Phase transitions, stability, and dielectric response of the domain structure in ferroelectric-ferroelastic thin films

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We present the first analytical study of phase transitions in ferroelastic-ferroelectric epitaxial thin films on exactly solvable model. The emerging domain structure with domains of equal width (which may be exponentially large on a “soft” substrate) always remains stable irrespective of the film thickness. The dielectric response of an epitaxial film is smaller than that of a free film, in striking contrast with assertions in the literature.

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Formation of ferroelastic domains in thin films due to elastic misfit between the film and the substrate was predicted by Roytburd \footnote{1}. The domain patterns are the focus of extensive studies, especially in epitaxial films of perovskite ferroelectrics that are improper ferroelastics \footnote{2}. However, the main results in this field are obtained by numerical methods or by making seemingly reasonable yet unjustifiable approximations. Additionally, all previous results refer to the case of equal elastic moduli of the film and the substrate. As a result, the physics of the epitaxial ferroelectric-ferroelastic films remains obscure, and this has led to generally accepted yet erroneous statements in the literature.

In this paper we consider an exactly solvable case of a ferroelectric-proper ferroelastic thin film described by a one-component order parameter, which is either a strain tensor component or a polarization component \footnote{3} exhibiting a second order phase transition. The model allows an analytical treatment at all temperatures, including that in the vicinity of the transition.

We shall begin with the case of the film in the absence of an external electric field. The film is assumed to be perpendicular to the z-axis and the order parameter the \(u_{xy}\) component of the strain tensor. It is assumed to be attached to an elastically isotropic substrate with the shear modulus \(\mu\), Fig. 1. The elastic moduli of the ferroelastic are supposed to be the same as in the substrate with the exception of the “soft” modulus corresponding to the \(u_{xy}\) component of strain. Thus, the Landau thermodynamic potential has the form

\[
F = \int dV [2Au_{xy}^2 + 2D(\nabla u_{xy})^2 + Bu_{xy}^4 + \mu (u_{ik}^2 - 2u_{xy}^2)]
\]

where \(A = \alpha (T - T_c)\), with \(\alpha, D, \mu\) positive constants, and we have only kept the most relevant terms. The equation of state is

\[
\sigma_{xy} = 2(A - D\nabla^2)u_{xy} + 2Bu_{xy}^3
\]

We first consider the loss of stability of the symmetric (paraelectric, paraelastic) phase at the phase transition. According to standard procedure, it corresponds to the first appearance of a non-trivial solution to the linearized equations of state. We shall look for the non-trivial solution for the \(x\)-component of the displacement vector \(u_x = u(y, z)\). One can swap the \(x\) and \(y\) axes to consider the \(u_y\) strains instead. This will only be the consideration of the inhomogeneous part of the strain. The homogeneous strain of the whole sample defines the change of its volume and shape and is described by six independent components of the (homogeneous) strain tensor. In our case, there is no loss of stability with respect to homogeneous deformation since it would cost an infinite elastic energy to produce such a strain with an infinitely thick substrate.

To find the inhomogeneous part of the strain \(u_x\) at the phase transition one should satisfy the equations of local equilibrium, \(\partial \sigma_{ik} / \partial x_k = 0\), which in the present case read

\[
\frac{\partial \sigma_{xy}}{\partial y} + \frac{\partial \sigma_{xz}}{\partial z} = 0.
\]

We shall use the Fourier representation

\[
u(y, z) = \int u_k(z) \exp(iky) dk
\]

and find the first appearance of the non-trivial solution for \(u\) for a given wave vector \(k\). We then determine the \(k\) where the instability sets in first, and this will be the point of the stability loss of the symmetric phase.

We obtain the following equations for the strain with the use of Eqs.\footnote{3}.\footnote{4}

\[
\frac{d^2u_k}{dz^2} - \frac{A_k}{\mu} k^2 u_k = 0, \quad 0 < z < l; \quad (5)
\]

\[
\frac{d^2u_k}{dz^2} - k^2 u_k = 0, \quad -\infty < z < 0, \quad (6)
\]
where \( A_k = A + Dk^2 \). At the free surface \((z = l)\) the boundary condition reads \( \sigma_{xz}(l) = 0 \), which is equivalent to \( du_k(z)/dz = 0 \). In addition, the displacement \( u_k(z) \) and the stress \( \sigma_{xz}(z) \) should be continuous at the interface \( z = 0 \), and the stress should vanish at \( z \rightarrow -\infty \).

Let us first consider the case of \( A_k < 0 \), which would lead to a loss of stability of the paraphase. The solution of Eqs. (3), (4) is

\[
\begin{align*}
    u_k(z) &= F \cos \eta k(z - l), \quad 0 < z < l; \\
    u_k(z) &= G \exp [k|z|], \quad -\infty < z < 0,
\end{align*}
\]

where \( \eta^2 = -A_k/\mu \). The boundary conditions give us the condition of the existence of the non-trivial solutions

\[
\cot \eta kl = \eta.
\]

This equation does have a solution for \( A_k < 0 \), while there is no solution at \( A_k > 0 \), hence the loss of stability takes place for \( A_k < 0 \). For the region of interest \((\eta \ll 1)\) the approximate solution is \( \eta \simeq \pi/2kl \) or

\[
|A| \sim Dk^2 = \frac{\pi^2 \mu}{4kl^2}.
\]

The minimum value \(|A|_c\) corresponds to

\[
k_m = \left(\frac{\pi}{2}\right)^{1/2} \frac{\mu^{1/4}}{D^{1/4}l^{1/2}} \sim \frac{1}{d_{at}^{1/2}l^{1/2}}.
\]

where usually (not on very “soft” substrates) \((D/\mu)^{1/2} \sim d_{at}\), with \(d_{at}\) the interatomic distance (see, e.g. [3]). This means that the loss of stability of the symmetric phase takes place at

\[
|A|_c = \frac{\pi D^{1/2} \mu^{1/2}}{l} \sim \mu d_{at} \frac{l}{l},
\]

or at

\[
T = T_{c1} = T_c - \frac{\pi D^{1/2} \mu^{1/2}}{al}.
\]

The temperature of the phase transition is lowered by about \( T_{at}\), where \( T_{at}\) is the characteristic “atomic” temperature. Since normally \( T_{at} \sim (10^2 - 10^3) T_c \), one may expect a complete suppression of the second order transition for films with thicknesses of hundreds of atomic layers depending on the particular materials parameters. The inhomogeneous structure that forms when the system loses stability is a domain structure close to the phase transition, where the widths of the domain walls and the domains themselves are comparable (see, e.g. [4]). One can readily see that this is valid in the present case since the domain wall width \( W = (D/2 |A|)^{1/2} \).

We consider next the domain structure not very close to the phase transition in a state with the spontaneous strain \( u_{xy}^0 \). There the domain wall width is much smaller than the width of the domains and one can use the linearized equation of state, obtained by expanding the free energy (3) about the spontaneous deformation,

\[
\begin{align*}
    \sigma_{xy} &= 2M(u_{xy} - u_{xy}^0), \\
    u_{xy}^0 &\equiv u_0 = \pm (-A/B)^{1/2},
\end{align*}
\]

where \( M \equiv -2A \) is \( \ll \mu \) when the system is close to the transition (“soft” modulus), with the gradient term being the origin of the domain wall energy.

Initially we shall assume that all the domains have the same width, which we will find by minimizing the sum of the elastic energy and the (surface) energy of the domain walls. We shall follow the standard procedure (see e.g. [3]). Firstly, we consider the film without a contact to the substrate where we create a distribution of the spontaneous deformation, \( u_{xy}^0 \).

We consider a stripe-like domain structure with the spontaneous strain

\[
\begin{align*}
    u_{xy}^0(y, z) &= u_0, \quad 0 < z < l, \quad (2n - 1) a < y < 2na; \\
    u_{xy}^0(y, z) &= -u_0, \quad 0 < z < l, \quad 2na < y < (2n + 1) a,
\end{align*}
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with the period \(2a\). There would be no stresses in the structure if \( u_0^2 = -A/B \). We have to find the displacements appearing after the film is attached to the substrate, \( u_x(y, z) \equiv u(y, z) \). For the film \((0 < z < l)\) Eq. (3) takes the form

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\[
M \frac{\partial^2 u}{\partial y^2} + \mu \frac{\partial^2 u}{\partial z^2} = 2M \frac{\partial^2 u_{xy}}{\partial y^2}.
\]
(17)

Since the domain pattern is periodic, the elastic displacements may be represented as a Fourier series
\[
u(y, z) = \sum_k u_k(z) \exp(iky), \quad k = \frac{\pi n}{a},
\]
(18)

where \(n = \pm 1, \pm 2, \ldots\). After solving the resulting ordinary differential equations with the above conditions one finds the elastic energy by e.g. using the formula \([6]\)

\[
F_{el} = \frac{1}{2} \int \sigma_{ij} u_{ij}^0 dV
\]
(19)

with the result for the elastic (stray) energy per unit area of the film:

\[
\frac{F_{stray}}{A} = \frac{16\mu u_0^2}{\pi^3} \eta \sum_{j=0}^{\infty} \frac{1}{(2j + 1)^3} \coth \eta k l + \eta,
\]
(20)

where \(\eta = \sqrt{M/\mu}.\) We shall first consider temperatures not very far from the transition, where \(\eta \ll 1.\) Since \(\coth x > 1\) for any argument, one can then omit the second term in the numerator. We shall suppose that the equilibrium period of the domain structure satisfies the condition \(\eta k l \gg 1\) and check later that this condition is fulfilled. We can then put \(\coth \eta k l \simeq 1\) for all terms in \([21]\) and find the energy of the domain structure

\[
\frac{F}{A} = \frac{\gamma l}{a} + \frac{14\zeta(3)}{\pi^3} \mu u_0^2 \eta a,
\]
(21)

where the first term is the energy of the domain walls, with \(\gamma\) the domain wall surface energy. Therefore, the equilibrium period of the domain structure is

\[
a = \left( \frac{\pi^3}{14\zeta(3)} \frac{\gamma l}{\mu u_0^2 \eta} \right)^{1/2} = \left( \frac{4\pi^3}{21\zeta(3)} \frac{D^{1/2}}{\mu^{1/2}} \right)^{1/2},
\]
(22)

since \(\gamma = 8\sqrt{2D^{1/2}} \left| A \right|^{3/2}/3B\). We must check now if the above assumption \(\pi \eta l/a \gg 1\) is fulfilled together with \(\eta \ll 1.\) Together those constraints read

\[
\left( \frac{D/\mu}{l} \right)^{1/2} \ll \frac{|A|}{\mu} \ll 1
\]
(23)

Since usually \((D/\mu)^{1/2} \sim d_{at} \ll l,\) the condition is satisfied very close to the transition.

The period of the domain structure becomes exponentially large when the modulus \(\mu\) is anomalously small, \((D/\mu)^{1/2} \gg d_{at},\) and the condition \((22)\) is violated. Then for very thin films \(l \ll (D/\mu)^{1/2}\) one has to reconsider the calculations of the sum in Eq. \(20\). The exact result for \(M = \mu\) (\(\eta = 1\)) is

\[
\frac{\Delta F_{stray}}{A} = 8\mu u_0^2 \eta \left[ \frac{7\zeta(3)}{8} - Li_3(e^{-b}) + \frac{1}{8} Li_3 (e^{-2b}) \right],
\]
(24)

where \(b = 2\pi l/a, Li_n(z) = \sum_{k=1}^{\infty} z^k / k^n\) \([3]\), cf. Refs. \([9, 10]\). The period of the domain structure for a very thin film on a "soft substrate" is exponentially large (cf. Refs. \([9, 10]\)),

\[
a = \frac{\pi l}{e^{1/2}} \exp \left( \frac{\pi \eta l}{8\mu u_0^2} \right) = 1.9l \exp \left( \frac{\pi D^{1/2}}{3\mu^{1/2} l} \right).
\]
(25)

Next, we shall show that there is no instability with respect to the structure with opposite domains of unequal widths, as suggested by Roytburd \([4]\). To this end we shall estimate the change of the energy of the system where the domains have different widths, \(a(1 + \delta)\) and \(a(1 - \delta)\). As we have discussed above, the homogeneous part of the strain is zero. This is possible with domains of unequal width only if the homogeneous strains in the domains, \(u_1 = u_0 + \Delta u_1\) and \(u_2 = u_0 + \Delta u_2\), are different. The condition of zero homogeneous strain reads

\[
u_1(1 + \delta) + u_2(1 - \delta) = 0.
\]
(26)

We must also minimize the elastic energy of this structure. The energy density of the homogeneous deformation can be found from the energy density in the ferrophase, \(2M(u_{xy} - u_{xy}^0)^2 + 2\mu u_{yz}^2\) [cf. Eq.(1)] which gives us the elastic energy of homogeneous stresses (cf. Ref. \([7]\))

\[
\frac{F_h}{A} = \frac{1}{2} \frac{(1 + \delta) 2M \left( \Delta u_1 \right)^2 + (1 - \delta) 2M \left( \Delta u_2 \right)^2}{l}.
\]
(27)

Minimizing Eq. \((27)\) with respect to \(\Delta u_1\) (which is equivalent to the condition that the force acting on the domain wall is zero), taking into account the constraint \((23)\), we obtain \(\Delta u_1 = \Delta u_2 = -u_0 \delta\) and

\[
F_h/A = 2MU_{stray}^2 \delta^2.
\]
(28)

One has to add the energy of inhomogeneous stresses, which depends on \(\delta\)

\[
\frac{\Delta F_{stray}(\delta)}{A} = \frac{8\mu u_0^2 \eta \left| A \right|}{\pi^3} \sum_{n=1}^{\infty} \frac{(-1)^n (1 - \cos \pi n \delta)}{n^3 \left( \coth \frac{\pi n \eta \delta}{a} + \eta \right)},
\]
(29)

where \(\Delta F_{stray}(\delta) = F_{stray}(\delta) - F_{stray}(0)\), to obtain the total change in energy.

We shall now analyze two limiting cases. *Rigid substrate not very far from \(T_c\) (\(\eta = \sqrt{M/\mu} \ll 1, \pi \eta l/a \gg 1\)).* The expression in parentheses in the denominator in Eq. \((29)\) can be replaced by unity, and we obtain

\[
\frac{\Delta F_{stray}}{A} = -\frac{4\ln 2}{\pi} \mu u_0^2 \eta \delta^2.
\]
(30)
In spite of the negative sign of this stray contribution, the total energy increases with $\delta$,

$$ \frac{\Delta F}{A} = 2\eta \mu u_0^2 (\eta \frac{1}{a} - 2\ln \frac{2\pi}{a}) \delta^2 > 0, \quad (31) $$

and, consequently, no instability sets in.

Soft substrate $[(D/\mu)^{1/2} \gg d_{at}, \eta = 1]$. There the contribution (29) can be found exactly with the result [8]

$$ \frac{\Delta F_{stray}(\delta)}{A} = -\frac{4}{\pi^3} \mu u_0^2 a \left[ \frac{3}{4} \zeta(3) + \text{Re} \ Li_3 (-e^{i\pi\delta}) \right. $$

$$ + Li_3 (-e^{-b}) - \text{Re} \ Li_3 (-e^{i\pi\delta-b}) \Bigg]. \quad (32) $$

In this case the domains may be wide, $l/a \ll 1$, Eq. (25), and we obtain

$$ \frac{\Delta F}{A} = \pi \mu u_0^2 \frac{l^2}{a} \delta^2. \quad (33) $$

This energy increases with $\delta$ and, therefore, the domain structure remains stable on a “soft” substrate too.

Finally, we shall evaluate the dielectric response of the above domain structure. We assume a linear coupling between $u_{xy}$ and $P_z$ given by the thermodynamic potential

$$ F = \int dV (2A_1 u_{xy}^2 + \frac{1}{2} A_2 P^2 + B u_{xy}^4 + gu_{xy} P) \quad (34) $$

with $A_2 > 0$, $P \equiv P_z$. Minimizing (34) with respect to $P$ we obtain

$$ A_2 P + gu_{xy} = 0, \quad (35) $$

hence the spontaneous strain $u_0$ leads to the spontaneous polarization in the domains $P_h = \mp gu_0/A_2$. The previous free energy functional [1] can be obtained from (34) with the use of (35), and $A = A_1 - g^2/4A_2$.

Let us now show that the net polarization does not change when the domain walls have moved, so that now $\delta \neq 0$. In a free standing film the change would be $2P_0 \delta$, but in a film on a substrate the polarization itself changes since it follows the changes of the mean strains in every domain. The homogeneous polarization $P_h$ is then, with the use of Eq. (35),

$$ P_h = \frac{1}{2} (1 + \delta) P_1 + \frac{1}{2} (1 - \delta) P_2 $$

$$ = -\frac{g}{2A_2} \left[ (1 + \delta) u_1 + (1 - \delta) u_2 \right] = 0, \quad (36) $$

because the average strain in the film (square brackets) is exactly zero, Eq. (23). In other words in a thin film on a substrate the shift of the domain walls does not lead to any change in the average polarization. They appear to be decoupled, while they are strongly coupled in a free standing film. Surprisingly, under an external field the domain walls do not shift in our case and the field produces $P_h = E/A_2$: one has to put the field $E$ in Eq. (34) and set $u_{xy} = 0$ because the homogeneous deformation remains zero.

The result (36) emphasizes the qualitative difference in the dielectric response of a ferroelectric-ferroelastic domain structure in a free standing film and in an epitaxial film: (i) there is a finite stiffness with respect to the domain wall shifts and (ii) these shifts change the polarization within the domains for the film on a substrate. In our specific case these changes completely compensate the polarization gain that would have taken place in a free standing film. In general, the compensation is not perfect but the effect should be taken into account. For example, these two aspects have been overlooked by Erbil et al. [11] who have only accounted for the energy change when the variation of the relative domain fraction. This has been ascribed to a pinning potential, while the other, much more important, terms were not considered. Their conclusion about enhancement of the permittivity due to the domain structure is incorrect. Our results, additionally, do not show any signs of instability of the domain structure with the film thickness, as has been speculated first by Roytburd [6] analytically and then by Pertsev et al. [7] numerically for perovskite ferroelectrics. Since their case is somewhat different (the spontaneous strain $u_{zz}$), it might be interesting to apply their numerics to the present simpler case to check the result.

In conclusion, we have demonstrated analytically how the domain structure sets in at the phase transition and that it remains stable with respect to spontaneous breaking of symmetry between the opposite domains irrespective of whether the substrate is rigid or “soft”. The dielectric response of the epitaxial films is qualitatively different from that of free standing films. In the present case the motion of the domain walls has zero effect on dielectric response in ferroelastic-ferroelectric thin films. Generally, the response of an epitaxial thin film is suppressed compared to a free film.

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