Turing Patterns in Ferroelectric Domains: Nine kinds of Nonlinear Instabilities

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Abstract

We show explicitly that the domain patterns in ferroelastic/ferroelectric crystals are those predicted by the Turing pattern model, with several basic structures: Chevron boundaries (with or without domain width change), dislocation zipping and unzipping (with velocities measured), bull's eye circular patterns, and spiral patterns. These all can be described by reaction diffusion equations, but the terms required in a Landau-Ginzburg approach differ, with for example complex coefficients required for spiral patterns and real coefficients for chevron patterns. There is a close analogy between spiral domains and Zhabotinskii-Belousov patterns, and between bull's eye circular patterns and Rayleigh-Bernard instabilities or Taylor-Couette instabilities with rotating inner cylinders, but not with each other. The evolution of these patterns with increasing strain (e.g., wrinkling/folding or folding/period-doubling) is well described by the model of Wang and Zhao, but the question of whether there is a separate rippling-to-wrinkling transition remains moot. Because these processes require diffusion, they should be absent (or qualitatively different) near Quantum Critical points. Other ferroelectric domain instabilities, including vortex and Richtmyer-Meshkov are also discussed.

Introduction

Alan Turing is perhaps best known for his work in solving the Enigma code in the 1940s and for his pioneering work on artificial intelligence, but he was also a superb theoretical biologist. Among his important contributions was the development of reaction-diffusion models [1] later used to explain patterning in chemical reactions, including the famous Zhabotinskii-Belousov reaction [2,3].

The idea that diffusion would destabilize a uniform distribution of atoms or molecules in nature is somewhat paradoxical and counter-intuitive, because diffusion usually stabilizes things. However, simple reaction-diffusion equations predict many observed patterns in chemistry and biology.

Starting with an equation of form

$$du/dt = f(u) + D \nabla^2 u \quad (4.)$$

for two components:

$$du_1/dt = f_1(u_1, u_2) + D_1 \nabla^2 u_1 \quad (5.)$$

$$du_2/dt = f_2(u_1, u_2) + D_2 \nabla^2 u_2, \quad (6.)$$

it can be shown that there is a threshold for a static pattern instability for a certain ratio $D_1 > D_2$. Here one component u_1 is termed an activator and the other, u_2 , an inhibitor. In fact the static pattern predicted by this approach – termed type I-s (s for static) [4,5] is rarely observed, because most chemical reactions involve diffusion coefficients D_1 and D_2 that are close in magnitude; however, specific reagents have been studied in the successful attempt to produce such patterns.

Although these static patterns are not common in nature, the non-static oscillatory patterns are. These are often labelled as type III-o (o for oscillatory) in the Turing scheme, which separates instabilities into those which are static in both space and time (s), those which are static in space but oscillate in time (I-o), and those which oscillate in both space and time (III-o). The spiral domain instabilities, like the Zhabotinskii-Belousov instability, oscillate in both space and time.

Figure 1: Theoretical domain instability patterns from Hohenberg and Krekhov.

There are a total of five patterns predicted for domain instabilities (shown below from Hohenberg and Krekhov), and we have recently illustrated all five diagrammed above experimentally [6]: Needles, chevrons, zippers, bulls-eyes, and spirals. Note that the chevron pattern (next to top panel) can maintain domain width on both sides of the reflection plane or change width; this width change can be an integer ratio (doubling, tripling...) but it can be a non-integer ratio also, resulting in incommensurate domain

Figure 2. (top left, right) Bull's eye patterns in PZT [6]; center: Spiral domains [6] ; bottom: dislocation twinning instabilities (panels a,c,d,f).

structures. Of these five patterns, the chevron and dislocation patterns are described by Hohenberg as arising from Turing static instabilities, meaning static in both space and time; however recent unpublished work by A. Hershovitz and Y. Ivry measure the zipping and unzipping velocity of the dislocation mechanism, so in that sense they are not truly static.

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The bull's eye pattern is analogous to the Taylor-Couette instability with rotating central cylinder; and the spiral pattern is related to the Zhabotinski-Belousov instability; but oddly enough, the bull's eye and spiral patterns are not related to each other.

Note that the oscillatory instabilities can occur in the context of faceting of ferroelectric nano-crystals (Ahluwalia et al.; Ng et al. [7-9]; Baudry [10-12]). The most important point is that unlike the theories of Landau and Lifshitz (1935) or Kittel (1946) for domains, these instabilities do not have straight rectilinear sides:

Fig.3. Nano-ferroelectric domains inside micro-ferroelastic domains. Note curvature. White spot is In particle from focussed ion beam RIB processing.

Several questions remain unanswered: Although most investigators agree that there is a well-defined wrinkling-to-folding phase transition (Wang and Zhao [13]; Metaxas et al.[14]), some recent researchers have inferred the existence of a preliminary precursor ripple-to-wrinkle transition.

In addition to the five nonlinear distortions shown above and detailed by Hohenberg and Krechov, there are several others. It is known that in conventional hydrodynamics the Taylor-Couette instability with a rotating central cylinder exhibits five different instabilities.[15-17] Only one of these is related to the “bulls-eye” figure shown. The other four have not been identified yet in ferroelectric domains. However, one of these is vortex-dominated, and it seems likely that this is closely related to the vortices in ferroelectrics; very recently S.-W. Cheol has claimed that vortex domains are universal in ferroelectrics (EMRS, Warsaw, Sept. 27, 2018), but in our view they are only one of nine unrelated possibilities.

The basic assumption of the present work is that domains have elastic moduli μ that are slightly larger than those of the underlying substrates. If the reverse is true, nothing very interesting happens: ferroelectric domains simply float around like islands on top of the substrate. But if the domain moduli exceed the substrate moduli, then under tensile or especially compressional stress, the domains undergo wrinkling, folding, bending, and other geometric nonlinear distortions. This is shown in detail by Wang and Zhao in the two figures below, which graph film/substrate moduli μ versus strain ϵ . The third dimension is proportional to film thickness.

Fig. 4. Wrinkling, creasing, folding, etc. in thin films: Film/substrate elastic moduli versus strain (Wang and Zhao [14]).

Fig.5. Some experimental data for Fig. 4 from Wang and Zhao [14].

Other kinds of nonlinear domain instability exist, outside the families considered by Hohenberg. Notable among this is the Richtmyer-Meshkov instability.

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Pb5Ge3O11 Gruverman

Fig.6

The Richtmyer-Meshkov instability is a well-known instability in fluids and in plasmas, including astrophysics.[18-20] In a configuration of two fluids with the more dense fluid above the other, a mechanical force from below will create nano-domains of the less dense fluid propagating upwards through the denser liquid. If the denser fluid is at the bottom, this phenomenon does not occur.

As Fig. 6 above shows in lead germanate $\text{Pb}_5\text{Ge}_3\text{O}_{11}$, this occurs in at least one ferroelectric: here the large white + domain wall first develops a wave or wrinkle analogous to a capillary wave, followed by ejection upwards in the presence of +E field from below. If the field is reversed, these nanodomain instabilities do not occur, and needle-like domains form instead. A. L. Gruverman, Ph.D. thesis, Univ. Ekaterinburg (1990) and [21].

In the present study we illustrate such wrinkles (first found by Gruverman in lead germanate domain walls in his 1990 thesis (Univ. Ekaterinburg), measure their velocities, and relate them to capillary waves.

Dimensionality Effects?

Very recently the fabrication of ultra-tetragonal PbTiO_3 has been reported (Zhang et al., Science 361, 494 (2018)), using epitaxial growth on PbO, which produced a switchable out-of-plane polarization of approximately $236 \mu\text{C}/\text{cm}^2$, nearly 200% of the previous record polarization in a ferroelectric. In the present paper we report via atomic force microscopy the nano-domain structure in this material. Surprisingly, there are two variants produced by the same processing: In addition to the switchable out-of-plane polarization, we find specimens in which the polarization is entirely in-plane fourfold closure domains of rather uniform ca. 50-nm diameter. Such fourfold vertices are rare in perovskites (McQuaid et al., Nano Lett. **14**, 4230-4237 (2014)); and mechanisms are suggested.

Introduction

Very recently we have shown [22] that some PbTiO_3 grown by sputtering onto PbO produced a remarkably strong out-of-plane polarization of $236 \mu\text{C}/\text{cm}^2$. This is somewhat surprising because earlier measurements on similar ultra-tetragonal PbTiO_3 give structures that were either initially planar (non-switching polarizations in planar fourfold closure domains), or otherwise gave out-of-plane polarization that was apparently metastable and disappeared totally with time.[23] In the present manuscript we report a similar phenomenon in which specimens prepared in the same way as those with large out-of-plane polarizations display only in-plane fourfold nanodomains ca. 50 nm in diameter; we suggest that the domain interface might be thicker ([3D] rather than [2D]).

Suggested mechanisms:

In addition to the previously published TEM, to demonstrate the ferroelectric properties of these specimens independent from hysteretic switching, we show in Fig. 7 the piezo-force microscopy (PFM) of domains and domain walls. Note the fourfold vertices in agreement with the model of Srolovitz and Scott. [24] This 4-state planar Potts model is often termed the Ashkin-Teller model after the scientists who first published an equivalent interaction model.[25] It is still studied in the case of a large applied external field,[26] which is the case here with a very large interfacial lattice mismatch strain. We emphasize that in the absence of such a large field, threefold vertices are generally dominant.

Here we consider another possibility: that the thickness of the domain, and whether it approximates a [2D] or [3D] structure is a dominant effect. (See the Wang and Zhao third dimension in Fig.4). In the domain vertex model of Srolovitz and Scott either fourfold domains are unstable and rapidly separate into closely spaced pairs of Y-shaped threefold vertices, or the pairs of threefold domains are unstable and rapidly coalesce into a single fourfold X-shaped vertex; this depends upon parameters in the Potts model used. To be specific, a four-state Potts model is required to describe the domain wall vertices in any case. However, to explain pairs of adjacent three-fold vertices, the Potts model is a scalar model (a simple extension of an Ising model); in this model any fourfold vertex quickly decomposes to adjacent pairs. But a vector Potts model (“clock model”) is required to describe the fourfold vertices. In this case, pairs of adjacent threefold vertices quickly coalesce to X-shaped fourfold vertices. Hence a given sample can exhibit threefold or fourfold vertices but not both. A few systems illustrate both cases, however. This does not violate the Srolovitz-Scott model, but it implies that the interaction parameter is anisotropic, with out-of-plane polarized domains satisfying a scalar $n=4$ Potts model and in-plane polarized domains satisfying a clock model. This has not been reported before in any ferroelectric, with the exception of lead strontium titanate (PST), [27] where pairs of threefold vertices are found and – “very rarely” – a few fourfold vertices (it is tempting to suggest that these very few may have been interrupted in a transient state after nucleation). $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) also exhibits both threefold and fourfold vertex geometries.[28] This may give some insight into the more complex circular domains reported recently.[29,30] Note in particular that applying an external electric field to rotate the polarizations will necessarily create and destroy vertex structures, which had not previously been known.

We can discuss further a physical reason for the out-of-plane domains satisfying a scalar Potts model but in-plane conforming to the vector Potts prediction. In this respect we can point out only that these domains are not topologically equivalent, with out-of-plane polarizations allowed to be only up or down. In recent studies by McQuaid et al., no intact fourfold closure vertices were observed; all were split by strain.[31] The collapse of fourfold vertices into adjacent pairs of threefold vertices is further considered by Opperman,[32] who emphasizes qualitative changes in dynamics due to axial anisotropy.[33]

We note parenthetically that $n=4$ Potts systems cannot produce Brerezinskii-Kosterlitz-Thouless melting in two-dimensions (although $n=6$ can); the $n=4$ systems do not form hexatic two-dimensional states.[34] It is also worth noting that the two-dimensional Potts model gives second-order phase transitions for $n < 4$ but first-order for $n = 4$ or greater, so the $n=4$ state is special.

Voronoi partitions and n-fold vertices

It is also useful to point out that the general question in nature of whether fourfold or threefold vertices are stable is rather well known. In two dimensions Voronoi partitions (domain walls in the present context) subdivide space into four quarters only when the objects of interest (nucleation sites at defects in the present examples) are symmetrically placed on the vertices of a rectangle. Otherwise, any other configuration generates closely spaced pairs of threefold vertices. This is a result of the growth of domains from initial nucleation sites to fill two-dimensional Euclidean space. Weaire and Aste describe this [35,36] as a two-dimensional law: “Only three states meet in a common vertex,” or “vertex connectivity = 3.” However, in three dimensions the opposite is true, and fourfold vertices are stable; we find 100% fourfold vertices in ultra-tetragonal PbTiO_3 on PbO . Therefore the change of vertex geometry from fourfold for in-plane PZT to threefold for out-of-plane polarization may derive from the effective dimensionality in the two cases: Are our thin films truly two-dimensional? The observation that these rules hold in general for Voronoi partitions implies that the phenomenon may be independent of the nature of interaction (“jamming”) between or among ferroelectric domains. Voronoi partitions are sometimes referred to as Dirichlet tessellations.

We prefer the strong axial field model [26] as an explanation (“Teller-Ashkin model”) for our observed fourfold vertices but include the Voronoi discussion for completeness.

Parenthetically, since the number of domains intersecting a vertex must be $n > 4$ for Kosterlitz-Thouless melting to occur in two dimensions, such melting is unlikely for most ferroelectric domain walls.

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