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Oscillatory Dynamical Switching System of Bulk Ferroelectrics

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Abstract: This study gives a detailed account of calculation of the bulk ferroelectric (FE) oscillatory dynamical system switching for first and second-order phase transition, respectively. All the formalism is delineated in the framework of Landau free-energy expansion and Landau-Khalatnikov (LK) equation of motion where effect of external energy may affray FE atoms similar to the spring damped oscillatory system. Here we scrutinized the switching properties from free-energy expansion and hysteresis loop. The polarization and current switching appropriate to the estimated complete switching time, changing of temperature, electric field and damping are scrutinized and discussed.

Keywords: Phase Transitions, Coercive Field, Polarization Switching

INTRODUCTION

Ferroelectric (FE) materials are of special interest to developers of the next generation of such devices because they manifest polarized electronic states that can symbolize bits of information. Moreover, these materials preserve their polarization states without consuming electrical power, making FE the subject of intense study for non-volatile memory applications in which data is stored even when the power is turned off. FE materials are characterized by reversible spontaneous polarization p_s. The spontaneous polarization p_s arises due to noncentrosymmetric set in order of ions unit cells which produce a permanent electric dipole moment affiliated with the unit cell. p_s in FE can be reversed by applying the external electric field e where the arrangement is $e>e_c$ (the coercive field). This reversal phenomenon is called switching. Lines and Glass[1] state that, p_s eventuated in FE phase correlates with the Curie temperature T_c where $p_s \neq 0$ if $T < T_c$ and $p_s = 0$ if $T > T_c$, the FE phase and paraelectric (PE) phase, respectively. In the first-order ferroelectric-paraelectric phase transitions, p_s may have an essential value at temperature approaching to T_c, while for second-order, the decrease of p_s as temperature $T{\sim}T_c$ is more continuous.

Ricinschi *et al.*[2] and Tan *et al.*[3] give details of switching behavior of bulk, semi-infinite and thin film FE in second and first-order phase transition respectively where both exchange options on relaxational switching system. As we know, in practice, the atoms in FE materials may fluctuate oscillatorily due to influence of external energy. As far as we know, there is no basic discussion to estimate the switching time of the FE bulk materials in terms of oscillatory dynamical system. It may be used as a preliminary step towards corresponding calculations for the symmetric and asymmetric FE thin film. Currently, there are many experimental observations to study the switching behavior for FE materials; for example, Merz[4] using optical method to observe the $BaTiO_3$ domain structure, recorded the motion of 90^o and 180^o domain walls in single crystal $BaTiO_3$ thin film using TEM and Shur *et al.*[5] found that the domain dynamics essentially depend on applied electric field.

From the theoretical consideration in this study, we focused our study to represent the estimate time of bulk FE for both cases: first and second-order phase transition. From previous results[6], we estimated that the switching time for second-order case verging on $t{\sim}1.064 \times 10^{-13}$s. Although this value may represent very fast switching, since in practice the value is in nanosecond but it is authentic because the effect of domain wall movement and geometry effect e.g films are neglected. On the other hand, the switching study of polarization in bulk FE gives us the clear view of what may happen in bulk ferroelectric and what are the fastest times of FE switching without any cause effect.

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Larsen *et al.*[7,8] related that the polarization switching time for PZT films using short voltage pulse technique was approximately 390×10^{-12}s. The switching data in FE were first analyzed by Ishibashi and Takagi[9] in the framework of the Kolmogorov-Avrami (KA) theory. As we know, the KA theory is based on nucleation and growth of domains of contradiction polarization. However, the KA theory being formulated for ideal systems frequently meets with obstacles while describing the kinetics of transformations in real objects characterized by violations of the two postulates: finiteness of transformed media and domain structure during polarization reversal in electric e.g in bulk single crystals, ceramics and thin films.

In the next portion, we will discuss the basic formalism on bulk FE switching in both transitions: first and second-order phase transition, respectively using Landau-Devonshire (LD) free-energy density and Landau-Khalatnikov (LK) equation of motion. The oscillatory switching formalism also implicates numerical approach where we use central finite-difference method (CFDM). Some basic discussion on switching based on free-energy and hysteresis loop are given in order to work out in detail the oscillatory switching behavior for bulk FE classifications.

DIMENSIONLESS FORMALISM

To deliberate the Landau model for switching, we may write all the formalism in dimensionless form to perform the universal results without any materials-parameter dependent using the conventional scaling[1,3,6,10] and the Landau free-energy expansion f for non-equilibrium behavior may be written as

$$f = \frac{1}{2}\alpha p^2 - \beta p^4 + \frac{1}{6}p^6 - ep \qquad (1)$$

where for the first-order case, $\alpha = t_r$, while for second-order, $\alpha = (t^* - 1)$. t_r and t^* represents the dimensionless temperature for first and second-order phase transition, respectively. $\beta = 1/2$ for first-order and $\beta = -1/4$ for the second-order case. The difference between these phase transitions is that first-order involves the expansion of p^6, whereas p^4 for second-order phase transitions. The last terms in (1) show the external electric field e as a driving force. Fig. 1(a) and (b) show the free-energy f curves switching due to the various electric field e (positive switching) for first and second-order phase transitions, respectively, the complete switching is affirmed by $e = e_C$ (coercive field). The non-equilibrium free-energy curves are at pure-stable FE phase, where $t_r = -1$ (below supercooling temperature) and t = 0.1, for first and second-order case, respectively. As we know, in first-order conditions, there are various ranges of temperature[1,3], but for this study we only focused on pure FE phase and it is enough for quantitative discussion. Differentiation of polarization due to the effect of e are given in both graphs, where A defined the bulk polarization p_B value in equilibrium state. The purple curves represent the complete switching since $e = e_C$. Fig. 1(a) and (b) show the positive-side switching, with the bulk spontaneous polarization hello shifting the value from A to $p_B = -1.16$ and $p_B = -0.55$ for first and second-order phase transition respectively and vice versa for negative-side switching.

Coercive field: In FE materials, the polarization response with the electric field is highly non-linear and discloses a hysteresis loop. Electric field that has been applied may increase the ferroelectric domain until total domain growth and reorientation of all the domains have occurred in a direction favorable to external field. At this juncture, the FE is tiveness deduced to acquire saturated polarization p_{sat} and if the electric field is abolished, some of the domains do not reorient into random configuration and, thus, the materials still polarized, so called remanent polarization, p_r. Then, the effect of electric field required to reestablish the polarization into zero called coercive field e_c. As mentioned above, $e > e_c$ is the inherent condition for spontaneous polarization to repeal their state.

Fig. 2(a) and (b) accord the dielectric hysteresis loops (DHL) curves (p versus e) at anomalous ranges of temperature at pure FE phase described by figure captions for first and second-order phase transitions, respectively, with the coercive field e_c assert by vertical arrows. The features in Fig. 2(a) and (b) directly comes from df/dp = 0 of (1) called the dielectric equation of state, given by

$$\frac{df}{dp} = e = \alpha p - 4\beta p^3 + p^5 \qquad (2)$$

On the other hand, the DHL curves in Fig. 2(a) and 2(b) also describe the thermodynamically stable and unstable state, which is de/dp > 0 and de/dp < 0, respectively. The coercive field e_c may be calculated directly from $d^2f/dp^2 = 0$ of (1), since e_c may be allocated at p-e curves as inflection points, therefore the quadratic equation in p^2 with solutions

$$p_C^2 = \frac{3}{5}\left(1 \pm \sqrt{1 - \frac{5}{9}t_r}\right) \quad \text{and} \quad p_C^2 = \frac{(1-t^*)}{3} \qquad (3)$$

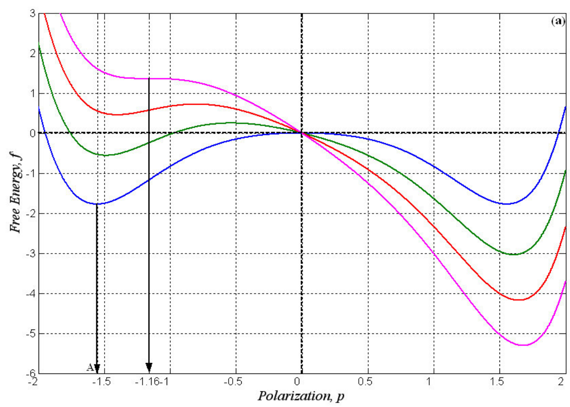
for first and second-order case, respectively which is stated in Fig. 2(a) and (b) in vertical axes. Substituting in (2) gives

$$e_C = \frac{4}{5}\left[\frac{3}{5}\left(1 \pm \sqrt{1 - \frac{5}{9}t_r}\right)\right]^{1/2}\left[t_r - \frac{3}{5}\left(1 \pm \sqrt{1 - \frac{5}{9}t_r}\right)\right] \quad (4)$$

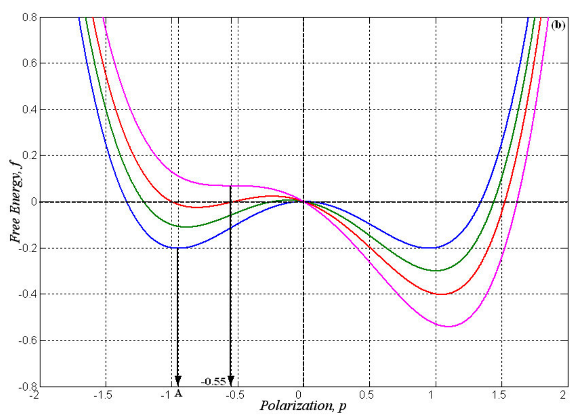
and

$$e_C = \pm 2\sqrt{\frac{(1-t^*)}{3}} \quad (5)$$

the coercive field for first and second-order, respectively. The coercive field decreases correspond to the increase in temperature. This clearly shown that the switching properties are highly affected by the temperature effect at high-temperature ranges-field-induced phase towards PE phase for first-order and near PE phase for second -order case. Both values are

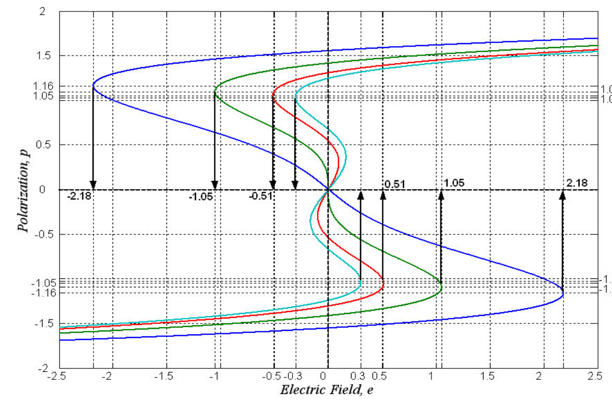


(a)

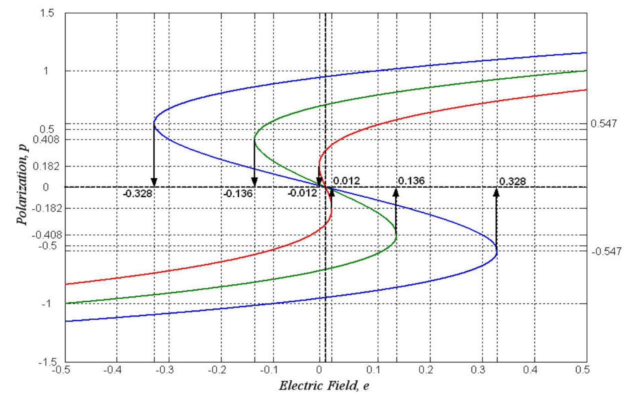


(b)

Fig. 1: Ferroelectric free energy f versus polarization p for (a) first-order and (b) second-order phase transition with temperature t_r = -1 and t^* = 0.1, respectively. The curves represent positive switching calculated from different positive electric field: (a) for first and second-order case e = 0, equilibrium state (blue), e_1 = 0.8, e_2 = 0.1 (green), e_1 = 1.5, e_2 = 0.2 (orange) and e_1 = e_{C1} = 2.18, e_2 = e_c = 0.33 (magenta). The polarization at equilibrium state labeled with A, where (a) p_B = 1.55 and (b) p_B = 0.95 for first and second-order case, respectively



(a)



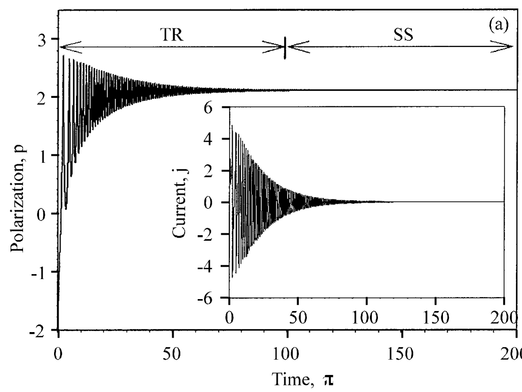
(b)

Fig. 2: Hysteresis loop p versus polarization e for (a) first-order and (b) second-order phase transition with different temperature at pure ferroelectric phase. For first-order case: t_r = -1 ($t<t_{SHB}$) (blue), tr = t_{SH} = 0 (green), t_r = 0.5 (red) and $t_r \approx t_{CB}$ = 0.7 (cyan) and for second-order case: t^* = 0.1 (blue), t^* = 0.5 (green) and $t^* \approx t_{CB}$ = 0.9 (red). The coercive field e_c and polarization p_c are labeled in both figures

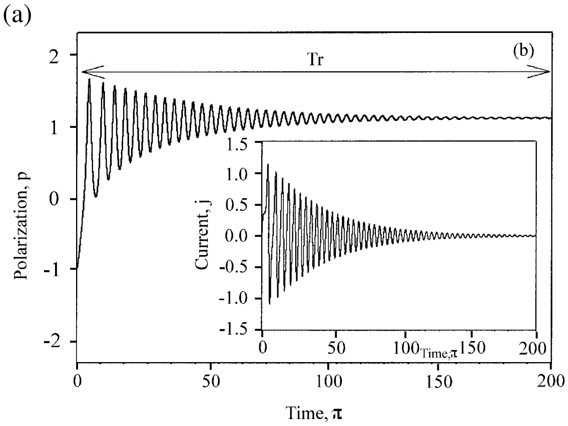
indicated by vertical arrows in Fig. 2(a) and 2(b) for various temperatures and may be used as a guardian to determine the switching behavior, since $e \geq e_c$ are the foremost conditions for the complete switching.

Oscillatory dynamic system switching: The atoms resonate proportionately to the effect of external electric field may described by Landau-Khalatnikov (LK) equation of motion as an oscillatory dynamical damped system, hence

$$\frac{d^2p}{d\tau^2} + g\left(\frac{dp}{d\tau}\right) = -\left(\frac{\delta f}{\delta p}\right) \quad (6)$$

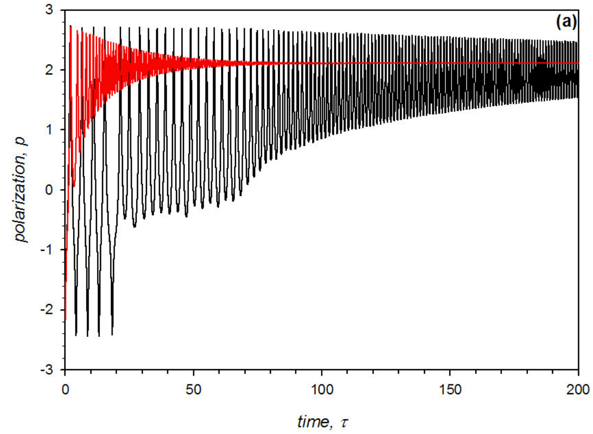


(a)

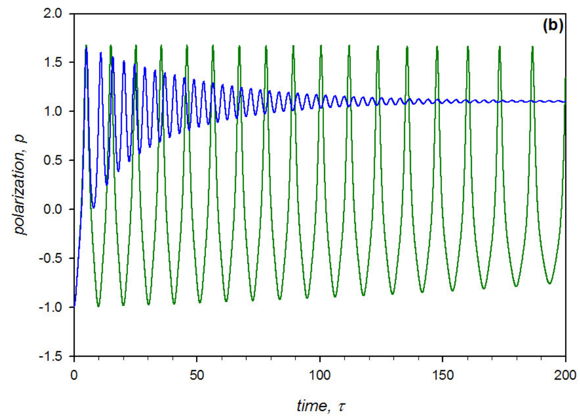


(b)

Fig. 3: Polarization p versus time t switching behaviors for (a) first-order and (b) second-order case with temperature $t_r = -1$ with $e = 2.2$ (coercive electric field $e_{c1} = 2.18$ and damping parameter $g = 0.1$) and $t^* = 0.1$ with $e = 0.35$ (coercive electric field $e_c = 0.33$ and damping parameter $g = 0.01$), respectively. The current, j, switching in the inset for both cases



(a)



(b)

Fig. 4: Damping g effect for polarization switching: (a) first-order with $t_r = -1$ and (——) $g = 0.01$, (▬) $g = 0.1$ and (b) second-order with $t^* = 0.1$ and (▬) $g = 0.001$, (▬) $g = 0.05$. The electric field on curve (a) and (b) are the same as in Fig. 3

which is evaluated from spring oscillatory damped system where restoring force is eliminated. The second and first-order differential equation in LHS of (6) describe the soft-mode dynamic properties in damped oscillatory system observed in many displacive FE. g refer to the damping parameter

$$g = \gamma(4\varepsilon_0 C / B^2 m)^{1/2} \quad \text{and} \quad g = \gamma(a^3 T_0^3 / m\varepsilon_0{}^3)^{1/2}$$

which is for first and second-order phase transitions respectively. By applying (1) into (2), then

$$\frac{d^2p}{d\tau^2} + g\frac{dp}{d\tau} = -\alpha p + 4\beta p^3 - p^5 + e \qquad (7)$$

In relaxational system, the problem may be solved analytically since the first term of (7) vanishes but for oscillatory dynamical case, the numerical method approach is needed since we considered the second derivative term in (7).

As described before in[6], we are using Central Finite-Difference Approximation (CDFA) to treat the nonlinear equation of (7) and simultaneously may be written as

$$p_{N+1} = \frac{(\lambda-1)p_{N-1} + \left(2-\alpha(\Delta\tau)^2\right)p_N + \left(4\beta p_N^3 - p_N^5 + e\right)(\Delta\tau)^2}{(1+\lambda))} \qquad (8)$$

where $\lambda = (1/2)g(\Delta\tau)$, p_{N+1} is the polarization to be computed, p_{N-1} is the previous calculated value and p_N the current value. The increment of time is given by $\Delta\tau$. Since the switching occurs in bulk FE, we take the initial polarization as $p_{N-1} = p_N = p_{BULK}$ for both cases, first and second-order, respectively. The current switching is defined as $j = (p_{N+1} - p_{N-1})/(2\Delta\tau)$ using backward finite-difference approximation. Using some experimental data of $BaTiO_3$ from Chew *et al.*[10] and Wang *et al.*[11], hence the estimation of damping value for first and second-order are g = 0.1 and g = 0.05, respectively. The conditions for complete switching have been mentioned above where they correspond to the coercive field e_c value and we assume the initial polarization occurred in negative state.

Fig. 3 shows the under-damped oscillatory switching system behavior for first and second-order phase transition in 3(a) and 3(b) respectively. Since our proposition is to investigate the bulk FE oscillatory switching phenomenon, thus the temperatures at pure stable-state FE are considered, where $t_r = -1$ and $t^* = 0.1$ for first and second-order phase transitions respectively. Clearly identifiable is that the transient response (*TR*) in first-order is two times faster than second-order case, where the steady-state (*SS*) occurred at $\tau \approx 100$. The transient response (*TR*) of the dynamical system refers to the behavior as it makes a transition from the initial condition to the final condition, while the steady-state (*SS*) is the area where the entire transient has died out[12]. The settling time which is the time to reach the *SS*, is $\tau \sim 100$ and $\tau \sim 200$ for first and second-order respectively. The presence of damping parameter g in terms of mechanical vibration point of view makes oscillator always comes to rest as indicated in Fig. 4 for both first and second-order phase transitions. These motions are also known as transient vibrations. From Fig. 3 and 4, the presence of damping in simple harmonic oscillator (SHO) describe mathematically by $A\exp(-\eta\omega t)$, where η is known as damping ratio, A is amplitude, ω is frequency and t is time.

RESULTS AND DISCUSSION

The oscillatory dynamical system for bulk ferroelectric in the first and second-order phase transitions has been studied in terms of switching time. All the calculations have been given in dimensionless form to perform the universal results. Details of dielectric hysteresis loops (DHL) for first and second-order behavior have been discussed by investigating the coercive field e_c. Since the purpose of this study is to investigate the switching time t for bulk FE, then from Fig. 3, we know that the approximation of switching time $t = \tau t_0$. From previous study[3,6], $t_0 = (m\varepsilon_0/aT_0)^{1/2}$ and $t_0 = (4m\varepsilon_0 C/B^2)^{1/2}$ for second and first-order phase transitions respectively. By using experimental data from Wang *et al.*[11], thus $t_0 \sim 5.32 \times 10^{-16}$ s for second-order case and $t_0 \sim 7.38 \times 10^{-15}$ for first-order case. As mentioned above, from Fig. 3, the transient response (*TR*) in first-order is two times faster than second-order case, where the steady-state (*SS*) occurred at $\tau \approx 100$. Thus, the approximation values for first and second-order phase transitions switching time in oscillatory dynamical system are $t \sim 7.38\times10^{-13}\,s$ and $t \sim 1.064 \times 10^{-13}$s respectively. These results show that the approximation of theoretical calculation for bulk FE oscillatory switching time are in the ranges of $\sim 10^{-13}$s. Our theoretical estimation is valid since we have neglected other effects i.e domain wall movement and surface effect which occur in FE thin film. The bulk switching time estimation that we calculated here may be used as theoretical-guide-value to estimate the oscillatory switching in symmetric and asymmetric FE films and we are currently pursuing to investigate this behavior and hope to publish the results soon.

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REFERENCES

1. Lines, M.E. and A.M. Glass, 2001. Principles and Applications of Ferroelectrics and Related Materials*,* Clarendon Press, Oxford. New Edn.
2. Ricinschi, D., C. Harnagea, C. Papusoi, L. Mitoseriu, V. Tura and M. Okuyama, 1998. Analysis of ferroelectric switching in finite media as a Landau-type phase transitions. J. Phys. Condens. Matter, 10: 477.
3. Tan, E.K., Junaidah Osman and D.R. Tilley, 2001. Theory of switching in bulk first-order ferroelectric materials. Phys. Stat. Sol., 228: 765.
4. Merz, W.J., 1954. Domain Formation and Domain Wall Motions in Ferroelectric $BaTiO_3$ Single Crystals**.** Phys. Rev., 95: 690.
5. Ya Shur, V., A.L. Gruverman, N. Yu Ponomarev, E.L. Rumyantsev, N.A. Tonkachyova, 1992. Integrated Ferroelectrics, 2: 51.
6. Halif, M.N.A. and Junaidah Osman, 2004. Analysis of bulk second-order ferroelectric switching in oscillatory dynamical system. KUKUM J. Eng. Res. and Education, 1: 97.
7. Larsen, P.K., G.L.M. Kampschoer, M.B. van der Mark and M. Klee, 1992. Proc. of the 8th IEEE Intl. Symposium on Applications of Ferroelectrics (ISAF ’92), pp: 217.
8. Larsen, P.K., R. Cuppens and G.J.M. Dormans, 1995. Science and Technology of Electronic Thin Films. Ed. By Auciello O and Waser R (Kluwer Academic, Dodrecht, The Netherlands), 284: 201.
9. Ishibashi, Y. and Y. Takagi, 1971. Note on ferroelectric domain switching. J. Phys. Soc. Jpn, 31: 506.
10. Chew, K-H., Junaidah Osman, R.L. Stamps, D.R. Tilley, J.F. Webb, 1999. Theory of far-infrared spectroscopy for ferroelectric size effect. Integrated Ferroelectrics, 23:161.
11. Wang, Y.G., W.L. Zhong and P.L. Zhang, 1994. Size effect on Curie temperature of ferroelectric particles. Solid State Commun., 92: 519.
12. Woods, R.L. and K.L. Lawrence, 1997. Modeling and Simulation of Dynamic Systems, Prentice Hall, New Jersey.