Formation and rapid evolution of domain structure at phase transitions in slightly inhomogeneous ferroelectrics and ferroelastics

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We present the analytical study of stability loss and evolution of domain structure in inhomogeneous ferroelectric (ferroelastic) samples for exactly solvable models. The model assumes a short-circuited ferroelectric capacitor (free ferroelastic) with two regions with slightly different critical temperatures $T_{c1}>T_{c2}$, where $T_{c1}-T_{c2}\ll T_{c1},T_{c2}$. We show that even a tiny inhomogeneity like 10^{-5} K results in splitting the system into domains below the phase transition temperature. At $T<T_{c2}$ the domain width a is proportional to $(T_{c1}-T)/(T_{c1}-T_{c2})$ and quickly increases with lowering temperature. The minute inhomogeneities in T_c may result from structural (growth) inhomogeneities, which are always present in real samples, and a similar role can be played by inevitable temperature gradients.

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I. INTRODUCTION

The idea that the phase transition in electroded short-circuited ferroelectric proceeds into homogeneous monodomain state[1] is very well known. Similar result also applies to free ferroelastic crystals. However, it has *never* been observed. Surprisingly, both electroded ferroelectrics and free ferroelastics do split into domains, although they should not. The present paper aims to answer why.

It is generally assumed that in the finite nonelectroded ferroelectric samples the domain structure appears in order to reduce the depolarizing electric field if there is a nonzero normal component of the polarization at the surface of the ferroelectrics[1,2] (in complete analogy with ferromagnets[3]), if the field cannot be reduced by either conduction (usually negligible in ferroelectrics at low temperatures) or charge accumulation from environment at the surface.[4] On the other hand, in inhomogeneous ferroelastics (e.g., films on a substrate, or inclusions of a new phase in a matrix) the elastic domain structure accompanies the phase transition in order to minimize the strain energy, as is well understood in the case of martensitic phase transformations[5] and epitaxial thin films.[6–8]

In search for reasons of domain appearance in otherwise perfect electroded samples, which is not yet understood, we shall discuss (i) a second-order ferroelectric phase transition in slightly inhomogeneous electroded sample and (ii) a second-order ferroelastic phase transition in slightly inhomogeneous free sample. We consider an exactly solvable case of a system, which has two slightly different phase transition temperatures in its two parts. While the phase transition occurs in the "soft" part of the system, the "hard" part may effectively play a role of a "dead" layer[10] and trigger a formation of the domain structure in the soft part with fringe electric fields (stray stresses) penetrating the hard part. One has to check this possibility, but the behavior of the corresponding domain structure is expected to be unusual: it should strongly depend on temperature since further cooling transforms the hard part into a soft one, while the first soft part becomes "harder." Since the inhomogeneity is small, one might expect that the domains would quickly grow with lowering temperature. We indeed find a rapid growth of the domain width linearly with temperature in the case of slightly inhomogeneous short-circuited ferroelectric and free ferroelastic. This behavior is generic and does not depend on particular model assumptions. Generally, the inhomogeneous ferroelectric systems pose various fundamental problems and currently attract a lot of attention. In particular, *graded* ferroelectric films and ferroelectric *superlattices* have been shown to have giant pyroelectric[11] and unusual dielectric response.[12]

II. PHASE TRANSITIONS IN SLIGHTLY INHOMOGENEOUS FERROELECTRIC

We shall first consider the case of slightly inhomogeneous uniaxial ferroelectric in short-circuited capacitor that consists of two layers with slightly different critical temperatures, so that, for instance, a top part "softens" somewhat earlier than the bottom part does. We assume the easy axis z perpendicular to electrode plates, and make use of the Landau free-energy functional for given potentials on electrodes φ_a (zero in the present case)[9] $\tilde{F}=F_{LGD}[\vec{P}]+\int dV(E^2/8\pi)-\Sigma_a e_a\varphi_a$, with

$$F_{LGD}[\vec{P}]=\sum_{p=1,2}\int dV\left(\frac{A_p}{2}P_z^2+\frac{B}{4}P_z^4+\frac{D}{2}(\nabla_\perp P_z)^2+\frac{g}{2}(\partial_z P_z)^2+\frac{A_\perp}{2}\vec{P}_\perp^2\right), \tag{1}$$

where P_z ($\vec{P}_\perp$) is the polarization component along (perpendicular to) the "soft" direction, index $p=1(2)$ marks the top (bottom) part of the film:

$$A_1=A,\quad 0<z<l_1,$$

$$A_2=A+\delta A,\quad -l_2<z<0.$$

Here $A_{1(2)}=\alpha(T-T_{c1(2)})$ and $\delta A>0$ (meaning $T_{c2}<T_{c1}$). We shall assume in the following that $l_1\sim l_2$. The constant

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$\alpha = 1/T_0$, where $T_0 \sim T_{at}$ (T_c) for displacive (order-disorder) type ferroelectrics, $T_{at} \sim 10^4 - 10^5$ K is the characteristic atomic temperature.

The equation of state is $\delta F_{LGD}[\vec{P}]/\delta \vec{P} = \vec{E} = -\nabla \varphi$, where φ is the electrostatic potential, or in both parts of the film $p = 1,2$:

$$E_z = -\partial_z \varphi = A_p P_z + B P_z^3 - D \nabla_\perp^2 P_z - g \partial_z^2 P_z, \tag{2}$$

$$\vec{E}_\perp = A_\perp \vec{P}_\perp . \tag{3}$$

These equations should be solved together with the Maxwell equation, $\mathrm{div}(\vec{E} + 4\pi \vec{P}) = 0$, or

$$(\partial_z^2 + \epsilon_a \nabla_\perp^2) \varphi = 4\pi \partial_z P_z, \tag{4}$$

where the dielectric constant in the plane of the film is $\epsilon_a = 1 + 4\pi/A_\perp$.

A. Loss of stability

We shall now find conditions for loss of stability of the paraelectric phase close to T_{c1} with respect to inhomogeneous polarization. The stability loss corresponds to appearance of a nontrivial solution to linearized equations of equilibrium. Indeed, at the brink of instability the system is in neutral equilibrium, defined by linear terms. We are looking for a nontrivial solution in a form of the "polarization wave,"

$$P_z, \varphi \propto e^{ikx}. \tag{5}$$

We shall check later that the stability will be lost for the wave vector $kl_1 \gg 1$ while the scale of change of P_z with z is l_1 so that $\nabla_\perp^2 P_z = k^2 P_z \gg g \partial_z^2 P_z \sim P_z / l_1^2$, and the last term in the right-hand side of Eq. (2) should be dropped. Going over to Fourier harmonics indicated by the subscript k, we obtain for the Poisson equation:

$$\varphi_k'' - \epsilon_a k^2 \varphi_k = 4\pi P_{zk}', \tag{6}$$

where the prime indicates derivative ($f' \equiv df/dz, f'' \equiv d^2 f/dz^2$). We can exclude P_{zk} with the use of the linearized equation of state (2), which gives

$$-\varphi_k' = (A_p + Dk^2) P_{zk}. \tag{7}$$

Substituting this into Eq. (6), we obtain $\varphi_k'' - [\epsilon_a k^2 (A_p + Dk^2) 4\pi] \varphi_k = 0$, where we have used $|A + Dk^2|/4\pi \ll 1$, which is always valid in ferroelectrics. We shall see momentarily that the nontrivial solution appears only when $A_1 + Dk^2 < 0$, while $A_2 + Dk^2 > 0$. The resulting system is

$$\varphi_{1k}'' + \chi_1^2 k^2 \varphi_{1k} = 0, \tag{8}$$

$$\varphi_{2k}'' - \chi_2^2 k^2 \varphi_{2k} = 0, \tag{9}$$

where $\chi_1^2 = -\epsilon_a (A_1 + Dk^2)/4\pi, \chi_2^2 = \epsilon_a (A_2 + Dk^2)/4\pi$. The corresponding solutions satisfying the boundary conditions for electroded surfaces ($\varphi = 0$ at $z = l_1, -l_2$) read

$$\varphi_{1k} = F \sin \chi_1 k (z - l_1), \tag{10}$$

$$\varphi_{2k} = G \sinh \chi_2 k (z + l_2). \tag{11}$$

The boundary condition at the interface ($z = 0$) reads as

$$\frac{\varphi_{1k}'}{A_1 + Dk^2} = \frac{\varphi_{2k}'}{A_2 + Dk^2}, \tag{12}$$

where we have used $|A_1 + Dk^2|/4\pi \ll 1$. We obtain from Eqs. (8)–(12) the condition for a nontrivial solution,

$$\chi_1 \tan \chi_1 k l_1 = \chi_2 \tanh \chi_2 k l_2, \tag{13}$$

which allows us to find the value of $|A|$ corresponding to the loss of stability of the symmetric phase for a given wave vector k. It will be shown below that the actual instability sets in for the value of k where $\chi_2 k l_2 \gg 1$, so that tanh can be replaced by unity. Close to the transition $\chi_2/\chi_1 \gg 1$, and the solution is

$$\chi_1 k l_1 = \frac{\pi}{2} \frac{\chi_2 k l_1}{1 + \chi_2 k l_1} \approx \frac{\pi}{2}, \tag{14}$$

when $\chi_2 k l_1 \gg 1$. This gives the condition of stability loss in the form $|A| = Dk^2 + \pi^3/\epsilon_a k^2 l_1^2$. There is no solution for $\chi_1^2 < 0$. The minimal value of A for the nontrivial solution (the actual onset of instability, if the transition with $k = 0$ does not occur earlier) is defined by

$$k_c = \left(\frac{\pi^3}{\epsilon_a D l_1^2} \right)^{1/4} \approx \frac{\pi^{3/4}}{\epsilon_a^{1/4}} \frac{1}{\sqrt{d_{at} l_1}}, \tag{15}$$

$$|A|_c = 2Dk_c^2 = \frac{2\pi^{3/2} D^{1/2}}{\epsilon_a^{1/2} l_1} \approx \frac{2\pi^{3/2}}{\epsilon_a^{1/2}} \frac{d_{at}}{l_1}, \tag{16}$$

where we have introduced the "atomic" size $d_{at} \sim \sqrt{D}$ comparable to the lattice parameter. We obtain the corresponding tiny shift in the critical temperature [see estimates below Eq. (18)] $T_{c1} - T_c \sim T_0 d_{at}/\epsilon_a^{1/2} l_1$. Hence the system loses its stability with respect to an inhomogeneous structure very quickly below the bulk transition temperature. It is readily checked that the assumptions we used to obtain the solution are easily satisfied. Indeed, $\chi_2 k l_2 \gtrsim 1$ and $\chi_2 k l_1 \gg 1$ both correspond to approximately the same condition when $l_1 \sim l_2$: $\delta A \gg (4/\pi^{1/2} \epsilon_a^{1/2})(d_{at}/l_1)$, meaning that the difference between T_c should be larger than the shift of T_c.

Now we have to determine when the transition into inhomogeneous state occurs prior to a loss of stability with respect to a *homogeneous* polarization. The homogeneous loss of stability corresponds to $A = A_h$ found from

$$A_h l_1 + (A_h + \delta A) l_2 = 0. \tag{17}$$

For the inhomogeneous state to appear first, there must be $A_c > A_h$, or $\delta A > [\pi^{3/2}(l_1 + l_2)/\epsilon_a^{1/2} l_1](d_{at}/l_1)$. This means that very *tiny inhomogeneity* in the sample is enough to split it into the domain structure,

$$T_{c1} - T_{c2} = T_0 \frac{\pi^{3/2}(l_1 + l_2)}{\epsilon_a^{1/2} l_1} \frac{d_{at}}{l_1}, \tag{18}$$

which, for a film 1 mm thick, is estimated as $T_{at}(d_{at}/\epsilon_a^{1/2}l_1)\lesssim\epsilon_a^{-1/2}(10^4\text{–}10^5)10^{-7}$ K$=10^{-3}\text{–}10^{-2}$) K for displacive systems, and $T_c(d_{at}/\epsilon_a^{1/2}l_1)\lesssim 10^{-5}\text{–}10^{-4}$) K for order-disorder systems. Certainly, such a small temperature and/or compositional inhomogeneity exists in all usual experiments.

B. Domain structure at $T_{c2}<T<T_{c1}$ ($A<0$, $A+\delta A>0$)

After stability loss the resulting "polarization wave" quickly develops into a domain structure, as we shall now demonstrate. The notion of the domain can be applied when the domain width $a=\pi/k_c$ becomes comparable and larger than the domain-wall thickness $W\sim\sqrt{D/|A|}$. The relation $W\lesssim a$ gives [see Eqs. (15 and 16)]

$$|A|\gtrsim\left(\frac{D}{\pi\epsilon_a}\right)^{1/2}\frac{1}{l_1}\approx\frac{d_{at}}{\epsilon_a^{1/2}l_1}\ll 1. \tag{19}$$

This is the same tiny temperature interval where the present scenario unfolds, and the system quickly goes over into the domain state well above the lower transition temperature T_{c2}, if it is larger than the value defined by Eq. (18).

In the region below T_{c1} where the domain structure forms (as shown above, it occupies most of the temperature interval $T_{c1}-T_{c2}$), we can use the linearized equation of state

$$E_z=(A+3BP_{01}^2)(P_z-P_{01})=-2A(P_z-P_{01}), \tag{20}$$

where $|P_{01}|=\sqrt{-A/B}$ is the spontaneous polarization in the top layer, which gives $P_{z1}=P_{01}+(1/2|A|)E_z$, $P_{z2}=(1/A_2)E_z$, for the top and bottom layers, respectively. In this case the equation for the potential φ (4) reduces to a standard Laplace equation $(\epsilon_c\partial_z^2+\epsilon_a\nabla_\perp^2)\varphi=0$, with the boundary condition

$$\epsilon_{c1}\partial_z\varphi_1-\epsilon_{c2}\partial_z\varphi_2=4\pi P_{01}(x), \tag{21}$$

where $\epsilon_{c1}=1+2\pi/|A|$, $\epsilon_{c2}=1+4\pi/A_2$.

The spontaneous polarization in the top layer alternates from domain to domain as $P_{01}(x)=\pm|P_{01}|\equiv\pm\sqrt{-A/B}$. We are looking for a solution in a form of a domain structure with a period $T=2a$ (Fig. 1),

$$P_{01}(x)=\sum_k P_{01k}e^{ikx},\quad \varphi(x)=\sum_k \varphi_k e^{ikx}, \tag{22}$$

with $k\equiv k_n=2\pi n/T=\pi n/a$, $n=\pm 1,\pm 2,\ldots$. Going over to the Fourier harmonics, we can write the Laplace equations for both parts of the film as

$$\epsilon_{c1}\varphi_{1k}''-\epsilon_a k^2\varphi_{1k}=0, \tag{23}$$

$$\epsilon_{c2}\varphi_{2k}''-\epsilon_a k^2\varphi_{2k}=0, \tag{24}$$

with the boundary conditions at the interface $z=0$

$$\varphi_{1k}=\varphi_{2k},\quad \epsilon_{c1}\varphi_{1k}'-\epsilon_{c2}\varphi_{2k}'=4\pi P_{01k}. \tag{25}$$

The corresponding *electrostatic* (stray) field part of the energy is found as[10]

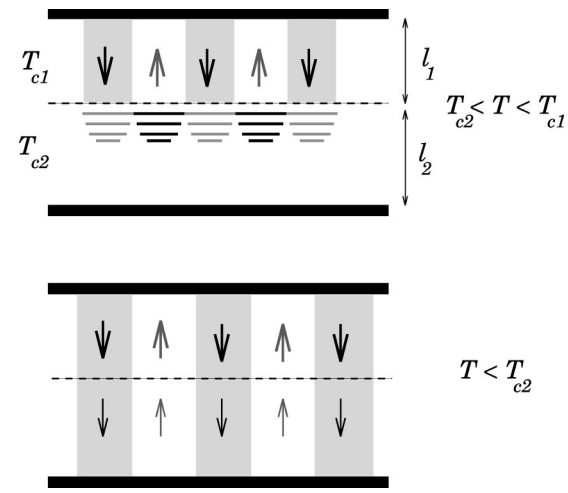

FIG. 1. Schematic of the domain structure with the period $2a$ in inhomogeneous ferroelectric film of the thickness l_1+l_2. Top and bottom layers have slightly different critical temperatures $T_{c1}>T_{c2}$, $T_{c1}-T_{c2}\ll T_{c1},T_{c2}$. Slightly below T_{c1} the top layer splits into domains with electric fringe field propagating into the bottom layer (fringe field shown as the hatched area in the top panel). The domains persist and evolve below T_{c2} when both layers exhibit a ferroelectric (or ferroelastic) transition (bottom panel).

$$\tilde{F}_{es}=\frac{1}{2}\int d\mathcal{A}\sigma_s\varphi(z=0), \tag{26}$$

where σ_s is the density of bound charge at the interface, corresponding to *only* the spontaneous part of the polarization $P_{01}(x)$, and integration goes over the area $\mathcal{A}$ between two parts of the film. We calculate this expression by going over to Fourier expansion (22) and using the fact that in the present geometry $\sigma_s(x)=-P_{01}(x)$ (and, therefore, its Fourier component $\sigma_{sk}=-P_{01k}$),

$$\frac{\tilde{F}_{es}}{\mathcal{A}}=\sum_{k>0}\frac{4\pi|P_{01k}|^2}{kD_k}, \tag{27}$$

$$D_k=\epsilon_a^{1/2}\left[\epsilon_{c1}^{1/2}\coth\sqrt{\frac{\epsilon_a}{\epsilon_{c1}}}kl_1+\epsilon_{c2}^{1/2}\coth\sqrt{\frac{\epsilon_a}{\epsilon_{c2}}}kl_2\right], \tag{28}$$

with $k=\pi n/a$, $n=1,2,\ldots$, similar to Ref. 13. Note that here $P_{01k}=2|P_{01}|/i\pi n$, $n=2j+1$, $j=0,1,\ldots$ and zero otherwise. Adding the surface energy of the domain walls, we obtain the free energy of the domain pattern,

$$\frac{\tilde{F}}{\mathcal{A}}=\frac{\gamma_1 l_1}{a}+\frac{16P_{01}^2a}{\pi^2}\sum_{j=0}^{\infty}\frac{1}{(2j+1)^3D_{2j+1}}, \tag{29}$$

where $D_n=D_{k_n}$. Not very close to T_{c1} the argument of coth is $\sqrt{\epsilon_a/\epsilon_{c1}}kl_1\gtrsim 1$ even for the smallest $k=\pi/a$ what is checked by the subsequent result [Eq. (30)], so that $D_k=\epsilon_a^{1/2}(\epsilon_{c1}^{1/2}+\epsilon_{c2}^{1/2})$. Minimizing the free energy, we find the domain width,

$$a=\left[\frac{\pi^2\epsilon_a^{1/2}(\epsilon_{c1}^{1/2}+\epsilon_{c2}^{1/2})}{14\zeta(3)}\Delta_1 l_1\right]^{1/2}, \tag{30}$$

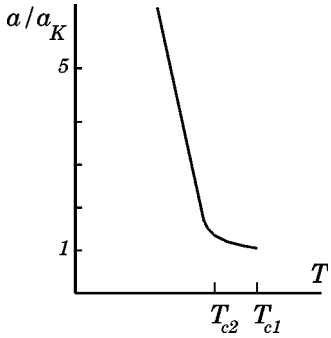

FIG. 2. The domain width in slightly inhomogeneous ferroelectric or ferroelastic in the units of a_K, the Kittel width (31). $a=a_K$ when the domain structure sets in at $T\approx T_{c1}$, and then it grows linearly with the temperature to large values $a\gg a_K$.

where $\Delta_1\equiv\gamma_1/P_{01}^2=d_{at}|A|^{1/2}$ is the characteristic microscopic length, and $d_{at}\equiv(2^{3/2}/3)D^{1/2}$ is comparable to a lattice spacing ("atomic" length scale). The expression (30) is valid when $\sqrt{\epsilon_a/\epsilon_{c1}}kl_1\gtrsim 1$, or $|A|\gtrsim 2d_{at}/(\pi\epsilon_a^{1/2}l_1)$, meaning that one has to be below T_c by a tiny amount $T_{c1}-T\gtrsim T_0 d_{at}/(\epsilon_a^{1/2}l_1)$, estimated earlier. Note that close to T_{c1} one obtains for the domain width

$$a=a_K\equiv\left[\frac{\pi^{5/2}\epsilon_a^{1/2}}{7\sqrt{2}\zeta(3)}d_{at}l_1\right]^{1/2}, \tag{31}$$

and this value does *not* depend on temperature. We shall formally refer to this result as the Kittel domain width.

Incidentally, close to T_{c2} the domain width is $a\approx\{[\pi^2\epsilon_a^{1/2}\epsilon_{c2}^{1/2}/14\zeta(3)]\Delta_1 l_1\}^{1/2}\propto\epsilon_{c2}^{1/4}$, which formally diverges $\propto(T-T_{c2})^{-1/4}$. However, in the vicinity of T_{c2} the induced polarization in the formerly "hard" part has about the same value as the spontaneous polarization in the "soft" part, $P_{z2}\approx P_{01}$. Then the equation of state in the bottom part becomes strongly non-linear, since the cubic term is much larger than the linear term, $BP_{z2}^3\approx BP_{01}^3=AP_{01}\approx AP_{z2}\gg A_2P_{z2}$, in the equation of state (since $A\gg A_2$ close to T_{c2}), so the response of the bottom layer does not actually soften in this region. In this case our derivation does not apply, but it is practically certain that the domain structure in the vicinity of T_{c2} would evolve continuously upon cooling, Fig. 2.

C. Domain structure at low temperatures ($T<T_{c2}$, $A<0$, $A+\delta A<0$)

When the system is cooled to below the critical temperature T_{c2}, a spontaneous polarization $|P_{02}|=\sqrt{-A_2/B}$ also appears in the bottom layer. The domain structure simultaneously develops in the whole crystal with domain walls running parallel to the ferroelectric axis through the whole crystal (if they were discontinuous at the interface between the two parts of the crystal this would have created a large depolarizing electric field). The electrostatic energy requires a solution of the same Laplace equations (23) and (24), only the boundary condition (25) would now read

$$\epsilon_{c1}\varphi_{1k}'-\epsilon_{c2}\varphi_{2k}'=4\pi(P_{01k}-P_{02k}), \tag{32}$$

where $\epsilon_{c1(2)}=1+2\pi/|A_{1(2)}|\approx 2\pi/|A_{1(2)}|$. Note that the density of the bound charge at the interface, corresponding to this discontinuity of spontaneous polarization, is now $\sigma_k=-(P_{01k}-P_{02k})$. Therefore, we immediately obtain for the total free energy of the structure, analogously to the previous case (29),

$$\frac{\tilde{F}}{\mathcal{A}}=\frac{P_{01}^2\Delta_1 l_1+P_{02}^2\Delta_2 l_2}{a}+\frac{16(P_{01}-P_{02})^2 a}{\pi^2}\sum_{j=0}^{\infty}\frac{1}{(2j+1)^3 D_{2j+1}}, \tag{33}$$

where $\Delta_{1(2)}=d_{at}\sqrt{|A_{1(2)}|}$. Not very close to T_{c2} we would have $\sqrt{\epsilon_a/\epsilon_{c2}}kl_2\gtrsim 1$ even for the smallest value of $k=\pi/a$ which enables us to replace coth by unity. The minimum of the free energy $\tilde{F}$ is achieved for the domain width

$$a=\frac{1}{1-P_{02}/P_{01}}\left[\frac{\pi^2\epsilon_a^{1/2}(\epsilon_{c1}^{1/2}+\epsilon_{c2}^{1/2})}{14\zeta(3)}\left(\Delta_1 l_1+\Delta_2 l_2\frac{P_{02}^2}{P_{01}^2}\right)\right]^{1/2}. \tag{34}$$

Close to the critical point T_{c2} the domain width formally behaves as $a\propto\epsilon_{c2}^{1/4}\propto(T_{c2}-T)^{-1/4}$, as found just above T_{c2} before. The same argument indicates though that our derivation does not apply in this region, but nonlinearity should not cause a substantial change in the domain structure.

With lowering the temperature to the region where $|A|\gg\delta A$, we will have $P_{02}/P_{01}=\sqrt{(A+\delta A)/A}\approx 1+\delta A/2A$, so that $1-P_{02}/P_{01}\approx 2|A|/\delta A\gg 1$ becomes a large prefactor. Note that in this region $\epsilon_{c1}\approx\epsilon_{c2}=2\pi/|A|$, $\Delta_1\approx\Delta_2=d_{at}\sqrt{|A|}$, and the domain width evolves as

$$a=\frac{|A|}{\delta A}\left[\frac{2^{5/2}\pi^{5/2}\epsilon_a^{1/2}}{7\zeta(3)}d_{at}(l_1+l_2)\right]^{1/2}, \tag{35}$$

It becomes much larger than the Kittel width, $a/a_K=2^{3/2}[(l_1+l_2)/l_1]^{1/2}[(T_{c1}-T)/(T_{c1}-T_{c2})]\gg 1$, growing linearly with lowering temperature (Fig. 2). For large periods of the domain structure Eq. (35) becomes inapplicable because the coth in the formula for D_k (28) cannot be replaced by unity, and this corresponds to $|A|\simeq(\delta A)^2 l_2 d_{at}$. If we assume that the difference between the critical temperatures in the both parts of the system is, for example, just $T_{c1}-T_{c2}=0.1$ K. Since $|A|=(T_{c1}-T)/T_0$ and $\delta A=(T_{c1}-T_{c2})/T_0$, we see that in 1-mm-thick film ($l/d_{at}\sim 10^7$) the expression for the domain structure period, Eq. (35), is valid at least in the region

$$T_{c1}-T\lesssim\frac{l_2}{d_{at}}\frac{(T_{c1}-T_{c2})^2}{T_0}. \tag{36}$$

This interval is 1–10 K for displacive and 50–100 K for order-disorder systems.

It follows from the qualitative analysis of the expression for the electric energy, that the domain width a will keep growing with lowering temperature beyond this range to sizes much larger than the Kittel width (31), because the system quickly moves into the region $|A|\gg\delta A$. This result is

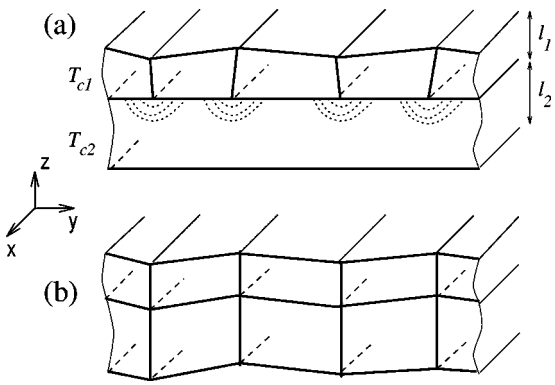

FIG. 3. Schematic of the domain structure in inhomogeneous ferroelastic film of the thickness l_1+l_2 with soft in-plane strain u_{xy}. Top and bottom layers have slightly different critical temperatures $T_{c1}>T_{c2}$, $T_{c1}-T_{c2}\ll T_{c1},T_{c2}$. (a) Slightly below T_{c1} the top layer splits into domains with fringe elastic field near the interface $z=0$ (schematically shown by the dotted lines). (b) The domains persist and evolve below T_{c2} when both layers exhibit a ferroelastic phase transition (bottom panel).

rather natural, since in this limit the relative difference between two parts of the system diminishes, and the system approaches the limit of a uniform free sample, which transforms into a monodomain state (i.e., $a=\infty$).

III. INHOMOGENEOUS FERROELASTIC PHASE TRANSITIONS

Very scenario applies in a case of slightly inhomogeneous proper ferroelastic in spite of some differences in the mathematics. Consider a ferroelastic slab with slightly different phase transition temperatures, $T_{c1}>T_{c2}$, in its two parts of a comparable size. In such a situation, the hard part will play a role of a rigid substrate for the top soft part of the sample at temperatures slightly below T_{c1}, and the sample will split into domains. The emerging domain structure should strongly evolve with temperature, since the bottom part of the film would also become "soft" at $T=T_{c2}$ slightly below T_{c1}.

A. Loss of stability ($T\approx T_{c1}$)

We assume that the film is perpendicular to the z axis, occupies the space $-l_2<z<l_1$, and is characterized by the u_{xy} (in-plane) component of the strain tensor as the order parameter. The hard shear modulus equals μ in both parts of the film, while the soft modulus corresponds to the u_{xy} component of strain. We shall consider a situation when the system consists of two layers with slightly different critical temperatures, Fig. 3. Thus the Landau thermodynamic potential has the form

$$F=\sum_{p=1,2}\int dV[2A_p u_{xy}^2+2D(\nabla u_{xy})^2+Bu_{xy}^4 +\mu(u_{ik}^2-2u_{xy}^2)], \tag{37}$$

where $A_1\equiv A=\alpha(T-T_{c1})$, $A_2=\alpha(T-T_{c2})\equiv A+\delta A$, with $\alpha,D,\mu>0$ positive constants, and $\delta A>0$ corresponding to $T_{c2}<T_{c1}$. Thus, the top layer of the system softens at T_{c1} $(A=0)$ while the other part of the system remains hard. Note that A designates now an elastic modulus and not reciprocal dielectric susceptibility as in the previously described case of ferroelectric. We designate the two parameters by the same letter to underline the similarities in the corresponding formulas.

The equation of state in each part p of the system is $\sigma_{ik}=\frac{1}{2}\delta F/\delta u_{ik}$, $i\neq k$:

$$\sigma_{xy}^p=2(A_p-D\nabla^2)u_{xy}+2Bu_{xy}^3, \tag{38}$$

$$\sigma_{xz}^p=2\mu u_{xz}, \quad p=1,2, \tag{39}$$

where $p=1$ (2) corresponds to the part $0<z<l_1$ $(-l_2<z<0)$.

The treatment of the stability loss is analogous to that of Ref. 7 and we omit some preliminary discussion presented in that earlier paper. To find the inhomogeneous part of the *displacement* vector u_x (or, equivalently, u_y) 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

$$\frac{\partial\sigma_{xy}}{\partial y}+\frac{\partial\sigma_{xz}}{\partial z}=0. \tag{40}$$

We shall use the Fourier expansion for the displacement vector

$$u(y,z)=\int u_k(z)\exp(iky)dk \tag{41}$$

and find the first appearance of the nontrivial solution for u for a given k wave vector. 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 displacement with the use of Eqs. (40) and (38),

$$\frac{d^2u_k}{dz^2}-\frac{A_{1k}}{\mu}k^2u_k=0, \quad 0<z<l_1, \tag{42}$$

$$\frac{d^2u_k}{dz^2}-\frac{A_{2k}}{\mu}k^2u_k=0, \quad -l_2<z<0, \tag{43}$$

where $A_{1k}=A+Dk^2$ and $A_{2k}=A+\delta A+Dk^2$. At the free surfaces $(z=l_1,-l_2)$ the boundary condition reads $\sigma_{xz}=0$, 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 $z=0$.

Let us first consider the case of $A_{1k}<0$, $A_{2k}>0$, which would correspond, as we will see shortly, to a loss of stability of the paraphase. The solution of Eqs. (42) and (43) is

$$u_k(z)=F\cos\chi_1 k(l_1-z), \quad 0<z<l_1, \tag{44}$$

$$u_k(z)=G\cosh\chi_2 k(z+l_2), \quad -l_2<z<0, \tag{45}$$

where $\chi_1^2=-A_{1k}/\mu=(-A-Dk^2)/\mu$ and $\chi_2^2=A_{2k}/\mu=(A+\delta A+Dk^2)/\mu$.

The condition of existence of a nontrivial solution, which we obtain from the boundary conditions, looks exactly the same as in the above case of ferroelectrics, Eq. (13). The subsequent analysis is also similar, and we obtain a condition for an existence of a nontrivial solution,

$$|A|=\frac{\pi^2\mu}{4k^2l_1^2}+Dk^2, \tag{46}$$

so the minimal value of $|A|=|A|_c$, when the solution first appears, corresponds to

$$k_c=\sqrt{\frac{\pi}{2l_1d_{at}}}, \tag{47}$$

$$|A|_c=2Dk_c^2=\frac{\pi\mu d_{at}}{l_1}, \tag{48}$$

where we have introduced the characteristic "atomic" length scale $d_{at}\sim(D/\mu)^{1/2}$, which is comparable to unit cell size. The corresponding shift of the critical temperature is very small. The coefficient α in Eq. (37) is μ/T_0, where $T_0\sim T_{at}$ in the case a displacive, and $\sim T_c$ in the case of order-disorder phase transition. Then, from Eq. (48),

$$T_c=T_{c1}-\frac{\pi\mu d_{at}}{\alpha l_1}\approx T_{c1}-T_0\frac{\pi d_{at}}{l_1}, \tag{49}$$

which is practically the same estimate, as for ferroelectrics, with the same (by the order of magnitude) values for the displacive and order-disorder phase transitions and the same condition for transition into inhomogeneous instead of a homogeneous state.

B. Domain structure in the top layer at $T_{c2}<T<T_{c1}$ ($A<0, A+\delta A>0$)

We consider next the domain structure below T_{c1} in a state with the spontaneous strain u_{xy}^0. One can apply the notion of the domain structure when the domain-wall thickness is much smaller than the domain width. This condition is fulfilled just below T_{c1} by a tiny amount given by the same small parameter d_{at}/l_1 as in the case of the ferroelectrics, Eq. (19). As in the previous case, one can apply the notion of the domain structure practically in the whole interval of temperatures between T_{c1} and T_{c2}, if the transition indeed proceeds into inhomogeneous state. Within this interval one can use the linearized equation of state for the top layer, obtained by expanding the free energy (37) about the spontaneous deformation,

$$\sigma_{xy}^1=2M_1(u_{xy}-u_{xy}^0),\quad 0<z<l_1, \tag{50}$$

$$u_{xy}^0\equiv u_0=\pm(-A/B)^{1/2}, \tag{51}$$

$$\sigma_{xy}^2=2M_2u_{xy},\quad -l_2<z<0, \tag{52}$$

where $M_1\equiv-2A>0$ is $\ll\mu$ when the system is close to the transition (soft modulus), $M_2=A+\delta A>0$. In both parts σ_{xz} is given by Eq. (39).

We shall assume that all the domains have the same width.[7] which we will find by minimizing the sum of the elastic energy and the (surface) energy of the domain walls. We consider a stripelike domain structure in the top layer with the spontaneous strain $u_{xy}^0(y,z)=\pm u_0$ with the period $2a$. There would be no stresses in the *free* top layer if $u_0^2=-A/B$. We have to find the displacements $u_x(y,z)\equiv u(y,z)$ appearing after the top layer experienced a phase transition. The equation of equilibrium (40) takes the form

$$M_1\frac{\partial^2u}{\partial y^2}+\mu\frac{\partial^2u}{\partial z^2}=2M_1\frac{\partial u_{xy}^0}{\partial y},\quad 0<z<l_1, \tag{53}$$

$$M_2\frac{\partial^2u}{\partial y^2}+\mu\frac{\partial^2u}{\partial z^2}=0,\quad -l_2<z<0. \tag{54}$$

Since the domain pattern is periodic, the elastic displacements may be represented as a Fourier series,

$$u(y,z)=\sum_k u_k(z)\exp(iky),\quad k\equiv k_n=\frac{\pi n}{a}, \tag{55}$$

where $n=\pm1,\pm2,\ldots$. After solving the resulting system of ordinary differential equations with the above conditions one finds

$$u_k(z)=u_0R_k\left(\frac{\eta_2\cosh\eta_1k(z-l_1)}{\eta_1\sinh\eta_1kl_1\coth\eta_2kl_2+\eta_2\cosh\eta_1kl_1}-1\right) \tag{56}$$

at $0<z<l_1$, and

$$u_k(z)=-\frac{u_0R_k\eta_1\cosh\eta_2k(z+l_2)}{\eta_1\cosh\eta_2kl_2+\eta_2\coth\eta_1kl_1\sinh\eta_2kl_2} \tag{57}$$

at $-l_2<z<0$, where $R_k=4/k^2a$, $k=\pi(2r+1)/a$, $r=0,\pm1,\ldots$ and $\eta_i=\sqrt{M_i/\mu}$, $i=1,2$, so that the amplitudes of the displacements $u_k(z)$ are proportional to the domain width a, as they should be. The elastic energy is found with the use of the formula[14]

$$F_{el}=-\frac{1}{2}\int\sigma_{ij}u_{ij}^0dV=-\int\sigma_{xy}u_{xy}^0dV \tag{58}$$

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

$$\frac{F_{stray}}{\mu u_0^2\mathcal{A}}=\frac{16\eta_1\eta_2a}{\pi^3}\sum_{j=0}^{\infty}\frac{1}{(2j+1)^3}\frac{1}{D_j} \tag{59}$$

with $D_j=\eta_1\coth\eta_2k_jl_2+\eta_2\coth\eta_1k_jl_1$. To find the equilibrium domain width, we have to add the energy of the domain walls

$$F_{dw}/A=\gamma_1l_1/a=\mu u_0^2\Delta_1l_1/a, \tag{60}$$

where[7]

$$\gamma_1 = \frac{8\sqrt{2}D^{1/2}|A|^{3/2}}{3B} \equiv \mu u_0^2 \Delta_1, \tag{61}$$

$$\Delta_1 \equiv \frac{8\sqrt{2}D^{1/2}|A|^{1/2}}{3\mu} \equiv d_{at}\sqrt{|A|/\mu} \tag{62}$$

and we have introduced the microscopic length scale Δ_1, with $d_{at} \equiv (8\sqrt{2}/3)(D/\mu)^{1/2}$ is, once more, of the order of the unit cell size. Note that the actual domain walls exist only in the top layer, which underwent a ferroelastic transition, with the stray displacement field penetrating into the bottom ''rigid'' part of the sample.

The equilibrium domain width is found from the total free energy,

$$\frac{F_{tot}}{\mu u_0^2 \mathcal{A}} = \frac{F_{stray}}{\mu u_0^2 \mathcal{A}} + \frac{\Delta_1 l_1}{a} \tag{63}$$

with the stray energy from Eq. (59). Assuming $\pi \eta_{1(2)} l_{1(2)}/a \gtrsim 1$ (to be checked later), we replace all coth in Eq. (59) by unity and easily obtain for the domain width

$$a = \sqrt{\frac{\pi^3 \Delta_1 l_1}{14\zeta(3)} \frac{\eta_1 + \eta_2}{\eta_1 \eta_2}}. \tag{64}$$

Slightly below T_{c1} one has $\eta_1 \ll \eta_2$

$$a = a_K \equiv \sqrt{\frac{\pi^3 \Delta_1 l_1}{14\zeta(3)} \frac{1}{\eta_1}} = \sqrt{\frac{\pi^3}{2^{3/2} 7\zeta(3)} d_{at} l_1}, \tag{65}$$

the limiting value which does *not* depend on temperature close to transition. We shall formally call this a Kittel period for the elastic domain structure, and the system, as we have shown, loses stability and quickly sets in the domain structure with this period, which is independent of the temperature close to the phase transition. As in the case of ferroelectrics, the period of the domain structure formally increases close to T_{c2}, but this conclusion is not reliable because the nonlinear effects in the former hard layer should be taken into account in this region.

C. Ferroelastic domain structure at low temperatures ($T < T_{c2}$, $A < 0$, $A + \delta A < 0$)

We consider next the domain structure not very close to the phase transition. There the domain wall width is much smaller than the width of the domains and one can use the linearized equation of state in both top and bottom parts of the film, obtained by expanding the free energy (37) about the spontaneous deformation,

$$\sigma_{xy} = 2M_1(u_{xy} - u_{xy}^0), \quad 0 < z < l_1, \tag{66}$$

$$\sigma_{xy} = 2M_2(u_{xy} - w_{xy}^0), \quad -l_2 < z < 0, \tag{67}$$

where $M_1 \equiv -2A$ is $\ll \mu$ (soft modulus), $M_2 = -2(A + \delta A)$ (note the change in the M_2 value below T_{c2}). Similarly to the previous case $u_{xy}^0 \equiv u_0 = \pm(-A/B)^{1/2}$, $w_{xy}^0 \equiv w_0 = \pm[-(A + \delta A)/B]^{1/2}$.

We have to find the inhomogeneous displacements in the film $u_x(y,z) \equiv u(y,z)$. For the film the equation of mechanical equilibrium (40) takes the form

$$M_1 \frac{\partial^2 u}{\partial y^2} + \mu \frac{\partial^2 u}{\partial z^2} = 2M_1 \frac{\partial u_{xy}^0}{\partial y}, \quad 0 < z < l_1, \tag{68}$$

$$M_2 \frac{\partial^2 u}{\partial y^2} + \mu \frac{\partial^2 u}{\partial z^2} = 2M_2 \frac{\partial w_{xy}^0}{\partial y}, \quad -l_2 < z < 0. \tag{69}$$

We look for a solution in the same periodic form (55) as earlier with the result

$$u_k(z) = R_k \left[\frac{(u_0 - w_0)\eta_2 \cosh \eta_1 k(z - l_1)}{\eta_1 \sinh \eta_1 k l_1 \coth \eta_2 k l_2 + \eta_2 \cosh \eta_1 k l_1} - u_0 \right], \tag{70}$$

for $0 < z < l_1$, and

$$u_k(z) = -R_k \left[\frac{(u_0 - w_0)\eta_1 \cosh \eta_2 k(z + l_2)}{\eta_1 \cosh \eta_2 k l_2 + \eta_2 \coth \eta_1 k l_1 \sinh \eta_2 k l_2} - w_0 \right] \tag{71}$$

for $-l_2 < z < 0$, where R_k is defined after Eq. (57). The elastic (stray) energy per unit area of the film is now found by integrating over both parts of the film, since now a spontaneous strain exists in both of them:

$$\frac{F_{stray}}{\mathcal{A}} = \frac{16\eta_1 \eta_2 \mu (u_0 - w_0)^2 a}{\pi^3} \times \sum_{j=0}^{\infty} \frac{1}{(2j+1)^3} \frac{1}{\eta_1 \coth \eta_2 k_j l_2 + \eta_2 \coth \eta_1 k_j l_1}, \tag{72}$$

where $\eta_i = \sqrt{M_i/\mu}$, $i = 1,2$, with $M_1 = -2A$, $M_2 = -2(A + \delta A)$ and $k_j = \pi(2j+1)/a$. Closer to $T = T_{c2}$ from below this expression becomes similar to that for the previous case, since $w_0 \to 0$. To find the total free energy one has to add the energy of the domain walls

$$\frac{F_{dw}}{\mathcal{A}} = \frac{\mu u_0^2 \Delta_1 l_1 + \mu w_0^2 \Delta_2 l_2}{a}, \tag{73}$$

where $\Delta_2 = d_{at}|(A + \delta A)/\mu|^{1/2}$, while Δ_1 is given by Eq. (62). The equilibrium period of the structure, is

$$a = \frac{1}{1 - w_0/u_0} \sqrt{\frac{\pi^3[\Delta_1 l_1 + \Delta_2 l_2 (w_0^2/u_0^2)]}{14\zeta(3)} \frac{\eta_1 + \eta_2}{\eta_1 \eta_2}}, \tag{74}$$

in the same approximation as before, $\pi \eta_2 l_2/a \gtrsim 1$, which enables us to replace coth by unity in Eq. (72).

We find in the vicinity of T_{c2}, where $\eta_2 \equiv \eta_2^- = \sqrt{-2(A + \delta A)/\mu} \ll \eta_1$, $\Delta_2 \ll \Delta_1$, $w_0 \ll u_0$), the equilibrium domain width,

$$a = \sqrt{\frac{\pi^3 \Delta_1 l_1}{14\zeta(3)} \frac{1}{\eta_2^-}} \propto \frac{1}{\sqrt{\eta_2^-}}. \tag{75}$$

We see that the period of the domain structure formally diverges when one is approaching T_{c2} from below but this behavior will be modified by the nonlinear effects.

Let us check the behavior of the domain width at temperatures deep into the ferroelastic region for both parts of the film, where $|A| \gg \delta A$. There $\eta_2 \approx \eta_1$, $\Delta_2 \approx \Delta_1$ and $1 - w_0/u_0 \approx \delta A/2|A| \ll 1$, and we obtain

$$a = \frac{2|A|}{\delta A}\sqrt{\frac{\pi^3}{7\sqrt{2}\zeta(3)} d_{at}(l_1+l_2)}. \tag{76}$$

We see that far below the temperature where a spontaneous strain sets in the whole system, the period of the domain structure grows with respect to the Kittel period of initial domain structure a_K, Eq. (65), as

$$\frac{a}{a_K} = \frac{2^{3/2}|A|}{\delta A}\left(\frac{l_1+l_2}{l_1}\right)^{1/2} = 2^{3/2}\left(\frac{l_1+l_2}{l_1}\right)^{1/2}\frac{T_{c1}-T}{T_{c1}-T_{c2}} \gg 1. \tag{77}$$

Since the period is linearly growing with lowering temperature, $a \propto |A|$, and becomes very large, $a \gg a_K$, and the replacement of the coth by unity becomes unjustified. The condition of applicability of Eq. (77) is the same as for Eq. (35) in the case of ferroelectrics.

IV. SUMMARY

Summarizing, in an electroded ferroelectric or free ferroelastic sample with a tiny inhomogeneity of either the critical temperature or temperature itself (i.e., in the presence of a slight temperature gradient and/or minute compositional inhomogeneity across the system) the domain structure abruptly sets in when the spontaneous polarization appears in the softest part of the sample (i.e., the part with maximal T_c). This takes place when the difference in T_c in the parts of the sample is just 10^{-3}–10^{-2}) K for the displacive systems, and even smaller, 10^{-5}–10^{-4} K, for the order-disorder systems. The period of the structure then grows linearly with lowering temperature and quickly becomes *much larger* than the corresponding Kittel period.

This result does not depend on specific geometry assumed in the present model. Indeed, if local $T_c = T_c(z)$ varies continuously, it can be approximated by a piecewise distribution of a sequence of ''slices.'' Upon cooling the system first loses stability in the softest part of thickness l_s, which is derived from the position of the boundary where local $T_c = 0$, with respect to a domain structure with fine period $\propto \sqrt{l_s}$. The domains extend into the bulk of the system and become wider with further cooling, since l_s increases. In electroded sample there will be no domain branching and domain walls would run straight across all transformed slices. Otherwise, discontinuities would have resulted in very strong depolarizing field. If the overall inhomogeneity is small, the picture would obviously remain very similar to the two-slice model solved above. The same arguments remain valid if the inhomogeneity were to have more complex form/distribution in a sample. The interesting feature of the present effect in case of *ferroelectics* is that the depolarizing field appears not due to surface charges, which are screened out by the electrodes, but because of the bulk inhomogeneity. In the case of *ferroelastics*, inhomogeneity in the sample results in the *bulk stresses* that cause the splitting of the system into domains. In this case too the domain wall would run straight through the soft part of the crystal, since the discontinuities would result in large stray elastic stresses.

We have shown that a very tiny temperature gradient, or a slight compositional inhomogeneity, etc., would result in practically any crystal eventually splitting into domains no matter how high the quality of it is. The rapid evolution of the domain pattern, found in the present paper, when it starts from very fine domains at T_c, which then grow linearly with temperature to very large sizes is similar to what has been reported in Ref. 15 for ~1-mm-thick triglycine sulfate (TGS) crystals. It would be very interesting to perform controlled experiments for the domain structure close to the second-order phase transitions. One could check, in particular, the basic assumption of the present theory that the electric fields (elastic stresses) accompanying ferroelectric (ferroelastic) phase transitions even in slightly inhomogeneous media are compensated by formation of the domain structures rather than, for example, by screening of the electric field by charge carriers in ferroelectrics. Further understanding of the domain formation at phase transitions in real crystals is very important given that many properties of ferroelectrics and ferroelastics, used in applications, are mainly determined by the domain structures.

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