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Perturbation analysis and memory in ferroelectric materials

A. K. Bandyopadhyay[a] and P. C. Ray[b]
College of Ceramic Technology, University of Calcutta, 73, A. C. Banerjee Lane, Calcutta-700 010, India

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Many ferroelectric materials like $LiTaO_3$ and $LiNbO_3$ exhibit peculiar behavior in terms of showing a large discrepancy between experimental and theoretical values of coercive field by the use of Landau–Ginzburg model. If a perturbation is given at zero field, then there is also perturbation or fluctuation in polarization with respect to the nondimensional value of domain-wall width. An eigenvalue problem is deduced through a linear Jacobian transformation to show that there is a finite value of ''memory,'' when the perturbation in the electric field is lifted. The eigenvalue gives a characteristic value of polarization, which also gives rise to a zone of stability for polarization. This perturbation formalism also allows the calculation of the limits of the coercive field and, subsequently, the values of the domain-wall width can also be estimated, which show both the lower and upper limits of theoretical values for both the above ferroelectric materials, deduced as the theoretical limits of the coercive fields. The theoretical framework is developed in this article.
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I. INTRODUCTION

During the past decade or so, there has been a tremendous surge of research activities on various aspects of ferroelectrics (the huge experimental work done by the Penn State group in collaboration with various other labs is collectively referred to as Gopalan *et al.* which contains many important references).[1–6] Due to a strong possibility of using these materials as nonvolatile memory devices, their importance has grown up in an exponential mode. However, there are still several problems at hand.

The most important aspect of ferroelectric materials is the nonlinear hysteresis behavior in the polarization (P) versus electric-field (E) vectors. This needs to be properly understood. The experimental values of different important parameters from this hysteresis curve, like saturation polarization (P_s) at high value of E, remnant polarization (P_r) or memory effect at $E=0$ and coercive field (E_c) when $P=0$, cannot be always explained in theoretical terms. Most notably, the latter two terms, P_r and E_c, are difficult to reconcile with the well-known Landau–Ginzburg model for free energy functional relating polarization through a polynomial, in important ferroelectric materials like $LiTaO_3$ and $LiNbO_3$.[1]

Even before embarking on the application front with the fabrication of memory devices, we have to understand the nature of the evolution of memory function and consequent switching phenomenon in terms of so-called domain-wall movement or motion. If everyone is inclined to use the famous Landau–Ginzburg model (albeit in modified form) for free energy functional, we have to understand, then, why there is such a huge discrepancy between the experimental values of the coercive field of such materials and those found theoretically by using this model.[1] But, ultimately it is important to find out the domain-wall width, which is the main issue apart from understanding the hysteresis parameters, as mentioned above.

In the present article, a theoretical approach is developed through a perturbation formalism taking different variables in nondimensional form. This perturbation in E gives rise to a perturbation or fluctuation in P. From a purely eigenvalue problem, a characteristic or critical value of polarization is found out, which can explain the limiting values of P_r or memory, coercive field (E_c), and the domain-wall width, apart from deriving the stability zone for polarization.

II. THEORETICAL DEVELOPMENT

The relation of free energy (G) with the order parameter or polarization (P) is described by the famous Landau–Ginzburg model as:

$$G=-\frac{\alpha_1}{2}P^2+\frac{\alpha_2}{4}P^4+\ldots., \tag{1}$$

neglecting the higher-order terms. The differentiation of G with respect to the order parameter (P) yields the electric field (E) as

$$E=\frac{dG}{dP}=-\alpha_1 P+\alpha_2 P^3+\ldots. \tag{2}$$

The expansion coefficients (α_1 and α_2) are important parameters for these equations.

In mathematical approach, it is not an uncommon practice to put different variables in the nondimensional form to bring some kind of parity, eventually to be able to estimate the value of the concerned variable by putting it back in the dimensional form in order to understand its order of magnitude. In the present case of nonlinear hysteresis behavior of ferroelectrics nondimensional forms for the free energy G, electric field E, polarization P, and the coordinate system (x^+) with the domain-wall center as the origin are essential

[a]Electronic mail: asisbanerjee1000@yahoo.co.in
[b]Department of Mathematics, College of Leather Technology, LB Block, Sector III, Salt Lake, Calcutta-700 098, India.

to better understand the behavior of these variables. The nondimensional values of free energy (G'), the electric field (E'), the polarization (P'), and the parameter for domain dimension (x') are defined as follows:

$$G' = \frac{G}{\alpha_1 P_s^2}, \tag{3a}$$

given $\alpha_2 \approx \alpha_1 / P_s^2$, where P_s = saturation polarization,

$$E' = \frac{E}{\alpha_1 P_s}, \tag{3b}$$

$$P' = \frac{P}{P_s}, \tag{3c}$$

$$x' = \frac{x^+}{x_0}, \tag{3d}$$

where x_0 is the half of the domain-wall width (hereinafter mentioned simply as domain-wall width throughout the text). Then, we can write nondimensional forms of Eqs. (1) and (2) as

$$G' = \frac{G}{\alpha_1 P_s^2} = -\frac{\alpha_1}{2}\left(\frac{P^2}{\alpha_1 P_s^2}\right) + \frac{\alpha_2}{4}\left(\frac{P^4}{\alpha_1 P_s^2}\right) = -\frac{1}{2}P'^2 + \frac{1}{4}P'^4, \tag{4}$$

$$E' = \frac{E}{\alpha_1 P_s} = -\alpha_1 \frac{P}{(\alpha_1 P_s)} + \alpha_2 \frac{P^3}{(\alpha_1 P_s)} = -P' + P'^3. \tag{5}$$

Now, let us consider polarization as per reference of Lines and Glass[7] in order to take the variability of the domain wall width, and the polarization is expressed as

$$P = P_s \tanh(x^+/x_0), \text{ i.e., } P' = \tanh(x'). \tag{6}$$

Here, x_0 is the half of the domain-wall width. The prime notation from the above nondimensional values can be dropped for the sake of simplicity, and by using Eqs. (5) and (6), we get

$$E = -\tanh x + \tanh^3 x = -P \operatorname{sech}^2 x. \tag{7}$$

From Eqs. (6) and (7), by differentiating with respect to x, we get

$$\frac{dP}{dx} = \operatorname{sech}^2 x = -\frac{E}{P}, \tag{8}$$

$$\frac{dE}{dx} = -\frac{E}{P}(3P^2 - 1), \tag{9}$$

and

$$\frac{dG}{dx} = -E(P^2 - 1). \tag{10}$$

A. Perturbation approach

In the nonlinear hysteresis of P versus E behavior, after the electric field (E) is brought to zero from a very high value, a small perturbation in E (i.e., ΔE) will give rise to a perturbation or fluctuation in P (i.e., ΔP). These perturbations are also put in nondimensional form and are related to that of the x value, i.e., x^+/x_0, where x_0 is the half width of the ferroelectric domain wall. It should be mentioned here that the value of x was also put in the nondimensional form by Gopalan *et al.*[1] in the polarization function without actually pointing it out explicitly. Now, we can give a perturbation in E at the stationary or equilibrium point at $E=0$ and $P \neq 0$, i.e., as a special case, let us write $P = P_c$ (say). Then, the perturbation equations for the independent variable E and the dependent variable P are shown below along with that of the free energy (G):

$$\frac{d}{dx}(\Delta P) = \left(\frac{-1}{P}\right)\Delta E + \left(\frac{E}{P^2}\right)\Delta P. \tag{11}$$

Similarly, we get

$$\frac{d}{dx}(\Delta E) = -\left[\left(\frac{3P^2+1}{P^2}\right)E\Delta P + \left(\frac{3P^2-1}{P}\right)\Delta E\right], \tag{12}$$

$$\frac{d}{dx}(\Delta G) = -2EP\Delta P - (P^2-1)\Delta E. \tag{13}$$

At the stationary or equilibrium point at $E=0$ and $P=P_c \neq 0$, these perturbation terms are put in a matrix form in a perturbed state from the above system of equations and a linear Jacobian transformation is made as follows:

$$\begin{bmatrix} \frac{d}{dx}(\Delta G) \\ \frac{d}{dx}(\Delta E) \\ \frac{d}{dx}(\Delta P) \end{bmatrix} = \begin{bmatrix} 0 & -(P_c^2-1) & -2EP_c \\ 0 & \frac{-(3P_c^2-1)}{P_c} & -\frac{(3P_c^2+1)E}{P_c^2} \\ 0 & -\frac{1}{P_c} & \frac{E}{P_c^2} \end{bmatrix} \times \begin{bmatrix} \Delta G \\ \Delta E \\ \Delta P \end{bmatrix}. \tag{14}$$

The Jacobian transformation allows us to linearize the so-called chaotic nonlinear behavior in the hysteresis of P versus E. This linearization also helps us to understand the behavior of participating/concerned variables in the perturbation/fluctuation context.

From the above Jacobian matrix, the characteristic determinant must vanish at the stationary or equilibrium point, i.e., at $E=0$ and $P=P_c \neq 0$ as

$$\begin{vmatrix} 0-\lambda & -(P_c^2-1) & 0 \\ 0 & \frac{-(3P_c^2-1)}{P_c}-\lambda & 0 \\ 0 & -\frac{1}{P_c} & 0-\lambda \end{vmatrix} = 0, \tag{15}$$

or

$$-\lambda\left[\lambda\frac{(3P_c^2-1)}{P_c} + \lambda^2\right] = 0. \tag{16}$$

The eigenvalues from the above characteristic equation (i.e., Jacobian matrix) are found out as

$$\lambda = 0,\ 0,\ \text{and}\ -\frac{(3P_c^2-1)}{P_c}. \tag{17}$$

B. Stability zone

From the eigenvalue, it is possible to derive the ''zone of stability'' with the critical value of polarization, P_c, with the limiting stable value of $P_c = \pm 1/\sqrt{3}$. This factor containing number 3 in the denominator under the square root sign comes out of the second expansion coefficient of Landau–Ginzburg polynomial, as used by Gopalan *et al.*[1] Here, we give an explanation of this factor as the ''stability factor'' for the critical polarization at $E=0$, when there is a finite perturbation ΔE in the electric field.

This stability factor derived from the eigenvalue shows that the remnant polarization (P_r) cannot be less than $+1/\sqrt{3}$ in the upper half-plane (otherwise, the eigenvalue λ will be positive) and obviously as per the hysteresis curve, it cannot be greater than 1 (since the nondimensional form of $P_c = P/P_s$, and at $P=P_s$, $P_c=1$). Therefore, the ''stable zone'' of polarization (P) can be defined as lying between $+1/\sqrt{3}$ and $+1$ in the upper half-plane, and between $-1/\sqrt{3}$ and -1 in the lower half-plane. This is only revealed if the perturbation or fluctuation in polarization is considered to be present at $E=0$, as shown above. Therefore, this critical value of polarization fixes the stability range of the remnant polarization or memory.

The solution of the Jacobian matrix and subsequent integration leads to the values of ΔE, ΔG and ΔP as

$$\Delta E = C\exp\left[\left(-\frac{3P_c^2-1}{P_c}\right)x\right], \tag{18}$$

when $x = x^+/x_0 = 0$, i.e., at the domain-wall center, $\Delta E = C$ = integration constant, which can be explained as the perturbed value of E at $x=0$. This implies that $C=-\Delta x$, since $\Delta P = \Delta x$ and, consequently, $\Delta E = -\Delta x$ from Eqs. (6) and (7) at the domain-wall center at $x=0$. The perturbed value of G is given by

$$\Delta G = \frac{C.P_c(P_c^2-1)}{(3P_c^2-1)}e^{-(3P_c^2-1)/P_c x} + B = \frac{P_c(P_c^2-1)\Delta E}{3P_c^2-1} + B. \tag{19}$$

Here, B = integration constant for ΔG [Eq. (19)]. When $x=0$, $\Delta G = 0$ (i.e., at the domain-wall center), this implies that

$$B = \frac{-\Delta E P_c(P_c^2-1)}{3P_c^2-1} = \frac{\Delta x P_c(P_c^2-1)}{3P_c^2-1}, \tag{20a}$$

by putting $\Delta P = \Delta x$ and $\Delta E = -\Delta x$. Hence, the value of ΔG can be written as

$$\Delta G = \frac{P_c(P_c^2-1)(\Delta E + \Delta x)}{3P_c^2-1}. \tag{20b}$$

This helps to map the free energy in terms of a critical value of polarization as well as domain-wall width, and the stability zone can be found out in a G versus P plot. The perturbed value of P is given by

$$\Delta P = D + C\exp\left[\left(-\frac{3P_c^2-1}{P_c}\right)x\right] \Big/ (3P_c^2-1) = D + \frac{\Delta E}{3P_c^2-1}, \tag{21}$$

where D = integration constant for ΔP Eq. (21).

When the perturbation in E is lifted, i.e., $\Delta E = 0$, we get $\Delta P = D$, i.e., a remnant value of memory. This is an interesting result in that by applying a perturbation and then removing it at $E=0$, we find it easier to show that there is a ''finite value'' of polarization (P) at zero electric field, which can be surely represented as the existence of a finite memory (i.e., equal to D). In other words, the perturbation or fluctuation in P should always give rise to a value of a finite memory in ferroelectric materials. By maintaining the perturbation in E, we also get some interesting results in terms of P_c as follows.

When $P_c = +1$ (i.e., upper limit of the stable zone), $\Delta P = D + \Delta E/2$. But when $P_c = +1/\sqrt{3}$ (i.e., lower limit of the stable zone), $\Delta P = D + \infty = +\infty$, i.e., an essential singularity occurs. Both physical and mathematical implications are immense in and around this essential singularity. According to Picard's theorem (also known as Weirstrasse–Casorati equations), near an essential singularity, any function, i.e., the polarization function in this particular case oscillates.[8] This oscillation might be damped as $P \to 0$ when $E \to E_c$. These points are not considered at present, which is a matter of further study. For the moment, we can try to avoid this singularity point.

In order to find the value of the finite memory, D, let us use Eqs. (18) and (21) as

$$D = \left(1 + \frac{1}{3P_c^2-1}\right)\Delta x = \left(\frac{3P_c^2}{3P_c^2-1}\right)\Delta x, \tag{22}$$

where $\Delta P = \Delta x = a/x_0$ (a = lattice spacing) and, consequently, $\Delta E = \Delta - x$ from Eqs. (6) and (7) at the domain-wall center at $x=0$.

C. Coercive field and domain-wall width

The linear Jacobian transformation and the consequent characteristic equation give rise to a critical polarization (P_c), which could easily explain the finite memory value in the clear context of perturbation or fluctuation model. From the memory value, when P will tend to zero as $E \to E_c$, we can still use the above perturbation approach to derive the limiting values of E_c, when $P=0$, corresponding to $P_c = 1/\sqrt{3}$ to 1 at $E=0$.

For a square-loop hysteresis behavior for near-stoichiometric single crystals of say, $LiTaO_3$ and $LiNbO_3$, containing no dipolar defects, the sharp fall of P_s or P_r to $P=0$ with the application of an electric field E from $E=0$ up to E_c makes Gopalan *et al.*[1] used $(dE/dP)_{E=E_c} = 0$, since the steep fall implies $dP/dE = \infty$. The assumption on the

square-loop hysteresis leads to a very high value of E_c, although the experimental value of E_c has been found to be much lower. But in our case, this is not necessary, nor we have to invoke Landau–Ginzburg model. By simply resorting to the perturbation Eqs. (18) and (21), we get the value of E_c as follows.

If we change the electric field to $E+\Delta E$ in such a way that P_c changes to $-P+\Delta P$, and let $E+\Delta E=-E_c$ ($E_c>0$ at the domain-wall center at $x=0$), then $\Delta E=-E_c$, when $E=0$, when the total perturbation or fluctuation in P will tend to zero, i.e., $-P_c+\Delta P=0$. Thus, $\Delta P=P_c$ at $\Delta E=E_c$. In this case, the value of the perturbation in E, i.e., ΔE is the coercive field with the consequent critical value of polarization (P_c) as the perturbation term in polarization. Hence, from Eqs. (21) and (22), we get

$$P_c=D+\frac{-E_c}{3P_c^2-1}, \tag{23}$$

or

$$-E_c=(P_c-D)(3P_c^2-1)=P_c(3P_c^2-1)-3P_c^2\Delta x. \tag{24}$$

Thus, the singularity in the calculation of E_c is removed. In terms of using the characteristic value of polarization (P_c) in the stability zone (i.e., 1 and $1/\sqrt{3}$), we also get the limiting values of E_c as

$$(3\Delta x-2)\geqslant E_c\geqslant\Delta x \quad \text{or} \quad \Delta x\geqslant E_c\geqslant(3\Delta x-2). \tag{25}$$

This is in nondimensional form, and we can now put it in the dimensional form to estimate the limiting values of coercive field as

$$[3(a/x_0)-2]\alpha_1 P_s\geqslant E_c'\geqslant(a/x_0)\alpha_1 P_s, \tag{26a}$$

or

$$(a/x_0)\alpha_1 P_s\geqslant E_c'\geqslant[3(a/x_0)-2]\alpha_1 P_s, \tag{26b}$$

where a is the lattice spacing, and E_c' is the dimensional form of the value of coercive field. Now, as Gopalan *et al.*[1] did, if we take the experimental values for a single domain crystal of $LiTaO_3$ (17 kV/cm) and $LiNbO_3$ (40 kV/cm) taking the values of $\alpha_1 P_s$ as 7150 kV/cm and 14 137 kV/cm, respectively, then we can find an unique value of the domain-wall width (x_0) for each limiting critical value of P_c as follows:

(a) For $LiTaO_3$ ferroelectric: $3(a/x_0)-2=17/7150$ or $x_0=3a/(17/7150+2)=0.7491$ nm$\approx$0.75 nm, when $P_c=1$ (taking the lattice spacing as $a=0.5$ nm). The value of $x_0=210$ nm when $P_c=1/\sqrt{3}$, as also calculated by Gopalan *et al.*,[1] which was considered by these authors as the upper limit of the domain-wall width. Therefore, by taking the same experimental value of $E_c=17$ kV/cm of Gopalan *et al.*[1] and by putting $P_c=1$, the above value of x_0 of 0.75 nm seems to be close to that estimated by Padilla *et al.*[9] of about one lattice spacing (0.5 nm) by first-principle calculations. Surely, this can be considered as the lower limit of the width of 180° domain walls.

(b) For $LiNbO_3$ ferroelectrics: The value of domain-wall width $x_0=3a/(40/14\,137+2)\approx0.75$ nm when $P_c=1$, as also found above, which is again considered as the lower limit of domain-wall width and which is also close to that estimated by Padilla *et al.*,[9] as mentioned above. The upper limit of the value of x_0 has been estimated in the same manner to be = 177 nm when $P_c=1/\sqrt{3}$, as also found out by Gopalan *et al.*[1]

III. DISCUSSION

The linear Jacobian transformation of the matrix formulation by a set of perturbed equations clearly gives us the necessary insight for the calculation of various hysteresis parameters of ferroelectric materials, apart from delineating a stability zone with the critical limiting values of polarization (i.e., P_c). This critical polarization value gives us a clear concept of polarization behavior when the perturbation in the electric field is removed, thereby indicating the existence of a remnant polarization or memory (D) arising out of the perturbed state, and also its order of magnitude in terms of P_c.

This value of P_c might have a significance for the calculation of nonvolatile memory depending on the stoichiometry of ferroelectric crystals with or without dipolar defects. This should also help mapping different stoichiometry levels of a given ferroelectric crystal onto the P_c domain in the stability zone. Then, the task remains on how the switching process will take place vis-à-vis the domain-wall width, which is inversely proportional to the coercive field, as established from the present theoretical work.

The above values of domain-wall width appear to be reasonable, by using the perturbation or fluctuation model, giving two limiting values for each of the ferroelectric crystals. When P_c is high close to 1, the lower limit of domain-wall width (0.75 nm) is obtained. When P_c is low close to $1/\sqrt{3}$, the upper limit is found out, which is very close to those estimated theoretically by the direct use of the Landau–Ginzburg model by Gopalan *et al.*,[1] i.e., 216 nm and 181 nm for the above two ferroelectric materials, respectively. Finally, from Eq. (25), the theoretical values of the coercive field which can be estimated show only its limiting values. The value of E_c is known to be inversely proportional to the domain-wall width. Due to the strong dependence of E_c on P_c in the perturbation or fluctuation context, the sensitivity of P_c (and hence of E_c) on the domain-wall width seems to be quite pronounced [Eq. (24)].

It should be mentioned here that a large value of domain-wall width, although considered as the upper limit, in $LiTaO_3$ and $LiNbO_3$ crystals was ascribed to wide regions of strains and optical birefringence around individual domain walls. This can be strongly correlated with the presence of nonstoichiometry in the crystal, which could extend to micrometers level as per Gopalan *et al.*[1] The question of mapping this stoichiometry level onto the values of P_c in the stability zone should possibly throw some light on this issue, as mentioned above.

In the context of Landau–Ginzburg model, it can be easily construed that unless perturbation or fluctuation in polarization is considered in the right perspective, the discrepancy in the theoretical and experimental values of E_c will remain.

Moreover, the calculation of the domain-wall width from the theoretical values of 2750 and 5420 kV/cm for the above two crystals, respectively, from Landau–Ginzburg model[1] give rise to smaller values less than 1 nm, as per our perturbation approach. This implies again a lower limit for domain-wall width. Therefore, the domain-wall width, which is a strong function of P_c, also needs to be mapped onto P_c with the limiting values, as estimated in the present work.

From a comparison of the values of the domain-wall width of the above ferroelectric crystals, it is now clear that the discrepancy between the theoretical and experimentally observed values are much reduced in terms of our calculation of two limiting values. The upper limit arises from the lower limit of P_c equal to $1/\sqrt{3}$ and the lower limit comes out from the uppermost limit of P_c equal to 1.0. The perturbation model might need to be mathematically fine tuned by taking care of the electroelastic effect or other similar factors for different ferroelectric crystals in order to be able to further explain this large limit of domain-wall width.

IV. CONCLUSIONS

After taking the nondimensional forms of electric field, polarization, and domain-wall direction coordinate, if we apply perturbation in E at $E=0$, it gives rise to a perturbation or fluctuation in P. These perturbations along with that of free energy are put as an eigenvalue problem, and then by a linear Jacobian transformation, it has been possible to calculate a critical value of polarization, which also shows a zone of stability for polarization when $E=0$. The perturbation approach also shows a finite value of the remnant polarization or memory, when we put the perturbation in E, i.e., $\Delta E=0$. From this same perturbation approach, by taking a perturbation or fluctuation on the domain-wall width, it has been possible to calculate its limiting value for lithium tantalate and lithium niobate ferroelectric materials, as well as their limiting values of the coercive field E_c when $P=0$. There is a tremendous scope of work in this particular area.

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