



National Physical Laboratory

# The interplay between time and temperature effects in ordered ferroic systems

**Melvin M. Vopson**

- previously known as Marian Vopsaroiu -

**National Physical Laboratory, Hampton Road, Teddington, UK**

## Introduction

- **The understanding of fundamentals of polarization dynamics is important for the operation of devices where the rate of switching is critical to their operation**
- **Experimental evidence suggests that polarization reversal occurs via a nucleation of domains process**
- **The main domain nucleation-switching model, treats polarization reversal as a nucleation process and was given by Kolmogorov-Avrami-Ishibashi (KAI)**
- **According to the KAI model, upon the application of a E field, nuclei of reversed polarization are generated and the polarization switching takes place in a few steps:**
  - nucleation of domains
  - rapid growth of nuclei along polarization direction
  - sidewise growth and coalescence of the domains until the entire polarization is reversed
- **The KAI model predicts the following temporal dependence of polarization / electric displacement during the switching process:**

$$\Delta D(t) = 2p_s \cdot \left(1 - e^{-(t/t_{sw})^n}\right)$$

## Motivation

- **KAI model is not fully applicable to the reversal behavior over larger time periods or the reversal behavior of polycrystalline thin films**
- **KAI model does not explain the microscopic mechanisms that lead to the nucleation process of the domains**
- **One of the main limitations of the KAI model, is the failure to predict the relationship between the switching time to the applied electric field and temperature**
- **Several empirical expressions, linking the switching time to the applied electric field, have been obtained**

**Miller & Weinreich**

$$t_{sw} = Be^{b/E}$$

**Miller R C and Weinreich G 1960  
*Phys. Rev.* 117 1460**

**Stadler**

$$t_{sw} = AE^{-n}$$

**Stadler H L (1958) *J. Appl. Phys.* 29  
1485**

**Fatuzzo**

$$t_{sw} = CE^{-n} e^{\alpha/E}$$

**Fatuzzo E *Phys. Rev.* 127 (1962)  
1999 - 2005**

**Merz**

$$t_{sw} \cong \frac{\beta d}{E - E_C}$$

**W. J. Merz, (1954) *Phys. Rev.* 95  
690**

## Proposed model

- We assume that all nucleation sites are already present at any time in the sample
- We assume the ferroelectric material as an assembly of  $N$  elementary polar sites
- The switching is provided by the nucleation of a domain per an elementary polar site
- The nucleation occurs once a critical domain (volume  $V^*$ ) has reversed polarization and can expand unrestrictedly under the applied E field
- The switching rate is controlled by the switching rate of the nucleation site, rather than the rate of expansion of the nuclei or the rate of formation of critical nuclei (KAI)
- The time taken to reverse the polarization is called the switching time ( $t_{sw}$ ) and is assumed to be equal to the time required for the nucleation site to reverse, while the time for the expansion of the domain until it reverses the entire polarization of the elementary polar site is negligible in comparison with the nucleation time

## Proposed model

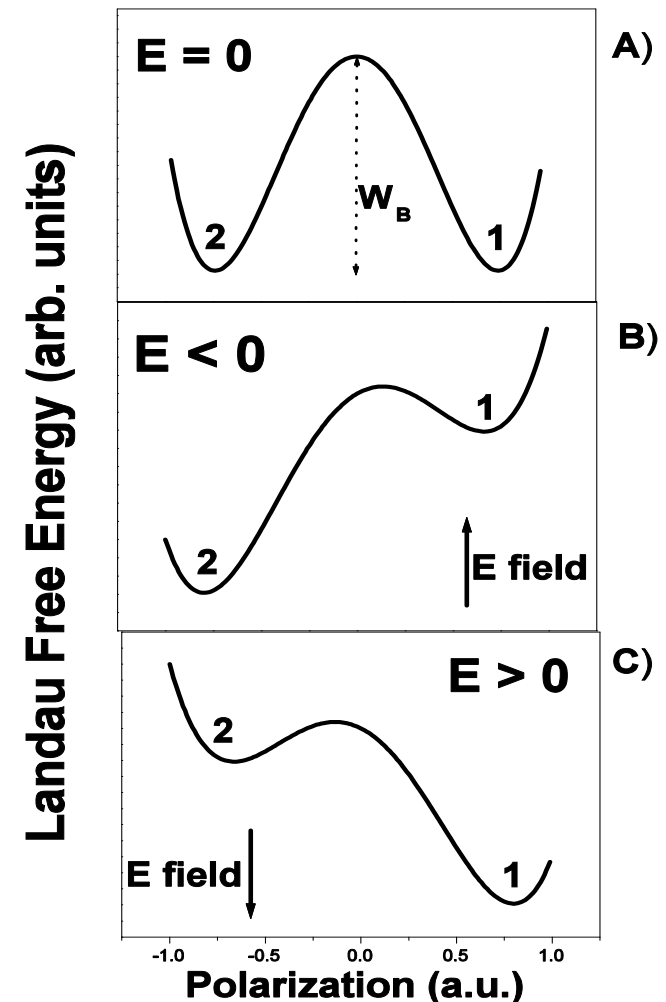
- We introduce the Landau-Devonshire free energy of the elementary ferroelectric polar site “*i*” under applied electric field as:

$$\frac{F_i}{V^*} = \frac{\alpha}{2} D_i^2 + \frac{\beta}{4} D_i^4 - D_i E_{app} \cos(\theta)$$

- The two possible states are separated by an energy barrier, representing states with polarization up / down

$$W_{1,2} = \left( -W_B \mp p_s E_{app} \right) \cdot V^*$$

- Transitions between the two states are physically permitted on a continuous basis
- A nucleation site is fundamentally a non-equilibrium two state system, with the occupation probabilities  $P_1$  and  $P_2$  of states 1 and 2 also time dependent



## Non-equilibrium statistics

- $P_l(t)$  and  $P_m(t)$  are the probabilities that the system is in the state  $l$  or  $m$  at the time  $t$
- $a_{l,m}$  and  $a_{m,l}$  are the transition rates per unit time from the state  $m$  to state  $l$  and vice versa, respectively

$a_{l,m} dt \cdot P_m(t)$  Probability that the system is in state  $m$  at time  $t$  and state  $l$  at time  $t + dt$

$a_{m,l} dt \cdot P_l(t)$  Probability that the system is in state  $l$  at time  $t$  and state  $m$  at time  $t + dt$

- The change  $dP_l(t)$  of probability  $P_l(t)$  when  $t \rightarrow t + dt$  is the difference of the two terms:

$$dP_l = \sum_{m \neq l} \left( a_{l,m} dt \cdot P_m(t) - a_{m,l} dt \cdot P_l(t) \right)$$

- The time evolution of the probabilities when a non-equilibrium system goes through different possible states are described by the general Pauli master equation

$$\frac{dP_l}{dt} = \sum_{m \neq l} \left( a_{l,m} P_m(t) - a_{m,l} P_l(t) \right)$$

## Solutions of Pauli – Master equation

- We solved the Pauli master equation for  $l, m = 1, 2$ , which describes the energy states of a nucleation site
- We assume the system in contact with a temperature reservoir and that the initial state is set to  $P_l(0) = 1$
- Solutions / time dependent probabilities of the two states are:

$$P_1(t) = e^{-\left(\frac{t}{t_{SW}}\right)} + P^1_{eq} \cdot \left(1 - e^{-\left(\frac{t}{t_{SW}}\right)}\right)$$

$$P_2(t) = (1 - P^1_{eq}) \cdot \left(1 - e^{-\left(\frac{t}{t_{SW}}\right)}\right)$$

where

Probability of state 1 at equilibrium

$$P^1_{eq} = \left(1 + e^{\frac{W_1 - W_2}{k_b T}}\right)^{-1}$$

Relaxation time / switching time

$$t_{SW}^{-1} = \nu_0 \cdot \left( e^{-\left(\frac{W_B - p_s E_{app}}{k_b T}\right) \cdot V^*} + e^{-\left(\frac{W_B + p_s E_{app}}{k_b T}\right) \cdot V^*} \right)$$

For the full derivation, please check:

M. Vopsaroiu, et. al Phys. Rev. B, vol. 82, (2010)

## Derivation of the switched polarization

- For  $N$  elementary polar sites, we define  $N_1(t) = P_1(t) \cdot N =$  number of sites in state 1 at time  $t$  and  $N_2(t) = P_2(t) \cdot N =$  number of sites in state 2 at time  $t$ , with  $N = N_1 + N_2$
- We assume the two probabilities describe the state of each nucleation site at time  $t$
- We also assume that the sample has been initially poled so that all polar sites are reversed into state 1,  $P_1(0) = 1$ , which results in  $N = N_1(0)$  and  $N_2(0) = 0$
- In order to reverse the polarization into state 2, we now apply instantaneously a constant electric field  $E_{app}$ . Over a period of time  $t$ , the total amount of polarization (electric displacement) switched from state 1 into state 2 is equal to:

$$\Delta D(t) = 2p_S \cdot N_2(t) / N = 2p_S \cdot P_2(t) = 2p_S \cdot (1 - P_1(t))$$

- Using the derived expression for  $P_1(t)$ , we obtain:

$$\Delta D(t) = 2p_S \cdot (1 - e^{-(t/t_{sw})}) \cdot (1 - P_{eq}^1)$$

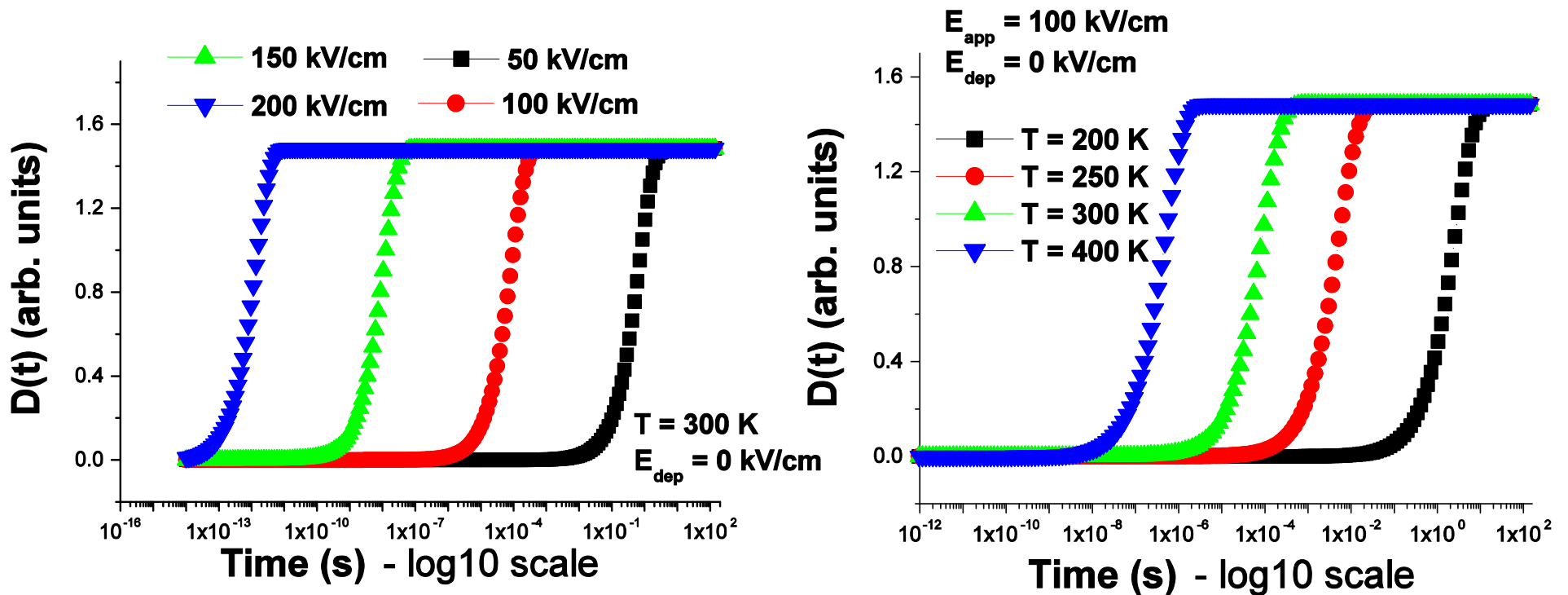


# Theoretical estimations

## Numerical parameters

$$\alpha = -11.57 \times 10^7 \text{ Vm/C}; \beta = 2.1 \times 10^8 \text{ Vm}^5/\text{C}^3; k_b = 8.61 \times 10^{-5} \text{ eV/K (or } 1.38 \times 10^{-23} \text{ J/K)}; V^* = 10^{-26} \text{ m}^3$$

This results in  $W_B = 0.99 \text{ eV}$  and  $Ps = 0.74 \text{ C/m}^2$



# Switching time

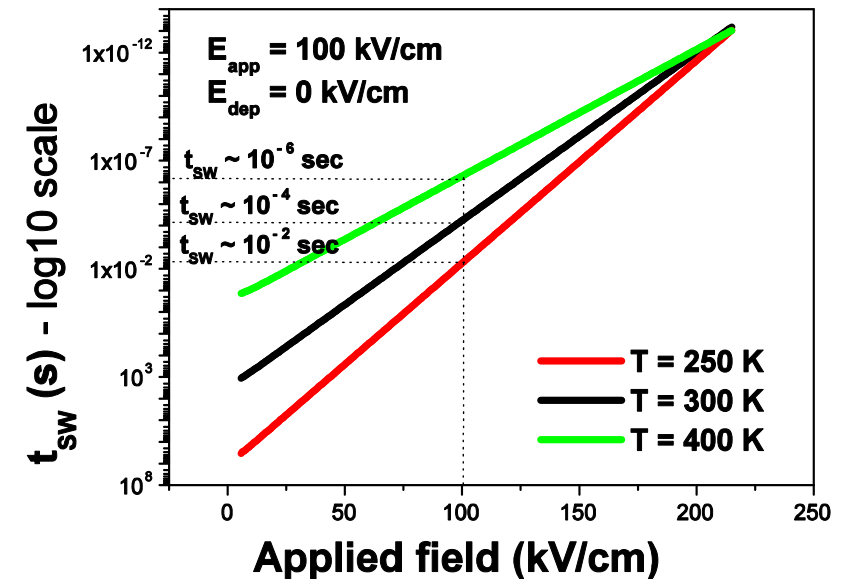
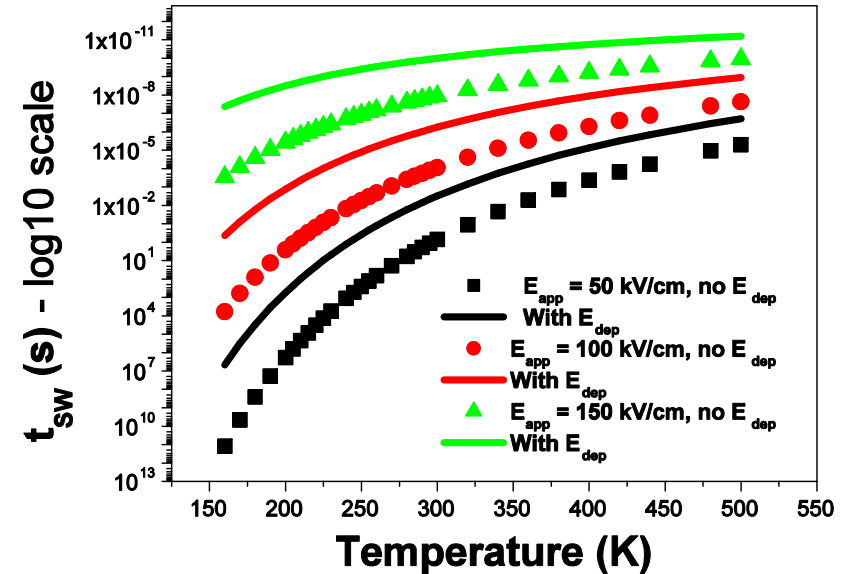
$$t_{SW}^{-1} = \nu_0 \cdot \left( e^{-\left(\frac{W_B - p_s E_{app}}{k_b T}\right) \cdot V^*} + e^{-\left(\frac{W_B + p_s E_{app}}{k_b T}\right) \cdot V^*} \right)$$

Numerical results indicate that the second exponential term is very small and can be ignored, especially for larger energy barriers

$$t_{SW} \cong \frac{1}{\nu_0} \cdot e^{\left(\frac{W_B - p_s E_{app}}{k_b T}\right) \cdot V^*}$$

For the case  $E_{app} = 0$ , the switching time is only function of the energy barrier and the temperature:

$$t_{SW} \cong \frac{1}{2\nu_0} \cdot e^{\frac{W_B \cdot V^*}{k_b T}}$$



## Derivation of the $E_c$

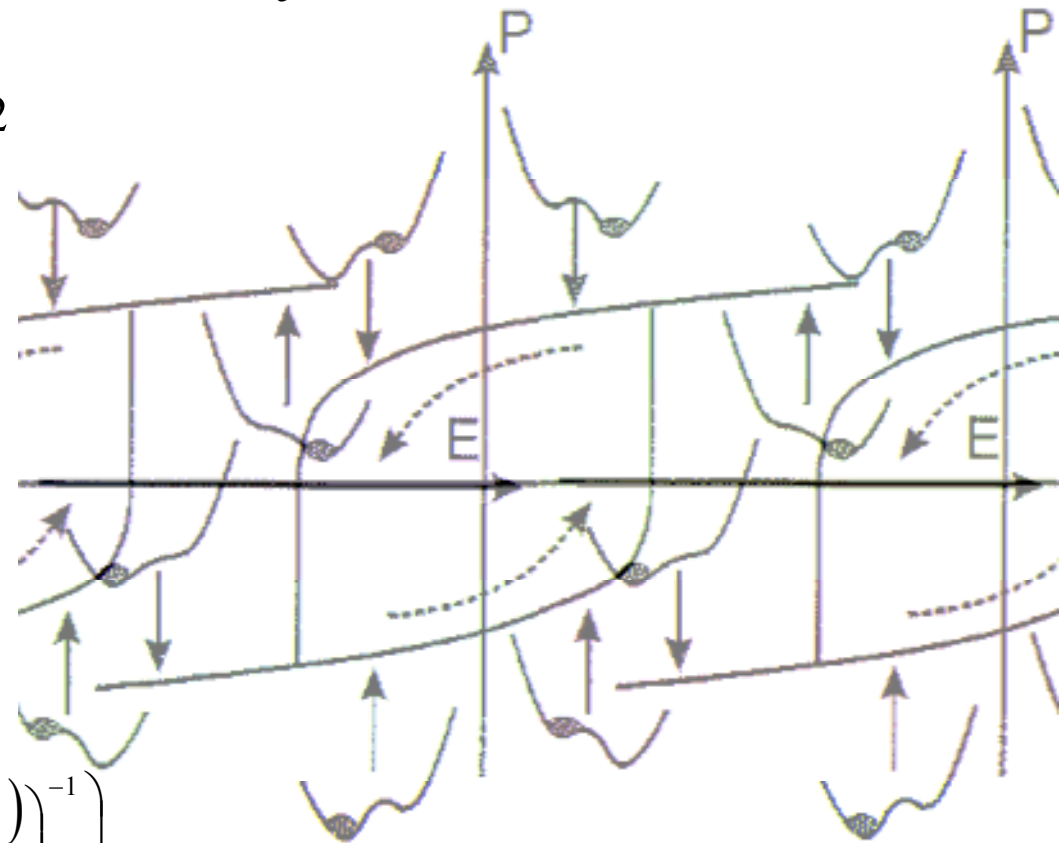
- Within the framework of our model, at the coercive field the occupation probabilities of the two possible states are equal:  $P_1(t) = P_2(t)$  at  $E_c$
- Since  $P_1(t) + P_2(t) = 1$ , it results that  $P_1(t) = 1/2$  at  $E_c$

$$P_1(t) = e^{-\left(\frac{t}{t_{SW}}\right)} + P_{eq}^1 \cdot (1 - e^{-\left(\frac{t}{t_{SW}}\right)}) = 1/2$$

$$\frac{t}{t_{SW}} = \ln\left(\frac{2(1 - P_{eq}^1)}{1 - 2P_{eq}^1}\right)$$

$$t_{SW} \cong \frac{1}{\nu_0} \cdot e^{\left(\frac{W_B - p_s E_c}{k_b T}\right) \cdot V^*}$$

$$E_c(t, T) = \frac{W_B}{p_s} - \frac{k_b T}{V^* p_s} \cdot \ln\left(\nu_0 t \cdot \ln\left(\frac{2(1 - P_{eq}^1)}{1 - 2P_{eq}^1}\right)^{-1}\right)$$

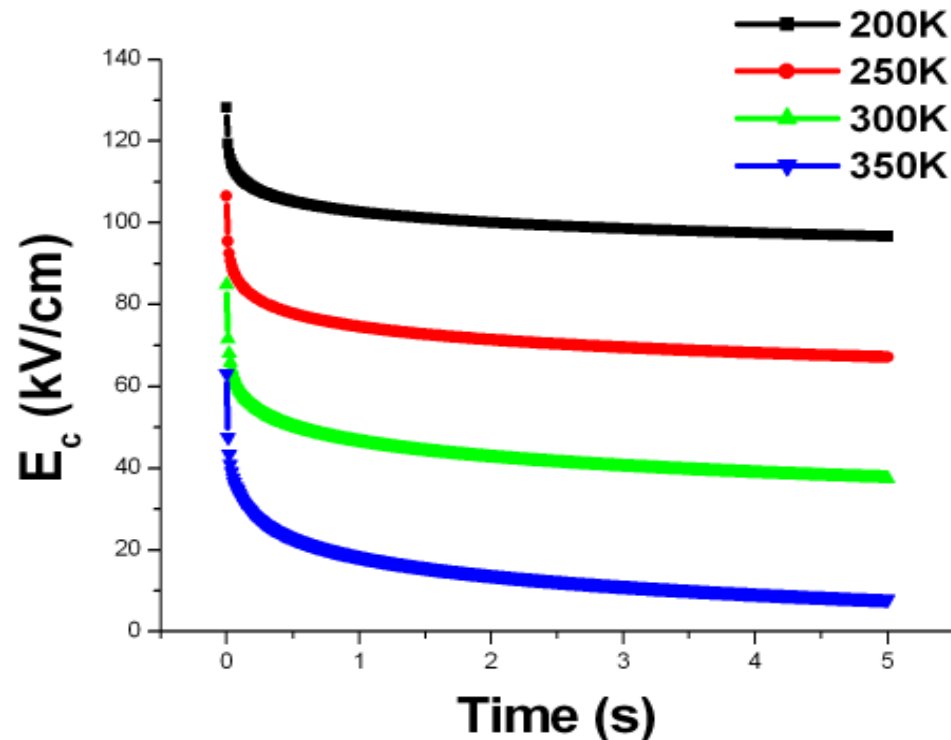


## Time / temperature dependence of $E_c$

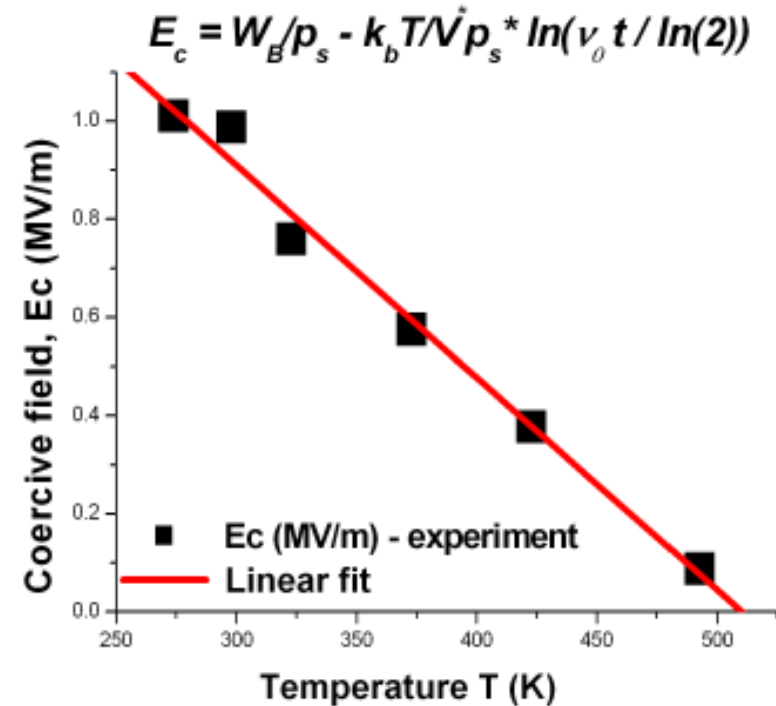
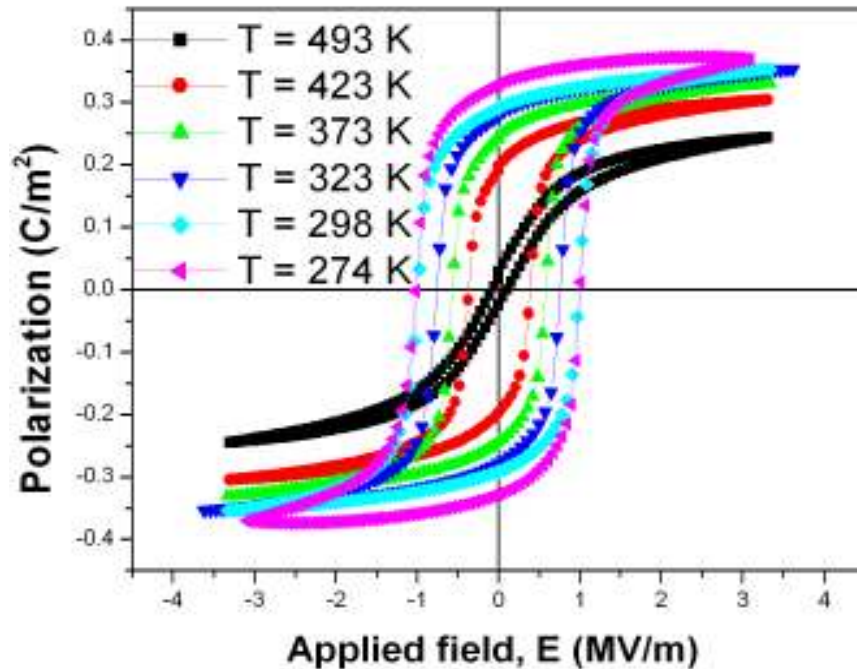
- For large enough applied fields we numerically determined that  $P_{eq}^l \ll 1$ , resulting in a simplified expression for the  $E_c$

$$E_c(t, T) \cong \frac{W_B}{p_s} - \frac{k_b T}{V^* p_s} \cdot \ln\left(\frac{\nu_o t}{\ln(2)}\right)$$

- The above relation shows that the coercive field decreases with the measurement time / frequency
- Also the coercive field varies linearly with the temperature with a negative slope:  $E_c(T) = a - b \times T$
- Standard P-E loops of “soft” PZT-5H at various temperatures has been measured to test the theoretical predictions



# Experimental evidence



From the linear fit:  $W_B/p_s = 2.206$        $k_b/(V^* p_s) \times \ln(v_0 t / \ln(2)) = 4324$   
 From experiment:  $p_s = 0.32 \text{ C/m}^2$   
 Measurement time  $t = 1 \text{ sec}$  (frequency 1 Hz)

The values obtained are:  $V^* = 3 \times 10^{-25} \text{ m}^3$        $W_B = 0.7 \text{ eV}$

The activation volume ( $V^* = 3 \times 10^{-25} \text{ m}^3$ ) calculated from our model compares well with ( $V^* = 1.62 \times 10^{-25} \text{ m}^3$ ) calculated for the same sample using a different model [K.B. Chong, F. Guiu, M.J. Reece, *J. Appl. Phys.* **103**, 014101 (2008)]; This corresponds to the volume of a sphere with a 4.1 nm radius

## Conclusions

- **The model makes a set of simplifications: 1D model, uni-axial domains, defects, polarization gradients or size effects not included, energy barrier is kept constant, etc**
- **However, within the limits of the system / model described in this paper, we were able to demonstrate the temperature, time and E field dependence of the polarization switching**
- **Analytical equations are based on quantified and documented physical quantities rather than fit to the experimental data**
- **Modelling results suggest that the switching process is dominated by the applied electric field, but it is also very susceptible to the thermal effects**
- **Coercive field predictions of the model fit well with the experimental data**
- **Additional effects such as depolarizing fields, crystal defects, energy barrier distributions, etc. can be easily built into the model presented here as a further development of it**
- **This can potentially be used for time dependent P-E loop simulations, fatigue studies, aging effects and other time / temperature dependent effects in ferroelectrics**