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Nonequilibrium Ferroelectric-Ferroelastic 10-nm Nanodomains: Wrinkles, Period-doubling, and Power-law Relaxation

James F. Scott,1* Donald M. Evans,2,3 Ram S. Katiyar,4 Raymond G. P. McQuaid,5 J. Marty Gregg5

1School of Chemistry and School of Physics and Astronomy, University of St. Andrews, North Haugh St., St. Andrews, Fife, U. K., KY16 9ST
2Earth Sciences Dept., Cambridge University, Cambridge, U. K., CB2 3EQ
3Depart. of Materials Science and Engineering, Norwegian University of Science and Technology, Trondheim, NO 208
4Speclab, Dept. Physics, University of Puerto Rico, San Juan, P. R. (USA) 00936
5School of Physics, Queen’s University, Belfast, N. I., U. K. BT7 1NN
*jfs4@st-andrews.ac.uk

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Abstract: Since the 1935 work of Landau and Lifshitz and of Kittel in 1946 all ferromagnetic, ferroelectric, and ferroelastic domains have been thought to be straight-sided with domain widths proportional to the square root of the sample thickness. We show in the present work that this is not true. We also discover period doubling domains predicted by Metaxas et al. (Phys. Rev. Lett. 2008, 217208) and modeled by Wang and Zhao Q. (Sci. Rpts. 2015, 5, 8887). We examine non-equilibrium ferroic domain structures in perovskite oxides with respect to folding, wrinkling, and relaxation and suggest that structures are kinetically limited and in the viscous flow regime predicted by Metaxas et al. in 2008 but never observed experimentally. Comparisons are made with liquid crystals and hydrodynamic instabilities, including chevrons, and fractional power-law relaxation. As Shin et al. [Soft Mat. 2016, 12, 3502] recently emphasized: “An understanding of how these folds initiate, propagate, and interact with each other is still lacking.” Inside each ferroelastic domain are ferroelectric 90-
degree nano-domains with 10-nm widths and periodicity in agreement with the 10-nm theoretical minima predicted by Feigl et al. (Nat. Commun. 2014, 5, 4677). Evidence is presented for domain-width period doubling, which is common in polymer films but unknown in ferroic domains. A discussion of the folding-to-period doubling phase transition model of Wang and Zhao is included.

Introduction:

Ferroelectrics for energy harvesting and other engineering devices generally require embodiments that have poled polarizations in ceramics. Domain structures must be aligned in order for the photo-responses to add constructively. Most researchers assume that the equilibrium domain structures of Landau-Lifshitz-Kittel are present ("Kittel Law"), but recent studies reveal highly non-equilibrium domain patterns and folding, which might adversely affect device performance. The two most important things about oxide ferroelectrics are: (1) In general they are not insulators. PbTiO$_3$ has a band gap of approximately 2.96 eV, approximately that of wide-gap III-V semiconductors such as GaN or II-VI's such as ZnO. Therefore, especially in thin-film form, they are electrical conductors. Hence it is necessary for device development to understand their band structure, to know accurate effective masses (typically, for example BaTiO$_3$ and SrTiO$_3$, they are n-type with light and heavy electrons, and electron effective mass $m^*$ of order 5.5-6.5 $m_e$, in contrast to the values $m^* = 1.0$-$1.4$ $m_e$ used, for example, in Refs. 1-6), trap levels, and conduction mechanisms. (For example, In the present context, Turnbull$^6$ has shown that elastic instabilities in nematics depend upon the relative mobilities of electrode-Injected electrons and holes.) On large-energy Fermi-level metal electrodes such as Pt (work function $W = 5.34$ +/- 0.02 eV) or Pd or Au, their large electron affinities usually produce small Schottky barrier heights, of order 0.8-1.2 eV. Because their mean free paths are small compared to the Schottky barrier widths, conduction is usually in the Simmons-limit of Schottky conduction, which yields current $J(E)$ proportional to $E \ exp (aE)^{1/2}$. For low voltages the exponential is nearly unity, and $J = bE$ results, giving the illusion of ohmic conduction (but unlike ohmic transport, insensitive to thickness and interface-limited). This aspect of Schottky barriers has been widely misunderstood; most recently Ref. 7 has discriminated between Schottky currents and impurity banding and resulting space charge
limited currents, based upon a low-voltage linear current-voltage relationship; however, such a criterion is invalid for oxides, where the Simmons' form of the Schottky Equation (valid for short electron mean free paths) is generally linear in J(V) at low voltages. In order to design optimum oxide electronics, it is important to understand bulk versus interfacial processes and to get effective masses and mobilities correct. As Morozova and Eliseev\textsuperscript{8} have pointed out, these semiconductor properties dominate domain wall relaxation times (a main part of the present paper), with an increase of x3 in carrier concentration decreasing relaxation time by a factor of x180. (2) Six is bigger than three! Direct tunneling through oxide films is typically limited to thickness d < 6 nm, whereas ferroelectric polarization is stable for d > 2.4 nm. This gives a finite range of thickness for which ferroelectric tunnel junctions are attractive devices, as developed nicely by the THALES group of Barthelemy and Bibes et al.\textsuperscript{9} Unfortunately for three decades the scientific community was under the impression, based upon misleading publications, that the minimum ferroelectric film thickness for stability was tens or hundreds of nm. This error delayed progress for many years.

The fact that ferroelectrics are wide-gap semiconductors means that early work on them – including domain dynamics – that treated them as perfect insulators must be revised. In particular, the fact that domain walls can be charged or uncharged, straight or curved, makes the assumption of equilibrium structures less likely than appeared a generation ago. Depletion and accumulation layers occur at or near interfaces and domain walls. Charges accumulate or leak off with various relaxation times, and these and other causes can produce long-lived but non-equilibrium structures, which can be kinetically limited.

Since 1935 it has been known that magnetic or ferroelectric domains often stabilize in rectilinear structures that can be easily calculated by assuming mechanical equilibrium. Their domain stripe widths are found to be proportional to the square root of film thickness. Although first derived by Landau and Lifshitz,\textsuperscript{10} this was independently rediscovered by Kittel a decade later\textsuperscript{11} and is often referred to as the “Kittel Law.” It also applies to many ferroelastic domains, as shown later by Roitburd.\textsuperscript{12} Very recently, however, it was shown\textsuperscript{13-15} that some ferroics exhibit quite different patterns, with parabolic domain walls and stripe widths unrelated to the film thicknesses, or exhibit viscoelastic properties.\textsuperscript{16-18} Some of these
have 5 nm-scale ferroelectric domains embedded inside micron-scale ferroelastic domains, with the contact angles of 45 degrees between the two, with what Vaclav Janovec first termed “walls within walls.” The overall pattern is somewhat jumbled and described by Salje and Carpenter as a “domain glass.” The overlapping domains resemble those studied previously in smectic liquid crystals in terms of wrinkling and Helfrich-Hurault instabilities.

The idea that switching in ferroelectrics can be mediated by an ultra-thin transient layer of ferroelastic planes with a dipole glass structure has been presented in a different context recently for PZT. Hence the idea of glassy fluid layers and hence hydrodynamics playing a role in domain switching seems to be supported from different observations and models.

Very recently it has been shown that even glassy materials behave as having phase transitions where “standard elastic behaviour breaks down...and nonlinear elastic moduli diverge.” This may be important in the present context of folding instabilities in glassy domain systems. See also earlier work on jamming and disorder.

We emphasize that the basic ansatz in our discussion is that ferroelastic domain walls are a kind of folding, produced by stress; this is carefully argued previously by Lukyanchuk et al. as the origin of domains in free-standing ferroelectrics.

Experiment:

These patterns may be detrimental to energy applications of ferroelectrics. Figure 1 below shows the TEM patterns in multiferroic submicron single crystals 80-120 nm thick of lead zirconate titanate iron tantalate (PZTFT). The 5-nm ferroelectric domains can easily be seen inside the curved micron-diameter ferroelastic domains in Figure 1abcd with 45-degree intersections. Note however that they all seem to be right-handed tilts (no herringbone patterns). The ferroelectric domain tilts are at ca. 45° from the inside edges of the larger ferroelastic walls; this shows that the latter behave as external boundaries (such as surfaces or grain boundaries) and implies that the nm-wide ferroelectric stripes are 90° domains, since in-plane 180° walls cannot satisfy this 45° constraint. The observed walls satisfy the
requirement \((\mathbf{P}_1 - \mathbf{P}_2) \cdot \mathbf{n} = 0\) that the ferroelastic wall be uncharged [here \(\mathbf{P}_{1,2}\) are the polarizations of the two visible ferroelectric nanodomains and \(\mathbf{n}\) is the normal to the ferroelastic wall]; however, they are sometimes at mutual angles of ca. 80 degrees or 100 degrees, not 90, and hence have net strain

Models:

In order to discuss these phenomena, it is helpful to consider a few definitions. Table I lists some characteristic temperatures for ferroelectrics, together with some instabilities known better in liquid crystals. The temperature of most interest in the present context is probably the Kauzmann temperature.\(^{33}\) This is a theoretical temperature of great interest, because if it exists, it implies a true phase transition between supercooled liquids and crystalline states, a moot proposition for many years. In the present context we use it loosely to mean a temperature at which domain patterns freeze in. It is important that it lies below the Burns temperature (ordering of local, nanoscale polarizations), but despite its relationship with ordering, it has no known direct connection to Vogel-Fulcher freezing. The latter is a semi-empirical model parameter anyway, and generally it is not possible to infer a model from an empirical equation.

Table I also lists some hydrodynamic instabilities known in liquid crystals. The process we see in Fig.1 is likely to be caused by a sliding instability in which one layer of polarization domains pops up and slides over the adjacent layer. Other hydrodynamic instabilities are well known in liquid crystals; for example, Delov et al. (Table I below) discuss how “hydrodynamic flow develops inside the flexoelectric stripe pattern...(and) electro-convection sets in.

It is useful to note that not all parabolic domain shapes need arise from hydrodynamic flow. Fig. 4 from Ref. 40 illustrates the growth rates for residual stress of out-of-plane wrinkles from a model calculation based upon wrinkling in a viscoelastic film. This is for the case in which the film is rather isotropic and the stress ratio in the folded layer and viscoelastic underlayer is 80%.
Table I: Characteristic transition temperatures and hydrodynamic instabilities

(For a full list and discussion of non-equilibrium patterning, see refs. 17, 18.)

<table>
<thead>
<tr>
<th>Transition temperature:</th>
<th>Simple description</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burns temperature $T_b$</td>
<td>Localized polar nano-domains</td>
<td>(30)</td>
</tr>
<tr>
<td>Vogel-Fulcher freezing temperature $T_{vf}$</td>
<td>d.c. dielectric peak $T$ in relaxors</td>
<td>(31,32)</td>
</tr>
<tr>
<td>Kauzmann temperature $T_k$</td>
<td>Fluid-crystal entropy equality</td>
<td>(33)</td>
</tr>
<tr>
<td>Glass temperature $T_g$</td>
<td>Conventional label from brittle to rubbery</td>
<td>(34)</td>
</tr>
</tbody>
</table>

Instability:

- Richtmyer-Meshkov
  - Shock-driven globular emission in fluid bilayers (35, 36)
- Helfrich-Hursault
  - Sliding instability of layers under mechanical stress (22, 23)
- Kauzmann
  - Glass-fluid equi-entropy temperature (33)
- Parodi
  - Periodic instability in smectics under electric fields (37)
- Bobylev-Pikin
  - Flexoelectric patterning in nematics (38,39)

Theory:

In this short note an insufficient number of parameters are known for our viscous domain system; however, we can attempt some superficial contact with published theories: ref. 40 gives an expression for wrinkle wavelength $\Lambda$ at long times (quasi-equilibrium) as

$$\Lambda = \pi \ h \left\{\frac{[2(1-2\nu)HE]/[3(1-\nu) \ h \ \mu]}{1} \right\}^{1/4},$$

where $h/H$ is the ratio of folded layer to underlying viscoelastic substrate layer; $\nu$, Poisson’s ratio; $C_{11}$, elastic constant; $E$, Young’s modulus; $\mu$ is a short-time relaxation constant of order $C_{11}$. The value of $\mu$ varies by $10^4$ depending upon whether the folding process is slow viscous flow or rapid; we assume rapid folding. For our system $\nu = 0.35$, $E = 67$ GPa, $C_{11}$
= 1.8 x 10^{11} \text{ dynes/cm}^2 = 18 \text{ GPa} \) (taken as typical of oxide perovskites), \( H = 90-120 \text{ nm} \), and \( h = \text{ca. 8-15 nm} \) (accurate perhaps to only +/- 50\%). Although the ratio \( E/\mu \) is not accurately known, this ratio occurs within a fourth-root, and hence \( \Lambda \) is relatively insensitive to its exact value and is generally\(^{40, 41} \) an order of magnitude larger than the film thickness \( h \). This estimates wrinkle wavelength as \( \Lambda = 30-50 \text{ nm} \), in reasonable accord with Figure 1. Other models\(^{32} \) give slightly different wrinkle wavelengths, but all have in common an approximately linear proportionality \( (h^{3/4} \text{ in Equation 1}; h \text{ in ref. 41}) \) between wrinkle wavelength \( \Lambda \) and film thickness \( h \); note that this disagrees qualitatively with the square-root dependence of the Landau-Lifshitz-Kittel law.

The same model \(^{40} \) gives a critical folding stress of

\[
\sigma_c = \left\{ \frac{2(1-v) E \mu h}{3(1-2v)(1-v^2)H} \right\}^{1/2}
\]

which for our parameters predicts ca. 65 GPa. By comparison, the critical stress in BaTiO\(_3\) is ca. 40 GPa (another typical perovskite oxide, PZT, does not even de-pole\(^{42} \) until 200 MPa), showing some consistency in the model and justifying our estimate of \( h \).

We can use the recent phase diagram of stress versus elastic coefficient from Wang and Zhao\(^{43} \) to estimate in general the fold to period-doubling phase transition. They find this transition at a modulus ratio of ca. 10:1 for film/substrate (i.e., favored for soft substrates) and a large mismatch strain of ca. 30\%, Fig. 2(a). For further numerical modeling of the folding to period-doubling transition in soft (biological) materials, see also Ref 44, in which Lihua, finds period doubling at strains as low as 10\%. Additionally, Budday et. al.\(^{45} \) have shown that period doubling always precedes period tripling
Summary of folded domains:

We call attention to the fact that these instabilities and domain patterns, undesirable for energy applications, can be avoided by choosing ferroelectrics that are not also ferroelastic – a new criterion to consider. That is the situation in any crystal in which the ferroelectric and paraelectric phases belong to the same crystal class. Examples are lead germanate (rhombohedral-rhombohedral), lithium niobate or lithium tantalate (rhombohedral-rhombohedral), or KTiOPO$_4$ (orthorhombic-orthorhombic), and many others. If other materials are employed, which change crystal class at their Curie temperatures, then attention should be paid to their processing and especially their poling in order to maximize performance in energy devices. The relationship between folding and relaxation times is discussed in refs 50-52.

Further work: Absence of true chevron domains

We note in Fig.1 the absence of chevron domains for the nm-scale ferroelectric domains within each ferroelastic domain. Here the ferroelectric stripes are all at approximately 45 degrees to the constraining ferroelastic walls. This is reminiscent of the behaviour of ferroelectric liquid crystals, where according to the model of Handschy and Clark, the presence of an in-plane polarization P destroys the chevron bistability. The origin of chevron domains and their stability in smectic liquid crystals is discussed further by Rieker et al. An important point in both magnetic domains and liquid crystal domains is that chevron structures are generally found only in large, extended systems and are suppressed in those of very small lateral area, such as the present case. Lagerwall has pointed out that ferroelectric (smectic) films usually have polarization P out-of-plane, whereas chevrons are non-polar and therefore seldom favoured. The dynamics of folds under biaxial compressive stress has very recently been shown elsewhere to result in curved domain walls and lenticular shapes; however, these authors emphasize that “The gradual in-plane compression of a solid film bonded to a soft substrate can lead to surface wrinkling and even to the formation of a
network of folds for sufficiently high strain. An understanding of how these folds initiate, propagate, and interact with each other is still lacking.” It is this network of folds and walls and their propagation and interaction that the present manuscript has addressed.

Period doubling:

If you look at the nm-scale ferroelectric domains in Fig 2(b), where the added lines along domain walls are guides to the eye, you will see that some adjacent walls differ by x2 in wall spacing. Although it is possible that this arises simply because the overlapping domains differ in thickness, a factor of two can arise in a different way: The full phase diagram of shear modulus M versus film/substrate adhesion energy G gives an interesting result, with a triple point connecting buckling (delamination), creasing, and wrinkling. But at a higher shear strain, the wrinkled phase undergoes period doubling. So one possibility is that these data show a period doubling of domain stripe widths within a wrinkled phase. Period doubling is not possible within the Landau-Lifshitz-Kittel model, because they assume infinitesimally small strains, whereas doubling requires nonlinear (large) strains. Note that the exact doubling of domain stripe widths cannot arise from coincidentally having layers twice as thick, because the Kittel Law varies not linearly with thickness but as its square root; hence an accidental doubling of stripe widths due to differing layer thicknesses would require a very unlikely thickness ratio of 1.414 within Kittel theory.

Non-exponential stress relaxation:

If ferroic domains are sometimes not in mechanical equilibrium, the next question to ask is how they relax with time. There is a long-standing puzzle concerning the relaxation of stress in different systems and in particular whether this is best described by a power law or an exponential. It is not practical to try to measure stress relaxation in our submicron-diameter PZTFT samples (Figure 1), because of their size and the fact that they require FIB
and TEM processing. Therefore we turn to a simpler system of ferroelectric-ferroelastic domain patterns. Previously we showed\textsuperscript{61} that the kinetics of some nano-ferroelectric domain walls in BaTiO\textsubscript{3} satisfied the standard linear model of rheology with respect to spatial coordinates, with wall velocity v(x) = Ax, where x designates the distance from an external wall. However, no attempt was made to describe the temporal dependence. In the present section we show that this is a power-law, non-exponential decay, with some data compatible with a power ca. -1/4 on a time scale of hours. The data x(t) are too sparse to reveal any stick-slip behaviour. It may be important to note that the polarization time dependence P(t) in BaTiO\textsubscript{3} is also known\textsuperscript{62} to give an exact power-law dependence for thin films 5 nm < d < 20 nm over a wide range of fields from zero to 530 kV/cm; the authors of ref. 59 did not give the exponent n, but visual inspection of their data (Fig.2b in ref. 62) suggests a value near n = 6.

Non-exponential stress relaxation in thin films of viscoelastic materials, including polymers, has been a puzzle in recent years.\textsuperscript{40, 63-65} Typically a power law of t\textsuperscript{-1/4} is predicted by models of folding and creep,\textsuperscript{4} whereas Fondado et al. have shown\textsuperscript{66} that values equal to or greater than unity can be found for magnetic or dielectric relaxations, and Ikegami and Ueda showed fifty years ago\textsuperscript{67} that some BaTiO\textsubscript{3} ceramics exhibited a logarithmic time decay for the positions <x(t)> we measure in Fig. 3; rather recently the Belfast group\textsuperscript{68} also fitted single-crystal BaTiO\textsubscript{3} film domain wall positions to a logarithmic dependence. It is not trivial to distinguish logarithmic dependences from power laws with small exponents n for sparse data sets, and in general this question has no definitive answer and may depend upon specific geometry. Generally relaxations in dielectrics of form t\textsuperscript{n} are said to obey the Curie-von Schweidler Law.\textsuperscript{69} However, fitting such models in ferroelectrics has generally been limited to displacement currents, not domain wall positions, where 0.75 < n < 0.95. In the present work we show that these models are more accurate than exponential decay for data\textsuperscript{61} on ferroelectric BaTiO\textsubscript{3} nano-domain positions x(t) over periods of 30 minutes to 20 hours (2x10\textsuperscript{3} – 7x10\textsuperscript{4} s) and find n ca. 1/4 for typical data (Figure 3). However, the uncertainty in this exponent is large for existing data and can range from 0.1 < n < 0.3 with the addition or subtraction of a few points. These data are for domain walls colliding along an x-axis; after
this event walls recoil at 90 degrees along the y-axis and give a rather different relaxation exponent n (ca. 1.9). Because such data exhibit n greater than unity one should not assume that this is simply an example of Curie-von Schweidler dependence $t^n$, nor Jonscher’s generalization to “universal dielectric relaxation,” because in those models it is impossible for n to be greater than unity. Moreover, Jonscher’s universal relaxation law for dielectrics generally refers to displacement current $J(t)$, whereas the position $<x(t)> = x_0 t^n$ for a charged domain wall should contribute $<dx(t)/dt> = x_0 t^{n-1}$ to such currents, worsening the agreement in the present case. However, it is known$^{70-72}$ that values of n between 1.0 and 2.0 are observed in LiNbO$_3$ and NaNO$_3$ and generally imply long-range diffusion of ions (such as variable-range hopping), ignored in Jonscher’s theory.

Generally more data are required to make these models quantitative for ferroic domain wall relaxation. As emphasized in Ref. 8, these times are strongly dependent upon carrier concentration in BaTiO$_3$ (since the walls appear to be charged) and are therefore extrinsic. It has been known for thirty years$^{73}$ that relaxation of domain structures in BaTiO$_3$ is often dominated by “volume effects,” particularly the alignment of polarization with macroscopic strain and a gradual reorientation of polar defects. In the presence of applied electric fields of ca. 200 V/cm these gave relaxation times fitted to exponential decay with relaxation half-lives of order 100 s, much shorter than the zero-field values measured in the present work. However, domain relaxations on a time scale of 20 hours, as in the present study, were reported$^{74-77}$ in 2014 with 50% decay reached in a few thousand seconds, as in our data. Very low (sub-Hz) frequency dielectric studies imply that these long relaxation times involve oxygen vacancy motion.$^{78}$

The ferroelectric domain periodicity studied here is slightly larger than the previous lower 6-nm reported by Vlooswijk et al.$^{79}$ or the 4-nm shown by Daumont et al.$^{80}$ The wrinkled structure in the latter resembles some of the present data in Fig.1. Our measured 10-nm widths agree with the minimum value theoretically predicted by Feigl et al.$^{81}$ Those authors also find an $h^{4/9}$ law relating domain width w to film thickness h, the same exponent originally published for folding in thin films by Holmes and Crosby$^{82}$ (not cited in ref 81) but not yet
verified in ferroic domains. Finally, the Obukhov model of strain relaxation in polymeric lamellae gives a power law with $1/4 < n < 2$, as we observe. Although the present domains are not polymeric, they are lamellar, and hence this might be relevant.

The deeper question in this work is why BaTiO$_3$ has ferroelastic and ferroelectric domain walls that are coincident, whereas PZTFT has ferroelectric walls inside the ferroelastic ones (“walls within walls”). This is addressed by Janovec and Privratska and generally depends upon the coupling between mechanical strain and polarization, which is complex in systems with charged domains. This in turn relates to nano-size and coherence lengths, since strain is unscreened whereas polarization is screened.

Further details to be examined include whether the domain flows are thixotropic, like toothpaste (viscosity decreases with time at constant stress), or superplastic, or exhibit overshoot. A general review is given in ref. 84 and the specific application of Mittag-Leffler models of relaxation to dielectrics, with power laws, in ref. 85.

We emphasize in concluding that it has been known theoretically for some time that domains should exhibit three regimes: (1) creep; (2) depinning; and (3) viscous flow. However, it has not been experimentally practical to study the flow regime prior to the present work. In concluding we note that the first clear evidence of diffusion of domain walls in ferroelectrics was shown in ref 87, where the Brillouin spectra of Ba$_2$NaNb$_5$O$_{15}$ near its phase transition that exhibited linewidth $G$ proportional to the square of momentum transfer $q$. Such a $q^2$ dependence is an unambiguous signature of diffusion.

A whole issue of a journal has previously been devoted to nonequilibrium domain behavior, and in particular, power-law, nonexponential time dependences. See Salje and other papers in this special issue: E. K. H. Salje, Phase Trans., 1998, 64, 1.
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(13) D. M. Evans, Ph. D. thesis, 2013, Queen’s University, Belfast.


Fig. 1. Transmission electron micrographs of PZTFT, showing clearly in (a-d) 10-nm wide ferroelectric 90-degree domains nested inside ferroelastic domains at nearly 45-degree angles: Examples showing non-coplanar folds with chevron-like structures NOT at 90 degrees.
Fig. 2 (a) Phase diagram for folding to period-doubling transition in thin films. Modulus ratio film/substrate is shown with threshold near 10:1 (soft substrate) versus misfit strain (ca. 30%). The third axis is normalized adhesion energy between film and substrate. Adapted from Wang and Zhao (Ref 34); (b) domain stripe-width period doubling (straight lines are guides to the eye)
Fig. 3. a) Time dependence of ferroelectric domain wall relation $x(t)$, from Ref. 52. Note that there is a power law with exponent $n$, and like the case of wrinkling, $n$ approximates $1/4$; b) relaxation time after collision, showing exponent $n$ near 2; note however that exponents as small as 0.25 are not incompatible with the error bars and that there is an energy loss after collision (lower velocities in 3b than in 3a).
Fig. 4. Model calculation for wrinkling anisotropy in a viscoelastic layer,\textsuperscript{31} as discussed in the text. The ordinate and abscissa are dimensionless measures of growth rates for residual stress. The grapefruit-segment-like shapes are to be compared with experimental data for ferroelastic domains in Fig.1 and suggest an alternative non-hydrodynamic origin; however, note that growth rate patterns are not the same as the resulting shapes of the ferroelastic domains, but only show how the latter develop anisotropy and hence might appear elliptical or parabolic, rather than circular. Copyright, R. Huang, Ph.D. thesis, Harvard University (used by permission).
"TEM micrograph of lead zirconate-titanate iron-tantalate (PZTFT) on 500-nm scale, showing nonequilibrium creases and ridges, together with domain spatial period doubling (left side) and redoubling (center right), in agreement with theoretical predictions."