Abstract

Acknowledgements

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Chapter 1

Mechanical softening in Ferroelectric domain walls

1.1 Introduction

So far, the focus of this work was largely on the behavior of, and interaction between various orders in uniform domains. A thorough understanding of these physics is of fundamental importance, since it provides the building blocks for more complex scenarios. Reality, however, presents to us almost exclusively these more complex scenarios. The reason for this is that while going through a phase transition with an associated spontaneous symmetry breaking, different parts of the material which are separated in space will separately (and usually randomly) choose one of the degenerate states with different values of the order parameters. One could argue that second order phase transitions could happen coherently throughout the entire system, but this assumes that the crystals are completely uniform and without defects, and that the temperature variation happens at an infinitely slow rate. In reality these assumptions are almost always invalid, inevitably leading to domains separated by domain walls (DWs) in which one or more order parameters interpolate between the values in the neighboring domains. The fundamental difference between DWs and the domains themselves has led to a great amount of research interest, both from the fundamental and technological point of view. The latter can be attributed to the small size and the fact that their location can usually be controlled easily. For example, while external electric fields can efficiently reorient the polarization of ferroelectric domains, their insulating nature makes them rather useless in advanced electronic applications such as information storage. There are, however, materials in which domains of differing polarization are separated by conducting DWs, which can be created and moved efficiently by applying electric fields to the domains that they separate[citation]. This behavior can be exploited by sandwiching a ferroelectric that harbors these walls between two conducting plates, and utilizing electric fields to increase or decrease the amount of conductive domain walls. This constitutes the writing of information, since it directly corresponds to the amount of current that flows through the device, which can be probed to read back the information[citation].

While this kind of technological promise has driven much of the research

of DWs towards their electronic properties, the coupling between electric polarization and internal strain puts the spotlight on their mechanical properties. This field is much less developed and has many unanswered questions. [mention piezoelectrics?] It has been shown that ferroelectric-ferroelastic (ferroelastic walls separate domains with differing strain textures) DWs can be moved by applying stress [**Schneider2001**]. This is not surprising since the different strain textures couple differently to the mechanical perturbation, causing an imbalance and associated movement of the separating DW. More interesting is the fact that the polarization itself can also be influenced by purely mechanical means, for example by the flexoelectric effect, with energy density:

$$f_{fl} = \frac{1}{2} f_{jklm}(\varepsilon_{jk}\partial_m P_l - P_l \partial_m \varepsilon_{jk}), \tag{1.1}$$

where repeated indices are summed over, ε denotes the strain and P the ferroelectric polarization. An applied strain gradient will as an internal electric field, thus coupling to the dipoles that constitute P. While this effect is generally small (i.e. the elements of the flexoelectric tensor f_{jklm} are small), it scales inversely with the size of the sample, meaning that it becomes increasingly important at the nanoscale of current state of the art electronic devices. Thus, using a tip to apply a strain gradient to the surface of a ferroelectric material allows one to mechanically write domain patterns and DWs at will [**Lu2012**].

These developments have increased the research into the mechanical properties of these materials in recent years. Here we focus on the mechanical properties of purely ferroelectric, 180°, DWs. As it turns out, these walls appear mechanically softer than the domains they separate. A similar softening has been previously observed and studied for ferroelastic DWs [**Lee2003**], but purely electric DWs have largely flown under the radar of mechanical studies. One reason is that the size of the domain wall (i.e. the region where the order parameter switches between the two domains) is on the order of a couple of unit cells, and was thus perceived to be to small to be detected with mechanical means, seen as tip contact areas are generally at least 100 unit cells. As it turns out, however, there is a strain texture associated with these DWs, which extends much further than the region in which the primary order parameter changes. This can qualitatively be understood by considering the electrostriction energy density

$$f_q = -\frac{1}{2}\varepsilon_{jk} q_{jklm} P_l P_m, \tag{1.2}$$

which causes the up and down domains to both be stretched along the direction of P, but no such stress exists inside the wall itself, since $P = 0$. This causes an indentation to form with an associated long range strain texture, because sharp changes in the strain are very unfavorable from an elastic point of view. This texture can be picked up mechanically by the applied tips and allows to make the observations that are the subject of this Chapter.

1.2 Experimental

Before going into the theoretical details that describe the physics of this problem, we describe the experiments performed by the group of Prof. Catalan that were the impetus of this research. In order to determine the generality of the

softening of ferroelectric DWs, three single crystal systems were investigated experimentally: $LiNbO_3$, $BaTiO_3$ and $PbTiO_3$. All measurements are based on Contact Resonance Frequency Microscopy, a scanning probe microscopy technique that uses the resonance frequence of an atomic force microscopy tip in contact with the sample to measure its local stiffness [**Rabe2000**]. A higher sample stiffness leads to a higher frequency, sothat a mapping of the surface stiffness can be made where the main limit on resolution is time. The results are shown in Fig. **??**, where the main focus are the right panels, displaying a clear contrast between soft areas close to the wall and harder areas inside the domains. One observation that points to the strain texture of the walls as the main actor is the relatively large width of the soft areas around the domain walls. It is also important to realize that the tip is in contact with the surface at all times during the experiment, ensuring neutrality and thus excluding electrical excitation. Another feature of the measurements, most clearly present in Fig. **??**(f) is the diffence in constrast between the up and down domains. This can be attributed to the flexoelectric coupling between the tip induced strain gradient and the polarization. Even though the applied forces were too small to reorient the polarization, the asymmetry in mechanical response can still be observed, and has been proposed as a mechanism for voltage-free mechanical reading of polarization [**Cordero-Edwards2017**, **Cordero-Edwards2019**, **Abdollahi2015**]. A similar explanation can not be used for the DWs, though, since they are markedly softer than either domain, resulting in a reduction of the Young's modulus of $\approx 19\%$.

[should I go more into detail of the models used by the experimentalists for the Young's modulus calculation?]

1.3 Theory

Since the mechanical DW softening seems a general property of 180° ferroelectric DWs, we focus on $BaTiO_3$ (BTO) in the following. Due to the relatively large size of geometry that needs to be simulated, we adopt the continuum Ginzburg-Landau-Devonshire model as described in [**Marton2010**]. The free energy density written in terms of primary order parameter P and associated strain ε can be written as:

$$f = f_L + f_G + f_c + f_q + f_{fl}, \tag{1.3}$$

$$f_L = \alpha_{ij}P_{ij} + \alpha_{ijkl}P_iP_jP_kP_l + \alpha_{ijklmn}P_iP_jP_kP_lP_mP_n, \tag{1.4}$$

$$f_G = \frac{1}{2}G_{ijkl}\partial_iP_j\partial_kP_l, \tag{1.5}$$

$$f_c = \frac{1}{2}C_{ijkl}\varepsilon_{ij}\varepsilon_{kl}, \tag{1.6}$$

$$f_q = -\frac{1}{2}q_{ijkl}\varepsilon_{ij}P_kP_l, \tag{1.7}$$

$$f_{fl} = \frac{1}{2}f_{ijkl}(\varepsilon_{ij}\partial_kP_l - P_i\partial_j\varepsilon_{kl}), \tag{1.8}$$

where the indices run through x, y, z, and there is a summation over repeated indices. The first term is the Landau free energy for a uniform ferroelectic polarization, where terms up to sixth order have to included to bound P, since in BTO both α_{ij} and α_{ijkl} are negative below the transition temperature. The

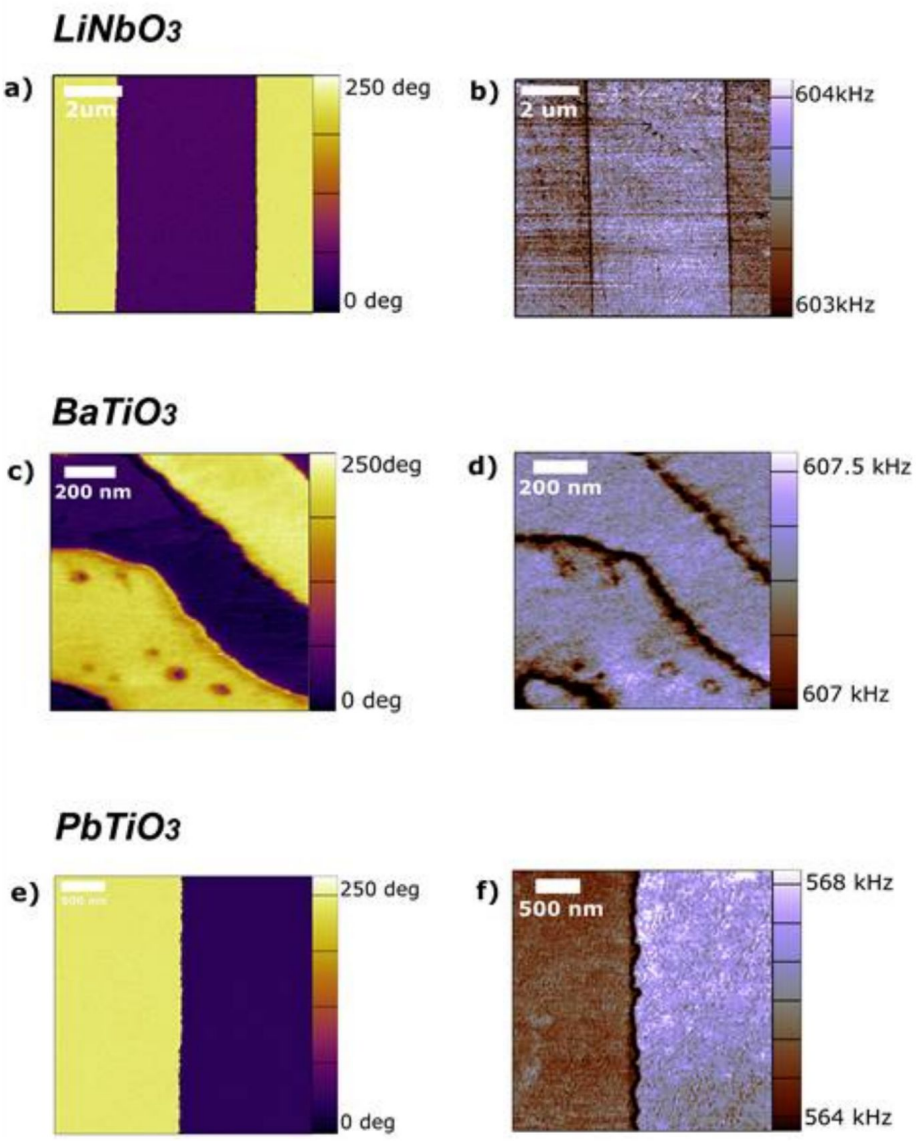

Figure 1.1: **Ferroelectric polarization and stiffness** (a-b) Periodically poled $LiNbO_3$ single crystal, (c-d) $BaTiO_3$ spontaneously polarized and (e-f) $PbTiO_3$ thin film. The contrast in figures (a,c,d) demonstrate the two opposite out-of-plane orientations of the ferroelectric polarization, and the differing stiffness in (b,d,f). The main focus are the DWs which appear most dark and are thus markedly softer than the domains.

second term denotes the Ginzburg part, i.e. the energy penalty for spatial variations of the polarization. This term influences the width of DWs, where a larger G leads to smaller walls and vice versa. The elastic energy density is described by f_c with stiffness tensor C_{ijkl}, which has the form of the standard Hooke's law. f_q signifies the electrostrictio, the main term coupling the polarization to the strain, and causes the domains to be stretched along the direction of the polarization [add some panels like in the discussion of the powerpoint]. Lastly, to be complete, we include the flexoelectric contribution, f_{fl}, since it leads to small but possibly important effects[rather vague].

The effective stiffness $\tilde{C}_{ijkl}$ can be found by taking the double derivative of the free energy with respect to ε:

$$\tilde{C}_{ijkl} = \frac{\partial^2 f}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}}. \tag{1.9}$$

In order to get an idea how having nonzero polarization influences the effective stiffness, we can solve this in the case of a single domain, leading to

$$\tilde{C}_{ijkl} = \tag{1.10}$$

The first possible source for the mechanical softening originates from the electrostriction term, and the strain texture it results in. As mentioned before, electrostriction stretches the domains in the direction of the polarization. Since we are investigating 180° domain walls, we can take the main polarization to be P_z, leading to a stretching of the domains in the z direction, or equivalently, $\varepsilon_{zz} \neq 0$ inside the domains. In the domain wall, however, P_z^2 is diminished and even zero at the center. This then causes ε_{zz} to be dimished, but never reduced to zero due to compatibility relations and the elastic coupling to neighboring unit cells. Nonetheless, this will result in an indentation that forms at the location of the domain wall, as shown pictorially in Fig. **??**(b), and more realistically in (c-d). As it turns out, the strain texture of this indentation stretches out relatively far [actual derivation and formula for this?] from the domain wall. This long-rangedness of strain is a general fenomenon, and depends on the morfology of the strain defect [more indepth on this?]. When the tip is then applied in an area where this strain texture is present, the wall will try to bend towards the tip in order to gain on the displacement. This will thus lead to a relatively big displacement to be caused by applying the tip, making the material appear soft.

Even though the interaction between the pinning potential, Peierls-Nabarro barriers, and electrostatics, with the force applied by the tip is hard to analytically describe, we can make statements about two extremes of the behavior: i) If the force of the tip is large enough, the wall slide towards it, maximizing the possible energy gain from the interaction with the tip. ii) A bending of the wall, where it remains inside the original Peierls-Nabarro potential, but deviates from the equilibrium position. [The situation that happens in the real material is more like a mix between the two, the top part of the wall bends almost completely towards teh tip, but it's not moved as a whole because the bottom/bending electrostatics pins it. Can we say that these things are causing the potential for the entire wall to behave like the one we describe below?]

The first case can be ignored because this would mean that in the experiments, the wall would be dragged along the tip since the tip moves at a relatively

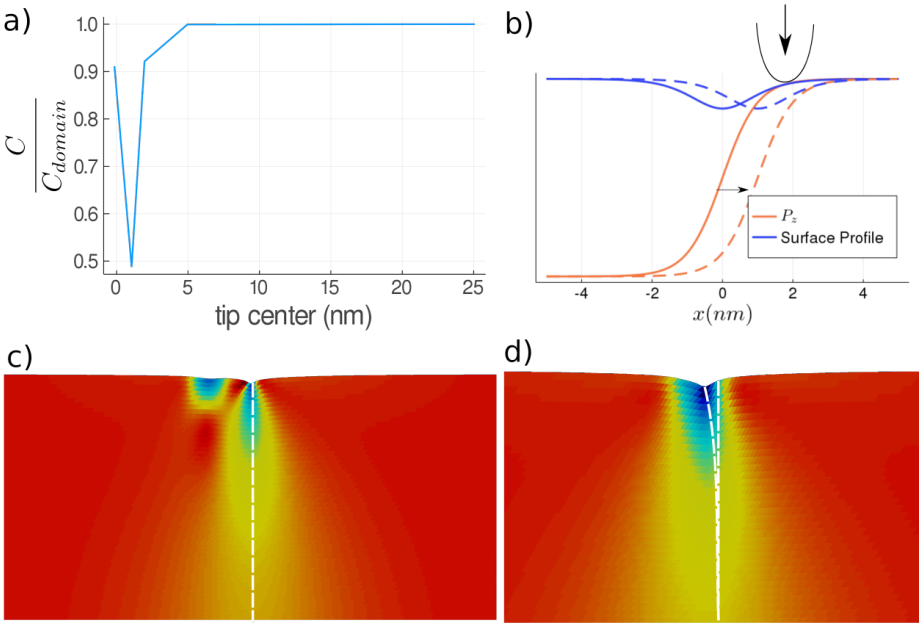

Figure 1.2

slow rate, which would lose any contrast between wall and domain during the full measurement. We therefore try to formulate a simple free energy expansion for the second situation, where we assume that the wall at x_{DW} is pinned by a parabolic potential, and perturbed by a tip applying a force F_z at x_{tip},

$$E = E_0 - F_z u_z(x_{tip} - x_{DW}) + \frac{m\omega^2 x_{DW}^2}{2}. \tag{1.11}$$

We can expand this equation under the assumption of a small x_{DW}, i.e. that the wall doesn't move far from the $x_{DW} = 0$ equilibrium situation. Together with minimizing the energy we obtain $x_{DW} = -Fu'(x_{tip})/m\omega^2$, with a compliance correction $\Delta c = u'(x_{tip})^2/(m\omega^2)^2$. Thus, we can conclude that to maximize the softening, the tip should be applied where $u'(x_{tip})$ is large, i.e. within the strain variation caused by the above discussed electrostrictive coupling. This part of the effect is pictorially depicted in panel (b) of Fig. **??**.

1.4 Results