Skyrmion model of nano-domain nucleation in ferroelectrics and ferromagnets

2006 J. Phys.: Condens. Matter 18 L71

(http://iopscience.iop.org/0953-8984/18/5/L03)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **18** (2006) L71–L79 doi:10.1088/0953-8984/18/5/L03

LETTER TO THE EDITOR

Skyrmion model of nano-domain nucleation in ferroelectrics and ferromagnets

M Dawber[1], A Gruverman[2] and J F Scott[3]

[1] Department of Physics, University of Geneva, Geneva, Switzerland
[2] Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695-7920, USA
[3] Earth Sciences Department, Cambridge University, Cambridge CB2 3EQ, UK

E-mail: matthew.dawber@physics.unige.ch, Alexei_Gruverman@ncsu.edu and jsco99@esc.cam.ac.uk

Received 2 November 2005, in final form 22 December 2005
Published 20 January 2006
Online at stacks.iop.org/JPhysCM/18/L71

Abstract

A skyrmion model of nano-domain ejection from large domain walls in ferroelectrics is presented, together with data on lead germanate $Pb_5Ge_3O_{11}$ and comparison data on ferromagnetic iron garnet. Notable is the occurrence of a short-wavelength transverse wall instability (wiggles) prior to the nano-domain emission. This nonlinear, defect-free model is qualitatively different from all known models of ferroelectric nucleation and propagation; nucleation in ferroelectrics has almost always been viewed as inhomogeneous, initiated at static impurity or defect sites that are fixed in space; the present model is also inhomogeneous but involves nucleation at existing domain walls, which are dynamic and not fixed in space. This defect-free ferroelectric nucleation model contrasts with the frequently invoked mechanism in thin-film switching of nucleation at electrode–dielectric interfaces and thus has significant implications for the ultimate switching speed in thin-film memory devices.

Skyrmions have not previously been applied to the problem of nucleation in ferroelectrics. In the present letter we use skyrmions to model high-field nucleation and test our predictions regarding nucleation sites with new experimental data.

Shur *et al* [1] discovered that in lead germanate ($Pb_5Ge_3O_{11}$), where 180° domains are optically distinct due to electro-gyration, at high applied electric fields $E(>150\ \mathrm{kV\ cm^{-1}})$, nano-domains are nucleated in front of an advancing macroscopic domain wall (figure 1(a)); figure 1(b) shows the distribution of nano-domain distances from the main domain wall after a time $t = 40$ ms. A very similar effect was reported in ferromagnets by Randoshkin *et al* [2] in a single-crystal film of iron garnet (figure 2). It is important to note in both figures 1(a) and 2 that the macroscopic domain wall surface becomes wavy just below the nano-domain

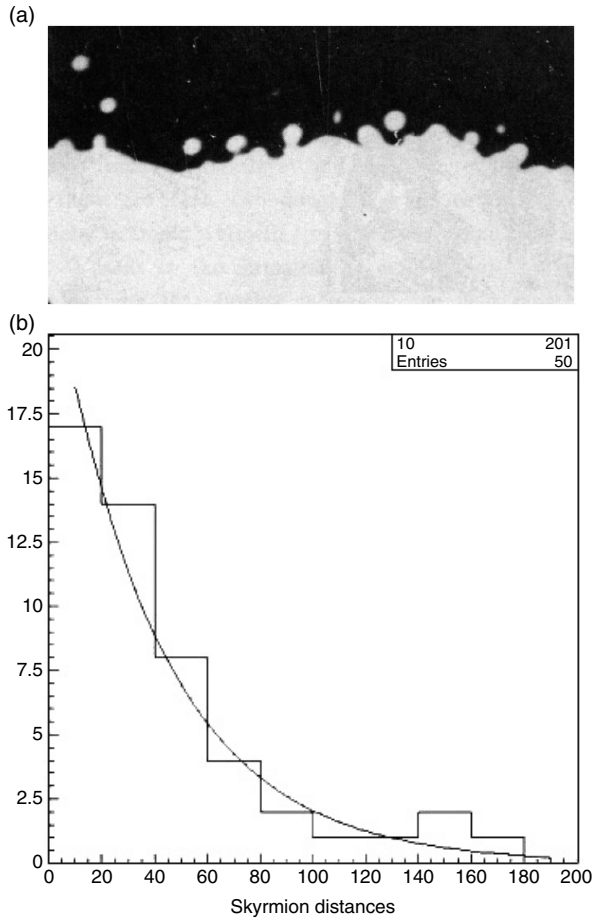

Figure 1. (a) Nano-domains in lead germanate near a large domain wall 40 ms after application of a field of ca. 100 kV cm^{-1} [1] with micrograph scale roughly 100 μm cm^{-1}; (b) graphed distribution of nano-domains from (a) versus distance in microns from the domain wall.

emission threshold; the walls at lower fields and velocities are quite flat. Therefore the nano-domain ejection from the wall has a precursor in the domain wall curvature. In magnets the phenomenon is modelled via a spin-wave formalism based upon the gyrotropic model of domain wall motion in uniaxial materials. When an applied magnetic field is sufficiently strong to exceed the Walker threshold, the magnetization vectors in the domain wall begin to precess around the applied field H with frequency $\omega = \gamma H$, where γ is the effective gyromagnetic ratio. By relating the precession frequency in the domain wall with the spin frequency in the domain, accurate predictions can be made for the threshold field at which the effect begins. We note that the domains nucleated in front of the large domain wall may be regarded as vortex-like skyrmions. The suggestion that follows then is that the domain wall phenomena in lead germanate might also be described by a gyrotropic model. Lead germanate has a strong gyrotropy (optical activity) associated with its ferroelectricity and its threefold helical C_3 point group symmetry, which is probably not coincidental in the context of nano-domain nucleation.

The modern theory of ferroelectricity, due primarily to Resta [3] and King-Smith and Vanderbilt [4], expresses ferroelectric polarization as the observable quantity in a geometrical

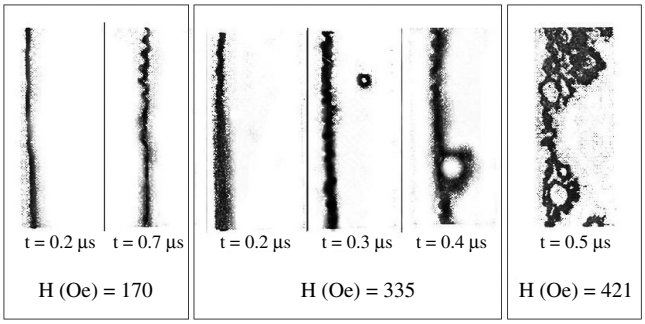

Figure 2. Nano-domains ejected from the ferromagnetic domain wall in iron garnet at different fields H and times t [2]. Coordinates are real space; the scale on the micrographs is ca. 10 μm cm^{-1}.

quantum phase. Resta treats this Berry phase via a vector potential, and the polarization is given as the surface integral of the curl of this vector potential, as an application of Stokes's theorem. Although the Berry phase was originally developed only for cases with electric field $E = 0$, it has recently been extended to insulators with nonzero field [5].

Domain walls in ferroelectrics are modelled as solitons, for example as those from a double sine–Gordon equation [6]. However, these models normally do not allow for vorticity, or topological charge [7, 8]. An extra term must be added to the Lagrangian for this, as first suggested by Skyrme [9]. Kudryavstev *et al* [10] developed a scheme by which topological charge is included in a (2+1)-dimensional vector O(3)-sigma model, spontaneously broken to $O(2) \times Z_2$, by addition of terms to the Lagrangian that permit stable skyrmion solutions. These authors mention that their Lagrangian (without the Skyrme term) can be derived from that of Pouget and Maugin [6]. In the present work we try to apply their model with the Skyrme term to a ferroelectric, thus creating ferroelectric skyrmions. In the paper by Kudryavstev *et al* they consider the situation where solitons with some degree of vorticity on the domain wall interact with each other to eject skyrmions in front of the domain wall. For there to be skyrmion emission in a ferroelectric there must be a threshold equivalent to the Walker threshold in a ferromagnet. Hence it is explicitly a nonlinear problem.

Lead germanate

The ferroelectric effects reported [1] are relatively slow, occurring on a millisecond timescale, as opposed to microseconds or nanoseconds. Typically, within $t < 40$ ms nano-domains are ejected 10–200 μm from the existing macroscopic domain wall. Figure 3 graphs a distribution of nano-domain numbers versus ejection distances at $t = 40$ ms. The nano-domains themselves are of order 10 μm in diameter, although this value is an upper limit on actual size that may depend upon both optics used and local strains around the nano-domains. The nano-domains themselves are cylindrical in shape with long axis along z and viewed through transparent electrodes in the experiments as circular cross-sections. The time resolution reported [1] is insufficient to determine whether the newly created nano-domains are formed at a distance ca. 30–200 μm from the advancing wall (as hypothesized in [1] and attributed to a 50 μm screening length) or are formed at the wall and ejected at high speeds (figure 2). Figure 1(b) shows that the nano-domains are unlikely to nucleate at a fixed distance (due, for example, to a screening length) from the large domain wall; in such a case their distribution should peak at this distance. New experiments, discussed below, show that, unlike data at low fields where

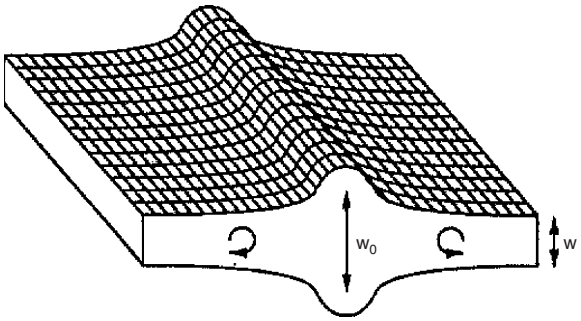

Figure 3. Bulging in domain walls predicted as transverse instabilities in [16] coordinates are real space; dimensions are arbitrarily adjustable according to parameters in the model.

nucleation occurs reproducibly at the same defect sites, this nucleation is not only arising from within existing domains, but occurs at spatially random sites with each voltage pulse. Instead we see that the distribution is monotonically decreasing from the wall, approximately exponentially, which is compatible with nano-domain ejection from the wall. The nano-domains have a lateral spatial distribution indicative of repulsion between nano-domain pairs, which is compatible with the substrate-mediated strain model of Andreev [11] and with the self-assembly data of Dawber *et al* [12] in other ferroelectrics.

Ferromagnets

Thresholds: in iron garnet the threshold for skyrmion domain ejection is [2] ca. 170 Oe, at which field the transverse instability (wiggles) arise after ca. 700 ns. At higher fields of 335 Oe, the instability becomes visible at ca. 200 ns and the first skyrmion nano-domain is ejected at ca. 300 ns. The nano-domain appears at about 10 μm from the wall after 300 ns at 335 Oe; an individual nano-domain can be tracked over 5 μm between nucleation at the wall at 400 ns and a time 100 ns later, yielding a nano-domain velocity of ca. 50 m s^{-1}. In ferroelectric lead germanate the domain wall velocity in samples with vertical growth layers is 230 m s^{-1} at $E = 420$ kV cm^{-1} ($T = 300$ K) and 14 m s^{-1} for horizontal growth layers; note that these numbers are comparable to the magnetic nano-domain ejection velocity inferred above for iron garnet. In lead germanate the bulk domain wall velocity increases exponentially with field, and the threshold for nano-domain emission is ca. 150 kV cm^{-1}. These velocities are all subsonic, so the phenomenon is apparently unrelated to the Cerenkov-like effects (coherent emission of acoustic phonons at a phase-matched angle to the domain wall propagation) observed for supersonic magnons [13]. The time required for domain formation in lead germanate is discussed in [14].

Chirality

Firstly, we note that domain walls in ferroelectrics and in ferromagnets are often chiral, even when there is no chirality in the bulk material. This problem is well reviewed by Coullet *et al* [15], with emphasis upon non-equilibrium systems (such as the ferroelectric switching in a large external field of interest to us) and applied to the particular case of ferroelectrics with bi-quadratic coupling between two order parameters by Houchmandzadeh *et al* [16]. The effect of chirality in the transitions between Ising walls and Bloch walls in magnets was first discussed

by Bulaevski and Ginzburg [17]. The important point of [10] in this context is that the domain wall (see figure 3) develops bulges prior to the onset of skyrmion-like ejection of nano-domains. One bulge is shown in figure 3. In reality there will of course be many bulges, resulting in the wiggles or transverse instability illustrated in figure 2. Thus, the bulges are precursors to the nano-domain emission. The presence of such bulges is probably typical in ferroelectric oxide domains; for example, Triscone showed [18] that the fractal dimensionality D of domain walls in perovskite oxide ferroelectrics is typically 2.5 and not the planar 2.0.

The theory developed [19] is applicable only to the case of systems with two coupled order parameters, η_1 and η_2. In such a situation the symmetry of the bulk ferroelectric need not be chiral; the bi-quadratic coupling and the presence of a Lifshitz invariant of form $\xi = \eta_1 \, \mathrm{d}\eta_2/\mathrm{d}x - \eta_2 \, \mathrm{d}\eta_1$ are sufficient for chirality within the domain walls. This is not an unusual case, but it is not the situation in lead germanate, which is a simple uniaxial ferroelectric. Therefore, in the case of lead germanate the chiral symmetry of the bulk ferroelectric is actually required, because there is no second order parameter. We note that many other ferroelastics and ferroelectrics have helical chiral structures, such as the D_3 point-group alpha-quartz structure of SiO_2 and berlinite $AlPO_4$ or the helical structures of the K_2SeO_4 family of incommensurate insulators.

Kudryavtsev–Piette–Zakrzewski model

The (2D) Lagrangian developed by these authors is of the form

$$L = F\big[(1/2)\partial_\alpha\phi\partial^\alpha\phi - (k^2/4)(\partial_\alpha\phi \times \partial_\beta\phi)(\partial^\alpha\phi \times \partial^\beta\phi) - (\mu^2/2)(1-\phi_3^2)\big] \tag{1}$$

(where y is along the domain wall and x normal to the wall) and results in small amplitude waves propagating along the wall (the waviness shown in figure 1) of amplitude $g(x, y, t)$ (NB two-dimensional waves independent of z, the normal to the crystal surface)

$$g_{tt} - g_{xx} - g_{yy} + \mu^2[1 - 2/\cosh 2(\mu x)]g = 0 \tag{2}$$

and skyrmion emission (chiral instability) from within a domain wall in a direction x normal to the wall; skyrmions are created as a superposition of a deformation and a topological wave:

$$w = \exp\big\{-\mu[x - (B/2)\tanh(\mu y + \mu t - \mu A) - \tanh(\mu y - \mu t + \mu A)] \times \exp((\mathrm{i}\pi/2) \times [\tanh(\mu y + \mu t - \mu A - \mu D) + \tanh(\mu y - \mu t + \mu A + \mu D) + 2)\big\}. \tag{3}$$

The time sequence shown in figure 4 is that for $A = 30$, $B = 20$, and $D = 10$ in equation (3), and corresponds reasonably well to data in figure 1, which occurs after the bulges shown in figure 3 develop. The nano-domain moves away from the larger wall at a speed which is half that of ripples along the wall, a prediction suitable for future testing in lead germanate. The theoretical model is more similar to the experimental data shown for iron garnet in figure 2. These comparisons suggest that the nano-domains in lead germanate (figure 1) do not nucleate at a distance from the large domain wall governed by depolarization fields, but rather originate within the wall and are ejected. If this is the case, it represents a completely new kind of nucleation in ferroelectrics: ferroelectric nucleation is almost always viewed as inhomogeneous with only a few exceptions [19, 20] on defect sites or interfaces; in the present situation it is inhomogeneous but nonlinear, arising at a threshold velocity, and in the complete absence of defects. This is further supported by the graph (figure 1(b)) of number of nano-domains versus distance from the wall of the advancing large domain. If these nano-domains nucleated at a fixed distance from the wall, this graph should exhibit a peak, whereas if the domains are ejected from within the wall the graph should be monotonically decreasing (as shown).

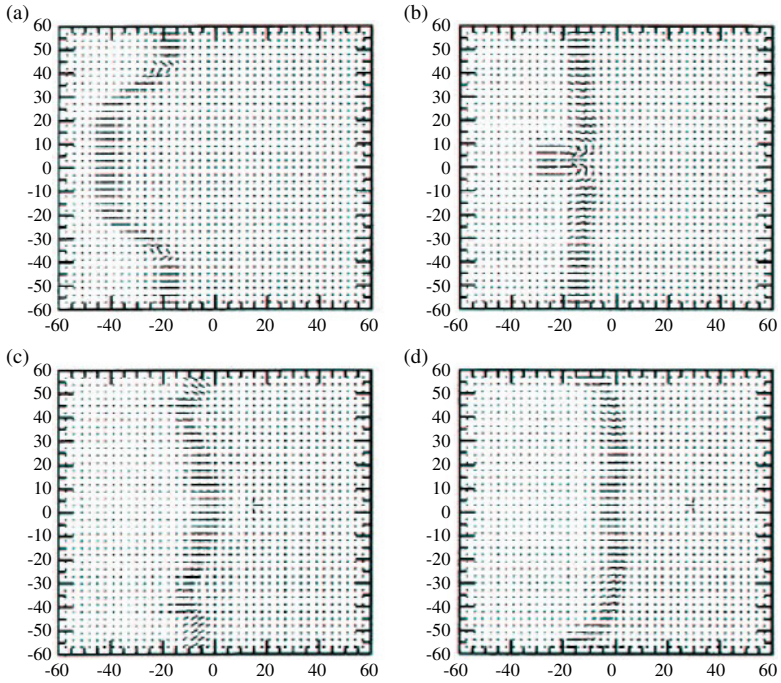

Figure 4. Change in shape in domain wall just before and after a skyrmion is emitted [10]. Axes are real space and units correspond approximately to μm in the case of lead germanate.

Gross–Pitaevski model

Peripheral to the discussion above concerning nonlinear transfer of domain wall energy is the idea that domain wall energy can be transferred via damping into acoustic phonons near the Brillouin zone boundary with abrupt thresholds. Indeed, this is the model of Dawber *et al* [21] in the 'perimeter effect'. We point out here that in a different context this is the Gross–Pitaevski model of general decay into a boson sea. See the theoretical developments by Frisch *et al* [22] The abrupt decay of domain wall energies as a function of frequency at high fields was recently reported experimentally in barium titanate by Zolotoyabko *et al* [23], but not interpreted in terms of any specific microscopic mechanism.

Classical model

Without dwelling upon the nonlinear dynamics or Lagrangians that follow the development of bulges or ripples in figure 3, we might first ask whether there is a simple mechanical model useful for estimating the threshold for creating such ripples. One of us has suggested elsewhere [24] that when the domain wall velocity exceeds the speed of domain wall ripples (transverse distortions) a new relaxation process sets in. Since the ripple velocity V is given by

$$V = (Tk/\rho), \tag{4}$$

where T is the surface energy of the domain wall (ca. 7 ergs cm^{-2} in most ferroelectric oxides); ρ is density (ca. 7 g cm^{-3}); and the wavevector $k = 2\pi/\lambda$ is determined visually from figure 1(a) from λ = ca. 100 μm. This gives a critical velocity v of order 10 cm s^{-1}, in agreement with [1], analogous to Cerenkov radiation or bow waves on a ship. Thus, although the phenomenon is not related to domain wall velocities approaching the speed of sound, there

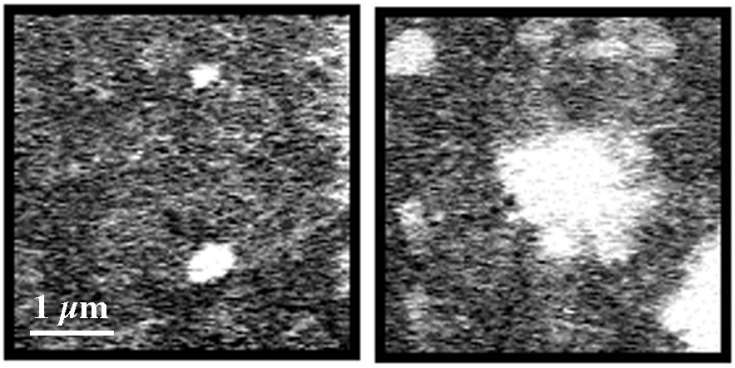

Figure 5. Nucleation in lead germanate with an initial voltage pulse (left) and subsequent pulse(s) (right), showing that the nucleation sites are not repeatable. Therefore, they do not occur at static defect sites. The dark areas are polarized down and an electric field is applied to reverse polarizations; the reversed 'up' domains appear as white.

may be other critical velocities in the problem related to ripple speed on macroscopic domain walls.

New experiments

A sample of PGO lead germanate crystal (polished plane parallel plate of about 300 μm thick) has been mounted on a metal plate using silver paint. The opposite surface of the sample has been inspected by piezoresponse microscopy (PFM). All PFM measurements have been performed using a commercial atomic force microscope (Park Scientific Instruments Autoprobe M5). A computer-controlled Keithley 236 source measure unit was used to apply switching voltage pulses to the PGO sample via a Pt coated Si cantilever (5 N m^{-1} force constant, MikroMasch). The same tip was used for domain imaging by applying a 10 kHz modulation voltage of 2.5 V (rms).

Figure 5(a) shows a PFM image of the PGO sample where two domains have been written by application of 25 V voltage pulses (two 1 s pulses have been used to write the upper domain of ∼300 nm in diameter and 4 pulses, 1 s each, have produced the lower domain of about 500 nm in diameter). Both domains exhibit sharp domain boundaries as is usually observed in PFM switching experiments, indicating a domain growth via progressive movement of the domain walls. Figure 5(b) shows a sample area where a domain has been produced by application of three 75 V, 1 s pulses applied to the same point. In this case, the domain exhibits irregular shape with blurry domain boundaries.

This figure shows that unlike earlier data [1] at low fields and slow (or dc) fields, application of higher fields at higher frequencies leads to nucleation at unreproducible sites. This strongly supports the present skyrmion model, which does not require defect sites for inhomogeneous nucleation.

Summary

Nucleation of ferroelectric domains in other systems has been shown to strongly favour nucleation sites on existing antiphase boundaries [25] rather than at impurity sites or electrode interfaces. Thus, lead germanate is not expected to be unusual in these respects, nor are the models limited to its symmetry class. The rapid nucleation of nano-domains in front

of an advancing macroscopic domain wall will produce a snow-plough effect that at high fields could mimic supersonic domain wall velocities, whereas real phase velocities of domain walls can remain subsonic. Furthermore, it has recently been demonstrated [26] that the original Kay–Dunn theory [27] of nucleation can be justified for inhomogeneous nucleation, in contrast to the original [27] homogeneous framework, such that the dependence of coercive field $E_c(d)$ upon thickness d is satisfied with $E_c(d) = Ad^{-2/3}$ over many decades of thickness down to sub-nanometre [28]. The present work may thus permit some insight into possible microscopic behaviour of coercive fields at very small thickness (nanometre films), important for optimizing and understanding the ultimate switching speed in ferroelectric thin-film memories, for which the fastest measured speed is 280 ps [29], a factor of two smaller than the theoretical estimate [30]; such a factor might conceivably be explained by the 'snow-plough' effect of skyrmion emission of nano-domains in front of advancing domain walls. Atomic force microscopy experiments [31] have supported the basic prediction of the skyrmion model, that nucleation, albeit inhomogeneous, does not occur at reproducible sites and hence is not defect initiated.

Work supported by EPSRC. We thank Pavel Zubko for preparing figure 1(b) and W Zakrzewski and B Piette for helpful discussions. We especially thank B J Rodriguez for his work on the data in figure 5.

References

[1] Shur V Ya, Gruverman A, Ponomarev N Yu, Rumyantsev E L and Tonkacheva N A 1991 Domain structure kinetics in ultrafast polarization switching in lead germanate *JETP Lett.* **53** 615
Shur V Ya, Gruverman A, Ponomarev N Yu, Rumyantsev E L and Tonkacheva N A 1990 Dynamics of plane domain walls in lead germanate and gadolinium molybdate *Ferroelectrics* **111** 197
Gruverman A 1989 *PhD Thesis* Ural State University, Ekaterinburg, Russia
[2] Randoshkin V V 1995 *Fiz. Tverd. Tela* **37** 356
Randoshkin V V 1995 Magnetic-field dependence of the domain-wall velocity in uniaxial films of iron garnets with various dampings *Sov. Phys.—Solid State* **37** 355 (Engl. Transl.)
[3] Resta R 1994 Macroscopic polarization in crystalline dielectrics: the geometric phase approach *Rev. Mod. Phys.* **66** 899
[4] King-Smith R D and Vanderbilt D 1993 Theory of polarization of crystalline solids *Phys. Rev.* B **47** 1651
[5] Souza I, Iniguez J and Vanderbilt D 2002 First principles approach to insulators in finite electric fields *Phys. Rev. Lett.* **89** 117602
[6] Pouget J and Maugin G A 1984 Solitons and electro-acoustic interactions in ferroelectric crystals *Phys. Rev.* B **30** 5306
[7] Dawber M 2003 *PhD Thesis* Cambridge Univ.
[8] Dawber M, Rabe K M and Scott J F 2005 Physics of thin-film ferroelectric oxides *Rev. Mod. Phys.* **77** 1083
[9] Skyrme T H R 1961 A nonlinear field theory *Proc. R. Soc.* A **260** 127
[10] Kudryavtsev A, Piette B M A G and Zakrzewski W J 1998 Skyrmions and domain walls in $(2 + 1)$ dimensions *Nonlinearity* **11** 783
[11] Andreev A F 1981 Faceting phase transisitions of crystals *JETP* **53** 1063
[12] Dawber M, Szfraniak I, Alexe M and Scott J F 2003 Self-patterning of arrays of ferroelectric capacitors *J. Phys.: Condens. Matter* **15** L667
[13] Democritov O *et al* 1988 Inelastic scattering of light by a dynamic domain wall *JETP Lett.* **48** 294
[14] Shur V Ya, Letuchev V V, Rumyantsev E L and Ovechkina I V 1985 Time needed for the formation of a through domain during polarization switching in lead germanate *Sov. Phys.—Solid State* **27** 743
Shur V Ya 1996 Fast polarization reversal process *Ferroelectric Thin Films* ed C Paz de Araujo, J F Scott and G W Taylor (Amsterdam: Gordon and Breach) pp 153–96
[15] Coullet P, Lega J, Houchmandzadeh B and Lajzerowicz J 1990 Breaking chirality in nonequilibrium systems *Phys. Rev. Lett.* **65** 1352
[16] Houchmandzadeh B, Lajzerowicz J and Salje E 1991 Order parameter coupling and chirality of domain walls *J. Phys.: Condens. Matter* **3** 5163

[17] Bulaevski L N and Ginzburg V L 1964 Temperature dependence of the shape of the domain wall in ferromagnets and ferroelectrics *Sov. Phys.—JETP* **18** 530
[18] Paruch P, Giamarchi T and Triscone J-M 2005 Domain wall roughness in epitaxial ferroelectric PbZr(0.2)Ti(0.8)O(3) *Phys. Rev. Lett.* **94** 197601
[19] Littlewood P B and Chandra P 1986 Delayed nucleation at a weakly first-order transition *Phys. Rev. Lett.* **57** 2415
[20] Chandra P 1989 Nucleation in the presence of long-range interactions *Phys. Rev.* A **39** 3672
[21] Dawber M, Jung D J and Scott J F 2002 Perimeter effect in very small ferroelectrics *Appl. Phys. Lett.* **82** 436
[22] Frisch T, Pomeau Y and Rica S 1992 Transition to dissipation in a model of superflow *Phys. Rev. Lett.* **69** 1644
[23] Zolotoyabko E, Quintana J P, Hoerman B H and Wessels B W 2002 Fast time-resolved x-ray diffraction in $BaTiO_3$ films subjected to a strong high-frequency electric field *Appl. Phys. Lett.* **80** 3159
[24] Scott J F 2003 Domain wall kinetics: nano-domain nucleation in lead germanate and Tilley–Zeks theory for PVDF *Ferroelectrics* **291** 205
Scott J F 2005 Unsolved problems in ferroelectrics for scanning probe microscopy *Scanning Probe Microscopy* ed P M Vilarhino *et al* (Amsterdam: Kluwer) pp 51–73
[25] Ganpule C S, Roytburd A L, Nagarajan V, Hill B K, Ogale S B, Williams E D, Ramesh R and Scott J F 2002 Polarization relaxation kinetics and 180-degree wall dynamics in ferroelectric thin films *Phys. Rev.* B **65** 014101
[26] Chandra P, Dawber M, Littlewood P B and Scott J F 2004 Scaling of coercive field with thickness in thin-film ferroelectrics *Ferroelectrics* **313** 7
[27] Kay H F and Dunn J W 1962 Thickness dependence of the nucleation field of triglycine sulphate *Phil. Mag.* **7** 2027
[28] Dawber M, Chandra P, Littlewood P B and Scott J F 2003 Depolarization corrections to the coercive field in ferroelectric thin films *J. Phys.: Condens. Matter* **15** L393
[29] Li J, Nagaraj B, Liang H, Cao W, Li Chi H and Ramesh R 2004 Ultrafast polarization switching in thin-film ferroelectrics *Appl. Phys. Lett.* **84** 1174
[30] Scott J F 2000 *Ferroelectric Memories* (Heidelberg: Springer) p 132
[31] Rodriguez B J, Nemanich R J, Kingon A, Kalinin S V, Terabe K, Liu X Y, Kitamura K and Gruverman A 2005 *Appl. Phys Lett.* **86** 012906