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Analysis of ferroelectric switching in finite media as a Landau-type phase transition

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Abstract. A detailed analysis of polarization reversal in ferroelectrics has been performed, in the framework of the Landau model for phase transitions. Some important characteristics of homogeneous switching have been emphasized and later used in studying the more general case of inhomogeneous switching. The two extremes of switching current correspond to the inflexion points of the dielectric hysteresis loop. Hysteresis loops of poled ferroelectric samples are expected to include negative-susceptibility regions, for high-frequency applied electric fields. The switching current minimum is eliminated by the experimental method used for recording the switching responses. Equivalent Landau coefficients and electric fields have been defined, in order to integrate the size effects and inhomogeneity contribution to switching of the global order parameter. We correlated the size effects on the critical parameters of the switching (the coercive field) and the ferroelectric-to-paraelectric phase transition (the Curie temperature). Polarization reversal in small-size ferroelectrics can be regarded as a diffuse phase transition, whereas its character is closer to normal for large-size samples. The size dependencies of the reversal speed and maximum current result from the size dependencies of the equivalent Landau coefficients and electric field inducing reversal.

1. Introduction

The interest in elucidating how the polarization reversal proceeds in a ferroelectric sample is justified by recent applications of ferroelectric thin films as non-volatile memories, adaptive learning neurodevices and sources for electron emission.

Early studies performed on barium titanate single crystals have shown that switching is an inhomogeneous process, based on nucleation of antiparallel domains followed by their growth under the influence of the applied electric field. Merz [1] and Little [2] directly observed the domain structure of barium titanate using optical methods. Yakunin *et al* used transmission electron microscopy [3] for recording the motion of both 90° and 180° domain walls in barium titanate single-crystal thin films.

Later, Shur *et al* [4] concentrated their attention on the switching behaviour of two uniaxial ferroelectrics having a very simple domain structure that contains 180° domain walls only: gadolinium molybdate and lead germanate. They showed that the domain dynamics essentially depends on the applied electric field strength. In weak electric fields the polarization reversal is achieved mainly by sideways growth of a few nucleated reversed domains. For stronger fields the nucleation of many new domains dominates the reversal.

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In the case of ceramics, the influence of grain dimensions is important as regards the ferroelectric properties. Frey and Payne [5] are the authors of an excellent review of the main experimental results describing the grain size effects in barium titanate ceramics. Among the possible causes of these effects, they analyse the relevance of: depolarization fields, the absence of long-range cooperative interactions, structural defects and elastic constraints. They advocate the idea of a critical size for the tetragonal phase of barium titanate, based on their results and those of other authors [6–8].

Ishibashi and Takagi [9] were the first to treat polarization reversal as an electrically induced phase transition, in the framework of the Kolmogorov–Avrami [10, 11] theory of crystal growth. Although it was successful in many respects, some changes to the original Avrami theory were required to explain the switching properties of ferroelectric samples with finite size.

Duiker and Beale [12] introduced changes in the growth regime of the 'new' phase domains using the geometrical condition of reaching the boundary. They performed computer simulations to verify the theory and showed that it successfully explains the qualitative features of the size-dependent switching polarization and current. Orihara and Ishibashi [13] further improved the theory, by introducing an average over the critical times when domains emerging from different parts of the sample touch different points of the grain boundary. Shur *et al* [14] divided a two-dimensional ferroelectric sample into strips along one of the directions. They treated the polarization reversal in terms of geometrical 'catastrophes' that occur when domains growing along the other direction stop reaching a chosen line because of size limitations.

All of the adaptations of Avrami theory to switching [12–14] have the drawback of not relating size-dependent effects occurring during switching with the detected size-dependent shift of the Curie temperature [6–8]. The boundary of the ferroelectric system influences the switching behaviour by means of a geometrical condition only.

A more promising approach is to maintain the original treatment of polarization reversal as an inhomogeneous change between two phases, but in the framework of Landau theory for phase transitions. This theory is the basis of what has become a standard method for describing the paraelectric-to-ferroelectric phase transition, predicting the occurrence of a non-zero order parameter below the Curie temperature [15]. In the past few years, Landau theory was extended in order to study the surface and size effects on the phase transitions of ferroelectrics with film or particle structure. The film thickness dependence of the transition temperature [16] and spontaneous polarization [17] have been obtained. Usually the surface ferroelectricity is weaker and a size-driven phase transition exists, at least for particulate media [18]. In another paper [19] the anisotropic correlation length of electric dipoles is taken into account in predicting the finite-size ferroelectric behaviour.

Ishibashi [20] was the first to use the Landau theory of phase transitions for modelling the polarization reversal, obtaining dependencies of switching times according with experiments. Omura *et al* [21] performed simulations on the basis of this model, computing the switching curves and hysteresis loops. In a previous paper [22] we introduced the depolarization-field energy in the Landau model and explained the grain size dependence of the switching properties of barium titanate ceramics. Wang and Smith [23] modelled a similar size effect, taking into account the non-ferroelectric passive layers that may exist at the system boundary.

Our recent paper [24] presented some simulations of partial switching experiments on the basis of a discrete Landau model and predicted a strong influence of the applied pulse sequence on the switching behaviour. A subtraction of the non-switching response from the switching response, as performed while using experimental data [25, 26], was shown to increase the agreement of the theoretical predictions with the experimental findings.

In the present paper we have analysed the ferroelectric switching process, and emphasized the consequences of treating polarization reversal as a Landau-type electrically induced phase transition. The first section contains a short review of the Landau model for switching. Some important particularities of homogeneous switching are pointed out in the second section. All of the values of the polarization during switching correspond to points of the dielectric hysteresis loop. The extremes of the switching current correspond to the inflexion points of the dielectric hysteresis loop. We have shown that polarization reversal has pronounced irreversible characteristics. The third section presents size-dependent effects in inhomogeneous ferroelectric switching. We have proved that size effects are intrinsic properties of finite ferroelectric media and that their explanation does not need additional hypotheses like those introduced in [12–14] and [22, 23]. The main idea is that inhomogeneous reversal of the interacting polar units in a finite sample can be reduced to homogeneous switching of a global order parameter. In order to integrate the inhomogeneities and size effects, we defined equivalent Landau coefficients and electric fields for the switching curves of global polarization. Under these circumstances, shifting of the Curie temperature and size effects on switching are both obtained from Landau theory. We have shown that polarization reversal in finite-size ferroelectrics can be regarded as a diffuse phase transition, especially at small sizes. The size dependencies of the maximum switching current and of the reversal speed reflect the size dependencies of the equivalent coefficients and the electric field. We believe that this is the first successful attempt to interpret various size-dependent effects on ferroelectric behaviour within the framework of a single model.

2. Review of the Landau model for switching

A simple form of the relevant free energy associated with paraelectric-to-ferroelectric phase transition is given by:

$$F = \frac{\alpha}{2}p^2 + \frac{\beta}{4}p^4 + \cdots. \tag{1}$$

Here p is the order parameter in the ferroelectric phase and α, β are Landau coefficients. The second-order term is temperature dependent: $\alpha = a(T - T_C)$, where T_C is the Curie temperature. For simplicity we retained in equation (1) only terms up to the fourth power of polarization. The processes studied do not differ significantly when more terms are added.

When we refer to switching as a phase transition, the energy of the applied electric field should be added to the free energy:

$$F = \frac{\alpha}{2}p^2 + \frac{\beta}{4}p^4 - pE. \tag{2}$$

The time variation of the order parameter during switching is described by the Landau–Khalatnikov equation [16]:

$$\gamma\frac{\mathrm{d}p}{\mathrm{d}t} = -\frac{\partial F}{\partial p} \tag{3}$$

where γ is a viscosity coefficient.

The switching current can be written as

$$j = \frac{\mathrm{d}p}{\mathrm{d}t}. \tag{4}$$

In order to account for the inhomogeneities of the polarization profile during switching (e.g. domains, impurities, imperfections), a new term must be added to the free energy. The energy should now be written in its discrete form [20–22], describing a one-dimensional ferroelectric lattice with N polar units:

$$F = \sum_{n=1}^{N} \left[\frac{\alpha}{2} p_n^2 + \frac{\beta}{4} p_n^4 + \frac{k}{2} (p_n - p_{n-1})^2 - p_n E \right] \tag{5}$$

where we have denoted the polarization at site n by p_n. The new term contains a contribution from the inhomogeneities present during the phase transition, yielded by the first-neighbour coupling constant k. In this case switching proceeds on the basis of the Landau–Khalatnikov equation written for each of the N polar units:

$$\gamma \frac{\mathrm{d}p_n}{\mathrm{d}t} = -\frac{\partial F}{\partial p_n} \tag{6}$$

where n varies from 1 to N.

The global order parameter is the average of the polarizations at all sites:

$$P = \frac{1}{N} \sum_{n=1}^{N} p_n. \tag{7}$$

The switching transient is described by equation (4), as in the homogeneous case, where p is the global order parameter.

In the next section some important characteristics of homogeneous switching are emphasized and these are used later in analysing the more general case of inhomogeneous polarization reversal.

3. Analysis of homogeneous switching and discussion

In this case, the polarization reversal is governed by equation (3), which takes the form of a non-linear first-order differential equation:

$$\gamma \frac{\mathrm{d}p}{\mathrm{d}t} = -(\alpha p + \beta p^3 - E). \tag{8}$$

We have chosen the following values of the coefficients: $\alpha = -1.6$, $\beta = 1.0$, $\gamma = 1.0$, $E/E_c = 1.54$. Unless stated otherwise, these values have been retained for obtaining all of the results presented in this paper. The polarization in the initial state is the negative remnant polarization, $p_r = -(-\alpha/\beta)^{1/2}$.

Figures 1(a) and 1(b) present the time dependencies of the polarization and current, computed from equations (8) and (4), respectively. We note the two extremes of switching current, i.e. a minimum for $p_m = -[-\alpha/(3\beta)]^{1/2}$ and a maximum for $p_M = [-\alpha/(3\beta)]^{1/2}$. The extreme values of the switching current are given by $\gamma i_m = E - E_c$ and $\gamma i_M = E + E_c$, respectively. Here E_c is the coercive field in the Landau model for switching:

$$E_c = \frac{-2\alpha}{3} \sqrt{\frac{-\alpha}{3\beta}}. \tag{9}$$

The saturation polarization from figure 1(a) corresponds to the solution of the following polynomial equation, denoted sometimes as the dielectric equation of state [27]:

$$\beta p^3 + \alpha p = E. \tag{10}$$

The electrically induced order parameter is the equilibrium polarization p_{eq}, for a given value of the electric field, obtained by solving the dielectric equation of state (10). The critical parameter limiting the existence of the two phases is the coercive field. This choice of quantities describing the phase transition leads to a power-law dependence of the order

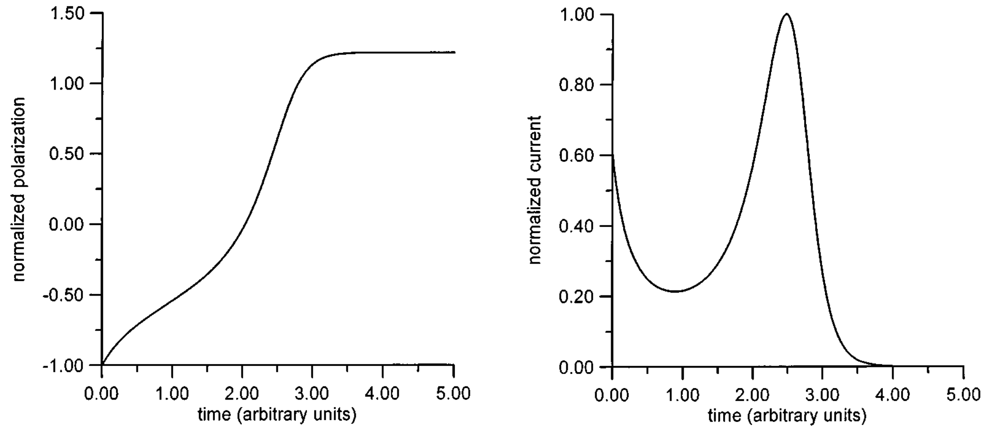


Figure 1. Time dependencies of the switching (a) polarization, normalized to its positive remnant value, and (b) current, normalized to its maximum value. The following values of the coefficients are adopted: $\alpha = -1.6$, $\beta = 1.0$, $\gamma = 1.0$, $E/E_c = 1.54$.

parameter in the critical region. When E approaches E_c, the order parameter scales with the electric field as $p_c - p_{eq} \propto (E_c - E)^{\mu}$, where p_c and E_c are the order parameter at the transition point and the coercive field, respectively. Our analysis based on equations (8)–(10) has shown that the critical exponent is $\mu \approx 0.48$, whereas its theoretical value in a thermally induced Landau phase transition described by the free energy in equation (1) is $1/2$ [15]. We believe that the existence of this power-law dependence of the order parameter emphasizes the similarity between switching as an electrically driven Landau phase transition and a conventional thermal one.

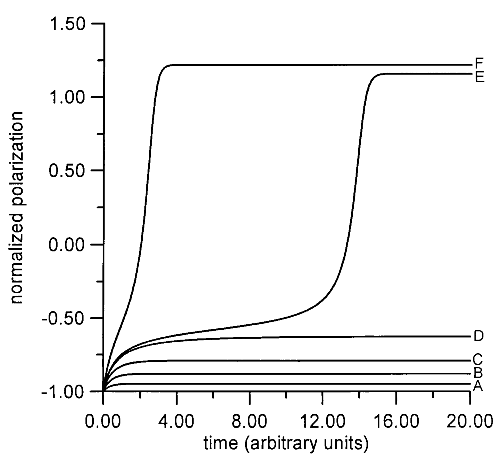


Figure 2. Time dependencies of the polarization after application of the electric fields indicated. The polarization is normalized to its positive remnant value. The electric field is given by the ratio E/E_c: (A) 0.26; (B) 0.51; (C) 0.77; (D) 0.99; (E) 1.03; (F) 1.54.

The order parameter p_{eq} varies discontinuously during the phase transition between the two oppositely polarized phases. Figure 2 contains the time dependencies of the

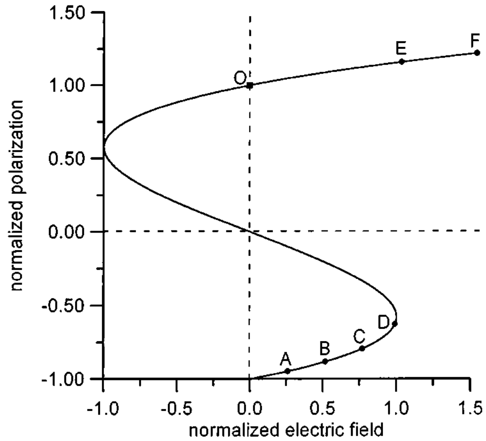


Figure 3. The dielectric hysteresis loop. The polarization is normalized to its positive remnant value and the electric field is normalized to the coercive field. The small full circles correspond to the curves depicted in figure 2. The line OF corresponds to the non-switching contribution. The values of the coefficients adopted are the same as for figure 1.

polarization change induced by the electric fields indicated, starting from the negative-remnant-polarization state. The saturated polarization for each curve is the order parameter p_{eq}. One observes the abrupt change of p_{eq} that occurs when the electric field inducing reversal becomes higher than the coercive field. An unstable-polarization range exists, where one could find the ferroelectric system in a transient state only. This is better illustrated by plotting the order parameter versus the electric field that confined the ferroelectric system in the respective state. Figure 3 contains such a plot, where the small full circles correspond to the curves indicated in figure 2. These points form the positive-susceptibility regions of the dielectric hysteresis loop (DHL), obtained from the dielectric equation of state (10). The unstable-polarization range obviously corresponds to the negative-susceptibility region of the DHL.

Equation (8) written as

$$\beta p^3 + \alpha p = E - \gamma \frac{\mathrm{d}p}{\mathrm{d}t} \tag{11}$$

shows that each state of the ferroelectric system during switching is associated with a point of the DHL. However, the presence of a negative-susceptibility region is only a mathematical way of illustrating that the states between the two inflexion points of the DHL cannot be accessed in equilibrium. Hence the equilibrium states of the ferroelectric system initially found in one of the remnant polarization states can only be outside of this range. This is why the negative-susceptibility region of the DHL is usually replaced by two vertical lines [27], suggesting that it is not stable. We shall describe below in what experimental circumstances the existence of the negative-susceptibility region is expected to be manifested directly.

Although not relevant as regards equilibrium, the states corresponding to the negative-susceptibility region are important for the switching process. The two inflexion points of the DHL are obtained for $E = E_c$ and $E = -E_c$, i.e. for $p_m = -[-\alpha/(3\beta)]^{1/2}$ and $p_M = [-\alpha/(3\beta)]^{1/2}$, respectively. This indicates that the two extremes of the switching current correspond to the inflexion points of the DHL. Consequently, while temporarily in a state associated with a negative-susceptibility point of the DHL, the ferroelectric system reverses its polarization with increasing speed. The states associated with positive-susceptibility regions of DHL are characterized by decreasing reversal speed. Simple calculations using the data from figure 1 show that 52% of the polarization change during reversal corresponds to the negative-susceptibility region of the DHL. On the other hand, only 22% of the intermediate states during switching are possible equilibrium states of the ferroelectric system. The above percentages allow us to conclude that polarization reversal is mainly a non-equilibrium process, with strongly irreversible characteristics.

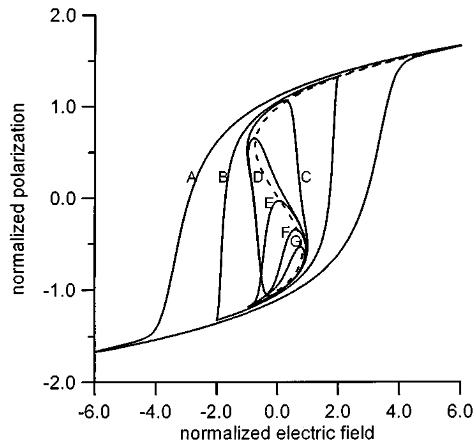


Figure 4. Hysteresis loops computed for sine waves of normalized amplitudes: (A) 7.70; (B) 2.57; (C) 1.28; (D) 1.24; (E) 1.23; (F) 1.22; (G) 1.16. The broken line is the DHL. The polarization is normalized to its positive remnant value and the electric field to the coercive field. The values of the coefficients are the same as for figure 1 and the period of the electric fields is $T = 16.0$.

When the electric field is removed, the polarization returns to its positive remnant value. This is a back-switching process. If a second positive pulse is applied after polarization reversal and removal of the electric field, a non-switching response is obtained. We described these processes by solving equation (8) with an appropriate initial condition and using the procedure involved in obtaining figures 2 and 3. In this way we have seen that in back-switching and non-switching processes, negative-susceptibility regions no longer exist. The polarization evolves on the upper branch of the DHL only, with decreasing speed (the line OF in figure 3). These observations prove that non-switching and back-switching processes are reversible. Hence, the time dependence of the polarization during reversal will inherently contain a reversible part, associated with the non-switching response.

Since negative-susceptibility regions are not usually found in experimental hysteresis loops, one could ask whether the DHL has a real physical meaning. Figure 4 shows some hysteresis loops computed when sine waves of different amplitudes are the external electric input of equation (8). The initial polarization has been set to its negative remnant value, as in the case of step-type applied fields. However, the hysteresis loops presented in figure 4 were recorded during the second period of the signal application, after the memory of the remnant initial state had been erased. The DHL of the same parameters (the broken line) is also shown. These hysteresis loops should be compared to those seen on the oscilloscope when sine electric fields were applied to a previously poled ferroelectric sample, in a Sawyer–Tower circuit. One observes that the positive-susceptibility regions of the DHL are parts of the hysteresis loops obtained for sine waves, if the amplitudes are well above the coercive field. The negative-susceptibility regions are avoided and replaced by normal hysteresis curves, as in experiments.

However, when switching is induced by high-frequency sine waves of amplitudes slightly higher than the coercive field, one expects that the hysteresis loops will tend to the DHL. Figure 4 shows that it is possible to obtain hysteresis loops entering the negative-susceptibility region, but certainly not in equilibrium. The ferroelectric system is prevented from reaching the equilibrium state corresponding to the amplitude employed (placed in the upper positive-susceptibility region of the DHL) by the decreasing and inversion of the applied sine wave occurring too early. Hysteresis loops like those depicted in figure 4 have already been reported in a paper describing the ferroelectric behaviour of some barium titanate poled ceramics [28].

The Landau theory has the apparent shortcoming of predicting a minimum of the switching current at early stages in addition to the maximum point always observed to exist experimentally (see, for example, [1, 26]). In order to explain why in usual switching experiments no minimum point in the time dependence of the switching current is detected, a short review of the experimental procedures is necessary. The switching current is usually recorded in a non-linear RC-circuit containing the ferroelectric sample (as a capacitor), connected in series with a linear resistor. As there is always a certain voltage drop across the resistor, polarization reversal will not be induced by an electric field applied in a stepwise fashion. So, in order to match the experimental conditions, the applied electric field in equation (8) should not have a stepwise time variation, as it had to have in order for us to obtain the results depicted in figure 1. More realistic would be to set the external field in equation (8) as varying exponentially from zero to the chosen amplitude. This correction takes into account the fact that the pulse applied to the ferroelectric capacitor used in measurements has a finite rising time.

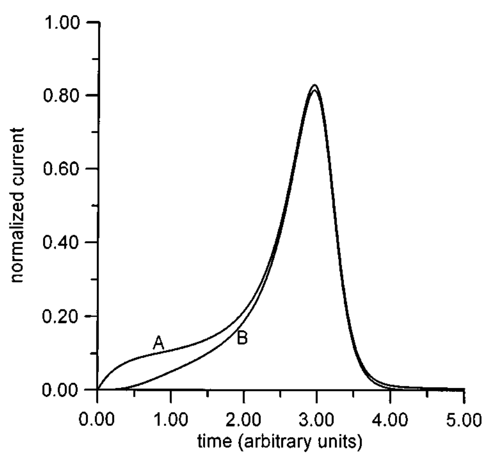


Figure 5. Corrected switching currents. The currents are normalized to the maximum value of the uncorrected switching transient. Curve A: the electric field varies exponentially from zero to $E/E_c = 2.82$, with the time constant $\tau = 2.0$. Curve B: the non-switching response was subtracted from the switching current plotted as curve A.

The currents depicted in figure 5 show the influence of the following two corrections. First, the applied electric field varied exponentially from zero to its amplitude (in this case $E/E_c = 2.82$), with the time constant $\tau = 2.0$. Now the only extreme value appearing in the time variation of the switching current (curve A) is the maximum detected in experiments. Furthermore, according to the experimental procedure [25, 26], we subtracted the non-switching response from the switching response plotted in figure 5 as curve A. Curve B shows that the agreement with experiments improved even more when we introduced this second correction. Thus the missing current minimum in experiments is not a false prediction of Landau theory, but merely an experimental artefact requiring model corrections. The minimum of the switching current is removed by the above-mentioned separation of the non-switching response and by the slowly time-dependent applied electric field.

The results of the next section were obtained using electric fields applied in a stepwise fashion. A precise comparison with experiments requires us to employ time-dependent (e.g. exponential) electric fields and to subtract the non-switching response. However, as we are primarily concerned with the qualitative features of inhomogeneous switching, the results presented below are not much different from the ones obtained with the above-mentioned corrections.

4. Analysis of inhomogeneous switching and discussion of finite-size effects

In this section we study the new effects that appear when the ferroelectric system is regarded as a one-dimensional lattice of interacting polar units. A polar unit at any site has the same Landau coefficients as in the case of homogeneous switching. Polarization reversal of one unit is described by the Landau–Khalatnikov equation, obtained after addition of a new inhomogeneity term in the free energy. We studied the new effects appearing in the switching curves because of this additional contribution to switching.

The time dependence of the polarization during its reversal can be obtained from equation (6), which becomes

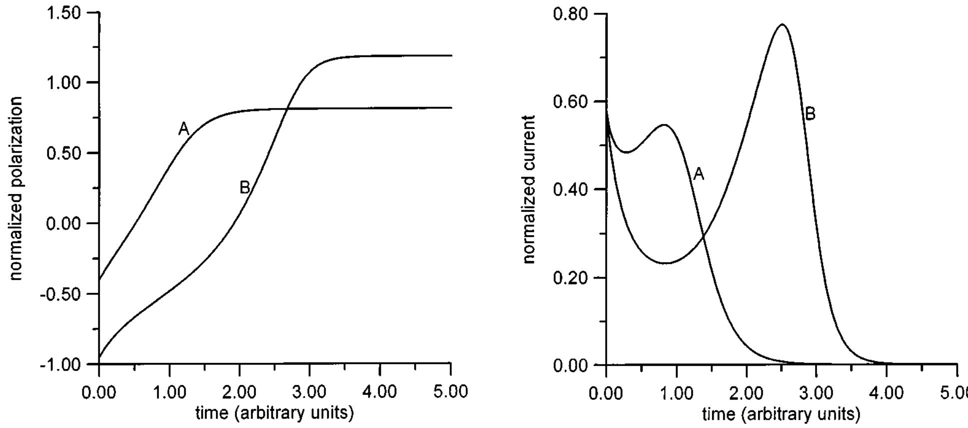
$$\gamma \frac{\mathrm{d}p_n}{\mathrm{d}t} = -\left[\alpha p_n + \beta p_n^3 + k(2p_n - p_{n-1} - p_{n+1}) - E\right] \tag{12}$$

and the global order parameter is now the average of the polarizations at all of the sites. The initial state for the differential equation (12) corresponds to the negative remnant polarization of all of the polar units.

In order to carry out computations of switching curves by solving equation (12), we adopted the free boundary condition (margin polar units have fewer first neighbours than the bulk ones). The inhomogeneity will gradually affect the polar units during switching, starting from the free boundary, leading to size-dependent effects. It appears that these effects can be accounted for in the framework of the Landau model with just the assumption of a free boundary, without needing the additional hypotheses introduced by other authors: geometrical 'catastrophes' [14], depolarization fields [22] or non-ferroelectric passive layers [23]. Although it is right to assume that the above phenomena could lead to size-dependent behaviour also, our approach has the advantage of a greater generality of the results.

Figures 6(a) and 6(b) show the time dependencies of the global switching polarization and current, for two samples with $N = 10$ and $N = 100$ polar units, respectively. They are in agreement with our experimental results for barium titanate ceramics with different grain sizes [22]. Both the maximum switching current and the time at which the current reaches its peak value decrease for small sizes.

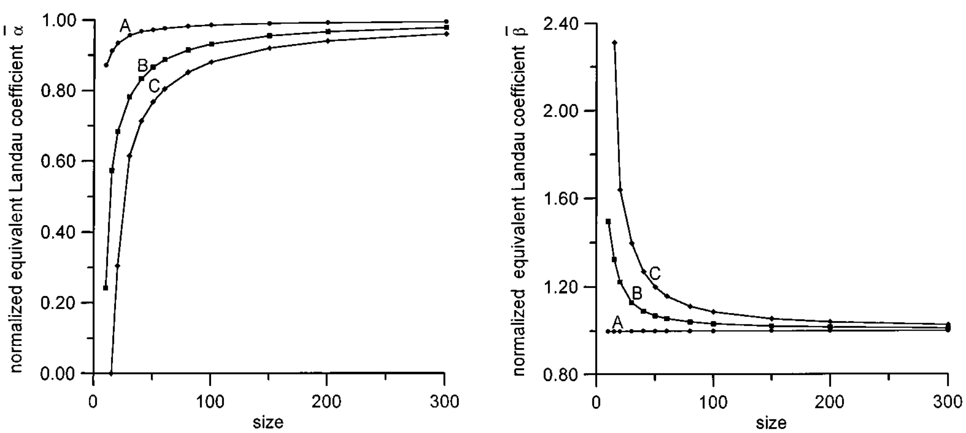
As the dependencies presented in figure 6 preserve the general features of the curves analysed in the preceding section (where we had neither inhomogeneities nor size effects), we investigated in what way the coupling between polar units of a ferroelectric with a free boundary contributes to switching of the global order parameter. Therefore we determined an equivalent homogeneous switching process, characterized by the equivalent Landau



(a) (b)

Figure 6. Time dependencies of the global (a) polarization, normalized to its positive remnant value in an isolated polar unit, and (b) current, normalized to its maximum value in an isolated polar unit, for a finite lattice having: (A) $N = 10$ sites; (B) $N = 100$ sites. The coupling constant is $k = 15$.

coefficients ($\bar{\alpha}$, $\bar{\beta}$) and electric field ($\bar{E}$) and governed by equations (8) and (4). The equivalent values are obtained by imposing the condition that the polarization and current time dependencies during this process are identical with those of the global order parameter, given by equations (12), (7) and (4). Obviously, the equivalent quantities are different from their values in a polar unit, as they integrate the coupling between units and size effects due to the free boundary.



(a) (b)

Figure 7. Size dependencies of the equivalent Landau coefficients (a) $\bar{\alpha}$ and (b) $\bar{\beta}$, normalized to their values in an isolated polar unit, for the following coupling constants: (A) $k = 1$; (B) $k = 15$; (C) $k = 50$.

Figures 7(a) and 7(b) present the size dependences of the $\bar{\alpha}$- and $\bar{\beta}$-coefficients, respectively, for the indicated values of the first-neighbour coupling constant k. One observes that $\bar{\alpha}$ and $\bar{\beta}$ approach their values for an isolated polar unit when the size increases.

For strong coupling, the equivalent Landau coefficients at large sizes are still different from their values corresponding to non-interacting polar units.

The size dependence of the $\bar{\alpha}$-coefficient can be related to the paraelectric-to-ferroelectric transition point shift to lower temperatures, at small sizes. This kind of dependence was reported to appear experimentally (see, for example, [6–8]) and was explained in the framework of the Landau model [16–19]. Our approach of treating size effects supposing there to be fewer neighbours at the boundary is similar to the hypothesis of weaker edge ferroelectricity employed in [16–19]. The main difference lies in the relationship between the two phases of the ferroelectric system involved, before and after the transition. Our results are relevant for a phase transition between two states having opposite values of the order parameter and not a thermal phase transition leading to a zero value of the polarization. We are therefore not primarily concerned with the transition temperature shift, as the relevant factor inducing polarization reversal is the electric field and not the temperature.

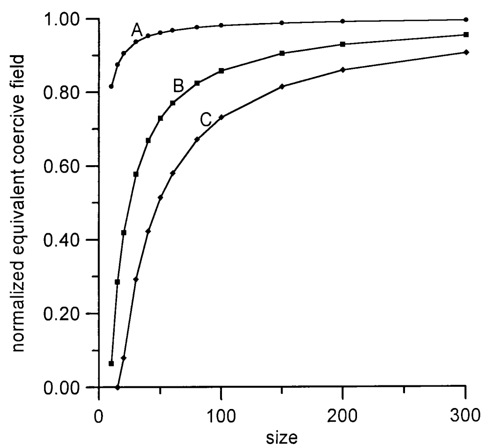


Figure 8. The size dependence of the equivalent coercive field, normalized to its value in an isolated polar unit, for the following coupling constants: (A) $k = 1$; (B) $k = 15$; (C) $k = 50$.

Figure 8 shows the size dependence of the equivalent coercive field, computed from equation (9) (for $\alpha = \bar{\alpha}$ and $\beta = \bar{\beta}$). As the coercive field is the critical parameter establishing the limit dividing the two phases, it is not surprising to see that it has a finite-size behaviour similar to that of the Curie temperature [16–19]. The existence of the 'old' phase is restricted at small sizes. Moreover, the ferroelectric system reaches the 'new' phase at a critical size, even though the electric field energy alone would not suffice to induce the phase transition.

An important difference from a thermally induced phase transition is that identifying just the equivalent Landau coefficients does not ensure correct integration of the inhomogeneity and size effects. In the case of switching, the presence of an electric field energy in addition to the thermodynamic free energy requires identification of the equivalent electric field also. An interesting result is that although a stepwise electric field induces switching of an isolated polar unit, the global polarization reverses under a time-dependent equivalent electric field.

Figure 9 contains an example of a time-dependent equivalent electric field ($\bar{E}$), computed for $N = 100$. We note that switching of the global order parameter is induced by an electric field close to its value in a polar unit only after a considerable time has elapsed. Figure 10 displays the size dependence of the time-averaged equivalent electric fields. One observes

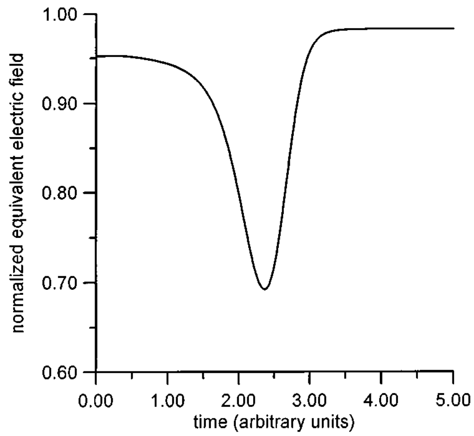


Figure 9. The time dependence of the equivalent electric field, normalized to its constant value in an isolated polar unit, for a finite lattice with $N = 100$ sites and the coupling constant $k = 15$.

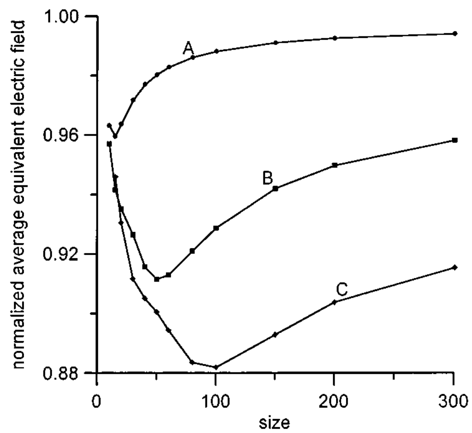
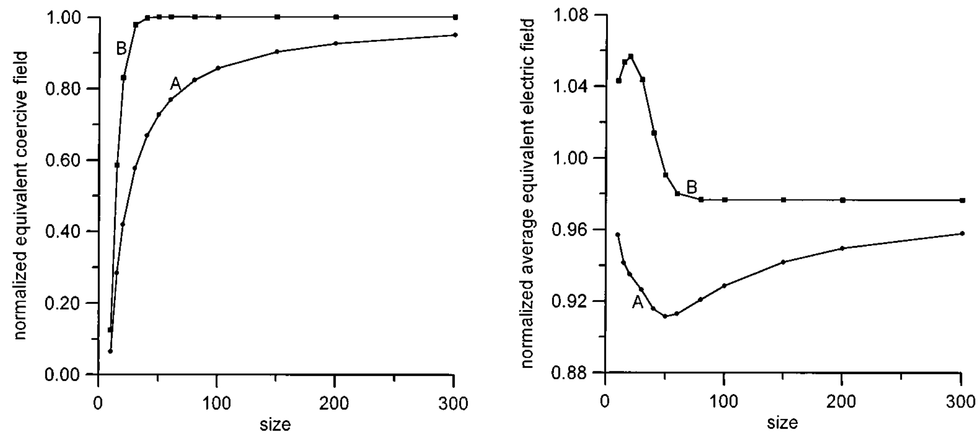


Figure 10. The size dependence of the time-averaged equivalent electric field, normalized to its value in an isolated polar unit, for the following coupling constants: (A) $k = 1$; (B) $k = 15$; (C) $k = 50$.

that large-size ferroelectrics have their global polarization reversed by equivalent electric fields whose time average approaches the external value more closely than in the case of small-size ferroelectric samples. The difference between the time average of the equivalent electric field and the external field is k-dependent.

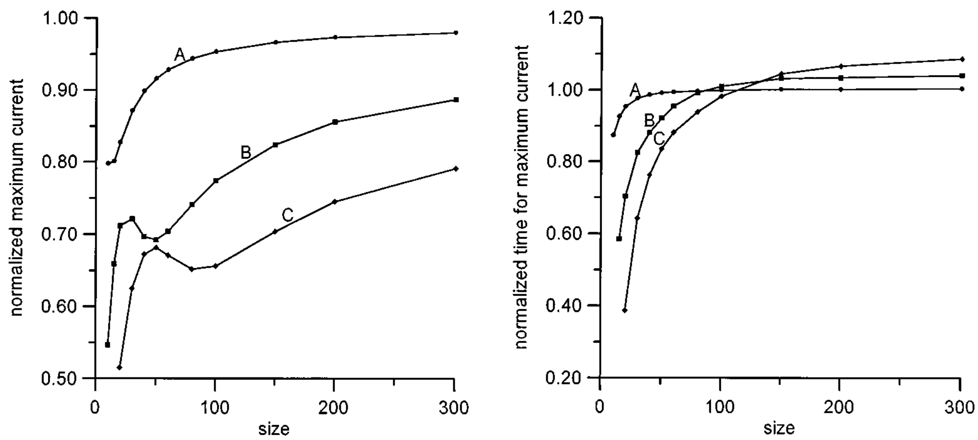
A comparative analysis of figures 7, 8 and 10 allows us to assess the way in which the inhomogeneity is manifested in the switching of the global polarization of ferroelectrics with different sizes. In the case of small samples, first-neighbour coupling tends to modify the equivalent thermodynamic coefficients rather than the electric field. Another feature is that the effect of inhomogeneity on the Landau coefficients is gradually extinguished at large sizes, as they approach the values corresponding to an isolated polar unit. The time-averaged equivalent electric field exhibits the same behaviour (i.e. approaches the external applied value) only at sizes larger than a k-dependent critical size. In the range of sizes that are lower than the critical size, considerable damping out of the effect of inhomogeneity on the equivalent thermodynamic coefficients occurs. Consequently, the spatial inhomogeneities begin to affect the equivalent electric field more significantly; its time average decreases from the external applied value down to a minimum. One expects the existence of this critical size to cause some peculiar behaviour of the global switching curves.

We are now going to point out an interesting feature of polarization reversal in a finite ferroelectric sample. We compared the time dependencies of the central-polar-unit current with the global switching current, for two samples having $N = 10$ and $N = 100$ sites. We observed that the central polar unit of a small-size system has a switching current that is significantly different to the global current (for example, it has no minimum). On the other hand, in a large sample, the current of the central polar unit looks more like the global current. Hence the weaker edge ferroelectricity is manifested in a size-dependent manner. According to the established method, we correlated this difference in switching behaviour with equivalent quantities described above. The dependencies of the equivalent coercive field and average equivalent electric field are presented in figures 11(a) and 11(b), respectively. The size dependencies of the two equivalent quantities computed for the global order parameters are also shown for comparison. We note that in the case of large sizes,



(a) (b)

Figure 11. Size dependencies of (a) the equivalent coercive field and (b) the time-averaged equivalent electric field for (A) global switching and (B) central-polar-unit switching, normalized to their values in an isolated polar unit. The coupling constant is $k = 15$.



(a) (b)

Figure 12. Size dependencies of (a) the maximum switching current and (b) the time taken to reach the maximum current, normalized to their values in an isolated polar unit, for the following coupling constants: (A) $k = 1$; (B) $k = 15$; (C) $k = 50$.

equivalent quantities for the central units have values approaching those corresponding to the global order parameter, whereas they differ considerably for small sizes. Since polar units from the central site to the boundary have different coercive fields, switching in small-size ferroelectric samples can be regarded as a diffuse phase transition. On the other hand, large-size ferroelectric samples contain polar units with equivalent coercive fields distributed over only a narrow range, so in this case the phase transition is of a fairly normal character. A similar behaviour has been reported by Lobo *et al* [29], for ferroelectric-to-paraelectric phase transitions in barium titanate ceramics with different grain sizes.

The switching parameters of a finite ferroelectric sample usually measured in experiments are the maximum of the switching transient and the time at which the switching current peaks. The latter is associated with the speed of the reversal. Some theoretical predictions of this model regarding the size dependence of these parameters are presented in figures 12(a) and 12(b), respectively. We note that the general trend is an increase of the maximum currents with size. However, they reach a minimum point at a k-dependent critical size, not detected in our measurements on barium titanate ceramics [22]. It is immediately obvious that the minimum of the switching current peak at the critical size detected in figure 12(a) is caused by the time-averaged equivalent electric field, which reaches its minimum value at the same size. On the other hand, the time at which the switching current reaches its maximum value increases monotonically with size, in agreement with our experiments showing higher speeds of the polarization reversal in fine-grained ceramics [22]. There is also a peculiar dependence of times taken to reach the maximum current on the coupling constant k. For large k, switching is faster at low sizes and slower at large sizes. According to figures 12(b), 7 and 10, the reversal speed at low sizes reflects the difference in equivalent Landau coefficients rather than different equivalent-electric-field time averages. The switching speed is higher when the polarization is reversed near the Curie point ($\bar{\alpha}$ at small sizes approaching zero, for large k, in figure 7(a)). When the size increases, the values of the equivalent electric fields gradually dominate over the reversal speed ($\bar{E}$ has the lowest value for large k in figure 10) and switching is slower, as seen in figure 12(b).

5. Conclusions

We have performed a detailed study of switching in ferroelectrics, in the framework of the Landau model for phase transitions. The order parameter is the equilibrium polarization under an applied electric field and the critical parameter limiting the two phases is the coercive field. These parameters describing the electrically induced phase transition exhibit Landau-type critical behaviour.

The time dependencies of the polarization and current during switching have been correlated with the dielectric hysteresis loop. Switching in ferroelectrics exhibits strong irreversibility characteristics, since many transient states of reversal are associated with negative-susceptibility regions of the dielectric hysteresis loop. Hysteresis loops of poled ferroelectric samples are expected to include negative-susceptibility regions. This happens when high-frequency sinusoidal electric fields are employed, that have amplitudes slightly higher than the coercive field.

Two corrections are proposed, in order to improve the agreement between the theoretical predictions of this model with experiments. According to experimental circumstances, switching curves have been computed with time-dependent (exponential) applied electric fields and the non-switching response has been subtracted from the switching current. Under these circumstances the switching currents look similar to the experimentally recorded ones, proving the validity of the model.

Inhomogeneous reversal of interacting polar units leads to finite-size effects in ferroelectric switching. We integrated the size and inhomogeneity effects in the switching of individual polar units to equivalent Landau coefficients and electric field, describing the evolution of a global order parameter. The size dependence of the equivalent coercive field is similar to the size dependence of the Curie temperature. The equivalent time-dependent electric field also has an important influence on the switching behaviour. We have shown that polarization reversal in small-size samples can be regarded as a diffuse phase transition, with coercive fields of polar units distributed over a wide range.

The size dependences of the maximum switching current and of the time at which it occurs are in good agreement with our previous experimental results on barium titanate ceramic samples with different dimensions of grains. Although the general trend is an increase of the maximum current with size, a range exists over which the maximum current decreases down to a minimum. The critical size at which the current peak is a minimum is identical to the size for which the equivalent electric field reaches its minimum value. The switching speed is higher for small sizes, in agreement with experiments. Highly inhomogeneous switching is faster for small sizes and slower for large sizes. Our analysis revealed that the speed of polarization reversal is controlled by the values of an equivalent Landau coefficients at small sizes and by the value of an equivalent electric field at large sizes.

This method of integrating size effects in switching using equivalent Landau coefficients and electric fields can be extended to two- or three-dimensional systems. Also a similar analysis can be performed for a ferroelectric with a first-order phase transition. This would increase the accuracy of the theoretical predictions, for the specific ferroelectric sample under examination.

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