Ferroelectric superlattices at nano scale: A Theoretical Investigation

A project report
submitted in partial fulfillment of the requirement for the award of
the degree of
Master of Science
in
Physics

by

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(PH17MSCST11003)

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Declaration

I hereby declare that the project work entitled "Ferroelectric superlattices at nano scale: A Theoratical Investigation" is a work carried out by me under the supervision of Dr. Manish K. Niranjan, Department of Physics, Indian Institute Of Technology, Hyderabad.
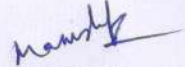
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08/05/2019

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Certificate

This is to certify that the project titled 'Ferroelectric superlattices at nano scale: A Theoratical Investigation' is a bonafide record of work done by Anuj Maurya towards the partial fulfilment of the requirements of the Master of Science degree in Physics at the Indian Institute of Technology, Hyderabad, Telangana, India. This thesis has not been submitted for the award of any other Degree/Diploma/Fellowship or any other similar title.

Dr. Manish K. Niranjan

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Contents

1 Abstract

In ferroelctrics, material size scales play a vital role in deciding its properties. Modeling of nano scale ferroelectric superlattices require different approach than bulk sized ferroelctrics. At smaller scales, thickness becomes a important parameter that can cause variation in critical value of properties of material and to study them choice of appropriate order parameter becomes crucial. This report mainly focuses on approach using spontaneous polarization as order parameter. Variation of Polarization, susceptibility and transition critical temperature with relative thickness of layers of ferroelectric superlattice is shown along comparison with different approach such as total polarization as order parameter, first principle calculation and experimental data using pre-existing curves from references.The most commonly observed anomalous phenomenon of ferroelectric superlattices is that the remanent polarization is much larger than their single-phase thin films. Going at very small scale of ferroelectric materials along with superlattice geomatry, one can see very interesting feature of it. In this type of structure, small variation in thickness of layers enhances dielectric constant and polarization of the sample.

2 Introduction

Ferroelectrics material exhibits electric dipole moment in absence of an external electric field. There is a relative displacemnt in position of positive charge and negative charge which causes polarization in crystals. Ferroelectricity usually disappear above a certain temperature called transition temperature. Above transition temperature crystal is said to be in paraelectric state. Ferroelectrics have phase transition temperatures. Second order phase transitions, there is no latent heat and the order parameter (spontaneous polarization) is not discontinuous in vicinity of transition temperature. But in First order phase transition it changes discontinuously at transition temperature. Structured ferroelectric bilayer, multilayer and superlattices shows phase transition temperatures, polarization and susceptibility which have dependency on ratio of thickness of different types of ferroelectric layers, structural periodicity, boundary conditions, elctrostatic ineractions, etc. It was found that the transition temperature of ferroelectric superlattices $BaTiO_3/SrTiO_3$ grown on $SrTiO_3$ can be changed upto 500k, depending on thickness of layers. At nano scale, critical properties of ferroelectric superlattices can be controlled by the thickness of different ferroelectric layers.

Properties of artificially structured ferroelectrics can be understood with thermodynamic models using Landau free energy expansion, simulations and First principle calculations. Landau theory provides description of a system's equillibrium behaviour near phase transition. There are different phenomenologies for ferroelectrics (e.g. Landau-Ginzburg Theory with boundary condition frames thin film ferroelectrics). Choice of order parameter becomes essential in case of thin films. In formulation of Landu free energy function it is found that total polarization as order parameter lead to significant variation in total free energy. It was investigated and suggested that the problem is underestimation of dielectric screening of electrostatic interaction between spontaneous polarization and depolarizing field and turned out use of spontaneous polarization as order parameter could be the solution.

Spontaneous polarization as order parameter in Landau free energy expansion includes the contribution from induced polarization explicitly in free energy functional, while this is excluded when expanded as total polarization. This report includes calculation of critical properties of ferroelectric superlattices, compared and discussed with different experimental data from references and existing calculations and enlighten very basic schematic of Dielectric susceptibility and polarisation in Ferroelectric multilayered superlattices.

3 Landau Devonshire theory

3.1 General phenomenology

Landau theory is symmetry based treatment and very promising in describing phase transitions in systems such as ferroelectrics and ferromagnets. Primarily this theory was used to establish the theory for second order phase transitions, later on Devonshire generalized Landau's approach to first order transitions. Free energy of ferroelectric thermodynamic state can be defined by specific variables like temperature(T), electric field(E), polarization(P), etc. Free energy of ferroelectrics can be expressed in terms of ten variables (three components of polarisation, six components of stress tensor and temperature). To understand the basic mechanism we shall make some assumption in order to simplify, consider one component of polarization and ignoring effect of the strain field. We need to write down an expression for this free energy using symmetry arguments.

Thermodynamic principle states that values of dependent variables in thermal equillibrium can be calculated when free energy is minimum. This theory validates in the vicinity of a phase transition and can expand the free energy in powers of the dependent variables (e.g. polarization) with coefficients that can be fitted to experiment from microscopic calculations. [1].

In order to understand behaviour of the system we can simplify the problem by taking a simple example where we can expand the free energy in terms of a single component of the polarization, ignoring the strain field, assumed crystal to be uniaxial ferroelectric and ignoring other contributions to free energy for now, We can write

$$F = \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 - EP \tag{1}$$

where F is free energy density and approximated to 6th power of ordered parameter. The equillibrium of state can be determined by minima of F , then we have

$$\frac{\partial F}{\partial P} = 0 \tag{2}$$

This eqaution give the expression for electric field as a non linear function of polarization P

$$E = aP + bP^3 + cP^5 \tag{3}$$

We can determine linear dielectric susceptibility by differentiating this equation with respect to P for zero polarization, we get

$$\chi = \frac{P}{E} = \frac{1}{a} \tag{4}$$

It is assumed that states are in the vicinity of phase transition (i.e. Curie point, T- T_0)

$$a = a_0(T - T_0) \tag{5}$$

from above two equations we will get

$$\chi^0 = \frac{1}{a_0(T - T_0)} \tag{6}$$

With the change in temperature in vicinity of phase transition 'a' changes its sign, phase transitions of ferroelectric depend upon sign of the coefficient in free energy expansion (eq. 1).
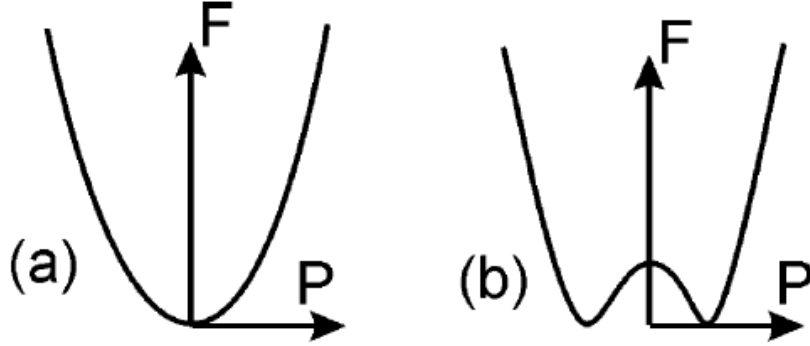

Figure 1: Free energy as a function of polarization for (a) a paraelectric state and (b) a ferroelectric state.

Now we have general expression for free energy along with temperature dependent coefficient

$$F = \frac{1}{2}a_0(T - T_0)P^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 - EP \tag{7}$$

where a_0 and c are both positive quantities in all known ferroelectric properties. Figure (1) shows Free energy as a function of polarization in paraelectric (T> T_0) and the ferroelectric (T< T_0) phases. Transformation of free energy from paraelectric to ferroelectric state can be seen by the sign of coefficient 'b',its sign will determine the nature of the paraelectric–ferroelectric transition.

3.2 Second-Order phase transition

If b> 0, second order transition occurs at transition temperature. The free energy will evolve continuously as a function of decreasing temperature i.e. from first schematic ($P = 0$) in Fig.(1) to the second schematic, that has minima at finite polarizations $P = \pm P_0$.

Spontaneous polarization can be obtained by putting E= 0. Since all coefficients are positive, we can neglect sixth and higher power of P.

$$P_0 = \left\{ \frac{a_0}{b}(T_0 - T) \right\}^{\frac{1}{2}} \tag{8}$$

Dielectric susceptibility can be written as

$$\chi_0 = \frac{1}{a_0(T - T_0)} \tag{9}$$

From Fig(2), We can see easily, with decreasing temperature spontaneous polarisation increases in vicinity of phase transition, χ_{-1}(dielectric stiffness) vanishes at $T = T_0$ and the dielectric suseptibility diverges.
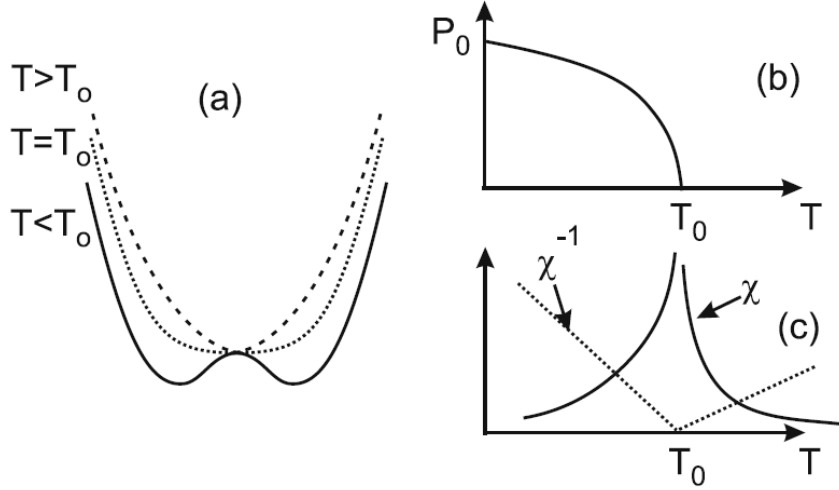
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Figure 2: Second-order phase transition. (a) Free energy as a function of the polarization at $T > T_0$, $T = T_0$ and $T < T_0$, (b) Spontaneous polarization $P_0(T)$ as a function of temperature, (c) The susceptibility χ and its inverse is evaluated at the equilibrium polarization $P_0(T)$

3.3 First-Order phase transition

If it happens to be b< 0, first order phase transition occurs at particular temperature T_c. In this phase transition, order parameter varies discontinuously at T_c which leads to spontaneous polarisation and dielectric susceptibiliy does not vanish at T_0.
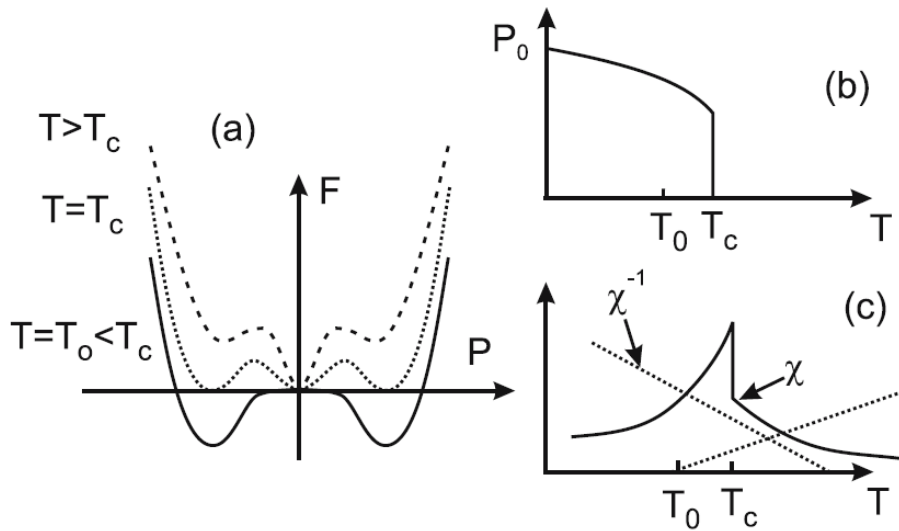

Figure 3: First-order phase transition. (a) Free energy as a function of the polarization at $T > T_c$, $T = T_c$ and $T = T_0 < T_c$, (b) Spontaneous polarization $P_0(T)$ as a function of temperature, (c) Susceptibility

The temperature at which this happens is Curie temperature T_c, which however now exceeds T_0. At

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any temperature between T_c and T_0 the unpolarized phase exists as a local minimum of the free energy. The procedure for finding the spontaneous polarization and the linear dielectric susceptibility is the same as its done earlier, but now we cannot neglect the sixth-order term. We then find dielectric stiffness does not vanish at T_0 and also find finite jump in both the susceptibility and the spontaneous polarization at the transition in Fig(3).

4   Landau-Ginzburg Theory

Ferroelectric materials are very sensitive to electromechanical boundary conditions due to the long-range nature of their underlying electrostatic interactions and to the strong coupling between the polarization and the strain. Thus, the influence of surfaces and other boundary conditions on their collective behavior is very pronounced. Possessing these, one can alter the ferroelectric behaviour of the material depending upon external environment through applied boundary conditions. This theory explains the ferroelectric behavior at small size scale with certain applied boundary condition. Because of reduced coordination number at a free surface compared to the bulk, we can expect the average polarization to display altered behavior at the boundary that could lead to changes in its overall thermodynamic behavior. Landau–Ginzburg approach assumes that the free energy can be expressed as a polynomial expansion of the average polarization, as finite-size effects become increasingly important.

4.1   Depolarisation effect

Consider a geometry where the polarization is normal to the boundary, it is expected, free surface charge to be increased, if it remains uncompensated and results into depolarizing electric field E_d. It is energetically difficult for the material sample to sustain its uniform polarization.The depolarization field increases with decreasing film thickness, its importance increases with reduced size must be included in phenomenological description of such finite-size ferroelectric systems. These depolarization effects can be significantly reduced by the presence of metal electrodes that provide charge compensation at the ferroelectric boundaries. Depolarisation effect contributes significantly to the free energy of the sample.

4.2   Misfit Epitaxial strain

The thermodynamic behaviour of a ferroelectric film is also sensitive to mechanical boundary conditions due to the strong coupling between the polarization and the strain. Application of pressure, both hydrostatic and biaxial, is known to affect the transition temperature of bulk perovskite ferroelectrics. Homogeneous epitaxial strain associated with substrate–film lattice mismatch has been included in a Landau free energy, this approach results in strain-induced shifts in the transition temperature and the spontaneous polarization whose signs depends on details of specific elastic compliances and electrostrictive constants. The elastic free energy takes the form,

$$F_e = \frac{u_m^2}{s_{11} + s_{12}} + \frac{2u_m Q_{12}}{s_{11} + s_{12}} + \frac{Q_{12}}{s_{11} + s_{12}} \tag{10}$$

where u_m is misfit strain, Q_{ij} is electrostriction tensors and s_{ij} are components of elastic compliance tensors. Misfit epitaxial strain can change the nature of the transition from first to second order. Some other effects can also be added to the contribution of free energy of ferroelectric film with boundary conditions.

5 Ferroelectric superlattices

In [2], they considered ferroelectric superlattice containing multilayer thin films of $PbTiO_3/SrTiO_3$ sandwiched between electrode with short-circuited boundary condition grown in substrate. These multilayer consists of alternative layers of $PbTiO_3$(typeA) and $SrTiO_3$(type B) having thickness d_A and d_B with length periodicity of superlattice (d_A+d_B). Total thickness of multilayer thin film L is large compared to its periodicity. Consider all vector fields are directed in z- direction to simplify the calculation.
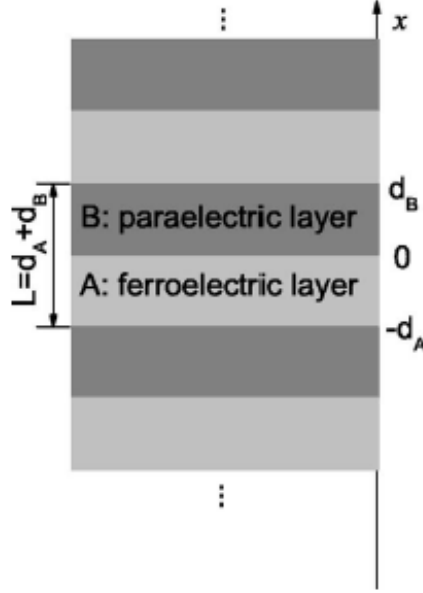

Figure 4: Arrangement of ferroelctrics A and B in a superlattice.

Investigation done by transmission electron microscopy (TEM) revealed excellent quality in superlattices with layers of $SrTiO_3$ thinner than 5 unit cells, though beyond this thickness the quality of the $SrTiO_3$ layers deteriorated with thickness (more likely due to low temperature). On the other hand, samples processed with higher temperatures found to be of lower quality, most likey because of lead losses from the $PbTiO_3$. Fig (5) shows TEM image of ferroelectric superlattices.

5.1 Susceptibility

The total dielectric susceptibility of ferroelectrics can be written in form of linear and non linear parts [4].

$$\chi^T = \chi^b + \left(\frac{\partial \chi^T}{\partial E}\right)_{\sigma,T} E + \left(\frac{\partial \chi^T}{\partial \sigma}\right)_{E,T} \sigma + \left(\frac{\partial \chi^T}{\partial T}\right)_{E,\sigma} T + \{higher order non-liniearities\}$$

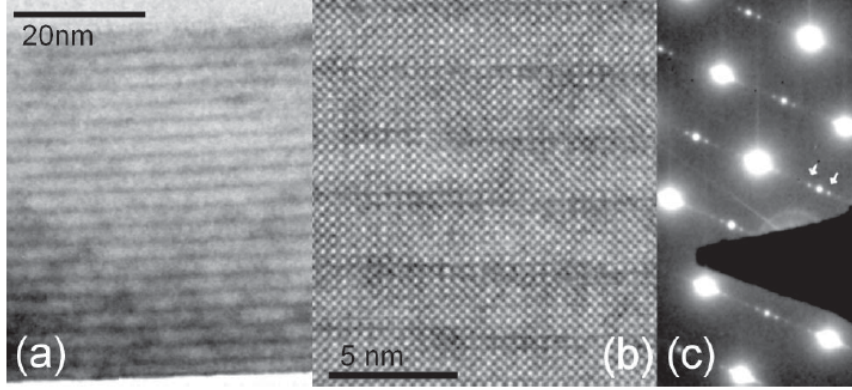$$= \chi^b + \chi(T, E, \sigma)$$

(11)

Figure 5: Cross-sectional TEM images of a 20 bilayer $PbTiO_3/SrTiO_3$ (a) Bright field image shows layering of the structure. (b) HRTEM shows the crystalline structure of the material. (c) Diffraction image demonstrating superlattice periodicity[3].

This shows dependence on Temperature $\mathbf{T}$, stress σ and electric field $\mathbf{E}$ through non-linear component of χ.

Non-linear term, which measures how applied electric field affected polarisation and total dielectric susceptibility can be calculated from equation (7). For $T > T_c$

$$\chi^T = \frac{\alpha_0}{(T - T_c)} + \chi_b \tag{12}$$

For $T < T_c$

$$\chi^T = \frac{\alpha_0}{2(T - T_c)} + \chi_b \tag{13}$$

where χ_b is the background susceptibility and should be determined experimentally. The schematic of equation is shown in fig (5). Total susceptibility in the limit of temperature far from transition temperature
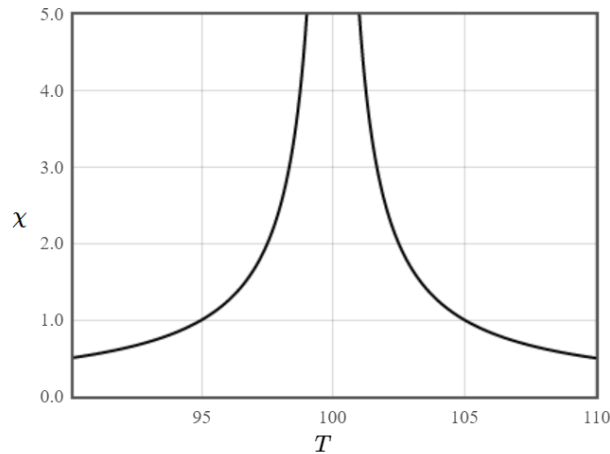

Figure 6: Dielectric susceptibility as a funcion of temperature.

is equivalent to background susceptibility of the sample.

5.2   Formulation of free energy

We consider ferroelectric superlattices structure made from multi-layered thin films sandwiched between electrodes under short-circuit boundary condition and grown on a substrate. In Spontaneous Polarisation as Ordered parameter approach, depolarization field E_{di} in layers are related to P_i in absence of external electric field, can be formulated using maxwell equations.

$$E_{dA} = -\frac{1}{\epsilon_{bA}}(P_A - <P>) \tag{14}$$

$$E_{dB} = -\frac{1}{\epsilon_{bB}}(P_B - <P>) \tag{15}$$

where

$$<P> = \frac{1}{L}\int_{-d_A}^{d_B} P dz$$

and ϵ_{bi} are background dielectric constant of ith layer.

The total free energy of a superlattice includes the bulk free energy, elastic energy, electrostatic energy as well as gradient energy, total free energy per unit volume for one period of superlattice can be written in the form $F = F_A + F_B + F_I$, where F_A and F_B are free energy for each of layer and F_I is free energy resulting from interfacial coupling [5]. F_A and F_B can be approximated using Landau-Ginzburg expansion from spatial dependence of P and is given by

$$F_A = \int_{-d_A}^{0}\left[\frac{1}{2}\alpha_A P_A{}^2 + \frac{1}{4}\beta_A P_A{}^4 + \frac{1}{6}c_A P_A{}^6 + \frac{D_A}{2}\left(\frac{\partial P_A}{\partial z}\right)^2 + \frac{1}{2\epsilon_{bA}}(P_A{}^2 - <P>^2) + \frac{u_{mA}{}^2}{S_{11A} + S_{12A}}\right]dz$$
$$+ \frac{D_A}{2\delta_{BA}}[P_A{}^2(0) + P_A{}^2(-d_A)] - \frac{\xi}{2}[P_A(0).P_B(0) + P_A(-d_A).P_A(d_B)]$$
$$\tag{16}$$

$$F_B = \int_{0}^{d_B}\left[\frac{1}{2}\alpha_B P_B{}^2 + \frac{1}{4}\beta_B P_B{}^4 + \frac{1}{6}c_B P_B{}^6 + \frac{D_B}{2}\left(\frac{\partial P_B}{\partial z}\right)^2 + \frac{1}{2\epsilon_{bB}}(P_B{}^2 - <P>^2) + \frac{u_{mB}{}^2}{S_{11B} + S_{12B}}\right]dz$$
$$+ \frac{D_B}{2\delta_B}[P_B{}^2(0) + P_A{}^2(d_B)] - \frac{\xi}{2}[P_B(0).P_A(0) + P_B(d_B).P_A(-d_A)]$$
$$\tag{17}$$

where α_A, β_A, α_B and β_B are renormalised Landau coefficients and can be written as

$$\alpha_A = a_{0A}(T - T_{c0A}) - \frac{2Q_{12A}u_{mA}}{S_{11A} + S_{12A}}$$

$$\beta_A = b_A + \frac{Q_{12A}{}^2}{S_{11A} + S_{12A}}$$

$$\alpha_B = a_{0B}(T - T_{c0B}) - \frac{2Q_{12B}u_{mB}}{S_{11B} + S_{12B}}$$

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$$\beta_B = b_B + \frac{Q_{12B}^2}{S_{11B} + S_{12B}}$$

where a_{0i}, b_i and c_i are expansion coefficient of free energyof layer i. Q_{12i} are electrostatic tensors. S_{11i} and S_{12i} are component of elastic tensor and u_{mi} are misfit strains between layers. ξ is short ranged coupling constant strength between layer A abd B and Δ_i are extrapolation length.

Now, the dynamic polarization distribution for a given temperature can be obtained in terms of free energy by solving time-dependent Ginzburg Landau equation [6] and is given by

$$\frac{\partial P_i(z,t)}{\partial t} = -L \frac{\partial F}{\partial P_i(z,t)} \tag{18}$$

L is kinetic coefficient related to domain wall mobility and polarisation distribution which describes time delay in evolution of polarization fields and can be written for both the layers as

$$\frac{\partial P_A(z,t)}{\partial t} = -L_A[\alpha_A P_A + \beta_A P_A{}^3 + c_A P_A{}^5 - D_A\left(\frac{\partial^2 P_A}{\partial z^2}\right) + \frac{1}{\epsilon_{bA}}(P_A - <P>)] \tag{19}$$

$$\frac{\partial P_B(z,t)}{\partial t} = -L_B[\alpha_B P_B + \beta_B P_B{}^3 + c_B P_B{}^5 - D_B\left(\frac{\partial^2 P_B}{\partial z^2}\right) + \frac{1}{\epsilon_{bB}}(P_B - <P>)] \tag{20}$$

Assuming, PTO and STO layers formed coherent interface, interfacial effects in equation (16) and (17) can be approximated and replaced by boundary conditions,

$$\begin{aligned}
\left[\frac{\partial P_A(z,t)}{\partial z}\right]_{z=-d_A} &= \frac{P_A(-d_A,t)}{\delta_A} - \frac{\xi P_B(d_B,t)}{D_A} \\
\left[\frac{\partial P_A(z,t)}{\partial z}\right]_{z=0^-} &= -\frac{P_A(0,t)}{\delta_A} + \frac{\xi P_B(0,t)}{D_A} \\
\left[\frac{\partial P_B(z,t)}{\partial z}\right]_{z=d_B} &= -\frac{P_B(d_B,t)}{\delta_B} + \frac{\xi P_A(-d_A,t)}{D_B} \\
\left[\frac{\partial P_B(z,t)}{\partial z}\right]_{z=0^+} &= \frac{P_B(0,t)}{\delta_B} - \frac{\xi P_A(0,t)}{D_B}
\end{aligned} \tag{21}$$

The above boundary condition equations can be obtained by considering interfacial coupling energy term into the free energy and then minimizing the free energy of the interface structure under applied electric field. Polarisation and susceptibility can be obtained by solving above reduced Landau-khalatnikov equation using finite differences method.

5.3 Polarisation and Susceptibility

The intrinsic average polarization and dielectric susceptibility was seen as a function of thickness and the spatial dependence of the polarisation and dielectric susceptibility for both symmetric and asymmetric superlattices. To be more precise to predict the polarisation, we need to consider effects of interfacial coupling and electrical conductivity. Different parameters assumed to be taken simple integer value in order to get the schematic of the polarisation and susceptibility which are shown in figure below [7] .
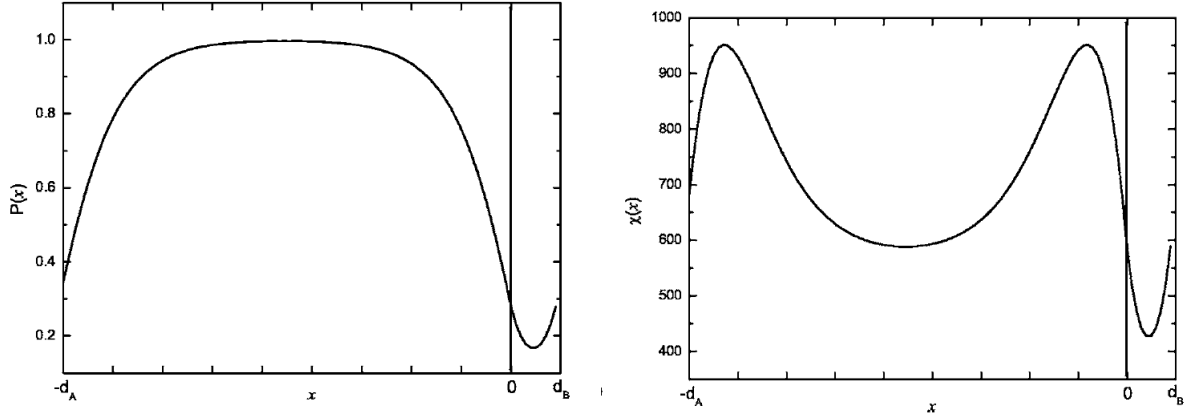
(a) Spatial dependence of polarization for an asymmetric (b) Dielectric susceptibility for an asymmetric ferroelectric-paraelectric superlattice ferroelectric-paraelectric superlattice

Figure shows the spatial variation of polarization (a) and dielectric susceptibility (b) of an asymmetric ferroelectric-paraelectric superlattice ($d_A \neq d_B$) with a larger local interaction coefficient and stronger interfacial coupling strength by taking electrical conductivity into account.

The interfacial coupling leads to the inhomogeneity of polarization across the interface between the ferroelectric and paraelectric layers. The interface structure in the ferroelectric-paraelectric superlattice corresponds to the region near the interface between the ferroelectric and paraelectric layers in which the inhomogeneity of polarization took place. This type of structure inherits a feature that the polarization of the ferroelectric layer near the interface is suppressed and there is induced polarization near the interface of the paraelectric layer. With increasing coupling strength, this induced polarization is enhanced, and the polarization profile near the interface is more bent. Similarly, the interfacial coupling leads to an enhancement of the local dielectric response near the interface. The enhancement of the local dielectric susceptibility near the interface is increased with increasing interfacial coupling strength. Infact, enhancement of local dielectric susceptibility is significantly greater in ferroelectric than paraelectric layer.

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6 Discussion

This report includes basic concepts to ferroelectric theory and modelling of different ferrroelectric system from bulk to multi-layered thin film. I tried to understand the behaviour of critical properties of ferroelectric superlattice with variation of thickness and temperature, in the vicinity of transition phase. This can be understood by example which has been taken in this report $PbTiO_3/SrTiO_3$ superlattices. Material constants and parameters in eq.(12) and eq.(13) are well known experimentally. I have taken data from different references to understand the methodology.
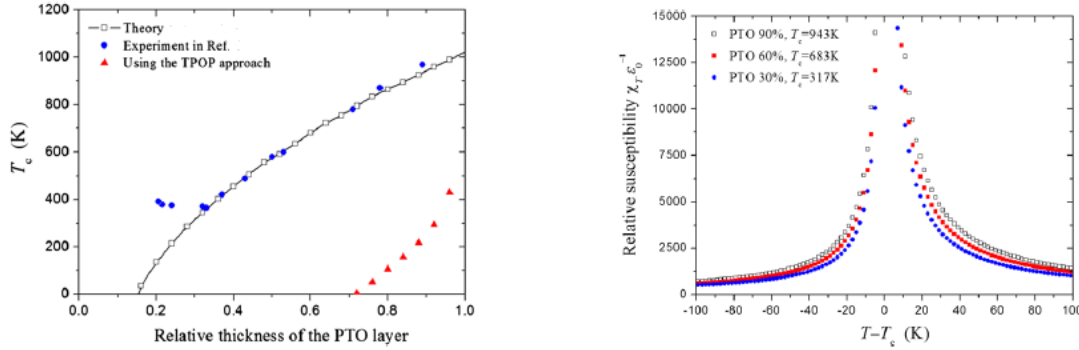
(a) Transition temp as a function of relative thickness of (b) Curie-Weiss type relatio of PTO/STO superlattice PTO and STO in PTO/STO superlattice.   with different relative thickness of PTO layer for L=10nm

Figure(a) (from [8]) shows that phase transition temperature increases with increase in relative thickness of PTO layer in PTO/STO superlattice. It is clearly seen that approach of Total polarization as order parameter shows a significant deviation from first principle calculation, but approach using spontaneous polarization as order parameter are in good approximation with first principle calculation.

Figure (b) shows that average relative susceptibility as a function of $(T-T_c)$, where depends upon relative thickness of PTO in supperlattice. In limit T$\to \infty$, susceptibility reduces to background suscepebility .

Figure (3) from [8] shows total average polarization as a function of ratio of thickness of layers in superlattice PTO/STO. From first principle calculation [3], n_s is kept constant at a value of3 and n_p is varied from 1to48. Curve from SPOP approach is in good approximation and again TPOP approach shows a significant deviation in polarizaion when Relative thickness of PTO is less than ten times of STO. But there is a critical thickness limit, below it PTO/STO does not show any polarization i.e. h_A^c=1.2nm and from TPOP approach its 6.8nm which is far from actual result[8].

The average polarization of the interface-coupled superlattice will be reduced while the average susceptibility will be enhanced with increasing interfacial coupling strength. The interfacial values for polarization and susceptibility of the ferroelectric and paraelectric layer become identical when there is significant difference between thickness of superlattices layers[7] i.e, thickness of PTO is greater than that of STO. Interesting
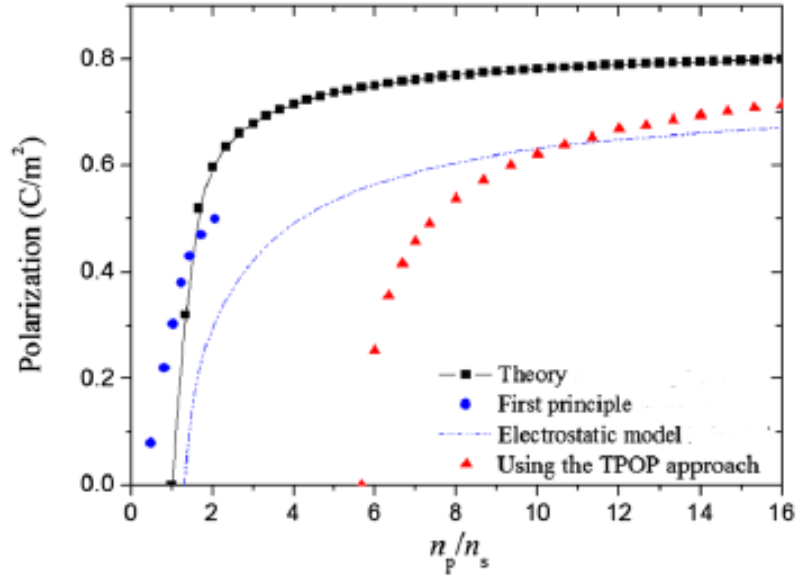
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Figure 9: The average total polarization as a function of ratio of thickness of two layers[8].

result is that, there is a better enhancement for the average dielectric susceptibility than the individual ferroelectric phase and the paraelectric phase.There are few more properties of ferroelectric superlattices which makes it matter of interest.

7   Conclusion

Different approaches discussed in report shows different results for parameters like polarization, susceptibility and phase transition temperature in ferroelectric superlattices. Spontaneous polarization as a ordered parameter explains ferroelectric superlattice system well and fitted the theorical modelling as well. Meanwhile, total polarisation as order parameter gives deviation for critical properties depending upon relative thickness in superlattices. SPOP approach results are in good approximation with the first principle calculations and experimental measurements. Interfacial interactions and depolarization field effects lead to better result in determining critical properties depending upon Relative thickness of layers in ferroelectric superlattices. Remarkable enhancement of dielectric susceptibility due to interfacial coupling makes ferroelectric superlattice more useful than any of its geometries.

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