Devonshire-Ginzburg-Landau phenomenological study of ferroelectric properties of PbTiO$_3$ thin films.

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Abstract— It is well known that the physical properties of ferroelectric thin films are considerably different from those of bulk ferroelectrics. The surface effect is one of this important properties observed in ferroelectric thin films. At the surface , the coordination of the atoms is different from that in the volume of the film. The influence of the surface effect on the ferroelectric properties of PbTiO$_3$ films has been investigated based on Ginsburg- Landau-Devonshire (GLD) thermodynamic theory, where the free energy coefficients are calculated for PbTiO$_3$ crystal from microscopic interactions based upon the statistical mean field approximation. In this study, the shift displacement profile, the average the maximal and minimal of central ion shift displacement, the phase transition and Curie temperature (Tc) dependence on the film thickness are numerically modeled and analyzed by an Euler-Lagrange equation with applying a corresponding boundary condition on ion displacement for various values film thickerss and levels of extrapolation length.

I. INTRODUCTION

Ferroelectric materials and in particular thin films have been the subject of considerable attention in the last decades, on the part of both experimental [1-5] and theoretical [6-13] researchers, to examine their properties such as, the surface effects, the size effects and phase transition. Regarding lead titanate PbTiO$_3$, M. de Keijser et al [14] and W. Ma et al [15] observed that the decrease in phase transition temperature with the decrease of film thickness. On the other hand, W.G. Liu [16] et al and Kenji Ishikawa et al [17] studies the phase transition of PbTiO$_3$ in the form of thin film and small particle. In the same direction B. Jiang et al [18] are studied the size dependence of second and fourth order GLD coefficients in order to explain the size effects in lead titanate properties.

The present work is based on the Ginzburg-Landau-Devonshire phenomenological theory which has been used for a long time (more than 60 years) to study the physical properties of ferroelectric thin films. In previous work [21], we have studied the phase transition in the ferroelectric crystal PbTiO$_3$ based on microscopic interaction and mean fileld statistical approximation. This study allowed us to explain the free energy as a function of the principal order parameter namely the shift of central ion. In the present work we performed the calculation of the profile of the ion shift, the average shift, the phase transition and the variation of transition temperature as a

function of PbTiO$_3$ film thickness. These calculations, we used the expression of free energy established in [21] for the volume part of thin film. The ion displacement depends on the distance from the surface; therefore the mean field approximation (applied in case of bulk) is no longer valid. Hence and in order to examine this property, we added the term gradient $|\nabla \bar{x}|^2$ to the LD free energy expression.

II. RELATED WORK

In the previous works [21], the phase transition in bulk PbTiO$_3$ is discussed quantitatively from the microscopic free energy based upon the mean field approximation, where the Ti ions shift is considered as the order parameter in the lattice having the spontaneous deformations. The spontaneous displacement of the central ion Ti is calculated by considering the variations in dipole-dipole interactions due to lattice deformations. Our calculations show that the spontaneous displacement decreases when the temperature increases and that it undergoes discontinuities at the level of the transition. The results obtained are in good agreement with the experimental results.

III. MODEL

Due to the lattice strains and shears and the potential the statistical free energy of the volume inside the film (far from the surface) is determined as a function of the crystal

energy U_{Cris} and the number of accessible states $\Omega(\bar{x}, \bar{y}, \bar{z}; T)$.

$F(\bar{x}, \bar{y}, \bar{z}) = U_{Cris} - k_\beta T \ln \Omega(\bar{x}, \bar{y}, \bar{z}; T)$

Since $\Omega(\bar{x}, \bar{y}, \bar{z}; T)$ can be expressed as a function of the potential V acting on the central ion Ti, the free energy becomes:

$F(\bar{x}, \bar{y}, \bar{z})$

$$= \frac{\eta}{2}\bar{x}^2 + \frac{d_1}{2}\bar{x}^4 - k_\beta T \ln \frac{\iiint \exp\left[-\frac{V(x,y,z;\bar{x},)}{k_\beta T}\right] dxdydz}{\iiint \exp\left[-\frac{V(x,y,z;0)}{k_\beta T}\right] dxdydz}$$

With the potential V is determined by summing on the short-range interactions, namely the Van der Waals interactions, the overlap interaction and that between the considered Ti ion and the neighboring ions. The expressions of η and d_1 are given in the following references [20,21]

In the present calculation, the starting point is the expression of free energy established in [21] is:

$$F = A(T)\bar{x}^2 + B(T)\bar{x}^4 \qquad (1)$$

With A(T) and B(T) are Landau temperature dependent coefficients and $\bar{x}$ is the displacement of the central ion Ti.

The most used method to model the surface effect consists of adding a term in the displacement gradient $|\nabla \bar{x}|^2$ [9] to the free energy expression.

Therefore the expression of the free energy per unit area of LD is given by:

$$F_S = \int_{-L}^{+L} dx \left[A(T)\bar{x}^2 + B(T)\bar{x}^4 + \frac{1}{2}K\left(\frac{d\bar{x}}{dx}\right)^2 \right] \qquad (2)$$

Where K, is a constant parameter independent of temperature. In this expression we neglected the effects of the depolarization field and that of the applied field ($E_{app}= 0$).

The minimization of this last equation using the Euler Lagrange equation gives:

$$F_S = \int_{-L}^{+L} f(x, \dot{\bar{x}}(x)) dx \qquad (3)$$

Where 2L is the film thickness and $\dot{\bar{x}} = \frac{d\bar{x}}{dx}$

Finally leads to the following second order differential equation:

$$K\frac{d^2\bar{x}}{dx^2} = 2A(T)\bar{x} + 4B(T)\bar{x}^3 \qquad (4)$$

With the boundary conditions: $\frac{\bar{x}}{\delta} + \frac{d\bar{x}}{dx} = 0$, δ is the extrapolation length which is a phenomenological parameter that represents the discrepancy surface and the interior of the film.

IV. RESULTS AND DISCUSSION

The numerical resolution of the differential equation (4) is performed by the Runge Kutta method. The adopted value of the constant parameter K is 10^{-13}J.

Figure 1 shows the variation of the spontaneous displacement along the film thickness. The displacement of the Ti ion decreases as we get closer to the surface, and the profile becomes non uniform in this area. The spontaneous displacement of the central ion represents the principal phase transition order parameter that triggers the transition; while spontaneous polarization is a macroscopic secondary parameter In addition spontaneous displacement and polarization are related to each other. This result is in agreement with published for the spontaneous polarization of ferroelectric thin films [5].
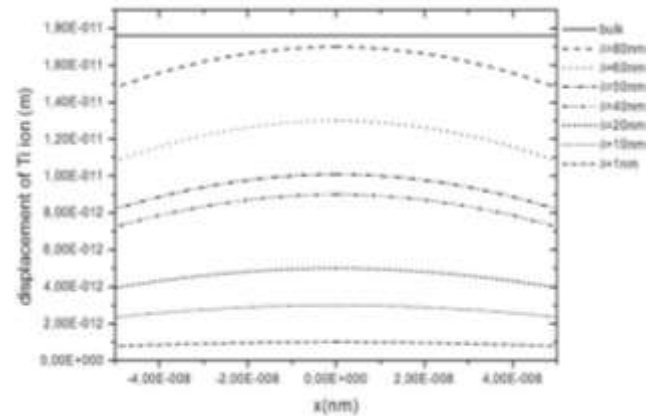

Figure 1. Spontaneous displacement profiles along the thickness direction of the film for T=300K, L=50nm and for a various values of extrapolation length δ.

We also notice that the displacement values increase with the extrapolation length until they take the values of the solid bulk material.

In Figure 2, we have shown the variation of the average displacement of the Ti ion as a function of temperature for several values of δ. We note that the transition temperature increases when δ increases.
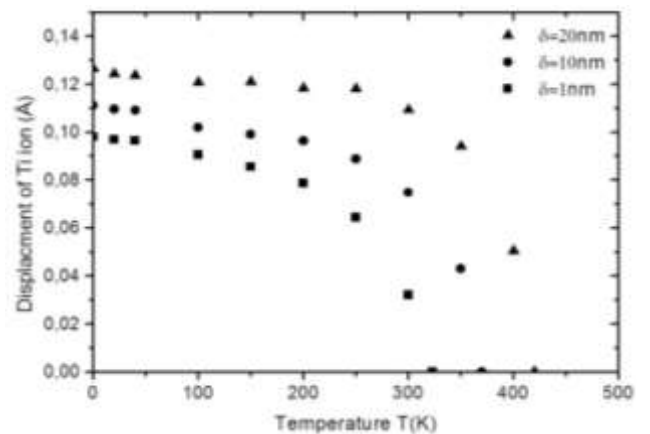

Figure 2. The calculated results of temperature dependence of Ti ions shifts for various values of δ in the case of L=120nm

Figure 3 shows the shift of the Tc as a function of film thickness. Tc increases monotonously with increasing the film thickness until it reaches the value of the bulk material for sufficiently large thicknesses.

Thickness dependence of the maximal x_0, the average x_m and the minimal x_L displacements of central ion Ti for several values of δ are represented in figure 4. The displacement of the central ion decreases with decreasing the film thickness and canceled out for a critical value L_0 below which the film is paraelectric. Figures 3 and 4 show the existence of a threshold thickness at which the film becomes ferroelectric It is worth noting that, the displacement of Ti at the center of thin film, is always greater than that at the surface of the film Moreover, when the thickness of the film decreases the displacement at the center decreases and quickly cancels out relative to the displacement of the Ti ion at the surface.
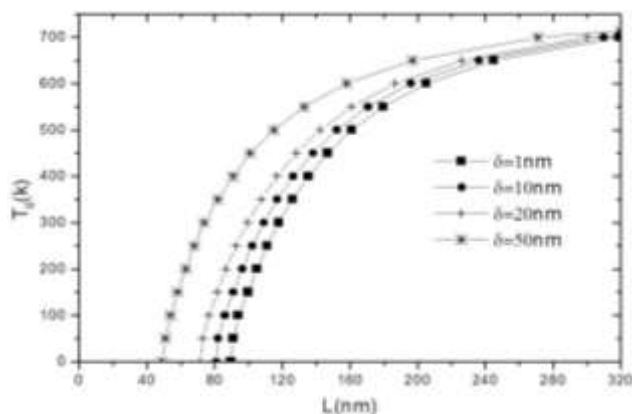

Figure 3: Thickness dependence of Curie temperature for a various values of δ.
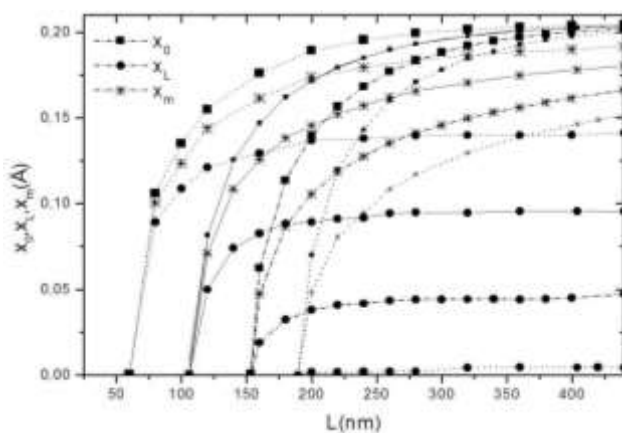

Figure 4: Thickness dependence of the minimal, the average and the maximal displacement of the central ion at T=0K for various values of δ (dashed line $\delta = 110°A$, solid line $\delta = 50°A$, dash dot line $\delta = 20°A$ and dot line $\delta = 1Å$)

V.   CONCLUSION AND FUTURE SCOPE

In this work we used the GLD model to study the ferroelectric properties of thin film $PbTiO_3$. It is found that the central displacement decreases in the vicinity of the surface. The values of displacement and transition temperature are always lower than those of the bulk material. The displacement decreases when increasing temperature, which shows a continuity in the vicinity of the transition, This suggests that the thin film is second order unlike the case of the solid bulk $PbTiO_3$.

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