, which indicates the reliability of the phase-field simulations. Thus, purely in-plane polarization is mainly considered hereafter.

In the Square, Honeycomb, and Triangular specimens, spontaneous polarizations orient along the lattice and form a rectilinear or single domain in each lattice, as shown in Fig. 4.2a-c. The single domain causes a significant decrease in the overall electrostatic interaction energy through the elimination or reduction of the depolarization fields at free surfaces, and is thus energetically favorable. The polarization vectors at lattice junctions gradually change their orientations to connect all single domains with polarization arranged in a head-to-tail manner, as shown in the magnified images in Fig. 4.2a-c. A continuous flow of polarization is thus formed in the entire structures of the Square, Honeycomb, and Triangular specimens.

In the SrCuBO, Star, and CaVO specimens, spontaneous polarization forms a single domain in most of the lattices and causes the continuous connection of single domains at the lattice junctions, as shown in Fig. 4.2d-f, respectively. Co-occurring with the formation of single domain, spontaneous polarizations in some lattices, however, terminate the continuous connection and then curl their orientations to form micro-vortex configuration. The coexistence of the micro-vortex and single domain results in an unusual polarization pattern characteristics for the domain structures of the SrCuBO, Star, and CaVO specimens.

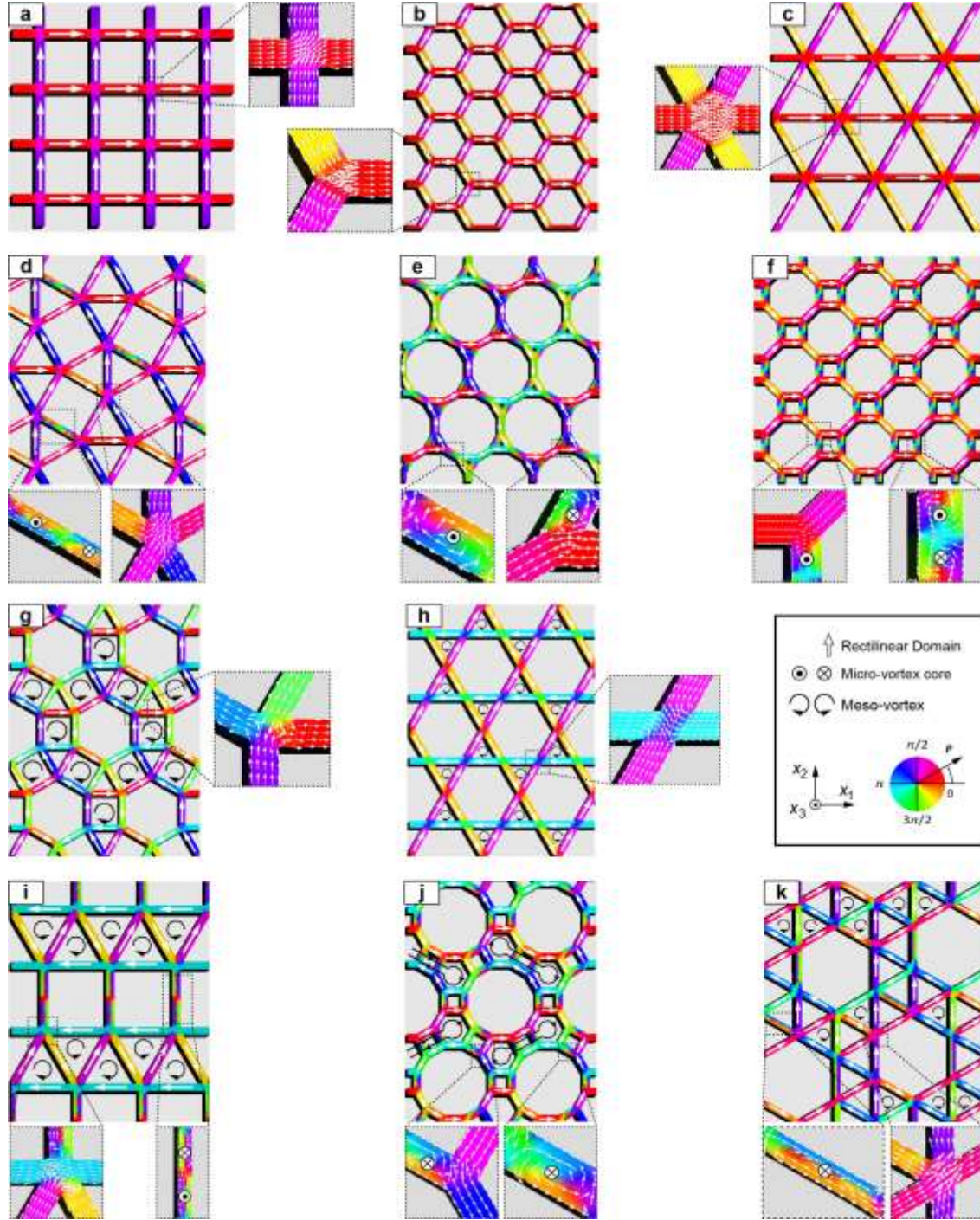


Figure 4.2. Polarization distribution in ferroelectric nano-metamaterials of (a) Square, (b) Honeycomb, (c) Triangular, (d) SrCuBo, (e) Star, (f) CaVo, (g) Bounce, (h) Kagome, (i) Trellis, (j) SHD, and (k) Maple-leaf specimens. The contour colors indicate the polarization direction.

Similar to the Square, Honeycomb, and Triangular specimens, continuous flow polarization patterns that consist of single domains are formed over the entire structures of the Bounce and Kagome specimens, as depicted in Fig. 4.2g and h, respectively. However, for the Bounce and Kagome specimens, the single domains in a complete loop of several neighboring lattices nest into flux-closure configurations at the mesoscopic scale to form a meso-vortex. Unlike the conventional vortex that appears in ferroelectric nanodots, the meso-vortex excludes the physical vortex core, which facilitates elimination of the energetic vortex core [32]. Therefore, the polarization patterns of the Bounce and Kagome specimens are characterized by the appearance of a meso-vortex in the continuous polarization flow.

Fig. 4.2i-k presents the striking characteristics of polarization patterns in the respective Trellis, Maple-leaf, and SHD specimens at the thermodynamic equilibrium state. Here, the polarization vortex occurs simultaneously at two different length scales within a single structure of the nano-metamaterial, thereby exhibiting hierarchical vortices. The coexistence of hierarchical rectilinear, micro- and meso-vortex polarizations results in the emergence of unusual and complicated patterns in the trellis, maple-leaf, and SHD specimens.

A previous study [18] revealed that the characteristics of polarization patterns in nano-metamaterials are strongly dependent on the internal structures of the ferroelectric nano-metamaterials and are governed by the parity of junctions that connect constituent nanostructures. This reveals an extrinsic route for control of the polarization in ferroelectric nano-metamaterials. Thus, Fig. 4.2 shows unique and controllable polarization patterns that can be tailored through deliberate design of the internal structure in these ferroelectric nano-metamaterials.

In addition to the polarization patterns, the macroscopic ferroelectric properties of nano-metamaterials are evaluated according to the average polarization $|P_{ave}|$, and its orientation with respect to the x_1 direction, θ . The magnitude of the average polarization is calculated by $|P_{ave}| = \sqrt{P_1^2 + P_2^2}$, in which $P_j = \frac{1}{V} \sum_i p_i \Delta V_i$, and V is total volume of the ferroelectric system, p_i are local polarization vector of i th element located at r_i , ΔV_i

is volume of i th element, respectively. $|P_{ave}|$ and θ , of which the magnitudes are summarized in Table 1, cover a wide range, depending on each type of internal structure in the ferroelectric nano-metamaterials.

Table 1. Average polarization magnitudes and directions, and average toroidal moments for ferroelectric nano-metamaterials.

	P_{ave} (C/m ²)	θ (degree)	G_3 (e/Å)
Square	0.536	45	0
Honeycomb	0.515	0	0
Triangular	0.501	0	0
SrCuBo	0.348	45	0
Star	0	0	0
CaVo	0.818	0	0
Bounce	0	0	12.20
Kagome	0.04	0	0
Trellis	0.151	0	0
SHD	0	0	11.50
Maple-leaf	0.212	0	0.37

4.3.2 Piezoelectric properties of ferroelectric nano-metamaterials

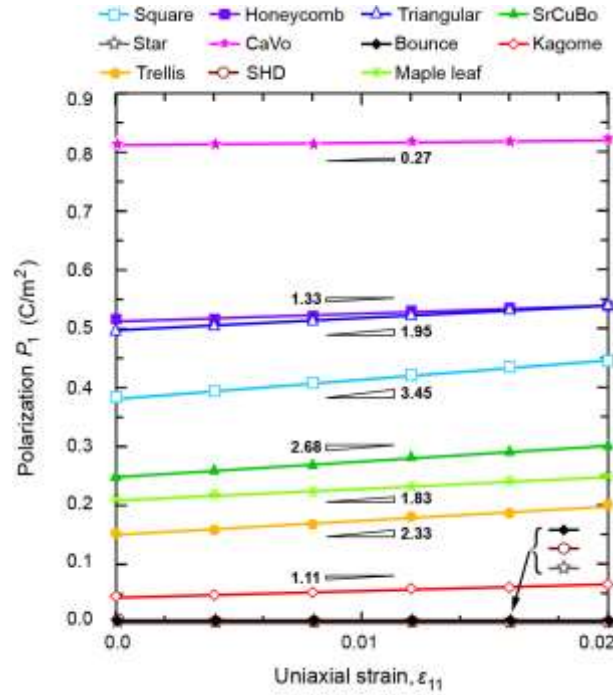


Figure 4.3. Average polarization P_1 in ferroelectric nano-metamaterials as a function of applied uniaxial strain ε_{11} . The slope of P_1 - ε_{11} relation represents the piezoelectric coefficient, e_{11} .

Fig. 4.3 represents the average polarization in the x_1 direction P_1 , as a function of the uniaxial strain, ε_{11} . P_1 changes linearly with an increase in ε_{11} for all specimens, whereby P_1 increases in most of the specimens, but is constant in the Star, Bounce, and SHD specimens. The piezoelectric coefficient e_{11} can thus be calculated through the derivative of polarization with respect to the applied mechanical strain, using the Maxwell relation $e_{11} = (\partial P_1)/(\partial \varepsilon_{11})$ [33]. In Fig. 4.3, e_{11} is represented by the slope of the P_1 - ε_{11} relations. A difference in the slopes of the P_1 - ε_{11} relations among the specimens is observed in Fig. 4.3, which indicates that e_{11} varies in the ferroelectric nano-metamaterials. The magnitude of e_{11} for the Square specimen, i.e., $e_{11(\text{Square})} = 3.45 \text{ Cm}^{-2}$, is even higher than that for the ideal PbTiO_3 bulk material of $e_{11(\text{bulk})} = 3.23 \text{ Cm}^{-2}$.

[34], while e_{11} for the remaining specimens are lower. I further calculated other piezoelectric coefficients e_{12} , e_{22} , e_{21} , e_{16} , and e_{61} . Similar tendencies to that observed in Fig. 4.3 are obtained for the other P - ε relations. The magnitudes of all piezoelectric coefficients are summarized in Table 2. All specimens are composed of the same material and have the same filling volume fraction; therefore, the difference in the magnitude of the piezoelectric coefficients among the specimens is due to the change of internal structure in the ferroelectric nano-metamaterials. This confirms that the piezoelectric coefficients in ferroelectric nano-metamaterials are strongly dependent on the internal structure.

Table 2. Piezoelectric and piezotoroidic coefficients for ferroelectric nano-metamaterials.

	Piezoelectric coefficients (C/m ²)						Piezotoroidic coefficients (e/Å)		
	e_{11}	e_{12}	e_{21}	e_{22}	e_{16}	e_{26}	e_{31}^g	e_{32}^g	e_{36}^g
Square	3.45	-0.75	-0.75	3.45	0.02	0.02	0	0	0
Honeycomb	1.33	1.11	0	0	-0.06	0	0	0	0
Triangular	1.95	0.99	0	0	-0.33	2.87	0	0	0
SrCuBo	2.68	-0.33	-0.33	2.69	0.76	0.76	0	0	0
Star	0	0	0	0	0	0	0	0	0
CaVo	0.27	-0.30	0	0.06	-0.11	-0.11	0	0	0
Bounce	0	0	0	0	0	0	18.37	18.37	-5.33
Kagome	1.11	-1.01	0	0	0.19	2.58	0	0	0
Trellis	2.33	-0.45	0	0	0	0	0	0	0
SHD	0	0	0	0	0	0	9.28	10.0	-6.43
Maple-leaf	1.83	-0.16	-1.07	0.39	-0.30	0.57	2.44	1.50	-3.82

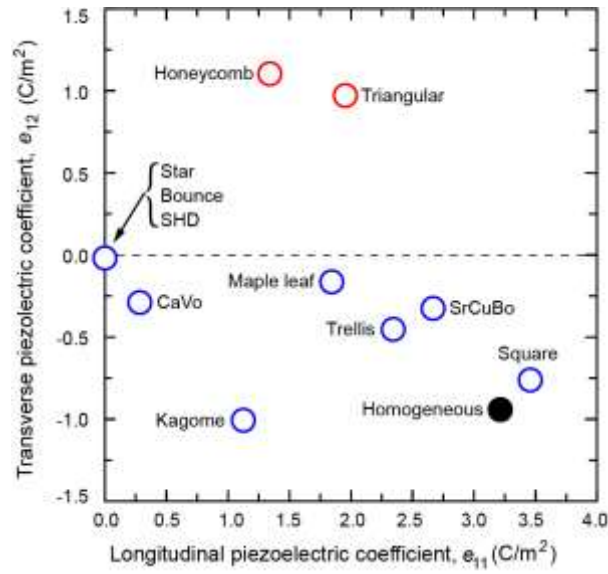


Figure 4.4. Longitudinal and transverse piezoelectric coefficients in ferroelectric nano-metamaterials with different internal structures. Blue and red circles correspond to the internal structures possessed negative and positive magnitudes of transverse piezoelectric coefficient, respectively.

Fig. 4.4 presents distributions of the longitudinal piezoelectric coefficients, e_{11} , and transverse piezoelectric coefficients, e_{12} , for all the considered ferroelectric nano-metamaterials. e_{11} and e_{12} for a homogeneous ferroelectric are also shown in Fig. 4.4 for comparison. e_{11} is positive for most of the nano-metamaterials, and the scatter of e_{11} is distant from that for homogenous ferroelectric. However, e_{11} for the Star, Bounce, and SHD structures are equivalent to zero. Piezoelectricity is an intrinsic property that appears in natural ferroelectric materials; therefore, the zero-magnitude of the piezoelectric coefficient suggests an unusual longitudinal piezoelectric response in the artificial ferroelectric nano-metamaterials, i.e., non-piezoelectricity in ferroelectric nano-metamaterials. On the other hand, for the transverse piezoelectric coefficients, most of the nano-metamaterials have a negative e_{12} , which is commonly observed in homogenous ferroelectrics [35,36]. Interestingly, the Honeycomb and Triangular specimens exhibit positive e_{12} , which gives rise to an anomalous transverse

piezoelectric response that goes beyond that for homogeneous ferroelectrics. Therefore, unusual piezoelectric responses are observed in ferroelectric nano-metamaterials and a wide range of piezoelectric coefficients can be achieved through deliberate design of the internal structure, which is distinct from common design methods such as doping [37] and domain wall engineering [38].

Given the rich variety of piezoelectric coefficients in the ferroelectric nano-metamaterials, I proceed by presenting material constants such as the piezoelectric anisotropy and hydrostatic coefficient to provide a comprehensive picture that can be used to assess the utility of piezoelectricity for applications. Fig. 4.5a summarizes the piezoelectric anisotropy coefficients ζ , for the ferroelectric nano-metamaterials, in which $\zeta = e_{11}/e_{12}$. The piezoelectric anisotropy of the homogeneous ferroelectric is also provided for comparison. Fig. 4.5a shows that the anisotropy coefficient is significantly altered by a change in the internal structure in the ferroelectric nano-metamaterials. For example, the highest absolute magnitude of the anisotropy coefficient, which is obtained for the Maple-leaf nano-metamaterial, is approximately four times of magnitude larger than that for the homogeneous material. Noted that the piezoelectric anisotropy of the homogeneous ferroelectric is dependent on the nature of the material, and it can be slightly enhanced in a small range of magnitude by rotation of the crystallographic orientation with respect to the imposed strain direction [36,39]. Since the same crystal orientation is considered for all of the nano-metamaterials, the significantly enhanced piezoelectric anisotropy indicates that the anisotropy coefficient of the ferroelectric nano-metamaterials becomes more susceptible to and strongly dependent on the internal structure. In addition, Fig. 4.5a shows that the anisotropy coefficient achieves a positive value in the Honeycomb and Triangular specimens that goes beyond the common negative value that appears in natural homogeneous ferroelectric materials [35,36]. Therefore, not only the piezoelectric anisotropy is significantly enhanced but its unusual positive value can also be achieved through deliberate design of the internal structure in these ferroelectric nano-metamaterials. This suggests that availability of an alternative strategy to freely and efficiently tailor piezoelectric anisotropy that is distinct from the conventional methods where the crystal orientation is controlled.

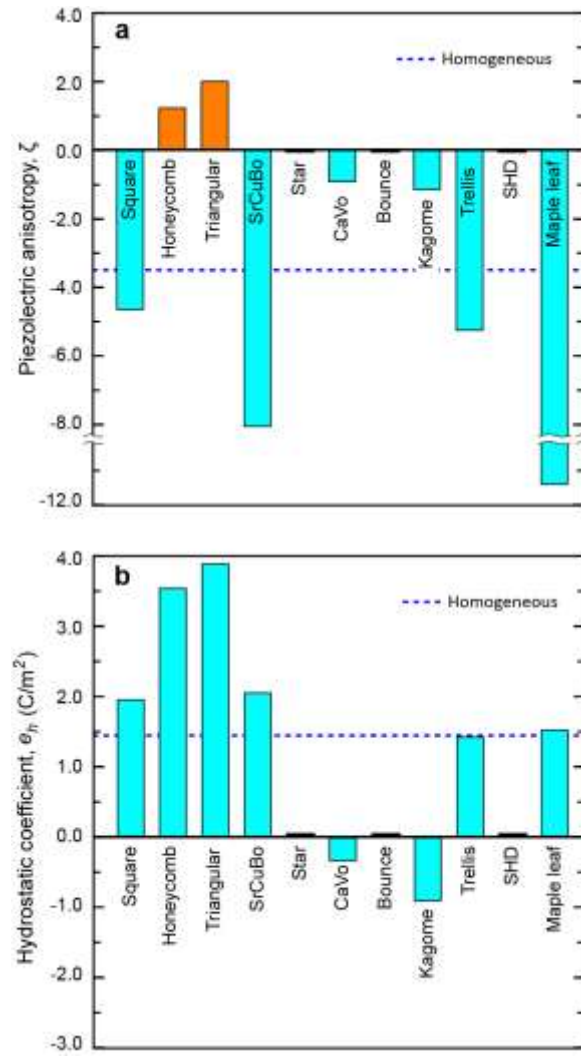


Figure 4.5. (a) Piezoelectric anisotropy coefficient, ζ , and (b) hydrostatic coefficient, e_h , in ferroelectric nano-metamaterials with different internal structures.

Fig. 4.5b summarizes the hydrostatic coefficients of the ferroelectric nano-metamaterials, which indicate the interactions between the longitudinal and transverse piezoelectric modes and are calculated according to $e_h = e_{11} + 2e_{12}$ [40]. The hydrostatic coefficient of the homogeneous material is also provided for comparison. An extreme magnitude of e_h is desirable and critically important for materials selected for hydroacoustic and other piezo-technical applications. Fig. 4.5b shows that e_h for the Square, Triangular, Honeycomb, and SrCuBo structures is larger than that for the

homogeneous ferroelectric, while e_h for the remaining structures is almost similar or lower. For the Square and SrCuBo specimens, e_h is approximately 150% greater than that for the homogeneous ferroelectric. Notably, e_h is significantly increased by approximately 260% in the Honeycomb and Triangular specimens. A Comparison of Fig. 4.5a and Fig. 4.5b demonstrates that the structures with positive anisotropy exhibit better hydrostatic properties. Although a sufficiently high hydrostatic coefficient is required for piezo-technical applications, achieving such a high value in homogeneous ferroelectrics is difficult due to the limited range of piezoelectric coefficients and their ratios. The variation of the enhanced hydrostatic coefficients in the present study suggests that this is a potential route for tailoring of the hydrostatic coefficient using ferroelectric nano-metamaterials. Thus, conscious design of nano-metamaterials provides an efficient way to significantly enhance hydrostatic coefficient, which is typically difficult to achieve in homogeneous ferroelectrics.

4.3.3 Piezotoroidic properties of ferroelectric nano-metamaterials

In the preceding section, novel and sophisticated polarization patterns that include polarization vortices at two different length scales appeared in ferroelectric nano-metamaterials (Fig. 4.2). A new ferrotoroidic order parameter has been introduced to describe and characterize for such a closure-flux configuration [41], in addition to the conventional order parameter of ferroelectric polarization. Although piezoelectricity or the interaction between ferroelectric ordering and a mechanical field has been widely considered for natural ferroelectrics and here for artificial ferroelectric nano-metamaterials through cross-coupling between ferroelectric polarization and ferroelastic strain, the interactions between new ferrotoroidic ordering and a mechanical field is not yet completely understood. Therefore, it is challenging, but of scientific interest, to study the toroidal moment-strain interaction and its properties in ferroelectric nano-metamaterials.

Adopting the concept of piezoelectricity, I probe a new functionality through consideration of the effect of strain on the toroidal moment in ferroelectric nano-metamaterials, excluding the Square, Honeycomb, and Triangular structures, due

to the absence of vortex configuration. Fig. 4.6 shows the toroidal moment G_3 , as a function of the uniaxial strain ε_{11} , in which the toroidal moment is determined as $G_3 = \frac{\sum r_i \times p_i \Delta V_i}{V}$, where p_i is local polarization vector of the i -th element located at r_i , and ΔV_i is the volume of the i -th element [41]. The magnitudes of the toroidal moments are also summarized in Table 1. Fig. 4.6 shows that G_3 changes linearly with the applied strain of ε_{11} in all specimens, whereby G_3 increases in the Bounce, SHD, and Maple-leaf specimens, while it is almost constant in the remaining structures. A coefficient that characterizes the linear change of G_3 under imposed ε_{11} is introduced in the same manner as the piezoelectric coefficient, i.e., the piezotoroidic coefficient, $e_{31}^g = \frac{\partial G_3}{\partial \varepsilon_{11}}$.

The slope of G_3 - ε_{11} represents the piezotoroidic coefficient, e_{31}^g . Fig. 4.6 shows that the slope of G_3 - ε_{11} is different for each of the Bounce, SHD, and Maple-leaf specimens. e_{31}^g for the Bounce specimen is approximately two times and ten times higher than that for the SHD and Maple-leaf specimens, respectively. In the remaining structures, e_{31}^g is zero because the total G_3 is suppressed due to the opposite chirality of polarization vortices. The significantly high magnitude of e_{31}^g and the diversity of the G_3 - ε_{11} relations demonstrate that the piezotoroidic effect is strongly dependent on the internal structure of the ferroelectric nano-metamaterials. Similar tendencies are obtained for the other piezotoroidic coefficients, including e_{32}^g and e_{36}^g . The magnitudes of the piezotoroidic coefficients are also summarized in Table 2. Thus, a new functionality of piezotoroidicity is achieved in ferroelectric nano-metamaterials, and its magnitude can be tailored through control of the internal structures in ferroelectric nano-metamaterials.

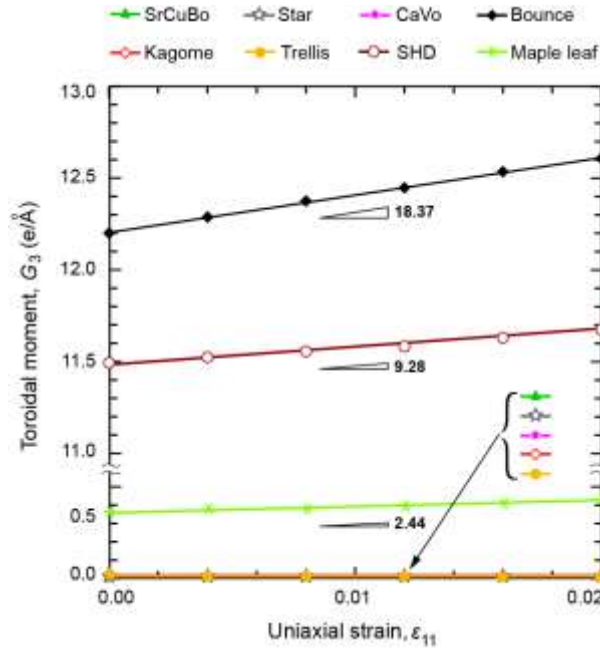


Figure 4.6. Average toroidal moment G_3 in ferroelectric nano-metamaterials as a function of applied uniaxial strain ϵ_{11} . The slope of G_3 - ϵ_{11} relation represents the piezotoroidic coefficient, e_{31}^g .

4.3.4 Discussion

In the present study, relatively simple 2D internal structures based on the architectures of 2D Archimedean lattices are employed to demonstrate the capability for control of the electromechanical properties of ferroelectric nano-metamaterials. The wide magnitude range of the piezoelectric and piezoelectric anisotropy coefficients manifests the tunability and controllability that is available through rational design of the internal structures. A wider range of the coefficients and even new electromechanical responses can be potentially realized in more complex internal structures, such as 3D metamaterials [42], auxetic metamaterials [13], and “Bucklicrystals” [43], in which the electromechanical response that is accompanied by structural responses can be enhanced. This suggests an alternative strategy to efficiently

tailor piezoelectric properties through the deliberate control of the internal structures of ferroelectric nano-metamaterials, which is distinct from conventional methods such as doping [37], and domain wall engineering [38].

Piezotoroidicity represents a new type of electromechanical coupling between ferrotoroidic ordering and a mechanical field, which could be considered as analogous to piezoelectricity for a ferroelectric material going from the bulk to the nanoscale, and would provide additional functionality that could be exploited for advanced electromechanical devices. Such a piezotoroidic effect may also provide solutions to some roadblocks encountered in the quest of miniaturized and efficient devices [44]. In addition, a strong piezotoroidic effect suggests that mechanical stress/strain could also be exploited to control the chirality of closure-flux configurations that exist in ferroelectric nano-metamaterials.

4.4 Conclusion

The electromechanical properties of 2D ferroelectric nano-metamaterials are investigated using a real-space phase field model based on Ginzburg-Landau theory. A wide range of piezoelectric coefficients are obtained for various structures of the ferroelectric nano-metamaterial, which demonstrates the strong dependence on the internal structure. Unusual positive transverse piezoelectric coefficients, and consequential positive piezoelectric anisotropy can be obtained in ferroelectric nano-metamaterials, which goes beyond that typically encountered in homogenous ferroelectrics. Significantly high piezoelectric anisotropy and hydrostatic coefficients can also be achieved in ferroelectric nano-metamaterials. A new functionality of piezotoroidicity is introduced, which is demonstrated to be dependent on the internal structure of ferroelectric nano-metamaterials. The present study thus opens exciting opportunities for tailoring the electromechanical properties through deliberate control of the internal structure in ferroelectric nano-metamaterials, and further extends the metamaterial concept to electromechanical nano-metamaterials. This is expected to further drive advances in metamaterials research and stimulate future experimentation

and simulation efforts to explore and realize more novel functionalities in ferroelectric nano-metamaterials.

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Chapter 5

Giant magnetoelectric coupling effect in 3-1 ferroelectric/ferromagnetic nanocomposites

5.1 Introduction

Multiferroic composites [1,2] of ferroelectric (FE) and ferromagnetic (FM) materials have recently attracted considerable research interest due to their large magnetoelectric (ME) coupling at room temperature and their excellent design flexibility [3-5], which provide the potential for advanced applications beyond those of the parent compounds, such as novel ME read-head sensors [6,7], data storage [8-10], and spintronic devices [11,12]. In these multiferroic composites, the ME coupling is based on the incorporation of magnetostrictive and piezoelectric effects through interfacial strain, and is thus primarily mechanical, while direct coupling between FE and FM order parameters occurs at the interfaces but is confined to the atomic scale [13]. The ME effect in multiferroic composites is therefore remarkably dependent on the magnetostrictive effect, piezoelectric effect, and elastic interactions between constituent phases.

Many bulk multiferroic composites have been found to exhibit strain-mediated ME effects [4,5,7]. Recent significant advances in manufacturing technology have enabled the nanostructure multiferroic composites to be controlled [1,2,14-17], providing a novel route to enhanced ME coupling by maximizing the interfacial area between the two phases of the nanocomposite. While the origin of the large ME coupling in multiferroic nanocomposites is, in a sense, simple, the exact details of the coupling mechanism are difficult to quantify due to the complexities of multiferroic nanocomposites, which critically prevent further tailoring of the ME coupling. This is because the ME coupling is crucially dependent on domain-level processes. Moreover, as the constituent materials approach nanoscale dimensions, the FE and FM domain structures are both altered, bringing about properties distinct from those of their bulk counterparts [18,19]. Despite their critical importance, a simultaneous understanding of the details of polarization and magnetization domain structures at the nanometer scale has remained elusive.

In this chapter, colossal ME coupling in 3-1 multiferroic $\text{BaTiO}_3/\text{CoFe}_2\text{O}_4$ nanocomposites is investigated based on mutual interactions between FE and FM domain structures using real-space phase-field method. I demonstrate that hierarchical ultrafine nanodomains are characteristically formed in the multiferroic nanocomposites and the consequent colossal ME coupling strongly depends on the arrangement of FM nanowires, suggesting a promising route to the tailoring of multiferroic domains and ME responses through the rational design of the nanostructure.

5.2 Simulation procedure

Here, I investigate multiferroic nanocomposites, in which uniform ferromagnetic CoFe_2O_4 nanowires are embedded in a ferroelectric BaTiO_3 matrix. Based on recent experimental reports [1,14,15,17], the lateral size of the FM nanowires is set to 64 nm. To study the effect of the constituent phase distribution on the FE and FM domain structures and the ME effect, three typical nanocomposite structures, with square, honeycomb, and triangular arrays of FM nanowires, are considered [20]. The

multiferroic nanocomposite structures and phase morphology are presented in Figure 5.1. The interface between the ferroelectric and ferromagnetic materials has an ideal bonding condition. On the basis of recent experimental results [1,14,15,17], a volume fraction ratio of 65:35 FE/FM is used for all multiferroic nanocomposites. Periodic boundary conditions are applied in the x_1 , x_2 , and x_3 directions. To obtain the thermodynamic equilibrium state for the multiferroic nanocomposites without an external field, small random fluctuations of polarization and magnetization are assigned as an initial state, and the simultaneous evolution of the polarization and magnetization fields is simulated by iteratively solving the time-dependent Ginzburg-Landau equations until no significant change in the polarization or magnetization is observed. In order to ensure that the equilibrium states for the multiferroic nanocomposites correspond to stable minima instead of only metastable minima, several preliminary calculations, are performed to test the formation of domain structures in each model, starting from different initial states. Then, an external magnetic field is applied to the nanocomposites step-by-step along a designated direction to consider the ME effect.

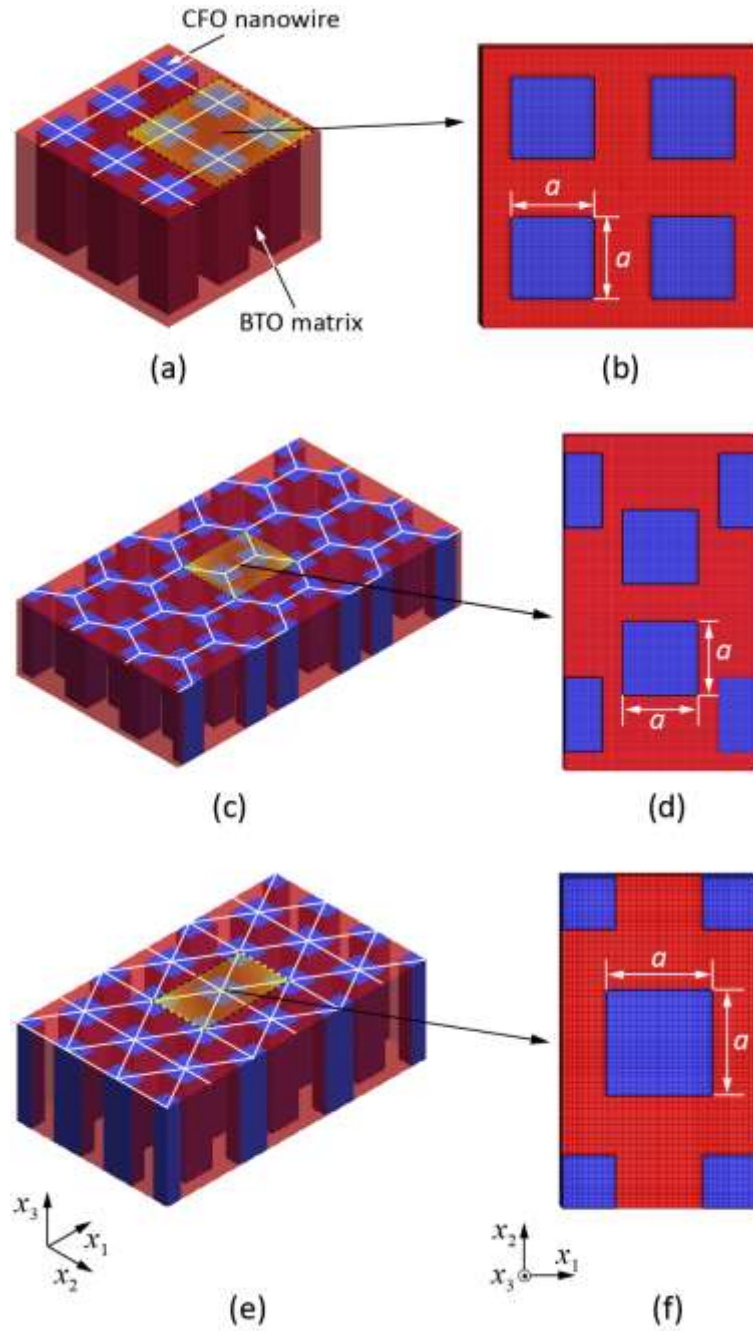


Figure 5.1. Three-dimensional of the 3-1 BaTiO₃/CoFe₂O₄ multiferroic nanocomposites and the simulation models with (a), (b) square array; (c), (d) honeycomb array; and (e), (f) triangular array of ferromagnetic nanowires. Red and blue color indicate ferroelectric BaTiO₃ matrix and ferromagnetic CoFe₂O₄ nanowire, respectively. The volume fraction ratio of 65:35 BaTiO₃/CoFe₂O₄ is used for all multiferroic nanocomposites. The square cross-section of ferromagnetic nanowire has dimension of $a = 64\text{nm}$. The periodic boundary conditions are applied in the x_1 , x_2 , and x_3 directions.

5.3 Results and discussion

5.3.1 Simultaneous polarization and magnetization configurations

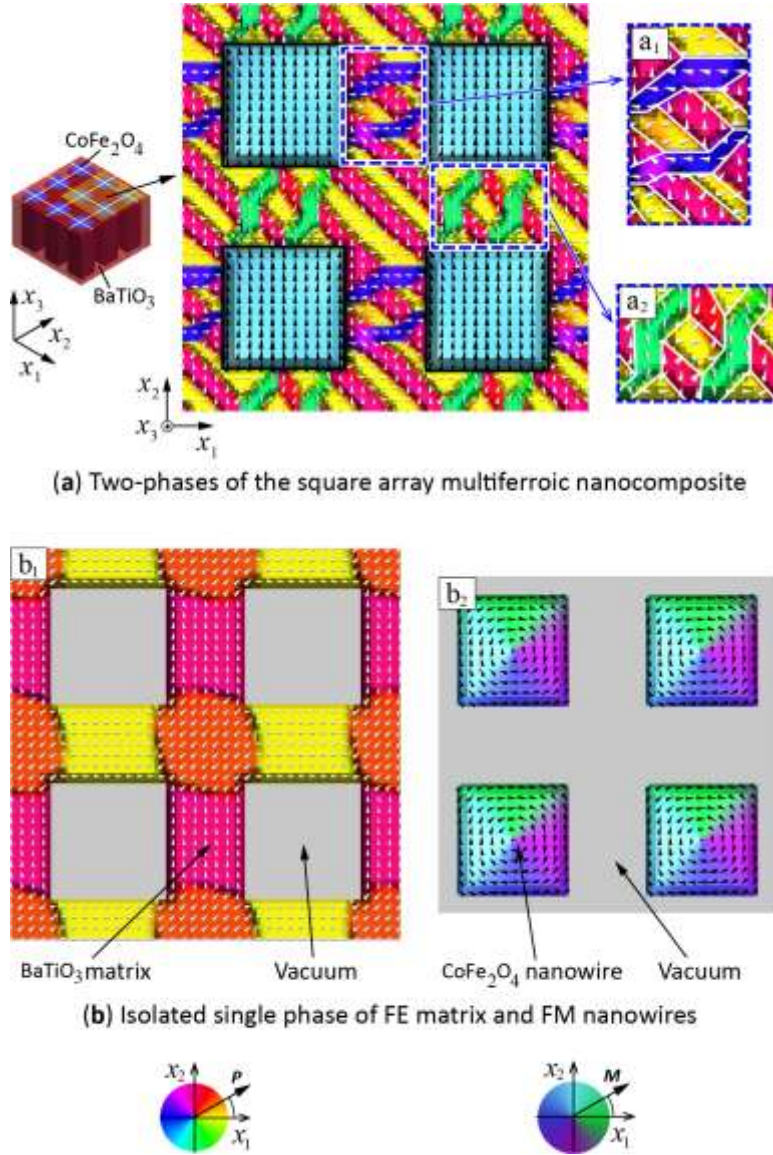


Figure 5.2. Distribution of polarization and magnetization in (a) the two phases of the square-array multiferroic nanocomposite and (b) isolated single phases of the ferroelectric matrix and ferromagnetic nanowires. The FE and FM domain variants are represented by different colors. The small white and black arrows indicate the directions of the polarization and magnetization vectors, respectively.

Fig. 5.2(a) shows simultaneously acquired domain polarization and magnetization configurations in the thermodynamic equilibrium state for the square-array nanocomposite. A bundle of 90° ultrafine striped FE nanodomains, elongated in the direction 45° from the x_1 axis, is stably formed. A more complicated cross-hatched pattern of ultrafine domains is found in the region between two neighboring FM nanowires (see Figs. 5.2(a₁) and (a₂)). The coexistence of ultrafine stripes and the cross-hatched pattern results in a hierarchical ultrafine FE domain structure in the multiferroic nanocomposite. Unlike the hierarchical ultrafine domains of the FE matrix, the constituent FM nanowire exhibits a single magnetization domain with a uniform orientation between the nanowires. Thus, a hierarchical ultrafine FE domain structure with a single FM domain characterize the domain configuration of the square-array multiferroic nanocomposite.

Insight into the formation of these coexisting domain structures in the multiferroic nanocomposite is obtained by considering the correlation and mutual influence between the FE and FM domain structures. I perform additional simulations to obtain spontaneous domain structures in isolated single phases of the FE matrix and FM nanowires with the same topologies as those of the nanocomposite, as shown in Fig. 5.2(b). A relatively simple multidomain structure emerges in the isolated FE matrix, where the polarization vector is mostly driven by the free surfaces, which is consistent with the case for FE nano-metamaterials [21]. In the isolated FM nanowires, a well-known closure-type vortex domain, which has been experimentally observed [22], appears in each nanowire to reduce the dominant demagnetization field at free surfaces. In comparison with their isolated counterparts, the FE and FM domain configurations in the multiferroic nanocomposite are both completely altered. The FE domain configuration acquires a more complicated hierarchical ultrafine FE domain structure, and the magnetic vortices are no longer stabilized in FM nanowires embedded in multiferroic nanocomposites. This change indicates that the FE domain structure is strongly correlated with and significantly influenced by the FM domain structure in the nanocomposites, and vice versa, through strain mediation at the interfaces. In addition, since the square FM nanowires are surrounded by the FE matrix in the nanocomposites, the permeability of the matrix is much larger than that of the free surface, leading to a

large reduction in the demagnetization field. On the other hand, the domain wall energy becomes important in nanoscale FM materials. A single domain is energetically more favorable than a vortex or multiple domains for FM nanowires in the nanocomposites.

I also observed coexisting FE and FM domain structures in honeycomb and triangular-array nanocomposites, as shown in Figs. 5.3(a) and 5.3(b), respectively, in order to show the effect of internal structure on the domain configuration of multiferroic nanocomposites. Cross-hatched and rectangular bubble-like patterns of ultrafine polarization domains are dominant in the FE matrix of the honeycomb array nanocomposite (Fig. 5.3(a)), whereas numerous triangular nanodomains coexisting with a sparse ultra-narrow band of domains emerge in the FE matrix of the triangular-array nanocomposite (Fig. 5.3(b)). Furthermore, Fig. 5.3 shows that the FM domains are different in the honeycomb and triangular array nanocomposites, which are multidomain and quasi-single domain, respectively. Therefore, the domain structure of multiferroic nanocomposites is sensitive to the distribution of the constituent phases, suggesting a promising route for the rational design of the internal structure of a nanocomposite in order to tailor the domain configuration, reminiscent of nano-metamaterial concepts [21].

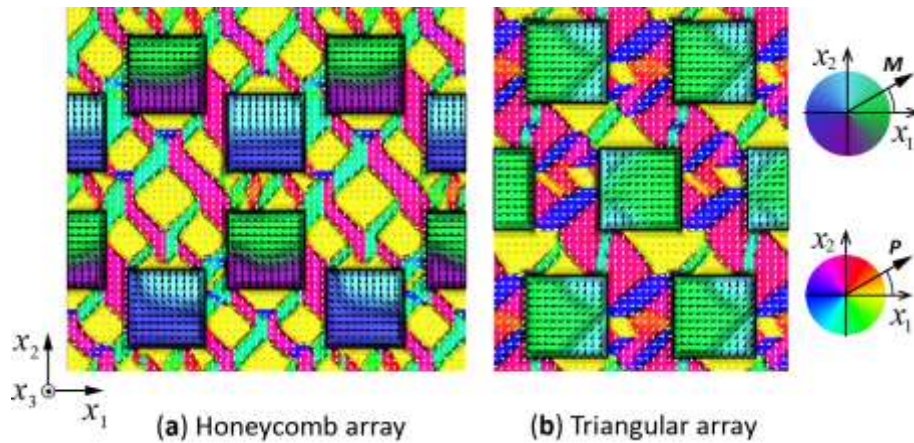


Figure 5.3. Distribution of polarization and magnetization in multiferroic nanocomposites with (a) a honeycomb array and (b) a triangular array of ferromagnetic nanowires.

5.3.2 Large magnetoelectric coupling effect

Having simultaneously determined the intriguing FE and FM domain structures of the multiferroic nanocomposites, I next consider the macroscopic ME properties, in order to provide a comprehensive picture of the interrelationship between microscopic domain structures and global behavior. The ME coefficient α_{ij} can be easily calculated as, $\alpha_{ij} = \Delta \bar{P}_i / \Delta H_j^{ext}$ [23], where $\bar{P}_i$ is the average polarization in the x_i direction and H_j^{ext} is the external magnetic field along the x_j direction. Fig. 5.4 summarizes the obtained ME coefficients for the square, honeycomb, and triangular-array nanocomposites. The magnitude of the ME coefficients is in the range of 10^{-9} - 10^{-8} s/m, which is much higher than that for bulk composites with the same composition [4,5], and is at least one order of magnitude higher than that for single phase multiferroic materials [24-26]. In addition, the magnitude of the ME coefficients obtained here agrees well with recent experimental observations and simulation-based predictions for multiferroic nanocomposites [2,27,28], which indicates the reliability of the present phase-field simulations. Thus, the colossal ME effect is characteristic of multiferroic nanocomposites. More interestingly, Fig. 5.4 shows that the ME magnitude is significantly altered by changing the FM nanowire arrangement in the multiferroic nanocomposites. For example, the highest ME coefficient for the triangular-array nanocomposite is approximately one order of magnitude larger than for the other nanocomposites. Note that all multiferroic nanocomposites considered in the present study have the same volume fraction and material composition. Therefore, the difference observed in Fig. 5.4 indicates that the ME coefficients are strongly dependent on the distribution of the constituent phases. This suggests an alternative strategy to efficiently tailor the ME effect that is distinct from the conventional methods of changing the volume fractions and/or material composition [4,23,29].

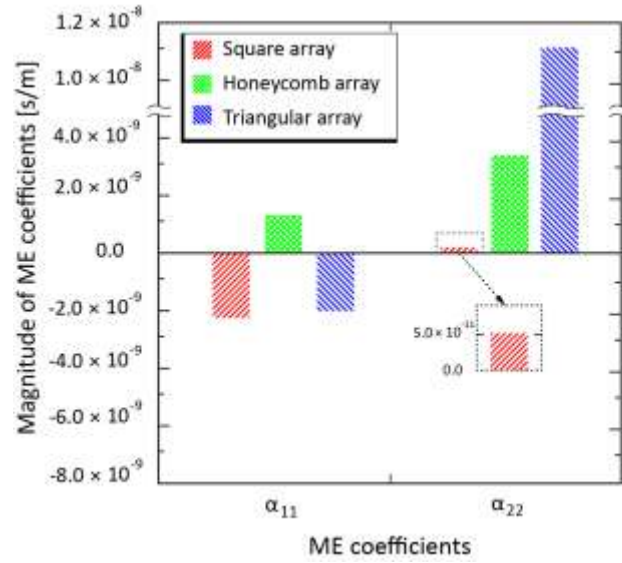


Figure 5.4. Magnetoelectric coefficients for multiferroic nanocomposites with square, honeycomb, and triangular arrays of ferromagnetic nanowires.

To clarify the underlying mechanisms responsible for the large ME coupling in the multiferroic nanocomposites and the difference in ME coefficients shown in Fig. 5.4, polarization behavior under an external magnetic field is investigated. The change in average polarization $\Delta \bar{P}$ under a magnetic field and a map of the domain walls for the FE configuration in a square-array nanocomposite are shown in Figs. 5.5(a₁) and 5.5(a₂), respectively. Fig. 5.5(a₁) shows that the polarization in the nanocomposite is sensitive to the magnetic field via interfacial strain mediation, particularly at the FE domain walls shown in Fig. 5.5(a₂). It is worth noting that experiments and first-principles simulations have proven that the response of the polarization to elastic strain is stronger at the domain wall than within an FE domain [30,31], which is consistent with Fig. 5.5(a₁). More importantly, the hierarchical ultrafine FE domain structure in the multiferroic nanocomposite results in an anomalously high density of domain walls, which occupy a substantial volume fraction of the FE domain region, unlike the case for conventional pure ferroelectrics [32,33]. Such a high density of domain walls may concentrate the local domain wall energy and elastic energy, leading to a regime of high domain wall mobility. Having a high density of mobile domain walls facilitates changes in domain populations under an external field, dramatically enhancing the ferroelectric

susceptibility. Therefore, the hierarchical ultrafine FE domains confer unique intrinsic properties to the multiferroic nanocomposites that result in strong ME coupling. On the other hand, the differences in the ME coefficients among the nanocomposites shown in Fig. 5.4 are attributed to the change in the domain wall distribution and internal strain distribution, which is accompanied by a change in the FM nanowire arrangement (as shown in the Figures 5.5 (b) and (c)).

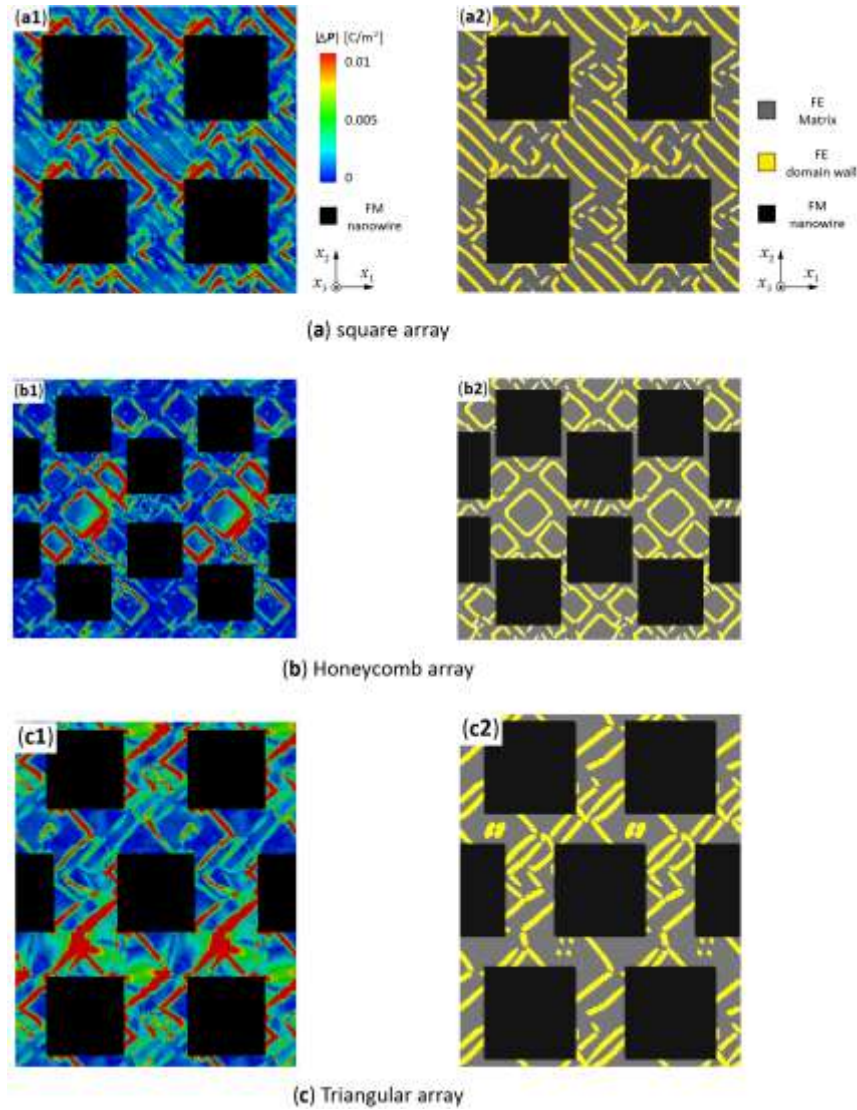


Figure 5.5. Distribution of the change in polarization under an external magnetic field and a map of the ferroelectric domain walls in (a) the square-array, (b) the honeycomb-array and (c) the triangular-array multiferroic nanocomposites.

5.4 Conclusion

In summary, I observed hierarchical ultrafine ferroic domain structures in 3-1 multiferroic BaTiO₃/CoFe₂O₄ nanocomposites. The unusual hierarchical ultrafine FE domains are intrinsically more susceptible to an external magnetic field via interfacial strain mediation because of the high domain wall density, giving rise to strong ME coupling that is consistent with recent experimental observations. This observation provides insight into the strong ME coupling and the complexities of multiferroic nanocomposites. The present study also provides a promising route for the design of ME response through microstructure-property correlation.

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Chapter 6

Instability criterion for ferroelectrics under multi-physics fields

6.1 Introduction

Ferroelectric materials are increasingly being considered as critical components in many advanced technologies, such as nonvolatile random access memory (FeRAM) devices [1,2], sensors, actuators, and transducers in micro(nano)electromechanical systems (MEMS/NEMS) [3,4], due to their large ferroelectricity and related electromechanical properties including a large piezoelectric response and high dielectric constant. The utility of ferroelectrics is derived from the ability to reorient or switch the spontaneous polarization between equivalent states under an applied electric field and/or mechanical loading, and by the coupling of such transition to other material properties such as strain [5,6], magnetic order [7], and surface charge [8]. Thus, instability in ferroelectric systems, viz., a rapid or catastrophic change in polarization ordering or reversal of the polarization vector with respect to the multi-fields that shift the system to another configuration with lower energy, essentially characterizes the polarization behavior of materials and leads to diverse functionalities or the critical malfunction of devices. Therefore, loss of stability in the polarization configuration becomes the general mechanism that underlies a wide variety of macroscopic and microscopic features of considerable importance with respect to the behavior of ferroelectric

materials under multi-field excitation. However, the instability in ferroelectric materials is generally complicated due to coherent nonlinear interactions between ferroelectricity and ferroelasticity [9-12], which critically prevent further exploitation of the advantageous aspects of these materials and the avoidance of problems associated with instability. Therefore, understanding the nature of the instability is both scientifically interesting and technologically important for ferroelectric materials.

The Ginzburg-Landau theory was proposed on the basis of the fundamental principles of thermodynamics and kinetics to describe the dynamic behavior of ferroelectrics using a polarization vector as an order parameter [13-16]. Phase field modeling based on the Ginzburg-Landau theory has been commonly used to study domain structures in ferroelectric materials, and polarization switching under static electric field and/or mechanical loading [17-21]. In recent years, phase field modeling has been extended for simulations in real-space [22-27], which has enabled any ferroelectric structures with arbitrary geometries and boundary conditions to be addressed [28,29]. Although the phase field model provides an unprecedented look at the temporal and spatial evolution of polarization, the absence of theory to describe instability in ferroelectric systems makes it difficult to capture the onset of instability events that occur not only globally but also more often locally. Therefore, an analytical criterion for instability in ferroelectrics is essential to detect their onset, from local to global events.

Various different criteria, such as the Maxwell stability criterion, lattice stability criteria, and phonon soft modes, have been proposed to separately describe each type of mechanical instability, including kink banding, buckling, dislocation, cleavage fracture, delamination of thin film from a substrate, and highly disordered amorphous metals [30-36]. Previous studies [37-41] proposed a criterion to rigorously describe the onset of mechanical instability and the deformation mode at the instability in arbitrary structures by explicitly taking into account the total energy of the system including the potential energy and work done by an external load and/or constraint with respect to all the degrees of freedom (DOFs) of the system. The advantage of the proposed theory is the capability to elucidate the nature of various mechanical instabilities in arbitrary structures without limitations or assumptions and its flexibility for other systems with

different DOFs [42-45]. Thus, it should also be possible to develop a criterion for instability in ferroelectric systems by extending this theory through the incorporation of the displacement, electrical potential, and polarization DOFs into the formulation.

In this chapter, I propose a criterion for instability in a continuum ferroelectric system by explicitly taking into account the total energy of the system including the potential energy and work done by an external field with respect to the displacement, electrical potential, and polarization DOFs on the basis of the Ginzburg-Landau theory. My theory gives an instability criterion where the minimum eigenvalue of the Hessian matrix of potential energy is zero. The proposed criterion is validated by application of the criterion to several situations of interest, such as domain switching in ferroelectric PbTiO₃ thin film under an electric field and successive ferroelastic transitions under mechanical excitation. I further demonstrate that the eigenvector according to the lowest eigenvalue directly yields the direction of polarization change associated with the instability mode, which readily allows identification of the type of instability.

6.2 Proposal of instability criterion for ferroelectrics

6.2.1 Theory of instability in ferroelectrics

Consider a finite element of a continuum ferroelectric system consisting of N nodes under an external electric field and/or mechanical load. The potential energy of the system U , can be described by the continuous displacements $\mathbf{d}$, electrical potential ϕ , and polarization vectors $\mathbf{P}$,

$$U=U(\mathbf{d}, \phi, \mathbf{P}), \quad (1)$$

where

$$\mathbf{d} = (d_x^1, d_y^1, d_z^1, d_x^2, d_y^2, d_z^2, \dots, d_x^N, d_y^N, d_z^N)^T, \quad (2)$$

$$\phi = (\phi^1, \phi^1, \dots, \phi^N)^T, \text{ and} \quad (3)$$

$$\mathbf{P} = (p_x^1, p_y^1, p_z^1, p_x^2, p_y^2, p_z^2, \dots, p_x^N, p_y^N, p_z^N)^T. \quad (4)$$

In the above, d_i^α , ϕ^α , and p_i^α denote the displacement, electrical potential, and the polarization vector at the node α ($=1, 2, \dots, N$) in the i ($=x, y, z$) direction. The irreducible number of displacement DOFs in the system is $I_R = 3N - 6$ because the DOFs for the rigid body translation (3) and rotation (3) are subtracted from the total DOFs of the node displacements ($3N$). The irreducible number of electrical potential DOFs is $I_\phi = N - 1$, since one nodal DOF for the potential should be fixed to represent connection to ground, i.e. zero voltage. On the other hand, the number of polarization DOFs is $I_P = 3N$. Therefore, the total irreducible DOFs in the system is $I = I_R + I_P + I_\phi = 7N - 7$. Here, an arbitrary deformation and/or perturbation of the polarization vector for the system can be represented by a change in the following m -dimensional vector $\mathbf{X}$, which consists of all DOFs:

$$\mathbf{X} = (d_z^2, d_x^3, d_y^3, d_x^4, d_y^4, d_z^4, \dots, d_x^N, d_y^N, d_z^N, \phi^1, \phi^2, \dots, \phi^N, p_x^1, p_y^1, p_z^1, p_x^2, p_y^2, p_z^2, \dots, p_x^N, p_y^N, p_z^N)^T \quad (5)$$

$$= (X_1, \dots, X_i, \dots, X_m)^T.$$

When the system is at equilibrium ($\mathbf{X} = \mathbf{X}_0$) under a static external electric field and/or mechanical load, the total energy of the system Π , consists of the potential energy U , the work done by an external mechanical load W , and the work done by an external electric field Φ , and is given by:

$$\Pi = U + W + \Phi \quad (6)$$

The total energy of the system in terms of an infinitesimal deformation and/or perturbation of the polarization vector, $\Pi(\mathbf{X}_0 + \Delta\mathbf{X})$, can be described by the Taylor series expansion of the total energy, $\Pi(\mathbf{X}_0)$, by $\Delta\mathbf{X}$, and is given by:

$$\Pi(\mathbf{X}_0 + \Delta\mathbf{X}) = \Pi(\mathbf{X}_0) + \sum_{k=1}^m \frac{\partial \Pi}{\partial X_k} \bigg|_{\mathbf{X}=\mathbf{X}_0} \Delta X_k + \frac{1}{2} \sum_{k=1}^m \sum_{l=1}^m \frac{\partial^2 \Pi}{\partial X_k \partial X_l} \bigg|_{\mathbf{X}=\mathbf{X}_0} \Delta X_k \Delta X_l + \dots \quad (7)$$

Stabilization of the ferroelectric system requires minimization of the total energy, which

yields the second term on the right-hand side (the first derivative of total energy) as zero, i.e.,

$$\sum_{k=1}^m \frac{\partial \Pi}{\partial X_k} \bigg|_{\mathbf{X}=\mathbf{X}_0} \Delta X_k = 0 \quad (8)$$

The external load is constant due to the static loading; therefore, the work is proportional to the displacement of nodes, which yields:

$$\frac{\partial^2 W}{\partial X_k \partial X_l} \bigg|_{\mathbf{X}=\mathbf{X}_0} = 0 \quad (9)$$

Similarly, the second derivative of the work done by a static external electric field is also zero, i.e.,

$$\frac{\partial^2 \Phi}{\partial X_k \partial X_l} \bigg|_{\mathbf{X}=\mathbf{X}_0} = 0. \quad (10)$$

Thus, by ignoring the higher-order terms, the change in total energy $\Delta \Pi$, can be rewritten in terms of an infinitesimal change in the system, $\Delta \mathbf{X}$:

$$\Delta \Pi = \Pi(\mathbf{X}_0 + \Delta \mathbf{X}) - \Pi(\mathbf{X}_0) = \frac{1}{2} \Delta \mathbf{X}^T \mathbf{A} \Delta \mathbf{X}, \quad (11)$$

where $\mathbf{A}$ is the $m \times m$ Hessian matrix of which the components are given by the second derivative of the total energy with respect to the DOFs,

$$\mathbf{A}_{kl} = \frac{\partial^2 \Pi}{\partial X_k \partial X_l} \bigg|_{\mathbf{X}=\mathbf{X}_0} = \frac{\partial^2 U}{\partial X_k \partial X_l} \bigg|_{\mathbf{X}=\mathbf{X}_0}. \quad (12)$$

$(k, l = 1, \dots, m)$

The eigenvalues of matrix $\mathbf{A}$ are represented by η_i ($\eta_1 \leq \dots \leq \eta_i \leq \dots \leq \eta_m$), whereby the matrix is diagonalized using the eigenvector, $\mathbf{v}_i$:

$$\mathbf{V}^{-1}\mathbf{A}\mathbf{V} = \mathbf{V}^T\mathbf{A}\mathbf{V} = \begin{pmatrix} \eta_1 & & 0 \\ & \ddots & \\ 0 & & \eta_m \end{pmatrix}, \quad (13)$$

where $\mathbf{V}=(\mathbf{v}_1...\mathbf{v}_m)$. Here, the eigenvector $\mathbf{v}_i$ is normalized. By introducing

$$\Delta\mathbf{Q} \equiv \mathbf{V}^{-1}\Delta\mathbf{X} = (\Delta Q_1, ..., \Delta Q_m)^T, \quad (14)$$

the total energy change in Eq.(11) becomes

$$\Delta I = \frac{1}{2}(\mathbf{V}\Delta\mathbf{Q})^T \mathbf{A}(\mathbf{V}\Delta\mathbf{Q}) = \frac{1}{2}\Delta\mathbf{Q}^T(\mathbf{V}^T\mathbf{A}\mathbf{V})\Delta\mathbf{Q} = \frac{1}{2}\sum_{i=1}^m \eta_i(\Delta Q_i)^2 \quad (15)$$

A similar discussion in previous work [37,38] indicated that the critical condition for instability, $\Delta I = 0$, appears when the minimum eigenvalue reaches zero, $\eta_1 = 0$, and the corresponding eigenvector $\mathbf{v}_1$ at $\eta_1 = 0$ represents the change in the polarization vector and the elastic deformation at the instability, i.e., the instability mode vector.

6.2.2 Ginzburg-Landau theory and formulation of the Hessian matrix

In the Ginzburg-Landau theory, the potential energy of the ferroelectric system U , can be described by [46]:

$$U = \int_V f dV = \int_V (f_{\text{Land}} + f_{\text{grad}} + f_{\text{elas}} + f_{\text{coup}} + f_{\text{dep}}) dV, \quad (16)$$

where f , f_{Land} , f_{grad} , f_{elas} , f_{coup} , and f_{dep} denote the potential energy density, Landau energy density, gradient energy density, elastic energy density, coupling energy density, and depolarization field energy density, respectively. V is the entire volume of the ferroelectric system.

The Landau energy density is expressed by a six-order polynomial of the spontaneous polarization [46,47] as:

$$\begin{aligned}
f_{Land} = & \alpha_1(P_x^2 + P_y^2 + P_z^2) + \alpha_{11}(P_x^4 + P_y^4 + P_z^4) \\
& + \alpha_{12}(P_x^2 P_y^2 + P_y^2 P_z^2 + P_z^2 P_x^2) + \alpha_{111}(P_x^6 + P_y^6 + P_z^6) \\
& + \alpha_{112}[P_x^4(P_y^2 + P_z^2) + P_y^4(P_x^2 + P_z^2) + P_z^4(P_x^2 + P_y^2)] \\
& + \alpha_{123}P_x^2 P_y^2 P_z^2
\end{aligned} \tag{17}$$

where α_1 is the dielectric stiffness coefficient, and α_{11} , α_{12} , α_{111} , α_{112} , and α_{123} are higher-order dielectric stiffness coefficients. The gradient energy density [13,17] in the second term of Eq. (16) is given by:

$$\begin{aligned}
f_{grad} = & \frac{1}{2}G_{11}(P_{x,x}^2 + P_{y,y}^2 + P_{z,z}^2) + G_{12}(P_{x,x}P_{y,y} + P_{y,y}P_{z,z} + P_{z,z}P_{x,x}) \\
& + \frac{1}{2}G_{44}[(P_{x,y} + P_{y,x})^2 + (P_{y,z} + P_{z,y})^2 + (P_{x,z} + P_{z,x})^2] \\
& + \frac{1}{2}G'_{44}[(P_{x,y} - P_{y,x})^2 + (P_{y,z} - P_{z,y})^2 + (P_{x,z} - P_{z,x})^2]
\end{aligned} \tag{18}$$

where G_{11} , G_{12} , G_{44} , and G'_{44} are the gradient energy coefficients, and $P_{i,j} = \partial P_i / \partial j$ denotes the derivative of the i th component of the polarization vector P_i , with respect to the coordinate j , and $i, j = x, y, z$. The gradient energy represents the energy penalty for inhomogeneous spatial distribution of the polarization in a ferroelectric system, such as domain walls. The elastic energy density is a pure mechanical strain energy density:

$$f_{elas} = \frac{1}{2}c_{11}(\varepsilon_{xx}^2 + \varepsilon_{yy}^2 + \varepsilon_{zz}^2) + c_{12}(\varepsilon_{xx}\varepsilon_{yy} + \varepsilon_{yy}\varepsilon_{zz} + \varepsilon_{zz}\varepsilon_{xx}) + 2c_{44}(\varepsilon_{xy}^2 + \varepsilon_{yz}^2 + \varepsilon_{zx}^2) \tag{19}$$

where c_{11} , c_{12} , and c_{44} are the elastic constants, and ε_{ij} is the total strain that includes the elastic and electrostrictive strains. The fourth term of Eq. (16) represents the energy density of electrostrictive coupling between the spontaneous polarization and mechanical strain, and is given by [47]:

$$\begin{aligned}
f_{coup} = & -q_{11}(\varepsilon_{xx}P_x^2 + \varepsilon_{yy}P_y^2 + \varepsilon_{zz}P_z^2) - 2q_{12}[\varepsilon_{xx}(P_y^2 + P_z^2) + \varepsilon_{yy}(P_x^2 + P_z^2) + \varepsilon_{zz}(P_x^2 + P_y^2)] \\
& - 2q_{44}(\varepsilon_{xy}P_xP_y + \varepsilon_{xz}P_xP_z + \varepsilon_{yz}P_yP_z)
\end{aligned} \tag{20}$$

where q_{11} , q_{12} , and q_{44} are electrostrictive constants. The depolarization energy is a self-electrostatic energy that corresponds to the long-range electrostatic interaction of

spontaneous polarization and is calculated by [48-50]:

$$f_{dep} = -\frac{1}{2} (E_x^d P_x + E_y^d P_y + E_z^d P_z), \quad (21)$$

where E_x^d , E_y^d , and E_z^d are the components of the depolarization field along the x, y, and z directions, respectively, which are induced inside ferroelectrics by incomplete screening of the polarization charges at truncated surfaces, and depends on the electrical boundary conditions. The depolarization field is derived as the negative gradient of the electrostatic potential, $E_i^d = -\partial\phi/\partial x_i$, with ϕ is electrostatic potential.

The work done by the external electric field E_i^a , is expressed as:

$$\Phi = \int_V f_{elec} dV = \int_V (-E_x^a P_x - E_y^a P_y - E_z^a P_z) dV. \quad (22)$$

The governing equation for determination of the polarization configuration can be derived using the variation or principle of virtual work [22]:

$$\mathbf{K} \cdot \mathbf{X} = \mathbf{F}. \quad (23)$$

In the above,

$$\mathbf{K} = \frac{\partial^2 \Pi}{\partial X_k \partial X_l} \bigg|_{\mathbf{X}=\mathbf{X}_0} = \frac{\partial^2 U}{\partial X_k \partial X_l} \bigg|_{\mathbf{X}=\mathbf{X}_0}, \quad (24)$$

$(k, l = 1, \dots, m)$

where $\mathbf{K}$ is the global stiffness matrix or the Hessian matrix and

$$\mathbf{F} = -\frac{\partial \Pi}{\partial \mathbf{X}} \bigg|_{\mathbf{X}=\mathbf{X}_0}. \quad (25)$$

The stiffness matrix $\mathbf{K}$ is expressed as [22]:

$$[K] = \begin{bmatrix} K_{dd} & 0 & -K_{dp} \\ 0 & K_{\phi\phi} & K_{\phi p} \\ -K_{pd} & K_{p\phi} & K_{pp} + K'_{pp} \end{bmatrix}, \quad (26)$$

where

$$[K_{dd}] = \int_V [B_d]^T [c] [B_d] dV, \quad (27)$$

$$[K_{dp}] = \int_V [B_d]^T [Q(P)] [N_p] dV, \quad (28)$$

$$[K_{pd}] = \int_V [N_p]^T [Q'(P_i)] [B_d] dV, \quad (29)$$

$$[K_{\phi\phi}] = \int_V [B_\phi]^T [\kappa_0] [B_\phi] dV, \quad (30)$$

$$[K_{\phi p}] = \int_V [B_\phi]^T [N_p] dV, \quad (31)$$

$$[K_{p\phi}] = \int_V [N_p]^T [B_\phi] dV, \quad (32)$$

$$[K_{pp}] = \int_V [B_p]^T [G] [B_p] dV, \quad \text{and} \quad (33)$$

$$[K'_{pp}] = \int_V [N_p]^T [\alpha(P_i)] [N_p] dV. \quad (34)$$

Details regarding all of the matrices are provided in Appendix C.

6.3 Application of the present criterion to domain switching in ferroelectric PbTiO_3

6.3.1 Simulation model and procedure

The instability criterion for ferroelectrics proposed here is applied to polarization switching in a ferroelectric thin film under electrical and mechanical excitation. A model size of $32\Delta x \times 32\Delta x \times 2\Delta x$ is used with a grid spacing of $\Delta x = 1.5$ nm. The periodicity is taken in the x and y directions. In addition, the mechanical clamped boundary conditions are also applied; that means the total strain of ε_{xx} and ε_{yy} equal to zero in the absence of external fields and no macroscopic shape deformation happens for the ferroelectric thin film during the polarization evolution. The thin film consists of a single crystal of ferroelectric PbTiO_3 , where the $[100]$, $[010]$, and $[001]$ axes correspond to the x , y , and z directions, respectively. To realize bare free surfaces in the model, the electrical boundary conditions for free surfaces are set to be open-circuited, i.e., $\mathbf{D} \cdot \mathbf{n} = 0$, so that the depolarizing fields from the polar surfaces are explicitly taken into account.

Formation of the spontaneous polarization configuration and domain switching in the ferroelectric thin film at room temperature are carefully tested using sophisticated real-space phase-field techniques based on the Ginzburg-Landau theory. To obtain the thermodynamic equilibrium state for the ferroelectric thin film without an external field, a small random fluctuation of polarization is assigned as the initial state, and the evolution of the polarization fields is simulated by iteratively solving the time-dependent Ginzburg-Landau equation [27,29] until no significant change in the polarization is observed. An external electric field or mechanical load is then applied to the ferroelectric thin film stepwise along a designated direction to consider the domain switching. Details of the phase field simulation and the properties of PbTiO_3 have been described previously [27,29].

6.3.2 Spontaneous polarization domain structure in the absence of external fields

Fig. 6.1 shows the spontaneous polarization configuration at the thermodynamic equilibrium state of the ferroelectric thin film under no external field. Strong confinement in the z direction of the ferroelectric thin film results in purely in-plane polarization [29,51-54]. A bundle of 90° stripe domains, which are elongated in the 135° from the x axis, are stably formed with favorable head-to-tail polarization arrangement. The characteristic of the 90° stripe domain configuration obtained here is consistent with that obtained from experimental observations [9,10,55,56] and simulation predictions for ferroelectric lamellae [48,57]. This consistency indicates the reliability of the present phase-field simulations. Therefore, the 90° stripe domains characterize the domain configuration of the ferroelectric thin film.

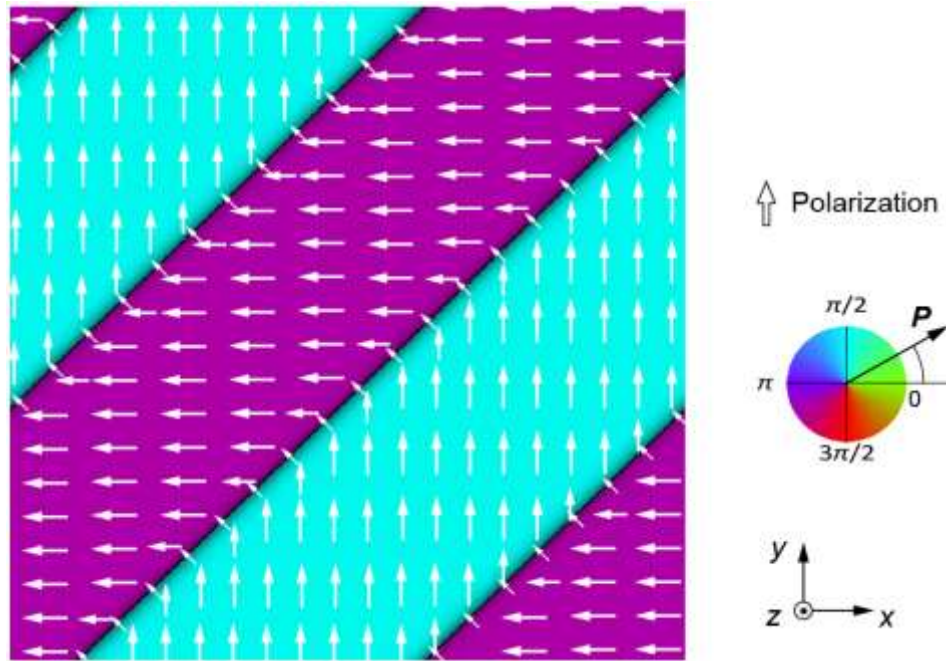


Figure 6.1. Spontaneous polarization domain structure of ferroelectric thin film. The background colors represent the orientation of the polarization vectors, as indicated by the color wheel. White arrows indicate the polarization vectors.

6.3.3 Application of instability criterion to domain switching under an external electric field

To consider the domain switching, a homogenous electric field is applied in the x direction. Fig. 6.2(a) shows the average polarization in the x direction $\overline{P}_x$, as a function

of the applied electric field, E_x . $\overline{P}_x$ is determined as $\overline{P}_x = \left(\sum_{j=1}^n P_x^j \right) / n$, where n is the

total number of the nodes of simulated models. $\overline{P}_x$ increases slightly with E_x . A small jump in the magnitude of $\overline{P}_x$ occurs as E_x reaches 0.125, then $\overline{P}_x$ increases monotonically with E_x . When $E_x = 0.18$, the magnitude of $\overline{P}_x$ abruptly changes from negative to positive. Fig. 6.2(b) shows the polarization configurations before and immediately after the sudden changes of $\overline{P}_x$, which correspond to the points A–E in Fig. 6.2(a). Comparison of the domain structures at points B and C indicates that the domains suddenly change their sizes under the electric field of $E_x = 0.125$, where the domains with the polarization originally anti-parallel to the electric field direction shrink while the other domains grow. The change of domain size results in a small jump in the magnitude of $\overline{P}_x$, shown in Fig. 6.2(a). In addition, the change of domain size originates from the motion of domain walls, which is driven by the applied electric field [57]. Note that the domain wall motion results in partial or local polarization switching, i.e., the regions swept by the domain walls are switched. Thus, the domain wall motion is regarded as a kind of instabilities that occurs in the ferroelectric system. After the domain wall motion, the domain structure has no significant change from point C to D; however, it completely changes from point D to E with $E_x = 0.18$, which indicates global domain switching. The coercive field for the domain switching is $E_c = 0.18$.

Typical snapshots during the temporal evolution of polarization switching are presented in Fig. 6.2(c), as indicated by points S₁–S₆. The domain walls first move to further shrink the domains with polarization anti-parallel to the electric field direction and expand the other domains (point S₂). The polarization vectors of the two growing domains then rotate their orientations clockwise, in an attempt to align themselves to the applied electric field (point S₃). The initial domain structure fades away, and new domains in which dipoles have aligned themselves completely with the electric field

(point S₄) begin to nucleate symmetrically about the original domain walls (point S₅). The newly formed domains then expand through the motion and change of the newly formed domain walls. At steady-state, all the domain walls are motionless under the external field, as shown by point S₆. It is noted that a reversed switching phenomenon can occur when the electric field is applied in the opposite direction, and a hysteresis response is thus obtained. This phenomenon is another case of instability in ferroelectrics that coincides with a rapid change in polarization vectors and can be analyzed by the proposed instability analysis method. However, the scope of this study is to propose and validate the method; therefore, for simplicity, I only focus on the first domain switching shown in Fig. 6.2.

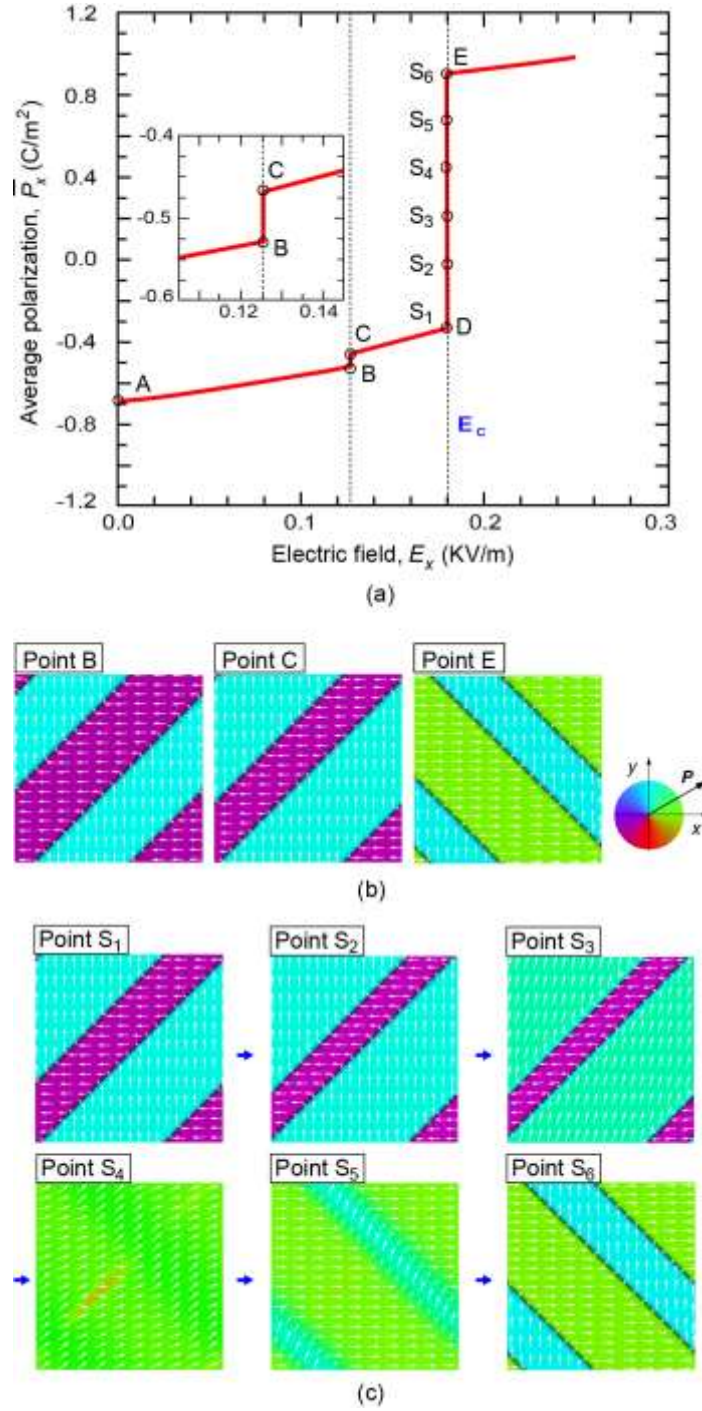


Figure 6.2. (a) Average polarization in the x direction $\bar{P}_x$, as a function of the applied electric field, E_x . E_c denotes the coercive electric field. (b) Polarization configurations under the applied electric field. Points A-E correspond to the different electric fields indicated in (a). (c) Snapshots of the polarization structure during the temporal evolution of polarization switching under the coercive electric field, E_c .

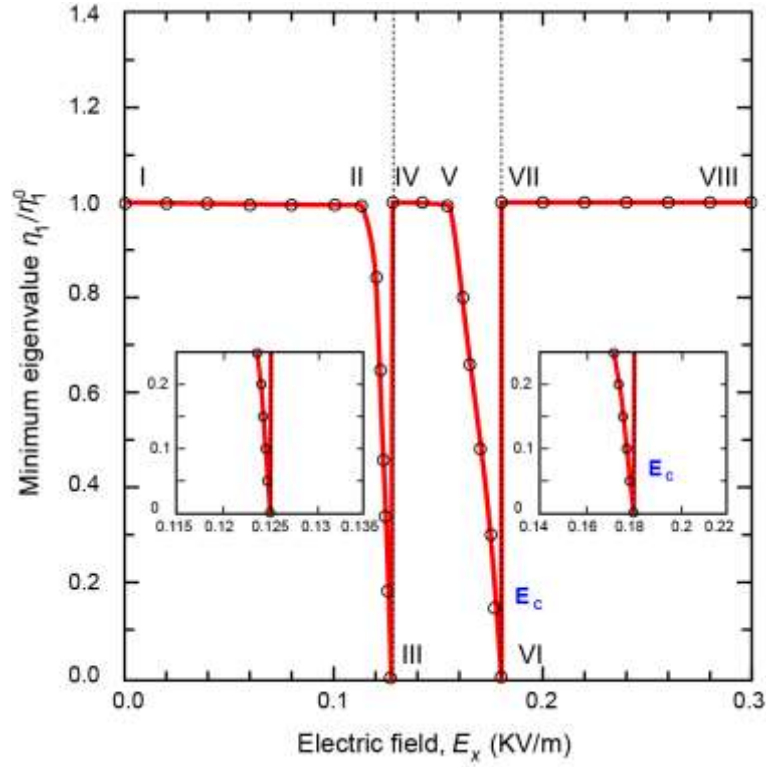


Figure 6.3. Minimum eigenvalue η_1 , normalized according to its value at zero electric field η_1^0 , as a function of the applied electric field, E_x .

To validate the instability criterion proposed here, the minimum eigenvalue of the Hessian matrix, or the global stiffness matrix, $\mathbf{K}$, is calculated as a criterion by considering all DOFs of the present model. Fig. 6.3 shows the normalized minimum eigenvalue η_1^* , as a function of the applied electric field, E_x . Here, the minimum eigenvalue η_1 is normalized according to its magnitude at zero electric field, η_1^0 . The minimum eigenvalue η_1^0 is positive at $E_x = 0.00$, indicating that the system is in stable. η_1^* is almost a constant when the external field increases from point **I** to point **II** in Fig. 6.3. η_1^* decreases as E_x increases from point **II** to point **III**, reaches zero at point **III** where $E_x = 0.125$, and then increases abruptly to a value of 1 at point **IV**. The

behavior of the $E_x - \eta_1^*$ curve from point **I** to **IV** is repeated for that from point **IV** to **VII**, in which η_1^* reaches zero at point **VI** with $E_x = 0.18$. It should be noted that the electric field at points **III** and **VI** with $\eta_1^* = 0$, which indicates the onset of instability according to my criterion, agrees exactly with the respective field of domain wall movement and domain switching obtained directly by the previously presented quasi-static simulations. This show that the instability criterion is valid for both the domain wall movement confined in a local area and global domain switching that expands to entire system.

Fig. 6.4 illustrates the eigenvector v_1 that corresponds to $\eta_1^* = 0$ at $E_x = 0.18$, which indicates the instability mode, i.e., the change of polarization with domain switching. The instability mode vector is dominant at the domain walls, while it is relatively small at the other areas, as shown in the magnified image of Fig. 6.4. This demonstrates that the domain wall is the area that is most sensitive to the applied electric field [10]. In addition, the instability mode vector at the domain walls demonstrates the clockwise change of the polarization vectors, which clearly corresponds to the onset of polarization switching under the coercive field (see also Fig. 6.2). A similar distribution of the eigenvector that corresponds to $\eta_1^* = 0$ is also observed at $E_x = 0.125$. Thus, the instability mode vector can represent the cause and mode of instability in ferroelectrics.

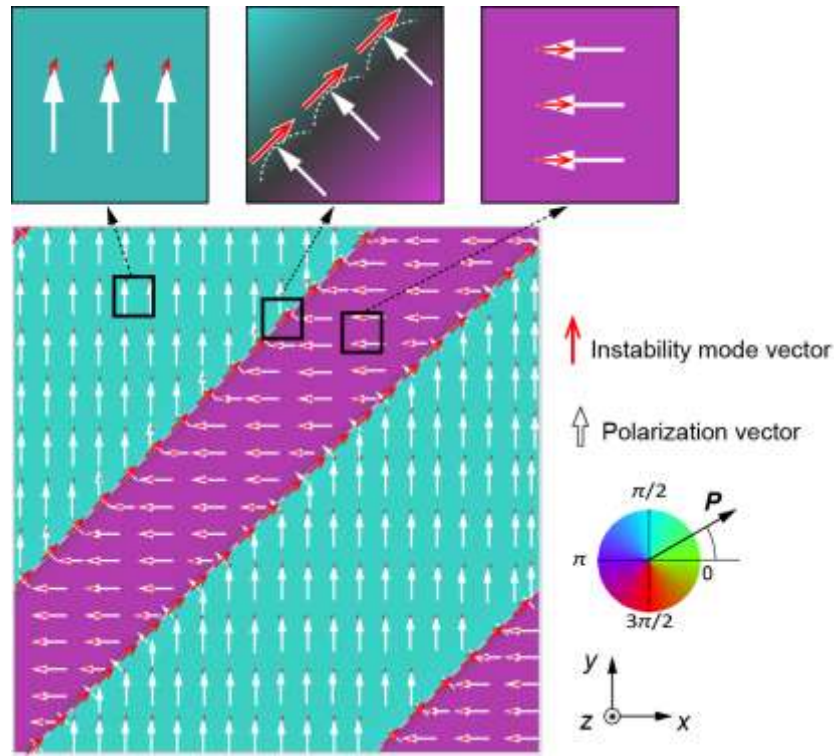


Figure 6.4. Instability mode vectors for polarization vectors. The mode vector v_1 , corresponds to the minimum eigenvalue of $\eta_1=0$ at domain switching. The background colors represent the orientation of the polarization vectors, as indicated by the color wheel. Red and white arrows indicate the instability mode vectors and polarization vectors, respectively.

6.3.4 Application of instability criterion to ferroelastic transition under external mechanical load

To consider the instability phenomenon that occurs in a ferroelectric system under an external mechanical load, a uniaxial compressive strain is applied along the y direction. Fig. 6.5(a) shows the average polarization in the x direction $\bar{P}_x$, as a function of the compressive strain, ε_{yy} . $\bar{P}_x$ gradually decreases with an increase of ε_{yy} . There are three small jumps in the magnitude of $\bar{P}_x$ as ε_{yy} reaches 0.017, 0.036, and 0.048

(Fig. 6.5(a)). Careful inspection of the polarization configurations presented in Fig. 6.5(b), which correspond to points A-H in Fig. 6.5(a), reveals that the three small jumps in $\bar{P}_x$ originate from successive 90° ferroelastic transitions. The ferroelastic switching results in shrinkage of the domains with the original polarization parallel to the y direction, while the other domains grow. At a large strain of $\varepsilon_{yy} = 0.048$, only a single domain with the direction of polarization perpendicular to the direction of compressive strain remains.

The minimum eigenvalue of the Hessian matrix $\mathbf{K}$ is calculated to validate the proposed instability criterion for the ferroelastic switching. Fig. 6.5(c) shows the normalized minimum eigenvalue η_1^* , as a function of the imposed compressive strain, ε_{yy} . The minimum eigenvalue η_1^0 is positive at $\varepsilon_{yy} = 0.00$, indicating that the system is in stable. A similar tendency to that of $E_1 - \eta_1^*$ in Fig. 6.3 is observed for $\varepsilon_{yy} - \eta_1^*$, in which η_1^* is dramatically reduced to zero at three different magnitudes of compressive strain. Comparison of Figs. 6.5(a) and 6.5(c) indicates that $\eta_1^* = 0$ at the exact same values of ε_{yy} that induce the 90° ferroelastic transitions presented in Fig. 6.5(b). This consistence demonstrates that the instability criterion is valid for the successive ferroelastic transitions.

Fig. 6.5(d) illustrates the instability mode vector v_1 , which corresponds to $\eta_1^* = 0$ at $\varepsilon_{yy} = 0.017$. The instability mode vector is also dominant at the domain walls, while it is relatively small at the other areas, as shown by the magnified image in Fig. 6.5(d). A similar distribution of the instability mode vector can be obtained for $\eta_1^* = 0$ at $\varepsilon_{yy} = 0.036$ and $\varepsilon_{yy} = 0.048$. This demonstrates that the motion of domain walls is the most favorable instability phenomenon that occurs in the ferroelectric material under mechanical load. The instability mode vector at the domain walls demonstrates a counter-clockwise change of the polarization vectors, which clearly corresponds to the onset of the polarization change under the mechanical load. In addition, recent

experiments [10] on ferroelastic switching revealed exactly the same mode of polarization rotation at the domain walls. Thus, the instability mode vector correctly represents the cause and mode of instability in the polarization configuration.

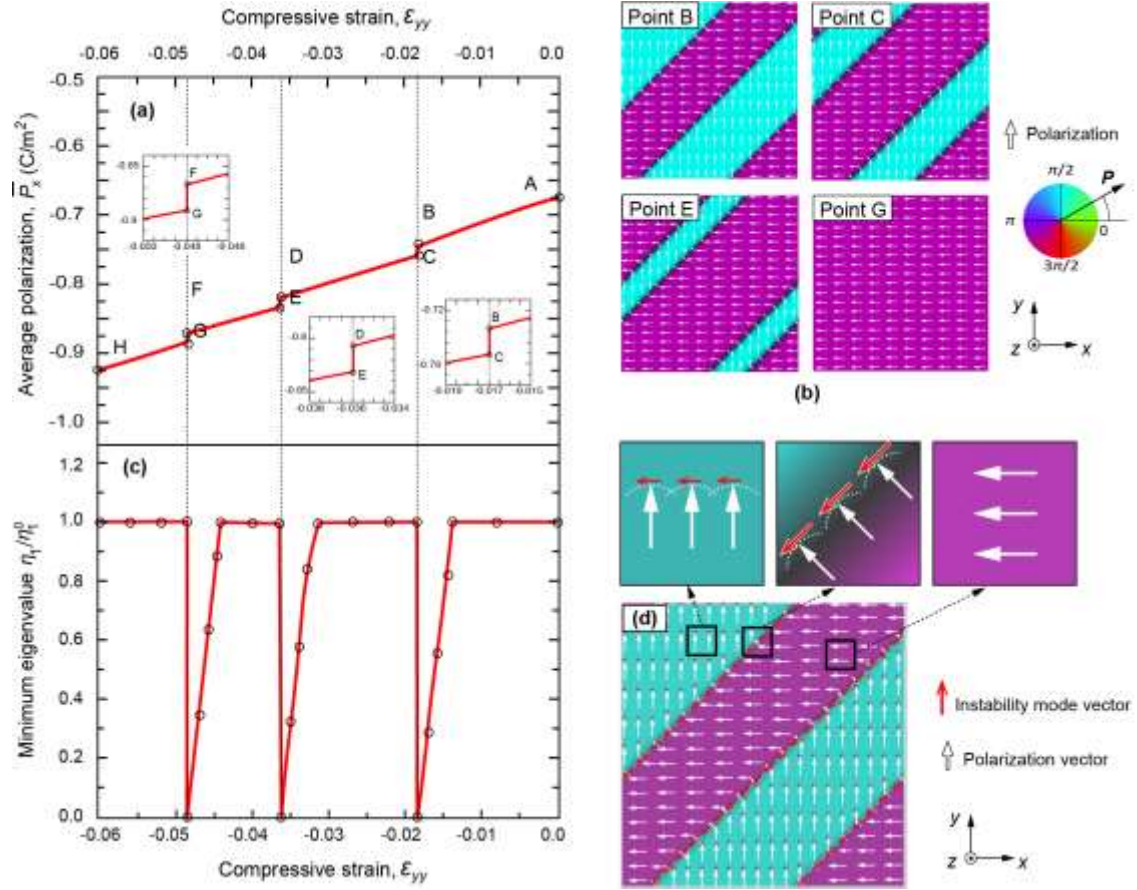


Figure 6.5. (a) Average polarization in the x direction $\bar{P}_x$, as a function of imposed compressive strain, ϵ_{yy} . (b) Polarization configurations under the imposed compressive strain. The background colors represent the orientation of the polarization vectors, as indicated by the color wheel. Points A-H correspond to the different strain indicated in (a). (c) Minimum eigenvalue η_1 , normalized according to its value at zero strain η_1^0 , as a function of the imposed compressive strain. (d) Instability mode vectors for polarization vectors. The mode vector v_1 , corresponds to the minimum eigenvalue of $\eta_1=0$ for the domain wall movement at point B in (a). Red and white arrows indicate the instability mode vectors and polarization vectors, respectively.

6.4 Discussion

In the present study, relatively simple ferroelectric thin film system was employed because both the critical magnitude of the external field and the behavior of polarization vectors at the instability must be sufficiently clear to determine from direct quasi-static simulations for comparison and validation of the proposed criterion. On the basis of my validated criterion, I can address more practical and complex instability issues for ferroelectric systems in realistic situations, where there are many types of polarization domains, including rectilinear domains, polarization vortices, and both of these interacting with numerous structural defects, such as grain boundaries, dislocations, and vacancies [9]. The proposed criterion enables the origin of instability to be determined, even in such complex ferroelectric systems. In addition, the corresponding instability mode vector provides details regarding the mechanism of instability, which enables elucidation of where and how the instability occurs in ferroelectrics. The information obtained through the proposed theory will further understanding of such instability and lead to new strategies for enhancement of the functionalities of ferroelectric devices.

I have further applied the proposed criterion to unusual polarization switching in an extremely small ferroelectric consisting of a nanodot with a polarization vortex under curled electric field, as shown in Fig. 6.6. The polarization vortex is characterized by toroidal moment of polarization G_z , which is defined as $G_z = \frac{1}{V} \int_V \mathbf{r} \times \mathbf{P} dV$, where $\mathbf{r}$ is the position vector of polarization $\mathbf{P}$ and V is volume of nanodot. The curled electric field is $\mathbf{E}^{Cur} = \frac{1}{2} \mathbf{S} \times \mathbf{r}$, where $\mathbf{S}$ is the vorticity vector of the curled field. Fig. 6.6 clearly shows that the proposed criterion rigorously captures the instability of the polarization vortex switching under curled electric field. On the other hand, the theory has flexibility for systems with different DOFs; therefore, it is possible to extend the criterion for a ferroelectric to the atomic-level, where the potential energy of the system can be described by the atoms' coordinates and polarization vectors. Noted that my proposed criterion can be applied to the mechanical instability due to buckling under compressive strain, however, I intentionally exclude the buckling phenomenon in the present study to

avoid distraction from my main purpose, i.e., proposing a new instability criterion mainly for the instability phenomena of ferroelectric and ferroelastic switching under mechanical/electric multi-fields. Thus, the proposed criterion is scale-independent, so that the instability phenomenon that occurs in any ferroelectric structures with arbitrary geometries can be addressed, thereby providing a general instability criterion for ferroelectrics. Furthermore, the flexibility of the DOFs is quite promising for extension of the proposed criterion to another important class of multiferroic materials that simultaneously exhibit at least two distinct ferroic order parameters, such as ferromagnetic order (or any other type of magnetic ordering) and ferroelectric ordering.

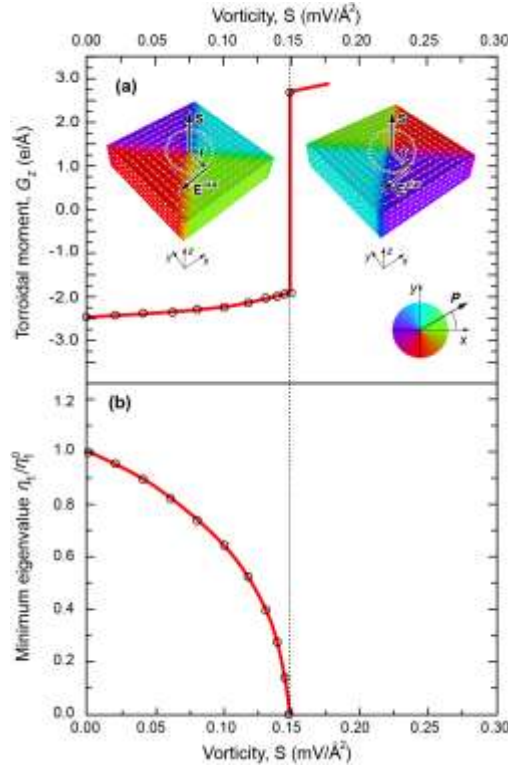


Figure 6.6. (a) Torroidal moment G_z as a function of vorticity S at room temperature. (b) Minimum eigenvalue, η_1 , normalized by the value at zero electric field, η_1^0 , as a function of vorticity S (or the applied curl electric field E^{Cur}). The illustration images represent domain configurations before and after the polarization vortex switching. The background colors represent the orientation of polarization in the xy plane as indicated by the color wheel.

6.5 Conclusion

I have presented an analytical method based on the Ginzburg-Landau theory to allow rigorous descriptions of instability in arbitrary systems of ferroelectrics under finite electric fields and/or mechanical loading to achieve an understanding of the microscopic nature of instability in these systems. The present theory yields, as an instability criterion, the condition that the minimum eigenvalue of the Hessian matrix of potential energy with respect to displacement, electrical potential, and polarization vector must be zero. Furthermore, the corresponding eigenvector represents the behavior of the polarization vector at the instability. The proposed theory is validated by application of the criterion to domain switching and successive ferroelastic transitions in ferroelectric PbTiO_3 thin film under an external electrical and mechanical excitation, respectively. This approach thus provides a novel insight into the cause of instability in ferroelectrics. In addition, the proposed criterion is scale-independent, which enables elucidation of the nature of various types of instability in arbitrary ferroelectric systems so that complicated instability issues in practical situations can be addressed.

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Chapter 7

Conclusion

In this study, I have investigated the multi-physics properties in topologically nanostructured ferroelectrics under mechanical and electric multi-fields from mesoscopic point of view by using phase-field modeling based on the Ginzburg-Landau theory. In addition, an analytical method to enable rigorous description of any type of instability in arbitrary morphologies and complex microstructures has been proposed as an extension for further investigations on the multi-physics properties in future.

In Chapter 2, unusual mechanical behavior of crack in nanoscale ferroelectrics, where polarization vortices characteristically emerge, is investigated. An anomalously large toughening effect is revealed in nanoscale ferroelectrics due to drastic stress release near the crack tip. Such anomalous toughening is attributed to an unusual switching behavior of the polarization vortices, which is no longer localized near the crack tip, but expands to the entire nanostructure. This local-to-global switching is intrinsically induced by strong cross-coupling between the ferroelectric polarization and mechanical strain that concentrates to the electro-elastic energy, not only in the vicinity of crack tip, but also to each polarization vortex due to its inhomogeneous distribution.

In Chapter 3, a new concept of ferroelectric nano-metamaterials has been introduced and demonstrated through simulations with periodic porous nanostructures of ferroelectrics. This new concept enables variety of unusual and complex yet controllable domain patterns to be achieved. A key design parameter to achieve such

complex patterns is explored based on the parity of junctions that connect constituent nanostructures. Variety of additional functionalities that are potentially obtained from ferroelectric nano-metamaterials have been highlighted, providing promising perspectives for novel multifunctional devices.

In Chapter 4, electromechanical responses in ferroelectric nano-metamaterials have been investigated. A wide magnitude range for apparent piezoelectric coefficients, which strongly depends on the internal structure, are obtained in ferroelectric nano-metamaterials. Unusual positive transverse piezoelectric coefficients, and consequently positive piezoelectric anisotropy can be achieved. A new functionality of piezotoroidicity, which represents a new type of electromechanical coupling between ferrotoroidic ordering and mechanical excitation, have been further introduced and demonstrated to emerge in ferroelectric nano-metamaterials.

In Chapter 5, colossal magnetoelectric coupling through interactions between ferroelectric and ferromagnetic nanodomains in 3-1 multiferroic $\text{BaTiO}_3/\text{CoFe}_2\text{O}_4$ nanocomposites has been investigated. A hierarchical ultrafine domain structure is characteristically formed in the nanocomposites, resulting in an extremely high density of domain walls, which causes polarization domains to be more susceptible to an external magnetic field via interfacial strain-mediation. This leads to an anomalously large magnetoelectric coupling effect in the multiferroic nanocomposites. The domain configuration and consequent magnetoelectric effect are strongly dependent on the constituent phase distribution.

In Chapter 6, an analytical method based on Ginzburg-Landau theory to enable rigorous description of any type of instability in arbitrary morphologies and complex microstructures under electric field and/or mechanical loading has been proposed. The present theory yields, as an instability criterion, the condition that the minimum eigenvalue of the Hessian matrix of potential energy must be zero. In addition, the corresponding eigenvector represents the polarization behavior at the onset of instability, which is successfully validated by application of the criterion to domain switching and successive ferroelastic transitions in PbTiO_3 ferroelectric thin film under electrical and mechanical excitations, respectively.

Appendix A

Phase field modeling for ferroelectric materials

A ferroelectric material changes from the paraelectric phase to the ferroelectric phase when the temperature is below its Curie temperature, where spontaneous polarization exists even in the absence of any external field. The ferroelectric materials is commonly investigated by using a phase-field approach based on the extended Ginzburg–Landau theory. The polarization vector $\mathbf{P} = (P_1, P_2, P_3)$ is used as the order parameter in the phase-field model to describe the free energies of ferroelectric phases. The total free energy F , of ferroelectric nano-metamaterial is obtained by integrating the total free energy density f , over the entire volume V , of the system [1]:

$$F = \int_V f dV = \int_V (f_{\text{Land}} + f_{\text{grad}} + f_{\text{elas}} + f_{\text{coup}} + f_{\text{elec}}) dV \quad (\text{A1})$$

where f_{Land} , f_{grad} , f_{elas} , f_{coup} , and f_{elec} represent the Landau free energy density, gradient energy density, pure elastic energy density, coupling energy density, and electrostatic energy density, respectively.

The Landau free energy density is described by a sixth-order polynomial of the polarization [1-4]:

$$\begin{aligned}
f_{\text{Land}} = & \alpha_1 (P_1^2 + P_2^2 + P_3^2) + \alpha_{11} (P_1^4 + P_2^4 + P_3^4) \\
& + \alpha_{12} (P_1^2 P_2^2 + P_2^2 P_3^2 + P_3^2 P_1^2) + \alpha_{111} (P_1^6 + P_2^6 + P_3^6) \\
& + \alpha_{112} [P_1^4 (P_2^2 + P_3^2) + P_2^4 (P_1^2 + P_3^2) + P_3^4 (P_1^2 + P_2^2)] \\
& + \alpha_{123} P_1^2 P_2^2 P_3^2
\end{aligned} \tag{A2}$$

where α_1 is the dielectric stiffness, and α_{11} , α_{12} , α_{111} , α_{112} , and α_{123} are higher order dielectric stiffness constants. The dielectric stiffness α_1 is given a linear temperature dependence based on the Curie–Weiss law:

$$\alpha_1 = (T - T_0) / 2\kappa_0 C_0, \tag{A3}$$

where T and T_0 denote the temperature and Curie-Weiss temperature, respectively, C_0 is the Curie constant, and κ_0 denotes the dielectric constant of a vacuum. The gradient energy density, which represents the energy penalty for the spatial polarization variation, is described by [1,3,4]:

$$\begin{aligned}
f_{\text{grad}} = & \frac{1}{2} G_{11} (P_{1,1}^2 + P_{2,2}^2 + P_{3,3}^2) + G_{12} (P_{1,1} P_{2,2} + P_{2,2} P_{3,3} + P_{3,3} P_{1,1}) \\
& + \frac{1}{2} G_{44} [(P_{1,2} + P_{2,1})^2 + (P_{2,3} + P_{3,2})^2 + (P_{1,3} + P_{3,1})^2] \\
& + \frac{1}{2} G'_{44} [(P_{1,2} - P_{2,1})^2 + (P_{2,3} - P_{3,2})^2 + (P_{3,1} - P_{1,3})^2]
\end{aligned} \tag{A4}$$

where G_{11} , G_{12} , G_{44} , and G'_{44} are the gradient energy coefficients, and $P_{i,j} = \partial P_i / \partial x_j$ denotes the derivative of the i th component of the polarization vector P_i , with respect to the j -th coordinate x_j , and where $i, j = 1, 2, 3$. The elastic energy density induced by mechanical strain is expressed by:

$$f_{\text{elas}} = \frac{1}{2} c_{11} (\varepsilon_{11}^2 + \varepsilon_{22}^2 + \varepsilon_{33}^2) + c_{12} (\varepsilon_{11} \varepsilon_{22} + \varepsilon_{22} \varepsilon_{33} + \varepsilon_{33} \varepsilon_{11}) + 2c_{44} (\varepsilon_{12}^2 + \varepsilon_{23}^2 + \varepsilon_{31}^2), \tag{A5}$$

where c_{11} , c_{12} , and c_{44} are the elastic constants, and ε_{ij} is the total strain that includes the elastic and electrostrictive strains. The coupling energy density between polarization

and strain is given by [1,3,4]:

$$f_{\text{coup}} = -q_{11}(\varepsilon_{11}P_1^2 + \varepsilon_{22}P_2^2 + \varepsilon_{33}P_3^2) - 2q_{12}[\varepsilon_{11}(P_2^2 + P_3^2) + \varepsilon_{22}(P_1^2 + P_3^2) + \varepsilon_{33}(P_1^2 + P_2^2)] - 2q_{44}(\varepsilon_{12}P_1P_2 + \varepsilon_{13}P_1P_3 + \varepsilon_{23}P_2P_3), \quad (\text{A6})$$

where q_{11} , q_{12} , and q_{44} are electrostrictive constants. The electrostatic energy density, which is obtained through Legendre transformation, is given as follow [1,3,4]:

$$f_{\text{elec}} = -\frac{1}{2}\kappa_0(E_1^2 + E_2^2 + E_3^2) - E_1P_1 - E_2P_2 - E_3P_3, \quad (\text{A7})$$

where E_i is the electric field due to the electrostatic potential distribution.

The temporal evolution of a polarization field toward its thermodynamic equilibrium state is driven by a decrease of the total free energy in the ferroelectric system, which is described by the time-dependent Ginzburg-Landau (TDGL) equation:

$$\frac{\partial P_i(r, t)}{\partial t} = -L \frac{\delta F}{\delta P_i(r, t)}, \quad (\text{A8})$$

where t denotes time, L is a kinetic coefficient, $r = (x_1, x_2, x_3)$ denotes the spatial vector, and $\delta F / \delta P_i(r, t)$ denotes the thermodynamic driving force for the evolution of polarization. In addition to Eq. (A8), the mechanical equilibrium equation,

$$\frac{\partial}{\partial x_j} \left(\frac{\partial f}{\partial \varepsilon_{ij}} \right) = 0, \quad (\text{A9})$$

and Maxwell's (or Gauss') equation,

$$\frac{\partial}{\partial x_i} \left(-\frac{\partial f}{\partial E_i} \right) = 0, \quad (\text{A10})$$

must be satisfied simultaneously with respect to charge-free and body force-free ferroelectric materials. For convenience, the following dimensionless values are used in the calculation [1]:

$$\begin{aligned}
r^* &= \sqrt{|\alpha_0|/G_{110}}r, & t^* &= |\alpha_0|Lt, & P^* &= P/P_0 \\
\alpha_1^* &= \alpha_1/|\alpha_0|, & \alpha_{11}^* &= \alpha_{11}P_0^2/|\alpha_0|, & \alpha_{12}^* &= \alpha_{12}P_0^2/|\alpha_0|, \\
\alpha_{111}^* &= \alpha_{111}P_0^4/|\alpha_0|, & \alpha_{112}^* &= \alpha_{112}P_0^4/|\alpha_0|, & \alpha_{123}^* &= \alpha_{123}P_0^4/|\alpha_0| \\
q_{11}^* &= q_{11}/|\alpha_0|, & q_{12}^* &= q_{12}/|\alpha_0|, & q_{44}^* &= q_{44}/|\alpha_0|, \\
c_{11}^* &= c_{11}/(|\alpha_0|P_0^2), & c_{12}^* &= c_{12}/(|\alpha_0|P_0^2), & c_{44}^* &= c_{44}/(|\alpha_0|P_0^2) \\
G_{11}^* &= G_{11}/G_{110}, & G_{12}^* &= G_{12}/G_{110} \\
G_{44}^* &= G_{44}/G_{110}, & G_{44}'^* &= G_{44}'/G_{110},
\end{aligned} \tag{A11}$$

where $P_0=0.757 \text{ C/m}^2$ is the magnitude of spontaneous polarization at room temperature, $\alpha_0 = \alpha_1(25^\circ\text{C}) = (T - T_0)/(2\kappa_0 C_0) = (25 - 479) \times 3.8 \times 10^5 \text{ m}^2 \text{ N/C}^2$ and $G_{110} = 1.73 \times 10^{-10} \text{ m}^4 \text{ N C}^{-2}$ is the reference value of the gradient energy coefficient. The normalized material coefficients are given in Table 1 [1].

The integral form of the governing equation is expressed in the following weak form [1,3,4]:

$$\int_V \left[\frac{\partial f}{\partial \varepsilon_{ij}} \delta \varepsilon_{ij} + \frac{\partial f}{\partial E_i} \delta E_i + \frac{\partial P_i}{L \partial t} \delta P_i + \frac{\partial f}{\partial P_{i,j}} \delta P_{i,j} + \frac{\partial f}{\partial P_i} \delta P_i \right] dV = \int_S \left[t_i \delta u_i - \omega \delta \phi + \left(\frac{\partial f}{\partial P_{i,j}} n_j \right) \delta P_i \right] dA, \tag{A12}$$

where t_i is the surface traction, ω is the surface charge, $\frac{\partial f}{\partial P_{i,j}} n_j$ is the surface gradient flux and n_j is the component of the normal unit vector of the surface.

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Appendix B

Phase field modeling for ferroelectric/ferromagnetic composites

In the phase field modeling of FE/FM nanocomposites, the multiferroic system is described by two vector fields: a polarization field $\mathbf{P}(\mathbf{r})$ and a magnetization field $\mathbf{M}(\mathbf{r})$. The total free energy of multiferroic nanocomposite is, then, expressed by:

$$F = \int_V [(1-\eta)f_p + \eta f_m + f_{b_elec} + f_{b_mag} + f_{elas}] dV \quad (B1)$$

Where $\eta=0$ is FE phase (BaTiO₃), $\eta=1$ is FM phase (CoFe₂O₄); $f_p = f_{Land} + f_{grad} + f_{elec}$ is the free energy density of FE phase with f_{Land} , f_{grad} , and f_{elec} representing the Landau, gradient, and the polarization related electrostatic energy (or electric field energy) densities, respectively, which can be expressed as [1,2]:

$$\begin{aligned} f_{Land} = & \alpha_1(P_1^2 + P_2^2 + P_3^2) + \alpha_{11}(P_1^4 + P_2^4 + P_3^4) + \alpha_{12}(P_1^2 P_2^2 + P_2^2 P_3^2 + P_3^2 P_1^2) \\ & + \alpha_{111}(P_1^6 + P_2^6 + P_3^6) + \alpha_{112}[P_1^4(P_2^2 + P_3^2) + P_2^4(P_1^2 + P_3^2) + P_3^4(P_1^2 + P_2^2)] \\ & + \alpha_{123}P_1^2 P_2^2 P_3^2 + \alpha_{1111}(P_1^8 + P_2^8 + P_3^8) + \alpha_{1122}(P_1^4 P_2^4 + P_2^4 P_3^4 + P_3^4 P_1^4) \\ & + \alpha_{1112}[P_1^6(P_2^2 + P_3^2) + P_2^6(P_1^2 + P_3^2) + P_3^6(P_1^2 + P_2^2)] \\ & + \alpha_{1123}(P_1^4 P_2^2 P_3^2 + P_1^2 P_2^4 P_3^2 + P_1^2 P_2^2 P_3^4) \end{aligned} \quad (B2)$$

$$\begin{aligned}
f_{\text{grad}} = & \frac{1}{2} G_{11} (P_{1,1}^2 + P_{2,2}^2 + P_{3,3}^2) + G_{12} (P_{1,1} P_{2,2} + P_{2,2} P_{3,3} + P_{3,3} P_{1,1}) \\
& + \frac{1}{2} G_{44} [(P_{1,2} + P_{2,1})^2 + (P_{2,3} + P_{3,2})^2 + (P_{1,3} + P_{3,1})^2] \\
& + \frac{1}{2} G'_{44} [(P_{1,2} - P_{2,1})^2 + (P_{2,3} - P_{3,2})^2 + (P_{3,1} - P_{1,3})^2]
\end{aligned} \tag{B3}$$

$$\text{and } f_{\text{elec}} = -E_1 P_1 - E_2 P_2 - E_3 P_3 \tag{B4}$$

where α_1 , α_{11} , α_{12} , α_{111} , α_{112} , α_{123} , α_{1111} , α_{1122} , α_{1112} , and α_{1123} are the phenomenological Landau expansion coefficients; G_{11} , G_{12} , G_{44} , and G'_{44} are the gradient energy coefficients; $f_{\text{b_elec}} = -\frac{1}{2} \kappa_c (E_1^2 + E_2^2 + E_3^2)$ is the electrostatic energy densities of background materials, in which κ_c is dielectric constant of the background materials; and E_1 , E_2 , and E_3 are the electric field due to the electrostatic potential distribution.

The FM term $f_m = f_{\text{ani}} + f_{\text{exch}} + f_{\text{mag}} + f_{\text{con}}$ is the free energy density of FM phase with f_{ani} , f_{exch} , f_{mag} and f_{con} denoting the magnetocrystalline anisotropy, magnetic exchange, magnetization related magnetostatic energy (or magnetic field energy) densities, respectively, which can be expressed as [3]:

$$f_{\text{ani}} = \frac{K_1}{M_s^4} (M_1^2 M_2^2 + M_2^2 M_3^2 + M_3^2 M_1^2) + \frac{K_2}{M_s^6} (M_1^2 M_2^2 M_3^2) \tag{B5}$$

$$f_{\text{exch}} = \frac{A}{M_s^2} (M_{1,1}^2 + M_{1,2}^2 + M_{1,3}^2 + M_{2,1}^2 + M_{2,2}^2 + M_{2,3}^2 + M_{3,1}^2 + M_{3,2}^2 + M_{3,3}^2) \tag{B6}$$

$$f_{\text{mag}} = -\mu_c (H_1 M_1 + H_2 M_2 + H_3 M_3) \tag{B7}$$

$$\text{and } f_{\text{con}} = A_s (M - M_s)^2 \tag{B8}$$

where K_1 and K_2 are the magnetocrystalline anisotropy constants, M_s is the magnitude of saturation magnetization, A is the exchange stiffness constant, μ_c is the permeability of the background material, and H_1 , H_2 , and H_3 are the magnetic field;

$M = \sqrt{M_1^2 + M_2^2 + M_3^2}$ is the magnitude of magnetization vector and A_s is the constraint energy constant; $f_{b_mag} = -\frac{1}{2}\mu_c(H_1^2 + H_2^2 + H_3^2)$ is the magnetostatic energy densities of background materials.

The elastic energy density of the whole system, f_{elas} , can be expressed as:

$$f_{elas} = c_{ijkl}(\varepsilon_{ij} - \varepsilon_{ij}^0)(\varepsilon_{kl} - \varepsilon_{kl}^0) \quad (B9)$$

where ε_{ij} is the total strain, ε_{ij}^0 is the stress-free strain due to the electrostrictive effect or magnetostrictive effect, and c_{ijkl} are the elastic stiffness tensors of FE or FM materials. For the particular BaTiO₃/CoFeO₄ nanocomposite, the ε_{ij}^0 can be written as [4]:

$$\varepsilon_{ij}^0 = \begin{cases} \eta \left[\frac{3}{2} \lambda_{100} \left(m_i m_j - \frac{1}{3} \right) \right] + (1-\eta) Q_{ijkl} P_k P_l & (i = j), \\ \eta \left(\frac{3}{2} \lambda_{111} m_i m_j \right) + (1-\eta) Q_{ijkl} P_k P_l & (i \neq j) \end{cases} \quad (B10)$$

where Q_{ijkl} are the electrostrictive coefficients and λ_{100} and λ_{111} are the magnetostrictive constants.

The simultaneous evolution of the polarization and magnetization fields toward their thermodynamic equilibrium distributions is driven by the decrease of total free energy in the multiferroic nanocomposite system, which is described the time-dependent Ginzburg-Landau (TDGL) equations:

$$\frac{\partial P_i(x, t)}{\partial t} = -L_{FE} \frac{\partial F}{\partial P_i(x, t)} \quad (B11)$$

$$\frac{\partial M_i(x, t)}{\partial t} = -L_{FM} \frac{\partial F}{\partial M_i(x, t)} \quad (B12)$$

where L_{FE} and L_{FM} are kinetic coefficient for the time evolution of spontaneous

polarization and magnetization, respectively. In addition to the TDGL equations, the following mechanical equilibrium equation:

$$\frac{\partial \sigma_{ij}}{\partial x_j} = \frac{\partial}{\partial x_j} \left(\frac{\partial F}{\partial \varepsilon_{ij}} \right) = 0 \quad (\text{B13})$$

and the Maxwell's (or Gauss) equations:

$$\frac{\partial D_i}{\partial x_i} = \frac{\partial}{\partial x_i} \left(- \frac{\partial F}{\partial E_i} \right) = 0 \quad (\text{B14})$$

$$\frac{\partial B_i}{\partial x_i} = \frac{\partial}{\partial x_i} \left(- \frac{\partial F}{\partial H_i} \right) = 0 \quad (\text{B15})$$

must be simultaneously satisfied for the body force, charge, and magnetic free in the multiferroic nanocomposites.

In order to solve the governing Eqs. (B11)-(B15) in real-space, a nonlinear multi-field coupling finite element method is employed. In the finite element method, the governing Eqs. (B11)-(B15) are expressed in the integral form (or weak form) as:

$$\begin{aligned} & \int_V \left\{ \frac{\partial f}{\partial \varepsilon_{ij}} \delta \varepsilon_{ij} + \frac{\partial f}{\partial E_i} \delta E_i + \frac{\partial f}{\partial H_i} \delta H_i + \left(\frac{1}{L_{FE}} \frac{\partial P_i}{\partial t} + \frac{\partial f}{\partial P_i} \right) \delta P_i + \frac{\partial f}{\partial P_{i,j}} \delta P_{i,j} \right. \\ & \left. + \left(\frac{1}{L_{FM}} \frac{\partial M_i}{\partial t} + \frac{\partial f}{\partial M_i} \right) \delta M_i + \frac{\partial f}{\partial M_{i,j}} \delta M_{i,j} \right\} dv \\ & = \int_S \left\{ t_i \delta u_i - w \delta \phi_P - B_n \delta \phi_M + \left(\frac{\partial f}{\partial P_{i,j}} n_j \right) \delta P_i + \left(\frac{\partial f}{\partial M_{i,j}} n_j \right) \delta M_i \right\} ds \end{aligned} \quad (\text{B16})$$

where t_i is the surface traction, u_i is the mechanical displacement, w denotes surface charge, ϕ_P is electrostatic potential, B_n is the normal component of the magnetic induction, ϕ_M is a scalar magnetic potential, and n_j denotes the components of normal unit vector of surfaces.

Tables BI and BII show the values of the material coefficients of BaTiO₃ and CoFe₂O₄, respectively, employed in the simulations.

TABLE BI. Material constants of BaTiO₃ used in the simulation [4].

Landau constants		Gradient constants	
α_1 [m ² N/C ²]	$4.124(T-115)\times 10^5$	G_{11} [m ⁴ N/C ²]	2.2×10^{-11}
α_{11} [m ⁶ N/C ⁴]	-2.097×10^8	G_{12} [m ⁴ N/C ²]	0
α_{12} [m ⁶ N/C ⁴]	7.974×10^8	G_{44} [m ⁴ N/C ²]	1.1×10^{-11}
α_{111} [m ¹⁰ N/C ⁶]	1.294×10^9	G_{44}' [m ⁴ N/C ²]	1.1×10^{-11}
α_{112} [m ¹⁰ N/C ⁶]	-1.950×10^9		
α_{123} [m ¹⁰ N/C ⁶]	-2.500×10^9		
α_{1111} [m ¹⁴ N/C ⁸]	3.863×10^{10}		
α_{1112} [m ¹⁴ N/C ⁸]	2.529×10^{10}		
α_{1122} [m ¹⁴ N/C ⁸]	1.637×10^{10}		
α_{1123} [m ¹⁴ N/C ⁸]	1.367×10^{10}		
Coupling constant		Elastic constants	
q_{11} [m ⁴ /C ²]	1.13×10^{10}	c_{11} [N/m ²]	1.78×10^{11}
q_{12} [m ⁴ /C ²]	2.86×10^8	c_{12} [N/m ²]	0.96×10^{11}
q_{44} [m ⁴ /C ²]	7.08×10^9	c_{44} [N/m ²]	1.22×10^{11}
Dielectric constant		Magnetic permeability	
ε [F/m]	4.427×10^9	μ [H/m]	5.02×10^{-6}

TABLE BII. Material constant of CoFe_2O_4 used in the simulation [4].

Magnetocrystalline anisotropy constants		Magnetostrictive constants	
K_1 [J/m ³]	3×10 ⁵	λ_{100}	-590×10 ⁻⁶
K_2 [J/m ³]	0	λ_{111}	120×10 ⁻⁶
Elastic constants		Saturation magnetization	
c_{11} [N/m ²]	2.86×10 ¹¹	M_s [A/m]	3.5×10 ⁵
c_{12} [N/m ²]	1.73×10 ¹¹		
c_{44} [N/m ²]	0.97×10 ¹¹		
Exchange stiffness constants		Magnetic permeability	
A [J/m]	7×10 ⁻¹²	χ_m	0.05
Dielectric constant		Magnetic permeability	
ε [F/m]	0.797×10 ⁹	μ [H/m]	1.56×10 ⁻⁴

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Appendix C

Details of Matrices

This appendix describes the details of matrices used in the paper. With the nodal values of each element, $\{d^I\}$, $\{\phi^I\}$, and $\{P^I\}$, the continuous displacements, electrical potential, and polarizations in the element are given by [1,2]:

$$\{d\} = [N_d]\{d^I\}, \quad \phi = \langle N_\phi \rangle \{\phi^I\}, \quad \{P\} = [N_p]\{P^I\} \quad (\text{A1})$$

where $[N_d]$, $\langle N_\phi \rangle$, and $[N_p]$ are interpolation functions (or shape functions) matrices.

The strain, electric field, and polarization gradients can also be described by the nodal values of displacements, electrical potential, and polarizations, respectively.

$$\{\varepsilon\} = [B_d]\{d^I\}, \quad \{E\} = -[B_\phi]\{\phi^I\}, \quad \{\xi\} = [B_p]\{P^I\} \quad (\text{A2})$$

where

$$\{\varepsilon\} = \begin{bmatrix} \varepsilon_{xx} & \varepsilon_{yy} & \varepsilon_{zz} & 2\varepsilon_{yz} & 2\varepsilon_{xz} & 2\varepsilon_{xy} \end{bmatrix}^T,$$

$$\{P\} = \begin{Bmatrix} P_x \\ P_y \\ P_z \end{Bmatrix}, \quad \{E\} = \begin{Bmatrix} E_x \\ E_y \\ E_z \end{Bmatrix}, \quad \{d\} = \begin{Bmatrix} d_x \\ d_y \\ d_z \end{Bmatrix},$$

$$\{\xi\} = \begin{Bmatrix} \xi_{xx} & \xi_{yy} & \xi_{zz} & \xi_{xy} & \xi_{yx} & \xi_{xz} & \xi_{zx} & \xi_{yz} & \xi_{zy} \end{Bmatrix}^T,$$

$$[c] = \begin{bmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{44} \end{bmatrix},$$

$$[Q(P_i)] = \begin{bmatrix} q_{11}p_x & q_{12}p_y & q_{12}p_z \\ q_{12}p_x & q_{11}p_y & q_{12}p_z \\ q_{12}p_x & q_{12}p_y & q_{11}p_z \\ 0 & q_{44}p_z & 0 \\ q_{44}p_z & 0 & 0 \\ q_{44}p_y & 0 & 0 \end{bmatrix},$$

$$[Q'(P)] = \begin{bmatrix} 2q_{11}p_x & 2q_{12}p_x & 2q_{12}p_x & 0 & q_{44}p_z & q_{44}p_y \\ 2q_{12}p_y & 2q_{11}p_y & 2q_{12}p_y & q_{44}p_z & 0 & q_{44}p_x \\ 2q_{12}p_z & 2q_{12}p_z & 2q_{11}p_z & q_{44}p_y & q_{44}p_x & 0 \end{bmatrix},$$

$$[\kappa] = \begin{bmatrix} \kappa_0 & 0 & 0 \\ 0 & \kappa_0 & 0 \\ 0 & 0 & \kappa_0 \end{bmatrix},$$

$$[G] = \begin{bmatrix} G_{11} & G_{12} & G_{12} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ G_{12} & G_{11} & G_{12} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ G_{12} & G_{12} & G_{11} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & G_{44} + G'_{44} & G_{44} - G'_{44} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & G_{44} - G'_{44} & G_{44} + G'_{44} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & G_{44} + G'_{44} & G_{44} - G'_{44} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & G_{44} - G'_{44} & G_{44} + G'_{44} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & G_{44} + G'_{44} & G_{44} - G'_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & G_{44} - G'_{44} & G_{44} + G'_{44} & 0 \end{bmatrix},$$

$$[\alpha(P_i)] = \begin{bmatrix} 2\alpha_1 + 4\alpha_{11}P_x^2 + 2\alpha_{12}(P_y^2 + P_z^2) & 0 & 0 \\ + 6\alpha_{11}P_x^4 + 2\alpha_{12}P_y^2P_z^2 & & \\ + \alpha_{112}[4P_x^2(P_y^2 + P_z^2) + 2(P_y^4 + P_z^4)] & & \\ 0 & 2\alpha_1 + 4\alpha_{11}P_y^2 + 2\alpha_{12}(P_x^2 + P_z^2) & 0 \\ + 6\alpha_{11}P_y^4 + 2\alpha_{12}P_x^2P_z^2 & & \\ + \alpha_{112}[4P_y^2(P_x^2 + P_z^2) + 2(P_x^4 + P_z^4)] & & \\ 0 & 0 & 2\alpha_1 + 4\alpha_{11}P_z^2 + 2\alpha_{12}(P_y^2 + P_x^2) \\ + 6\alpha_{11}P_z^4 + 2\alpha_{12}P_y^2P_x^2 & & \\ + \alpha_{112}[4P_z^2(P_y^2 + P_x^2) + 2(P_y^4 + P_x^4)] & & \end{bmatrix}. \quad (A3)$$

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List of Publications

Peer-reviewed papers

1. “Singular stress field near the free edge of interface in a bi-material” (in Vietnamese)
Do Van Truong, Le Van Lich
Journal of Science and Technology, 48, 733-740 (2010).
2. “Evaluation of interfacial toughness curve of bimaterial in submicron scale”
Do Van Truong, Hiroyuki Hirakata, Takayuki Kitamura, Vuong Van Thanh, Le Van Lich
International Journal of Solids and Structures, 49, 1676-1684 (2012)
3. “Plastic stress singularity near interface edge of elasto-plastic/elastic bi-material”
Le Van Lich, Do Van Truong
Computational Materials Science, 78, 140-146 (2013)
4. “Crack initiation site at the interface between a nano-component and substrate”
Le Van Lich, Takashi Sumigawa, Do Van Truong, Takayuki Kitamura
Mechanical Engineering Journal, Vol. 1, No.5, SMM0048 (2014)
5. “Anomalous toughening in nanoscale ferroelectrics with polarization vortices”
Le Van Lich, Takahiro Shimada, Koyo Nagano, Hongjun Yu, Jie Wang, Kai Huang, Takayuki Kitamura
Acta Materialia, 88, 147-155 (2015)

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6. “Hierarchical ferroelectric and ferrotoroidic polarizations coexistent in nano-metamaterials”
Takahiro Shimada, Le Van Lich, Koyo Nagano, Jie Wang, Takayuki Kitamura
Scientific Reports, 5, 14653 (2015)
 7. “Colossal magnetoelectric effect in 3-1 multiferroic nanocomposites originating from ultrafine nanodomain structures”
Le Van Lich, Takahiro Shimada, Kohei Miyata, Koyo Nagano, Jie Wang, Takayuki Kitamura
Applied Physics Letters, 107, 232904 (2015)
 8. “Instability criterion for ferroelectrics under mechanical/electric multi-fields: Ginzburg-Landau theory based modeling”
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 9. “Critical dimensional limit of continuum fracture mechanics for dislocation emission”
Takahiro Shimada, Le Van Lich, Kenji Ouchi, Yuu Chihara, Takayuki Kitamura
Engineering Fracture Mechanics (under review) (2016)
 10. “Polar and toroidal electromechanical properties designed by ferroelectric nano-metamaterials”
Le Van Lich, Takahiro Shimada, Shahmohammadi Sepideh, Jie Wang, Takayuki Kitamura
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 11. “Polar superhelices in ferroelectric chiral nanosprings”
Takahiro Shimada, Le Van Lich, Koyo Nagano, Jian-Shan Wang, Jie Wang, Takayuki Kitamura
Nano Letters (submitted) (2016)

Peer-reviewed conferences

1. “Investigation of elasto-plastic singularity stress field near the free edge of interface in a bi-material”
Do Van Truong, Le Van Lich, Nguyen Van Ben
The 10th National Conference on Solid Mechanics, 840-847, Thai Nguyen, Vietnam, November, 2010.
2. “The influence of bending deformation on the atomic structure and electric properties of carbon nanotubes”
Do Van Truong, Nguyen Tuan Hung, Le Van Lich
The 10th National Conference on Solid Mechanics, 828-833, Thai Nguyen, Vietnam, November, 2010.
3. “Simulation of crack propagation along interface in sub-micrometer scale by using virtual crack closure technique (VCCT)”
Le Van Lich, Do Van Truong
National Scientific Conference on Mechanical Engineering, Hanoi, Vietnam, October, 2011.
4. “The influence of anti-wear material properties on the stress distribution in a pair of mating gears”
Le Van Lich, Pham Van Thien, Do Van Truong
The 9th National Conference on Mechanics, Hanoi, Vietnam, December 2012.
5. “Evaluation of interfacial toughness curve of Cu/Si by using combination of experiment and numerical simulation”
Le Van Lich, Do Van Truong, Takayuki Kitamura
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6. “Unusual toughening in nanoscale ferroelectrics”

Le Van Lich, Takahiro Shimada, Koyo Nagano, Hongjun Yu, Jie Wang, Kai Huang, Takayuki Kitamura.. *The 8th Vietnamese-Japanese Students' Scientific Exchange Meeting (VJSE)*, Kyoto, Japan, October, 2015.

7. “Giant Strain-Mediated Magnetoelectric Coupling in Multiferroic Nanocomposites”

Le Van Lich, Takahiro Shimada, Kohei Miyata, Koyo Nagano, Jie Wang, Takayuki Kitamura

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8. “Unusual toughening in nanoscale SrTiO_3 originating from strain-induced ferroelectricity”

Le Van Lich, Takahiro Shimada, Takayuki Kitamura

APCFS2016: Asia-Pacific Conference on Fracture and Strength 2016, Toyama, Japan, September, 2016.

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