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High Junction and Twin Boundary Densities in Driven Dynamical Systems

X. Ding, Z. Zhao, T. Lookman, A. Saxena, and E. K. H. Salje**

The search for "exotic" interfaces can now be undertaken as we realize that interfaces and domain boundaries can contain structural elements which are not a simple juxtaposition of adjacent bulk materials. We know already that apparently simple twin boundaries in ferroelastic materials can be superconducting,[1,2] have high ionic mobilities,[3,4] can relate to a two-dimensional electron gas near compositional interfaces,[5–8] contain usual vortices,[9,10] exhibit multiferroicity[11–13] and show chirality.[14] Similar effects exist in ferroelectric domain boundaries.[10,15–18] Such properties can be exclusively contained in the twin boundaries and do not exist in the bulk. In this situation, the twin walls qualify as objects in the emerging field of "domain boundary engineering"[19] where domain boundaries are optimized to specific functionalities which remain localized in the domain boundaries.

Two elements are key for applications in ferroelastic materials: first the boundaries need to have the required functionality, which is already known for many materials with perovskite structure (WO_3, $CaTiO_3$)[1,20–24] and simple phase change materials (e.g., Cr:SnTe).[25] The second requirement is to produce a very dense array of twin walls to optimize the boundary effect. The movement of individual boundaries is already established in the IBM racetrack memory where moving magnetic domain walls in nanowires act as active memory elements.[26] Here we pursue the second route, namely, to show under what conditions high densities of twin walls and their junctions can be obtained. The desired breakthrough would be to use ferroelectric domain walls where the information can be written and read by simple electric fields in such dense arrays of twin walls.[27] In this paper we focus on the elastic properties (i.e., ferroelastic twin boundaries) which are part of most ferroelectric and multiferroic boundaries as a first step towards understanding how interfaces can be generated. The wider industrial consequence of such local structures as memory devices, conductors, holographic templates, or as membranes for batteries have already motivated a large research effort. Here we argue that high boundary densities can be achieved by shearing of ferroelastic (rather than ferroelectric) materials bearing in mind that many ferroelectric walls are also ferroelastic in nature.

The most common route to produce high twin wall densities is by fast temperature quench from a high temperature, paraelastic phase into a ferroelastic phase (see the model by Ball and James).[28] We will show here that an alternative method is to drive a single domain crystal by shear strain in the low temperature, ferroelastic phase. In this way a large number of long-lived metastable states are generated kinetically. In our computer experiment we simulate the shear in a thin film of a ferroelastic material. This situation is encountered when a thin film of one ferroelastic material (say $CaTiO_3$ with the required boundary functionalities) is deposited onto another ferroelastic material (say $LaAlO_3$) at high temperatures.[29,30] When the device is cooled to room temperature the template will shear and impose this shear to the thin film. When the shear strain increases to the yield strain, the thin film will spontaneously twin with a high twin boundary density. The twin pattern forms rapidly and remains essentially stable under further shear. We argue in this paper that the patterns are largely determined by the density of domain wall junctions which, in turn, depends on the elasticity of the thin film: soft films have much higher densities of domain wall junctions than hard films. Soft films have another crucial advantage: when the lateral dimensions of the thin film become smaller, the junction density increases whereas the same density decreases with smaller sizes for hard films.

The use of driven systems to generate high twin densities is motivated by the experimental observation of noise generation by moving twin boundaries[31–35] and the crossover from classical criticality to self-organized criticality in driven systems.[36] Hard driving (where the strain is prescribed) leads to a collapse of the mono-domain state at the yield stress into a highly structured, mesoscopic twin pattern which remains relatively stable under increasing strain. The initial nucleation of the domain patterns is well described by the theory of avalanches in sheared granular materials as recently proposed by Dahmen et al.[37] Note that in the case of stress driven (soft driving) loading, the pattern is much coarser and does not necessarily show the features described here.

We simulate the shear instability using a two-dimensional monoatomic lattice with linear springs between nearest and third nearest neighbors, as previously studied in ref.[38] where further details are given. The second nearest neighbor interaction is given by a double well spring (i.e., a Landau spring) which ensures that the two ground states are sheared lattices with shear angles ± 4°. The external driver is a shear strain at

Dr. X. Ding, Dr. Z. Zhao
State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University
Xi'an 710049, China
E-mail: dingxd@mail.xjtu.edu.cn
Dr. X. Ding, Dr. T. Lookman, Dr. A. Saxena, Prof. E. K. H. Salje
Theoretical Division and Center for Nonlinear Studies
Los Alamos National Laboratory
Los Alamos, NM 87545, USA
E-mail: ekhard@cam.ac.uk
Prof. E. K. H. Salje
Department of Earth Sciences
University of Cambridge
Cambridge CB2 3EQ, UK

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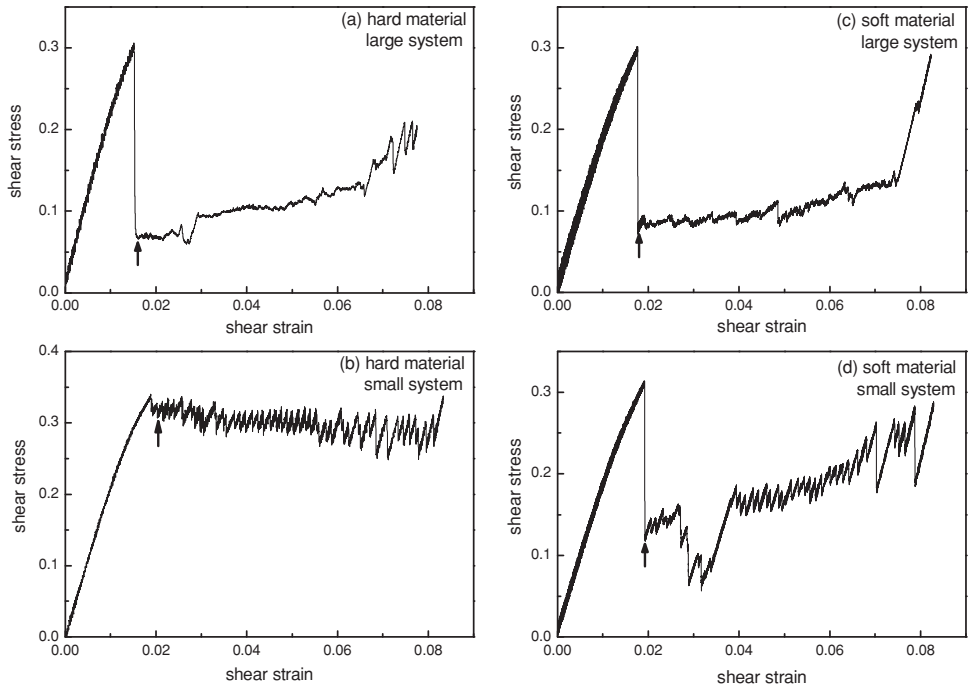

Figure 1. The shear stress versus shear strain curves for a large system with 641600 atoms (top) and small system (10200 atoms) (bottom). The arrows in the figures indicate points at which the domain patterns in Figure 2 are observed.

the upper and lower edge of the sample which stabilizes one domain orientation (–4°) and destabilizes the other (+4°). Increasing strain is initially compensated by an elastic deformation until a threshold is reached where the unstable domain decomposes into a multitude of twinned micro-domains. The stress-strain curves (**Figure 1**) and the domain patterns depend sensitively on the size of the system and on the elastic moduli of the sample. We tested a hard material (nearest neighbor spring constant $k_1 = 20$) and a soft material ($k_1 = 10$). The domain patterns after the yield points (arrows in Figure 1) are shown in **Figure 2**. A more detailed sequence of domain patterns during the yielding process is shown in the supplementary material (Figures S1-S4, Supporting Information). The hard material displays a small number of vertical domains and few horizontal

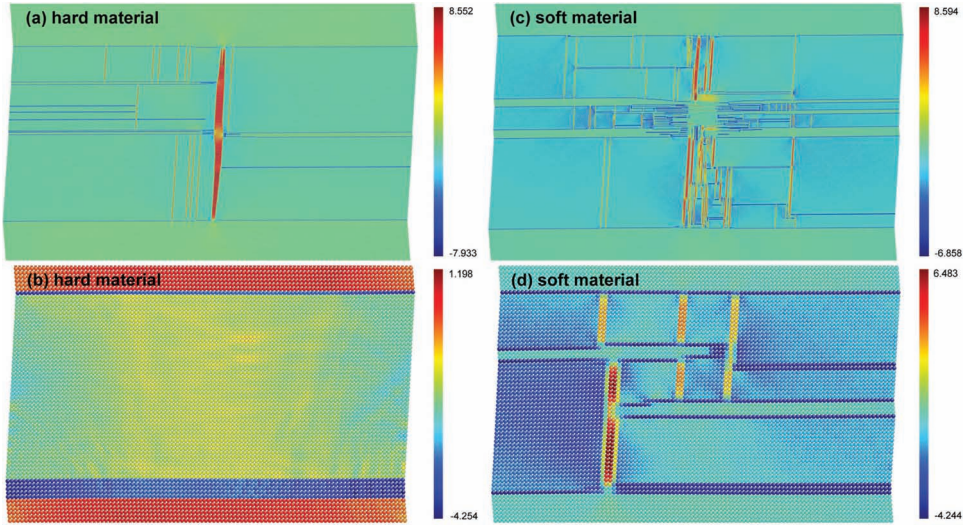

Figure 2. Domain patterns formed after the collapse at the yield stress for a large system with 641600 atoms (top) and a small system (10200 atoms) (bottom). The images on the left represent hard systems, those on the right are soft systems (the colors refer to the local shear angles $|\Theta_{vertical}| - 4° + \Theta_{horizontal}$).[38] The network of intersecting twin boundaries forms junctions which are still present for small systems of the soft material. The network is destroyed as the stable domain invades the unstable region. No vertical walls are seen in small systems of the hard material.

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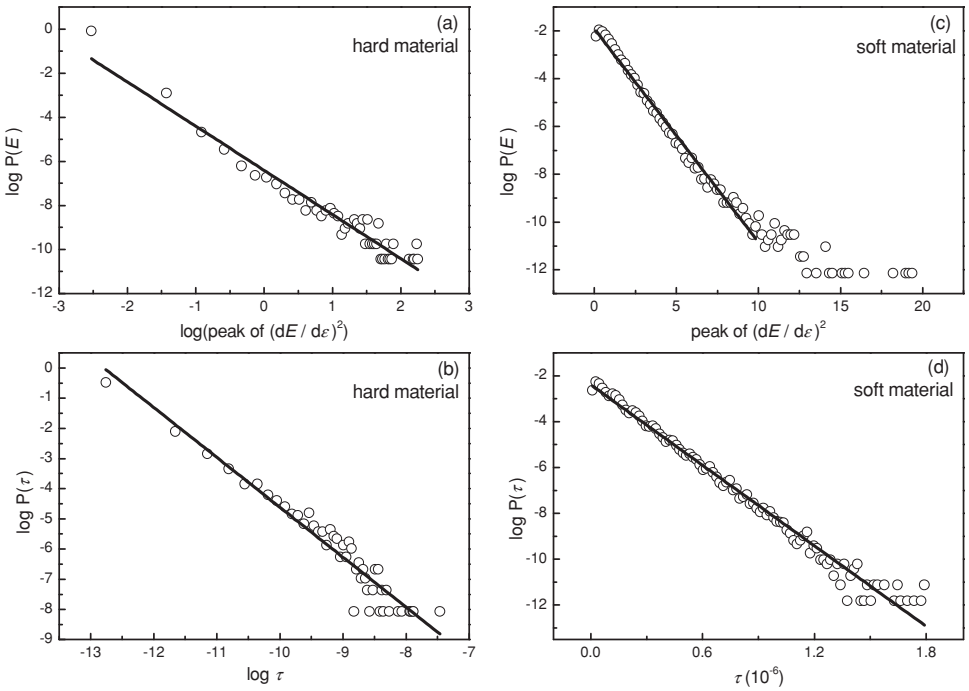

Figure 3. Time evolution of the microstructure for hard (left) and soft (right) materials. The probability to find a jerk of a certain energy content is plotted as a function of the energy of the jerk for systems with 641600 atoms. The graphs at the bottom show the waiting times between jerks. Soft systems show exponential energy and waiting time distributions while hard systems show power law distributions indicating strong correlations between the jerks. The energy exponent is $\alpha \approx 2$.

domain walls (Figure 2 left panel). The soft material has a much more complex domain pattern with a large number of vertical walls and some horizontal walls (Figure 2 right panel). The noise behavior of the jerks associated with depinning and propagation of the twin boundaries during shearing of the hard material follows a power law statistics with the probability of a noise jerk of energy E to be $P(E) \sim E^{-\alpha}$ with an energy exponent $\alpha \approx 2$ (**Figure 3**a). The statistics for the waiting times between jerks follows a power law correlated behavior for the hard material (Figure 3b) showing correlations between the jerks. The noise statistics is very different in the soft materials. The probability of finding a jerk with an energy E is now exponential, similar to the results in ref.[38] where Vogel-Fulcher dependences were observed at high temperatures (Figure 3c). The distribution $P(\tau)$ of waiting time between jerks τ is uncorrelated (exponential) for soft materials (Figure 3d).

The mechanical response of the system shows the typical yielding for shear strains of about 3.3×10^{-4} and a collapse of the stress from the upper yield stress to the lower yield stress by about 75% for large systems. The nucleation is extremely fast (the time scale is of the order of a few phonon periods), and creep phenomena are not seen near the yield point.[39,40] The geometrical analysis of this decay contains a network of intersecting twin boundaries which are destroyed when the stable domain invades the unstable region. The domain boundaries inside the unstable region do not change appreciably, all dynamics is dominated by the progressing front of the large stable domains at the top and bottom of the sample. The domain patterns within the unstable region are much "simpler" in small systems of the hard material. Here we find no vertical domain walls (Figure 2b) and the movement of domain boundaries is entirely related to the nucleation and annihilation of kinks in the advancing walls (Figure S2). The number of junctions converges to zero when the system size decreases. This behavior is very different for soft materials where a large number of junctions exists in large systems. In very small systems several junctions still exist (Figure 2d), even after parts of the complex twin patterns are destroyed by the progressing interfaces.

The complexity of the patterns dominates the kinetics of their formation as well as the density of twin walls. A convenient parameter to characterize "complexity" is the number density of intersections between different twin walls. We call these intersections, in accordance with previous experimental observations, "junctions" so that the junction density becomes the key parameter to describe the complexity of our twin patterns. In **Figure 4** we show the junction densities for hard and soft materials. The hard materials have fewer junctions (10^{-4} for large systems) and the junction density disappears for small systems when the sample cannot support complex patterns. In contrast to hard materials we find that soft materials generally have higher junction densities (2×10^{-3} for large systems). The junction density increases with smaller system sizes where the strong relaxation of the system allows the formation of junctions even for very small samples.[41–45] This shows that the desired materials properties for domain boundary engineering with high twin boundary and junction densities are best achieved for soft materials. Furthermore, small system sizes do not impede the formation of twin walls but, on the contrary, enable them. Small systems will show twinning in soft materials but not in

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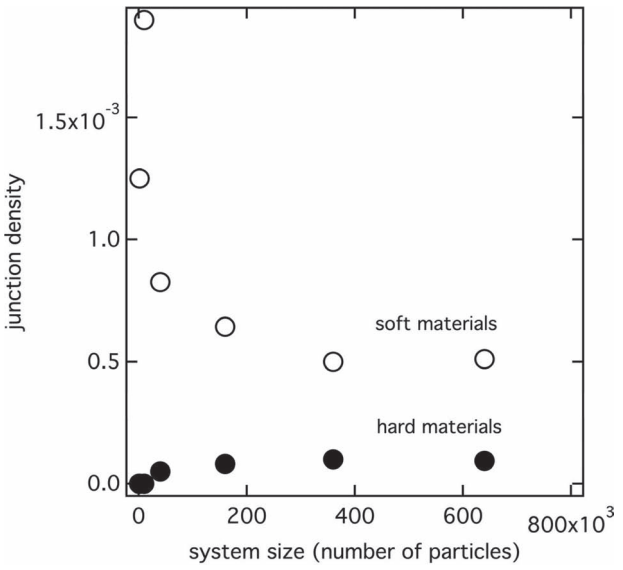

Figure 4. Junction density for hard (full circles) and soft (open circles) thin materials with a steep increase of the density for small systems sizes for soft materials. Hard materials have strong correlations between the twin walls and junctions which prevents the nucleation of junctions for small system sizes. This means that twin walls are parallel with little interaction between them. In soft layers, the strain energy related to junctions is smaller so that intersections between twin walls are common and lead to higher junction densities for small system sizes.

hard ferroelastics. The junction density has not been measured previously in ferroelastic crystals. We estimate the twin density in large, soft materials (Figure 2c) to be 5.0% of the total "volume". This value is in reasonable agreement with observed values in WO_3 and $LaAlO_3$ (0.3% found in a pattern with parallel walls),[46,47] in Co-doped YBCO (2.8%),[48] and in orthoclase (2%).[47]

Returning to ferroelectric materials, similarly high boundary densities may be anticipated, and, indeed, have been observed in quenched samples.[3,15,18,27,49–51] Quenched conducting ferroelectric walls[3,15] show very high densities, however, the proposed shear experiment has not yet been undertaken and may yield even higher densities. Although our model is limited to two dimensions, a possible way forward is to extend the third dimension from sheets to thin slabs to capture sample bending and surface nucleation to test the effective dimensionality of the twin walls. Another big step forward would be to incorporate dipolar electric interactions to model ferroelectric thin films.

In conclusion, a mechanism for the generation of device materials with high domain boundary densities is described. We considered here the shear of ferroelastic single crystals without changing the temperature. It was shown that such shear leads to the spontaneous nucleation of crystals with complex domain structures once the yield strain is overcome. The "volume" contribution of domain boundaries was estimated from computer simulations of a simple two-dimensional model to be ca. 5% of the total bulk material and is higher than in quenched materials. The observed trend is that the number of junctions between twin boundaries is found to be very high (about 0.2% of the number of bulk atoms) when the underlying elastic bulk moduli are soft but much lower in hard materials. Our microstructures, as generated by isothermal strain, show a very high wall and junction contribution which makes them suitable as functional materials where the functionality stems from the interfacial properties and not from the bulk.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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