Static and dynamic properties of ferroelectric thin film multilayers

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A thermodynamic theory of ferroelectric thin film multilayers is developed. The free energy functional is written down using a multilayer model in which c-domain layers of one ferroelectric material alternate with a-domain layers of a second ferroelectric material. We assume that the interfaces are perfectly sharp and that the polarization at these boundaries is zero. The renormalization of the free energy coefficients due to the stresses in the films and to the depolarizing field was taken into account, as well as the renormalization of the coefficients of the polarization gradients. The equilibrium inhomogeneous polarization temperature and its thickness dependence were determined from the solutions of the Euler-Lagrange equations resulting from the minimization of the free energy functional. A thickness induced ferroelectric phase transition is shown to exist and its transition temperature and critical layer thickness depend on the domain orientation. The criteria for "a/c", "c/c" and "a/a" domain multilayering are calculated and expressed via coefficients of the free energy density and the layer thickness.

The differential equation to calculate the inhomogeneous dielectric susceptibility was found to be a Lamé equation. The calculated multilayer susceptibility diverges at the transition temperature of the thickness induced ferroelectric phase. This divergence is shown to be the origin of the giant dielectric response observed in some multilayers. The theory gives an excellent fit to the temperature dependence of the giant susceptibility observed recently in multilayers of PbTiO$_3$-Pb$_{1-x}$La$_x$TiO$_3$ ($x = 0.28$). The equation determining the time and space dependence of the polarization is proposed and solved. The calculated dispersion law for the nonlinear polarization waves in multilayer structures reveals a critical wave vector for a given layer thickness, or a critical layer thickness for a given wave vector, for which the frequency $\omega = 0$. The frequency of the polarization waves is also shown to increase with layer thickness.

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I. INTRODUCTION

Artificial thin film multilayers composed of alternating layers of different materials have been the subject of study for many years. Much attention has been devoted to semiconducting [1], metallic [2], magnetic [3] and superconducting [4] multilayer structures. Increasingly frequent investigations of ferroelectric oxide multilayers are now taking place due to their technological promise: the artificial modification of structural and physical properties for use in dielectric capacitors, memory systems, pyroelectric detection and other types of devices makes them technologically attractive (see e.g. [5,6] and references therein), and there is also a basic interest in creating model structures for which to study fundamental questions related to ferroelectricity on increasingly smaller length scales. Recent experiments have revealed many unusual properties, such as giant dielectric response [7], anomalies in the ferroelectric-paraelectric phase transition temperature [8], in superlattice growth [9], and in superlattice structural anomalies [10]. In the latter work, investigation of PbTiO$_3$/BaTiO$_3$ (PT/BT) multilayers with bilayer PT/BT thickness between 50Å < $\Lambda$ < 360Å [10] shows that "c"-domain BT layers alternate with "a"-domain PT layers. This is in contrast both to the "c"-domain structure exhibited by thin single PT films of the same thickness grown on the same substrate. Raman spectra measurements reinforce this x-ray determined orientational anomaly in addition to revealing the existence of a superlattice wavelength dependent mode, whose frequency increases with increasing $\Lambda$. Up to now there have been few theoretical studies of ferroelectric multilayer structures. Calculation of the dielectric response has shown [11] that the spatial distribution of the layer thickness can lead to enhanced dielectric properties over a broad temperature range. A phenomenological theory has recently been developed [12] for thin film multilayers. The spontaneous polarization and
the dielectric susceptibility were calculated numerically with parameters appropriate to PT/BT. They showed that a thickness induced ferroelectric phase transition occurs only when the strength of the interfacial coupling is weak.

In this work we will consider a multilayer built up from alternating (100) and (001) ferroelectric thin films (such as PbTiO\textsubscript{3} and BaTiO\textsubscript{3}) epitaxially grown in the cubic paraelectric phase onto a cubic (001) substrate. We use a thermodynamic approach to describe the static and dynamic multilayer properties. The static properties are considered in section II in which section IIA is devoted to the description of the free energy of a multilayer with contributions coming from the internal stresses and the depolarizing field. Calculations of the inhomogeneous polarization and the thickness induced ferroelectric phase transition are performed in IIB. The criterion for the presence of "a/c", "a/a" or "c/c" layer structures in the superlattice is determined in IIC. The differential equation giving the static dielectric susceptibility of multilayers is considered in IID. The dynamic properties are treated in Section III. In IIIA the differential equation governing the time and space dependence of the polarization is written down and solved, and in IIIB the dispersion law for nonlinear waves formed by the polarization in the multilayer is reported. In the Discussion we show that the theory is in good agreement with the observed giant dielectric response in PLT/PT ferroelectric multilayers and in the Conclusion we discuss the applicability of our results and their future development. The Appendices contain the detailed calculations of (1) the criteria for "a/c", "a/a" and "c/c" layer structure of the superlattice, (2) the solution of the differential equation for the inhomogeneous dielectric susceptibility, (3) the multilayer susceptibility, (4) the value of the susceptibility for the thick film ferroelectric phase and for the thin film paraelectric phase, and (5) the Curie-Weiss law in the vicinity of the thickness induced ferroelectric phase transition.

II. STATIC PROPERTIES

A. Free energy

We consider a multilayer (see Figure 1) built up from "A" and "B" ferroelectric layers extending from \( z = -L/2 \) to \( L/2 \). Each layer has thickness \( l_i \) \( (i = A, B) \) so that the total multilayer thickness is \( L = N(l_A + l_B) \) where \( \Lambda = (l_A + l_B) \) is the multilayer wavelength and \( N \) is the number of wavelengths in the superlattice. The free energy of the multilayer system can be written as

\[
\Phi = \frac{1}{L} \int_{-L/2}^{L/2} \left( \Phi_A(z) + \Phi_B(z) + \Phi_{A,B}(z) \right) dz \tag{1}
\]

where \( \Phi_A \) and \( \Phi_B \) are the free energy densities of the \( A \) layers and the \( B \) layers respectively and \( \Phi_{A,B} \) is the free energy density resulting from the interaction between the layers.

We will start with the following forms for \( \Phi_A \) and \( \Phi_B \), which can be obtained from those free energies having cubic symmetry, and which allows for the symmetry lowering that is related to the nonequivalence of the \( z \) and the \( x, y \) polarization components in the film due to the contribution of the mechanical strains and to the depolarizing field. These effects are incorporated into the renormalized coefficients.

\[
\Phi_A = a_3 P_{Az}^2 + a_1 P_{Ax}^2 + P_{Ay}^2 + a_{11}(P_{Ax} + P_{Ay}) + a_{33} P_{Az} + a_{33} \left( \frac{\partial P_{Az}}{\partial z} \right)^2 + a_{11} \left( \frac{\partial P_{Ax}}{\partial x} \right)^2 + \left( \frac{\partial P_{Ay}}{\partial y} \right)^2 + \left( \frac{\partial P_{Az}}{\partial z} \right)^2 + \left( \frac{\partial P_{Az}}{\partial x} \right)^2 + \left( \frac{\partial P_{Ay}}{\partial y} \right)^2 + \left( \frac{\partial P_{Az}}{\partial z} \right)^2 \tag{2a}
\]

\[
\Phi_B = b_3 P_{Bz}^2 + b_1 P_{Bx}^2 + P_{By}^2 + b_{11}(P_{Bx} + P_{By}) + b_{33} P_{Bz} + b_{33} \left( \frac{\partial P_{Bz}}{\partial z} \right)^2 + b_{11} \left( \frac{\partial P_{Bx}}{\partial x} \right)^2 + \left( \frac{\partial P_{By}}{\partial y} \right)^2 + \left( \frac{\partial P_{Bz}}{\partial z} \right)^2 \tag{2b}
\]

Since we wish to take into account the change of \( P_{x,y} \) along the \( z \) direction, we have incorporated the additional gradient terms \( \partial P_{x,y}/\partial z \) into Eqs. (2).

Equations (2a) and (2b) correspond to the general case in which the \( x,y \), and \( z \) polarization components exist in both the \( A \) and in the \( B \) layers. Experimental data for multilayers usually show that \( c \)-domain layers alternate with \( c \)-domain layers, but recent experimental results on PbTiO\textsubscript{3}/BaTiO\textsubscript{3} multilayers have shown that \( c \)-domain BT layers alternate with \( a \)-domain PT layers in the multilayer structure. In order to be able to treat this interesting latter case we will assume that the \( A \) layers consist only of \( c \)-domains (i.e. \( P_A = P_{Ax}, P_{Ax} = P_{Ay} = 0 \)) while the \( B \) layers consist only of \( a \)-domains (i.e. \( P_{Bx} = P_{By} \neq 0, P_{Bz} = 0 \)). The variation of the polarization in the \( A \) and \( B \) layers in the vicinity of the \( z = 0 \) boundary is schematically depicted in Figure 2 in which the natural boundary condition for this configuration is \( P_{Ax}(z = 0) = P_{Bx}(z = 0) = 0 \). Since Fig. 2 represents one modulation period of the superlattice, this same boundary condition must be valid for all the interfaces that make up the multilayer structure, namely

\[
\Phi = \frac{1}{L} \int_{-L/2}^{L/2} \left( \Phi_A(z) + \Phi_B(z) + \Phi_{A,B}(z) \right) dz \tag{1}
\]
\[ P_{Az}(z_j) = P_{Bz}(z_j) = 0, \quad (3) \]

\[ z_j = - \frac{L}{2} + 2j l_{AB}; \quad z_j = - \frac{L}{2} + (2j + 1) l_{AB}; \]

\[ j = 0, 1, 2...N - 1. \]

The superlattice periodicity also implies the following periodic polarization condition,

\[ P_{Az}(z + j(l_A + l_B)) = P_{Az}(z) \]
\[ P_{Bz}(z + j(l_A + l_B)) = P_{Bz}(z) \quad (4) \]

Note that even in the case of a "c-domain/c-domain" or a "a-domain/a-domain" multilayer structure, zero polarization at the boundaries would be the most probable since the situation at the interfaces is physically similar to that of domain boundaries in bulk ferroelectrics.

We will, in this work, neglect the interaction energy term \( \Phi_{AB} \) due to the polarization interaction between the layers since this interaction decays rapidly, and because of the boundary conditions, we will also neglect any surface energy contributions. Hence we can rewrite the free energy density (2) equations as

\[ f_A = a_3 P_{Az}^2 + a_{33} P_{Az}^{4} + \alpha_{33} \left( \frac{dP_A}{dz} \right)^2 \quad (5a) \]

\[ f_B = 2b_1 P_{Bz}^2 + 2b_{11} P_{Bz}^{4} + 2\beta_{44} \left( \frac{dP_B}{dz} \right)^2 \quad (5b) \]

In Eqs.(5) we have conserved what is most essential for the analysis of thin film multilayers: the gradient terms which take into account the polarization change along the \( z \) direction (see Fig.2). Thus, in our model, the free energy density \( f(z) = f_A(z) + f_B(z) \) will replace \( \Phi_A(z) + \Phi_B(z) + \Phi_{AB}(z) \). The most important feature of the free energy density of thin films is its dependence on \( z \). In the most general case both the polarization \( P \) and the mechanical stresses \( \sigma \) can be inhomogeneous so that their gradients \( P' \) and \( \sigma' \) should also be taken into account. Because of this, the free energy \( \Phi \) is a functional of \( P, P', \sigma, \sigma' \), which we will write as:

\[ \Phi(P, \sigma) = \int_{-L/2}^{L/2} f(P(z), P'(z), \sigma(z), \sigma'(z)) dz \quad (6) \]

where, for the sake of clarity, we have omitted the vector and tensor component notation.

The equilibrium values of polarization and stresses or strains must then satisfy the Euler-Lagrange equations [3]

\[ \frac{\partial f}{\partial P} - \frac{d}{dz} \frac{\partial f}{\partial P'} = 0 \quad (7a) \]

\[ \frac{\partial f}{\partial \sigma} - \frac{d}{dz} \frac{\partial f}{\partial \sigma'} = 0 \quad (7b) \]

with the corresponding boundary conditions for \( P, \sigma, P', \sigma' \). Note that Eqs. (7a) and (7b) can be written for all components of \( P_i \) and \( \sigma_{ij} \) respectively.

In what follows we will calculate \( P(z) \) on the basis of Eq.(7a) and \( \sigma \) from first term in Eq.(7b) because we will here make the simplifying assumption that the interfacial stresses are homogeneous and so we will neglect the second term in Eq. (7b). For films, the coefficients of Eq. (2) are renormalized coefficients. The stresses as well as the depolarizing field act on the coefficients of the free energy of cubic symmetry. In general the thickness of the substrate is much larger than that of the multilayer structure. Taking this into consideration for the equilibrium condition of the mechanical forces, it can be shown [14] that the stresses induced by upper layers in the underlying films are negligibly small. Thus the nonzero stresses are \( \sigma_{xx} = \sigma_{yy} \) and \( \sigma_{xy} = 0 \) while \( \sigma_{zz} = \sigma_{xz} = \sigma_{yz} = 0 \) because of the existence of the unstressed free surface on top of the multilayer. The renormalization of the free energy coefficients \( a_i, a_{ij}, (i, j, k - \text{Voigt notation}) \) of bulk cubic symmetry by these stresses was previously performed [13] for a single thin film on a cubic substrate. Using the results of [13] along with the depolarizing field contribution, the coefficients \( a_3 \) and \( a_1 \) in Eq.(2a) can be written as:

\[ a_3 = a - \frac{2Q_{12}^A}{S_{11}^A + S_{12}^A} + \frac{2\pi}{\varepsilon_A} \quad (8a) \]

\[ a_1 = a - \frac{Q_{11}^A + Q_{12}^A}{S_{11}^A + S_{12}^A} \quad (8b) \]

Here \( a = a_0^A(T - T_{c0}^A) \), \( T_{c0}^A, Q_{ij}^A \) and \( S_{ij}^A \) are respectively the coefficients of the free energy, the ferroelectric phase transition temperature, the electrostriction constants and the elastic modulus of the \( A \) material. The strain \( X = X_1 + X_2 \) can be represented as

\[ X = X_{mf} + X_{th} + X_{dis} \quad (8c) \]

where \( X_{mf} = (b - a)/\alpha, X_{th} = (\alpha_B - \alpha_A)(T - T_g) \) and \( X_{dis} \) are respectively the misfit, thermal and disorder induced strains. In these expressions, \( b \) and \( a \) are the cubic lattice constants, \( \alpha_A \) and \( \alpha_B \) are the thermal expansion coefficients of the two materials in the cubic bulk phase and \( T_g \) is the growth temperature. We point out that the relaxation processes related to misfit dislocations, domain structure appearance and impurity diffusion processes can decrease \( X \), but full relaxation can only be achieved in bulk materials [17]. The last term in Eq.(8a) originates from the depolarizing field \( E_d \) whose contribution equals to \(-1/2E_dP_{Az}\) with \( E_d = -4\pi P_{Az}/\varepsilon_A \) for a free standing film without electrodes (\( \varepsilon_A \) is the dielectric
constant of the A material [18]). The renormalized coefficients in Eq.(2b) can be simply obtained from Eqs.(8) by the substitution \( a_3 \rightarrow b_3, a_1 \rightarrow b_1 \) and the index A \( \rightarrow \) B.

The renormalization of the transition temperature in the layer follows from Eqs.(8) and its analog for the B layer. For the A and B layers the transition temperatures can be written as:

\[
T_{e_x}^{A,B} = T_{e_x}^{A,B} + \frac{X^{A,B}2Q_{12}^{A,B}}{a_0^{A,B}(S_{21}^{A,B} + S_{22}^{A,B})} - \frac{2\pi}{a_0^{A,B} \varepsilon_{A,B}} \quad (9a)
\]

\[
T_{e_x}^{A,B} = T_{e_x}^{A,B} + \frac{X^{A,B}(Q_{11}^{A,B} + Q_{12}^{A,B})}{a_0^{A,B}(S_{11}^{A,B} + S_{12}^{A,B})} \quad (9b)
\]

where \( T_{e_x} \) and \( T_{e_x} \) are respectively the transition temperatures for the appearance of \( \sigma_3 \neq 0 \) (c-domain structure) and \( \sigma_3 = 0 \) (c-domain structure). It is seen that the depolarizing field contribution decreases the transition temperature of the c-domain layer whereas the influence of strain on this transition depends on the signs of the electrostrictive constants and whether the strains are tensile (\( X > 0 \)) or compressive (\( X < 0 \))[17].

We have omitted terms to the sixth power and above in the polarization, which is the correct procedure only for second order ferroelectric phase transitions. In general, bulk ferroelectric materials such as BaTiO\(_3\) and PbTiO\(_3\) undergo first order phase transitions, but calculations on BaTiO\(_3\) and PbTiO\(_3\) thin films have shown [16] that the renormalized coefficients of \( P_4^3 \) and \( P_4^3 \) have positive values and thus the ferroelectric thin film transition is second order rather than first order. For this reason we consider the free energy forms (2) and (5) to be those appropriate for multilayer films.

To the best of our knowledge there has been no consideration of how the stresses will renormalize the coefficients of the gradient terms in the free energy of cubic symmetry. We have performed calculations similar to those in [16], for which we have added the additional term \( \Delta F \) to the cubic symmetry free energy contained in Ref.16:

\[
\Delta F = \gamma \left[ \left( \frac{\partial P_x}{\partial x} \right)^2 + \left( \frac{\partial P_x}{\partial y} \right)^2 + \left( \frac{\partial P_y}{\partial y} \right)^2 \right] - \delta_{111} \left[ \left( \frac{\partial P_x}{\partial x} \right)^2 + \left( \frac{\partial P_y}{\partial y} \right)^2 \right] + \delta_{114} \left[ \frac{\partial P_z}{\partial x} \right]^2 + \left( \frac{\partial P_z}{\partial y} \right)^2 \right] \sigma_1,
\]

where \( \sigma_1 = \sigma_{xx} = \sigma_{yy} \neq 0 \) is the nonzero homogeneous stress in the film. Minimization of the free energy with respect to \( \sigma_1 \) gives the renormalized coefficients:

\[
\alpha_{33} = \gamma - \frac{X\delta_{133}}{S_{11} + S_{12}}
\]

\[
\alpha_{44} = -\frac{X\delta_{144}}{S_{11} + S_{12}}
\]

Obviously, the same relations hold for the free energy and the \( \beta \) coefficients of the B material. The parameters \( \gamma, S_{ij}, \delta_{ijk} \) are material parameters. The coefficient \( \alpha_{44} \) is proportional to \( X \), i.e. \( \alpha_{44} \neq 0 \) in films having nonzero homogeneous strain \( X \) (8c). The coefficients \( \delta_{ijk} \) are components of a sixth rank tensor which is the lowest rank (and so having the largest components) which will relate the squared gradient terms and the components of the stress tensor.

### B. Polarization

The Euler-Lagrange equation (7a) with \( f = f_A + f_B \) (see Eqs.(5)) for \( P = P_{Az} \) or \( P_{Bx} \) and \( P' = (dP_{Az})/(dz) \) or \( (dP_{Bx})/(dz) \) makes it possible to find the equilibrium values of the polarization on the basis of the equations:

\[
a_3P_{Az} + 2a_{33}P_{Az}^3 - \alpha_{33}(d^2P_{Az}/dz^2) = 0 \quad (12a)
\]

\[
b_1P_{Bx} + 2b_{11}P_{Bx}^3 - \beta_{44}(d^2P_{Bx}/dz^2) = 0 \quad (12b)
\]

The above equations have to be solved subject to the periodicity conditions (3) and (4). We shall demonstrate the solution for \( P_{Az} \) only, since \( P_{Bx} \) can be obtained from \( P_{Az} \) by substituting the corresponding coefficients. To integrate Eq.(12a) we let \( (dP_{Az})/(dz) = g(P_{Az}) \). This gives

\[
\frac{d^2P_{Az}}{dz^2} = \frac{g(P_{Az})}{dP_{Az}} \frac{dg(P_{Az})}{dP_{Az}} \quad (13)
\]

Substitution of Eq.(13) into (12a) leads to

\[
a_3P_{Az} + 2a_{33}P_{Az}^3 - \alpha_{33}g(P_{Az}) \frac{dg(P_{Az})}{dP_{Az}} = 0 \quad (14)
\]

which gives after integration

\[
a_3P_{Az}^4 + a_{33}P_{Az}^4 = \alpha_{33}g^2(P_{Az}) + c_{33} \quad (15)
\]

To obtain the constant \( c_{33} \) we introduce the maximum polarization in the layer \( P_{Azm} \) which satisfies the condition \( dP_{Az}/dz \bigg|_{P_{Az}=P_{Azm}} = 0 \), and we find

\[
c_{33} = a_3P_{Azm}^2 + a_{33}P_{Azm}^4 \quad (16)
\]

Substitution of Eq.(16) into Eq.(15) leads to

\[
a_3(P_{Az}^2 - P_{Azm}^2) + a_{33}(P_{Az}^4 - P_{Azm}^4) = \alpha_{33}(dP_{Az}/dz)^2 \quad (17)
\]
We now introduce the following parametrization
\[ P_{Az}(z) = P_{Azm} \sin \theta_A(z) \] (18)
\[ k^2_{Az} = \frac{P^2_{Azm}}{2P^2_{Az0} - P^2_{Azm}} \] (19)
where \( P^2_{Az0} = -a_3/(2\alpha_{33}) \) is the homogeneous polarization in a thick film - when the derivative in Eq.(12a) can be neglected. Note that this is not the polarization in the bulk material because the parameters \( a_3 \) and \( \alpha_{33} \) have been renormalized by the stresses in the layers (see Eqs.(8)). Because the homogeneous polarization corresponds to the mean field approximation, \( P_{Az0} \) can be considered as the film polarization calculated in this approximation. Substituting Eqs. (18) and (19) into (17) gives:
\[ \alpha_{33} \left( \frac{d\theta_A}{dz} \right)^2 = -\frac{a_3}{1 + k^2_{Az}} (1 - k^2_{Az} \sin^2 \theta_A) \] (20)
After separating the variables we obtain
\[ dz_3 = \sqrt{1 + k^2_{Az}} \frac{d\theta_A}{\sqrt{1 - k^2_{Az} \sin^2 \theta_A}} \]
\[ z_3 = \int_{-L_z/2 + 2jl_{Az}}^{\theta_A} \sqrt{1 + k^2_{Az}} \frac{d\theta_A}{\sqrt{1 - k^2_{Az} \sin^2 \theta_A}} \] (21)
where we have introduced the dimensionless variables
\[ z_3 = \sqrt{\frac{\alpha_3}{\alpha_{33}}} z; \quad l_{Az} = \sqrt{\frac{-a_3}{\alpha_{33}}} l_A; \quad L_z = \sqrt{\frac{a_3}{\alpha_{33}}} L \] (22)

It follows from the theory of elliptic functions that for the relation (21) the function \( \theta_A(z) \) has the form
\[ \theta_A(z_3) = \arcsin \left( \frac{z_3 + L_z/2 - 2jl_{Az}}{\sqrt{1 + k^2_{Az}}}, k_{Az} \right) \]
Hence from Eq.(18) we obtain the solution in terms of the elliptic sine function sn:
\[ P_{Az}(z_3) = P_{Azm} \sin \left( \frac{z_3 + L_z/2 - 2jl_{Az}}{\sqrt{1 + k^2_{Az}}}, k_{Az} \right) \] (23)

It can be seen that \( P_{Az}(z) \) satisfies Eq.(12a) and the periodicity conditions of Eqs.(4). \( P_{Az}(z) \) is depicted graphically in Fig.3.

The relation between \( P_{Azm} \) and \( l_{Az} \) can be found from the periodicity condition of the elliptic sine function (see [19–21]), namely
\[ \sin \left[ \frac{z_3}{2} + (2j + 1)l_{Az} \right] = 2K(k_{Az}) \] (24)
where
\[ K(k_{Az}) = \int_0^{\pi/2} \frac{d\theta}{\sqrt{1 - k_{Az}^2 \sin^2 \theta}} \]
is the complete elliptic integral of the first kind.

Substitution of (24) into (23) gives
\[ l_{Az} = 2 \sqrt{1 + k^2_{Az} K(k_{Az})} \] (25)

We plot the dependence Eq. (25) in Fig.4. Since we can write the polarization ratio as \( P^2_{Azm}/P^2_{Az0} = 2k^2_{Az}/(1 + k^2_{Az}) \) (see Eq.(19)), Fig.4 makes it possible to obtain the dependence of this ratio on the film thickness. We can see that for thick enough films (for the dimensionless length \( l_{Az} \approx 10 - 12 \) \( P_{Azm} \approx P_{Az0} \), and so this polarization ratio (see the additional scale in Fig.4) can be used as a criterion for distinguishing between thick and thin films. Moreover, Fig. 4 shows the existence of a critical layer thickness \( l_A = \pi \) such that the spontaneous polarization in the layer will exist only for \( l_{Az} \geq \pi \). Thus our calculations yield a thickness induced ferroelectric phase transition which was previously discussed for multilayer superlattices [12] and for single ferroelectric thin films [22–23].

The thickness induced phase transition temperature \( T_{cl}^A \) follows from \( l_{Az} = \sqrt{-a_0(T - T_{cl}^A)/\alpha_{33}} \) : \( l_A = \pi \alpha_{33}/a_0 \) (26a)

where \( T_{cl}^A \), the renormalized layer temperature, is given by Eq(9a). The reduced temperature \( T_{cl}^A/T_{cl}^A \) as a function of reduced thickness \( l_A/l_{Az} \) is plotted in Fig.5. The characteristic thickness \( l_A = l_{Az} \) at which \( T_{cl}^A = 0 \) is:
\[ l_{Az} = \frac{\pi}{\sqrt{a_0/T_{cl}}} \] (26b)

The Fig. 5 plot is in agreement with available experimental data on ferroelectric KNbO\(_3\)/KTaO\(_3\) superlattices for intermediate multilayer wavelengths. The range of the existence of the thickness induced phase transition is given by
\[ l_{Az} \geq l_A \leq \frac{\pi}{\sqrt{a_0(T_{cl}^A/T_{cl}^A - 1)/\alpha_{33}}} \] (26c)

with \( l_A \to \infty \) at \( T_{cl}^A \to T_{cl}^A \), the renormalized transition temperature. Below a certain thickness, \( l_A < l_{Az} \) there
is no thickness induced phase transition because $T^{A}_{cl}$ becomes negative. The thickness dependence of $T^{A}_{cl}$ (see Eq.(26a)) means that the thinner the film, the weaker its ferroelectricity.

The distribution of the polarization parallel to the multilayer growth axis, $P_{Bz}(z)$, can be obtained from (23) by simply replacing the coefficients (see (12a), (12b)):

$$a_3 \rightarrow b_1, \quad 2a_{33} \rightarrow b_{11}, \quad \alpha_{33} \rightarrow \beta_{33}$$  \quad (27)

The solution for $P_{Bz}(z)$ thus has the form

$$P_{Bz}(z_1) = P_{Bzm}sn \left[ \frac{z_1 + Lx/2 - (2j + 1)Lx}{\sqrt{1 + k^2_{Bz}}, k_{Bz}} \right]$$  \quad (28a)

$$k^2_{Bz} = \frac{P_{Bzm}^2}{2P_{Bz0}^2 - P_{Bz}^2}, \quad l_{Bz} = 2\sqrt{1 + k^2_{Bz}K(k_{Bz})}$$  \quad (28b)

where

$$z_1 = \sqrt{-\frac{b_1}{\beta_{44}}}z, \quad l_{Bx} = \sqrt{-\frac{b_1}{\beta_{44}}}l_B, \quad L_x = \sqrt{-\frac{b_1}{\beta_{44}}}L$$  \quad (29)

Fig. 3 of course also represents $P_{Bz}(z)$.

The temperature of the thickness induced ferroelectric phase transition can similarly be obtained from (26), (27) with the substitution $T^{A}_{cz} \rightarrow T^{B}_{cz}$, $a_0^A \rightarrow a_0^B$

$$T^{B}_{cl} = T^{B}_{cz} - \frac{\pi^2 \beta_{44}}{l_B^2 a_0^B}, \quad l_{B0} = \pi \sqrt{-\frac{\beta_{44}}{a_0^B T^{B}_{cz}}}$$  \quad (30)

Since the parameters in Eqs.(26) and (30) are different, the critical characteristics of the thickness induced phase transition should also be different in the A and the B layers. This may open up the prospect of engineering new multilayer materials constructed with several ferroelectric thin films (including superstructures consisting of several thin films in its unit cell) with a broad distribution of the transition temperature. This will result in a distribution of the material properties and also in any anomalous behavior, which may then be exploitable for device applications.

C. Criterion for "a/c", "c/c" and "a/a" domain structures

Up until now we have considered a multilayer built up of layers in which the polarization alternates between being in the plane of the film (a-domain layers) and perpendicular to the plane of the film (c-domain layers). This choice was motivated by the experimental results of Ref [14]. We will now look at the conditions for which this situation is energetically favorable compared to a-only or c-only layers throughout the multilayer structure (a/a and c/c layering respectively). The requirement for the a/c multilayer to occur is that the free energy should be less than that for c/c or a/a multilayers. In supposing that the A layers have "c"-domain structure, the criterion for the existence of an a/c multilayer can be written as

$$F_B(P_{Bz}) < F_B(P_{Bz})$$  \quad (31)

where $F_B$ can be obtained by integration of the free energy density (5) over $dz$ and summing over the layers. When the inequality (31) is not satisfied we will have the "c/c" domain criterion. Eq.(31) will correspond to "a/a" domain criterion if we suppose that the A layers are a-domain. To calculate $F_B(P_{Bz})$ and $F_B(P_{Bz})$ we have to substitute Eq.(23) into Eq.(5a) (with $A \rightarrow B$) and Eq.(28a) into Eq.(5b) and then perform the integration over $dz$. This integration and summation (see Appendix 1 for details) yield the following criterion for "a/c" domain structure:

$$\frac{b_3^2}{b_{33}} \varphi(k_{Bz}) < \frac{b_{11}^2}{b_{11}} \varphi(k_{Bz})$$  \quad (32)

Here

$$\varphi(k_{Bz}) = \frac{1}{(1 + k^2_{Bz})^2} \left[ \frac{1}{2}k_{Bz}^2 + 1 - f(k_{Bz}) \right],$$  \quad (33)

$$f(k_{Bz}) = (1 + k_{Bz}^2)E(k_{Bz}), \quad i = z, x,$$

where

$$E(k) = \int_0^{\pi/2} \sqrt{1 - k^2 \sin^2 \theta} d\theta$$

is the complete elliptic integral of the second kind. The function $\varphi(k)$ is calculated numerically and the results are shown in Figure 6. One can see that $\varphi(k)$ slowly increases for $0.3 \leq k \leq 0.8$ and for $1 \geq k \geq 0.8$ it changes much faster. In the scale of dimensionless thickness $l_z$ the region of slow increase corresponds to $5.5 \geq l_{z,x} \geq 3.5$. In the thick film limit ($k_{Bz} = 1$) $\varphi = 3/8$ and the criterion (32) transforms into

$$\frac{b_3^2}{b_{33}} < \frac{b_{11}^2}{b_{11}}$$  \quad (34)

This can be rewritten as

$$\frac{(T^{B}_{cz} - T)^2}{b_{33}} < \frac{(T^{B}_{cz} - T)^2}{b_{11}}$$  \quad (35)

where the transition temperatures in the thick films $T^{B}_{cz,x}$ are given by Eqs.(8). It is seen that for $T^{B}_{cz} > T^{B}_{cz}$ the preference is for a-domain orientation in the B layers (and
hence for a "c/a" domain multilayer). In comparing the formulas for \( T_{c2} \) and \( T_{c3} \) (Eqs. (9a) and (9b)), we see that for tensile strain \((X > 0)\) and for \( Q_{12} < 0 \) and \( Q_{11} + Q_{12} > 0 \), which is the case for many ferroelectrics with the perovskite structure, \( T_{c2} \) will be higher than \( T_{c3} \). However for compressive strain \((X < 0)\) it is possible for \( T_{c2} \) to be smaller or larger than \( T_{c3} \) depending on the depolarizing field. \( T_{c2}^B > T_{c3}^B \) can result from the depolarization field’s negative contribution to \( T_{c2} \). However, when the depolarization field can be neglected (e.g. a film with electrodes having high conductivity \([8]\)) compressive strains will lead to \( T_{c2} < T_{c3} \).

We point out that the criterion given by Eq.(35) corresponds to considering the film in the mean field approximation with homogeneous polarization \( P = P_0 \) (see Eq.(19)). It is the function \( \varphi \) which takes into account the contribution of inhomogeneous polarization related to the gradients in the free energy. Thus for the general case, one has to use criterion Eq.(32) for "a/c" domains in the multilayer structure, keeping in mind that the opposite condition (sign "\( > \)" substituted for sign "\( < \)" in Eq.(32)) implies the existence of a "c/a"-domain multilayer structure. The criterion for "a/a" domain coincides with Eq.(32) for the case when the A layers are "a"-domain. The criterion depends on the free energy parameters, the transition temperatures, and the ratio of the maximum polarization in a layer \( P_m \) to the thick film polarization \( P_0 \). The latter in turn depends on the film thickness, the coefficients of the gradient terms and the free energy constants \( b_3, b_1 \). With the help of Fig.4 or using the analytical formulas Eqs.(25) and (28b), Eq.(33) can be rewritten in terms of a dimensionless layer thickness \( I_{B_{2},z} \) which is presented as the second scale in Fig.6. By keeping in mind the analytical form of \( I_{B_{2},z} \) (Eq.29) one can see that the criterion (Eq.32) depends on the film thickness and the temperature dependent free energy parameters. Knowledge of these parameters will make it possible to calculate completely the criterion for a multilayer domain structure for a given layer thickness.

### D. Static dielectric susceptibility

We will now consider a multilayer system in an external electric field \( E = E_z \). In so doing we must add the term \(-E_z P_{Az}\) to the free energy density of the ferroelectric phase. From the general form of the Euler-Lagrange equation (7a), it follows that we have to add \(-E_z\) to Eq.(12a). Therefore this equation now has the form:

\[
2\alpha_3 P_{Az} + 4\alpha_3 P_{Az}^3 - E_z - 2\alpha_3 \frac{d^2 P_{Az}}{dz^2} = 0 \tag{36}
\]

The applied electric field induces an additional homogeneous polarization \( \Delta P_{Az} = \chi_{zz} E_z \), where \( \chi_{zz} \) is the linear dielectric susceptibility \((E_z \text{ is assumed to be small})\). Therefore the polarization in the A layer is now \( P_{Az} = P_{Az} + \Delta P_{Az} \). Putting \( P_{Az,E} \) in Eq.(36) and keeping only terms to the first power in \( \Delta P_{Az} \) leads to the equation:

\[
2\alpha_3 \frac{d^2 \chi_{zz}}{dz^2} - \chi_{zz} [2a_3 + 12a_3 P_{Az}^2] + 1 = 0; \quad T \leq T_{c1}^A
\]  

Eq.(37a) defines the static dielectric susceptibility for the case of inhomogeneous polarization \( P_{Az}(z) \). Homogeneous polarization \( P_{Az} = 0 \) leads to \( \chi_{zz}^{-1} = 2a_3 + 12a_3 P_{Az}^2(0) \). It is obvious that the \( \chi_{zz}^{-1} \) dependence originates from the \( z \) dependence of \( P_{Az} \). When the polarization is inhomogeneous, it is wrong to suppose that the susceptibility in the ferroelectric phase can be found by conventional differentiation of the free energy, i.e. \( \chi_{zz}^{-1} = 2a_3 + 12a_3 P_{Az}^2(z) \) is incorrect because \( \chi_{zz} \) obviously does not satisfy Eq.(37a) in general.

We will now discuss the solutions of Eq.(37a). By introducing the dimensionless variable

\[
\xi_t = (z_3 + L_z/2 - 2j_{Az}) / \sqrt{1 + k_{Az}^2} \quad \text{and keeping in mind that} \quad 2a_3 + 12a_3 P_{Az}^2(z) = 2a_3(1 + k_{Az}^2 - 6k_{Az}^2 \eta^2(\xi_3))/\left(1 + k_{Az}^2\right)
\]

we can rewrite Eq.(37a) in the form:

\[
\frac{d^2 \chi_{zz}}{d\xi_t^2} + \chi_{zz} \left(1 + k_{Az}^2 - 6k_{Az}^2 \eta^2(\xi_3)\right) = -2 \left(1 + k_{Az}^2\right) \chi_{zz}
\]  

where \( \chi_{zz}^{-1} = 4 |a_3| \) is the thick film susceptibility. The homogeneous part of Eq.(37b) is known to be a Lamé equation \([24]\). The general solution of Eq.(37b) can be written as a sum of the fundamental solutions of the inhomogeneous equation plus the particular solution of the inhomogeneous equation. Letting \( k_{Az}^2 = m_3 \) and denoting the susceptibility at the boundaries as \( \chi_s \) we obtain

![FIG. 1. Schematic diagram of a multilayer structure.](image-url)
\[
\chi_{zz}(\xi_3) = \chi_z \text{cn}(\xi_3) \text{dn}(\xi_3) + \frac{\chi_z (1-m_3)^2 + 2\chi_z (1+m_3)^2}{(1+m_3)E(m_3)} - \frac{1 - m_3}{K(m_3)} \text{cn}(\xi_3) \text{dn}(\xi_3) \times 
\left(\frac{\xi_3 - \frac{1 + m_3}{1 - m_3} E(am(\xi_3), m_3)}{\text{cn}(\xi_3) \text{dn}(\xi_3)}\right) + 
+ 2\chi_z \frac{1 + m_3}{(1 - m_3)^2} \left(1 + m_3 \text{cn}(\xi_3) \text{dn}(\xi_3) - (1 + m_3) + 2m_3 \text{sn}^2(\xi_3)\right).
\] (38)

Here \(\text{cn}(\xi_3)\) and \(\text{dn}(\xi_3)\) are the elliptic cosine and amplitude delta functions respectively. Their forms, properties and the relations between them are given in [19–21, 24, 25].

The details of the derivation of Eq.(38) are given in Appendix 2. It is seen from Eq.(38) that the behavior of \(\chi_{zz}(\xi_3)\) depends on \(m_3\), which is the polarization ratio (see Eq. (19)). This dependence is depicted in Fig.7a,b,c for two values of the susceptibility at the interfaces: \(\chi_s = 2\chi_t\) and \(\chi_s = 0\). The most interesting general feature of \(\chi_{zz}(\xi_3)\) is the appearance of peaks as \(m_3\) increases. The peaks become sharper and their maxima tend towards the interfaces as \(m_3\) approaches unity, which is when the maximum polarization of the layer equals the thick film polarization limit. In this limit \(\chi_{zz}(\xi_3)\) tends to \(\chi_t\) in the major portion of the film independent of the \(\chi_s\) value, as it should in a thick film (\(\alpha_{33} \rightarrow 0, P_{Azm} \rightarrow P_{A\xi}\)). From this we see that the solution (38) gives the correct value in the thick film limit.

For the electric field applied perpendicular to the multilayer surface, the susceptibility \(\chi_{zz}\) of the entire structure can be expressed as

\[
\frac{1}{\chi_{zz}} = \frac{1}{L_z} \sum_{j=0}^{N-1} \frac{dz_3}{\chi_{zz}(z_3)}
\] (39a)

This result follows from the fact that the capacitances \(C_i\) of serially connected capacitors obey the relation \(1/C = \sum 1/C_i\). When the electric field is applied parallel to \(x\) (which will interact with \(P_{Bx}\) only) we have the result

\[
\chi_{xx} = \frac{1}{L_x} \sum_{j=0}^{N-1} \int_{-L_x/2+(2j+1)l_x}^{-L_x/2+2j l_x} \chi_{xx}(z_1) dz_1
\] (39b)

since here the layers are connected in parallel. The inhomogeneous susceptibility \(\chi_{xx}(\xi_1)\) of the B layers can, of course, be obtained from Eq.(38) by substituting \(z_1\) for \(z_3\), \(b_1\) for \(a_3\), \(\beta_{44}\) for \(\alpha_{33}\) and \(\xi_1\) for \(\xi_3\). The substitution of the dimensionless parameters \(\xi_3\) for \(z_3\) and \(\xi_1\) for \(z_1\) in Eq.(39a) and Eq.(39b) respectively gives

\[
\frac{1}{\chi_{zz}} = \frac{1}{2K(k_{Az})} \int_0^{2K(k_{Az})} \frac{d\xi_3}{\chi_{zz}(\xi_3)}
\] (39c)

\[
\chi_{xx} = \frac{1}{2K(k_{Bz})} \int_0^{2K(k_{Bz})} \chi_{xx}(\xi_1) d\xi_1
\] (39d)

Since the available experimental susceptibility data for multilayers [8] corresponds to the case of the electric field applied along the \(x\) direction, we performed calculations on the basis of Eq.(39d). Details of these calculations are given in Appendix 3. They yield the following expression for the multilayer dielectric susceptibility \(\chi_{xx}\):

\[\text{FIG. 2. Variation of the polarization in a unit cell of a superlattice with an "a/c" domain structure.}\]

\[\text{FIG. 3. Periodic inhomogeneous polarization in a multilayer structure with "a/c" domains.}\]
\[ \chi_{xx} = \frac{1}{K(m_1)} \left( 1 + m_1 \right) \left[ \frac{(1 - m_1)^2 \chi_S + 2 \chi_t (1 + m_1)^2}{(1 + m_1)E(m_1) - (1 - m_1)K(m_1)} + 2 \chi_t (1 - m_1)K(m_1) - 2E(m_1) \right], \] (40)
\[ c_B = 2/c_B^B \]. The divergence at \( T = T_B^B \) is the most significant feature here.

It will be shown later, by comparison with the experimental data \[ \text{[1]} \], that the giant dielectric response observed in some multilayers originates from the susceptibility anomaly related to thickness induced phase transition considered above. Of course the internal fields induced by misfit dislocations, growth imperfections and impurities will smear out the dielectric response of the multilayers and thus reduce infinity to a more realistic value.

We will now discuss the possibility of calculating the thin film susceptibility as the second derivative of the free energy instead of solving the Lamé equation. To do this we assume that in the ferroelectric phase the role of the second term in Eq.(37) will increase with increasing polarization, and so it should be possible to neglect the contribution of the second derivative. In this case the susceptibility becomes \( \chi_{zz}^{-1} \approx 2a_3 + 12a_3P_A z^2 \). Integration of this expression over the layer thickness (with \( P_A(z) \) given by Eq.(23)) and then summing over the layers leads to the following expression

\[
\frac{1}{\chi_{zz}} = 2a_3 \left[ 1 - \frac{6}{1 + k_A^3} \left( 1 - \frac{E(k_A z)}{K(k_A z)} \right) \right] (49)
\]

where \( k_A z \) is given by Eq.(19).

Equation (49) gives the correct expression for the susceptibility in the thick film paraelectric phase \( (k_A z = 0, \chi_{zz}^{-1} = 2a_3, T > T_A^0) \) and in the thick film ferroelectric phase \( (k_A z = 1, \chi_{zz}^{-1} = -4a_3, T < T_A^0) \). However, problems arise with this approximation for intermediate values of \( k_A z \). For \( k_A z < k_A^0 z = 0.674 \) we obtain a negative expression for \( \chi_{zz} \) (including the region of thin film paraelectric phase \( T \geq T_A^0 \)) and a positive expression when \( 1 \geq k_A z > k_A^0 \) with \( \chi_{zz} \) diverging at \( k_A z = 0.674 \) \( (k_A^0 z \) sends the expression (49) for \( \chi_{zz}^{-1} \) to zero). It is obvious that for \( k_A z < k_A^0 \) the susceptibility must be calculated from the differential equation Eq.(37) instead of the approximation derived Eq.(49) since the latter leads to the physically unreasonable negative susceptibility. The validity of Eq.(49) in the region \( k_A^0 < k_A z \leq 1 \) when \( 1/\chi_{zz} > 0 \) can be checked by a \( 1/\chi_{zz} \) calculation on the basis of the exact solution of Eq.(37). Thus we see that Eq.(49) will be valid only in the thick film limit of \( k_A z = 1 \). Therefore, for the majority of thin films and multilayers, the dielectric susceptibility will be defined by Eq.(37) whereas the normally used free energy second derivative (see, e.g. \[ \text{[1]} \]) is valid in the ferroelectric phase only for thick films. We also point out that Eq.(37) will be applicable to bulk ferroelectrics with inhomogeneous polarization, i.e. when there is a strong contribution of the polarization gradient since the mean field approximation is no longer valid.

### III. Dynamic Properties

#### A. Polarization

To consider the dynamic properties of a periodic spatial structure, we should add the time derivatives of the polarization to equations (12a) and (12b). This can be done by the procedure suggested in \[ \text{[25,26]} \]. This procedure permits the investigation of low frequency dynamics in ferroelectrics. Its essence is to expand the polarization in powers of frequency or the time derivative operator \( d/dt \). The first order term gives, as usual, the decay of the polarization, while the second order term provides an "oscillatory response" and contains the mass coefficient \( \mu \).

The equations of motion can be written as

\[
\begin{align*}
\mu_A & \frac{\partial^2 P_A z}{\partial t^2} + \gamma_A \frac{\partial P_A z}{\partial t} + \frac{\delta F_A}{\delta P_A z} = 0 \quad (50a) \\
\mu_B & \frac{\partial^2 P_B x}{\partial t^2} + \gamma_B \frac{\partial P_B x}{\partial t} + \frac{\delta F_B}{\delta P_B x} = 0 \quad (50b)
\end{align*}
\]

The free energy variation \( \delta F/\delta P \) in the Euler-Lagrange Eqs.(12a) and (12b), yields the equations for \( P_A z \) and \( P_B x \).

![FIG. 4. Dimensionless thickness of an "A" or a "B" layer versus the polarization ratio.](image)

![FIG. 5. Temperature of the thickness induced ferroelectric phase transition as a function of layer thickness.](image)
\[
\mu_A \frac{\partial^2 P_{Az}}{\partial t^2} + \gamma_B \frac{\partial P_{Az}}{\partial t} + a_3 P_{Az} + 2a_{33}P_{Az}^3 - \alpha_{33} \frac{\partial^2 P_{Az}}{\partial z^2} = 0
\]  

(51a)

\[
\mu_B \frac{\partial^2 P_{Bz}}{\partial t^2} + \gamma_B \frac{\partial P_{Bz}}{\partial t} + b_1 P_{Bz} + 2b_{11}P_{Bz}^3 - \beta_{44} \frac{\partial^2 P_{Bz}}{\partial z^2} = 0
\]  

(51b)

Since Eqs. (51a) and (51b) are essentially the same we will consider the solution for \(P_{Az}\) keeping in mind that \(P_{Bz}\) can be written, as usual, by substitution of the relevant coefficients and constants in Eq.(51).

We will look for solutions of Eq.(51a) in the form of stationary nonlinear waves in the conventional self-similar form

\[
P_{Az} = P_{Az}(z - vt) = P_z(kz - \omega t), \quad \omega = kv
\]  

(52)

where \(\omega, k\) and \(v\) are the frequency, the wave number, and the velocity respectively and both vectors are directed along the \(z\) axis. Since the wave propagates along the normal to the multilayer structure (\(k\) and \(v\) are parallel to \(z\)) we have suppressed the index \(z\) in \(k\) and \(v\) in Eq.(52).

Using the relations

\[
\xi = z - vt; \quad \frac{\partial}{\partial t} = -v \frac{d}{d\xi}; \quad \frac{\partial^2}{\partial t^2} = v^2 \frac{d^2}{d\xi^2}; \quad \frac{d^2}{d\xi^2} = \frac{d^2}{d\xi^2}
\]  

(53)

we obtain from (51a)

\[
(\mu_A v^2 - \alpha_{33}) \frac{d^2 P_{Az}}{d\xi^2} - \gamma_A v \frac{dP_{Az}}{d\xi} + a_3 P_{Az} + 2a_{33}P_{Az}^3 = 0
\]  

(54)

Since we are interested in the dispersion law for nonlinear waves (which at \(t = 0\) gives us our static periodic structure (23)) we shall neglect the decay term. In doing so \((\gamma_A = 0)\) Eq.(54) coincides with Eq.(12a) but with \(\alpha_{33} \rightarrow \alpha_{33} - \mu_A v^2\), so that the solution of Eq.(54) can be written in the form of Eq.(23) :

\[
P_{Az}(z - vt) = P_{Azm}\text{sn} \left( \frac{\tau z - \tau t + L_z/2 - 2j\tau_p}{\sqrt{1 + k_{Az}^2}}, k_{Az} \right)
\]  

(55)

where \(\tau = \sqrt{-a_3/(\alpha_{33} - \mu_A v^2)}v\) and the renormalized values of \(\tau, L_z, \text{and} \ L_{Az}\) can easily be obtained from (22) by substituting \(\sqrt{-a_3/(\alpha_{33} - \mu_A v^2)}\) for \(\sqrt{-a_3/\alpha_{33}}\).

The solution of Eq.(51b) can be similarly obtained and written in the form:

\[
P_{Bz}(z - vt) = P_{Bzm}\text{sn} \left( \frac{\eta z - \eta t + L_z/2 - 2j\eta_p}{\sqrt{1 + k_{Bz}^2}}, k_{Bz} \right)
\]  

(56)

with \(\eta = \sqrt{-b_1/(\beta_{44} - \mu_B v^2)}v\) and \(\eta, L_z, \eta_{Az}\) follow from Eq.(29) after the substitution of \(\sqrt{-b_1/(\beta_{44} - \mu_B v^2)}\) for \(\sqrt{-b_1/\beta_{44}}\). Eqs. (55) and (56) give the time-dependent inhomogeneous polarization of a multilayer structure.

\[\text{B. Dispersion law}\]

To find the dispersion law of the stationary nonlinear waves formed from Eqs. (55) and (56) in the A and B layers respectively we first recall that the wave number \(k = 2\pi/(\lambda_{Az} + \lambda_{Bz})\), where \(\lambda_{Az}\) and \(\lambda_{Bz}\) are the wavelengths of the \(P_{Az}\) and \(P_{Bz}\) nonlinear waves respectively. They are actually determined by Eqs.(25) and (28b) with respect to the substitution \(\alpha_{33}(or \beta_{44}) \rightarrow \alpha_{33}(or \beta_{44}) - \mu_{A,B}v^2\). Hence

\[\lambda_{Az} = 2\sqrt{\alpha_{33} - \mu_A v^2} \sqrt{1 + k_{Az}^2} \text{K}(k_{Az})\]

(57)

\[\lambda_{Bz} = 2\sqrt{\beta_{44} - \mu_B v^2} \sqrt{1 + k_{Bz}^2} \text{K}(k_{Bz})\]

It then follows that

\[\varphi(k_{Az})\]

FIG. 6. Form of the function \(\varphi(k)\) in Eq.(32) which determines the criterion for the multilayer domain structure.
\[ k = \frac{2\pi}{\lambda_A + \lambda_{Bx}} = \frac{\pi}{\sqrt{(\alpha_{33} - \mu_A v^2)/(-\alpha_3) + 1 + k_{A3}^2 K(k_{A3}) + \sqrt{(\beta_{44} - \mu_B v^2)/(-\beta_1) + 1 + k_{Bx}^2 K(k_{Bx})}} (58) \]

Expression (58) implicitly determines the dispersion law, since \( v = \omega/k \), and so Eq. (58) can give the \( \omega(k) \) dependence. Let us simplify Eq. (58). It follows from Eqs. (25) and (28b) that

\[
\begin{align*}
    l_A &= 2\sqrt{\frac{\alpha_{33}}{-\alpha_3}} \sqrt{1 + k_{A3}^2 K(k_{A3})}; \\
    l_B &= 2\sqrt{\frac{\beta_{44}}{-\beta_1}} \sqrt{1 + k_{Bx}^2 K(k_{Bx})} 
\end{align*} (59)
\]

Thus we can rewrite Eq. (58) as:

\[
k = 2\pi \frac{1}{l_A \sqrt{1 - \mu_A v^2/\alpha_{33}} + l_B \sqrt{1 - \mu_B v^2/\beta_{44}}} (60a)
\]

or

\[
l_A \sqrt{k^2 - \frac{\mu_A}{\alpha_{33}} \omega^2} + l_B \sqrt{k^2 - \frac{\mu_B}{\beta_{44}} \omega^2} = 2\pi (60b)
\]

To facilitate the analysis of the dispersion law given by Eqs. (60) we will first assume that \( \eta = \eta_A = \eta_B \), where \( \mu_A/\alpha_{33} = \eta_A, \mu_B/\beta_{44} = \eta_B \) and \( l_A = l_B = \ell \). In this case we have from Eq. (60):

\[
\omega^2 = \frac{1}{\eta} \left[ k^2 - \frac{\pi^2}{l^2} \right] (61)
\]

It is seen from Eq. (61) that the dispersion law has the familiar long wavelength form. It also exhibits the peculiar dependence of the nonlinear wave frequency on its amplitude via relation between \( \ell \) and \( k_{z,x} \) (Eq. (59)), see e.g. [23].

We schematically plot the dispersion law in Fig. 9a. First of all since \( \omega^2 > 0 \) we have some critical value \( k = k_c = \pm \pi/\ell \) for which \( \omega = 0 \).

On the other hand for any specific value \( k = k_0 \) there is a critical thickness \( l_c = \pm \pi/k_0 \) at which \( \omega = 0 \) and \( \omega \neq 0 \) for \( \ell > l_c \) only. The thickness dependence of the frequency has the form:

\[
\omega = \pm \sqrt{\frac{\pi k_0}{\eta} \frac{1}{\ell} \sqrt{l^2 - l_c^2}} (62)
\]

which in the vicinity of \( l = l_c \) gives \( \omega \approx \pm \sqrt{\frac{\pi k_0}{2\eta} \frac{1}{l_c} \sqrt{l^2 - l_c^2}} \). Thus the frequency increases as the square root of \( \ell \). This dependence is represented in Fig. 9b.

For the general anisotropic case, \( \eta_A \neq \eta_B \) and \( \omega(l) \) and \( \omega(k) \) will be represented by more complicated expressions. They can be derived by squaring both sides of Eq. (60b). We obtain for \( l_A = l_B = l \):

\[
\begin{align*}
    \sqrt{\frac{\alpha_{33}}{-\alpha_3}} \sqrt{1 + k_{A3}^2 K(k_{A3})} &+ \sqrt{\frac{\beta_{44}}{-\beta_1}} \sqrt{1 + k_{Bx}^2 K(k_{Bx})} \\
    \sqrt{\frac{\beta_{11}}{-\beta_1}} \sqrt{1 + k_{Bx}^2 K(k_{Bx})} &+ \sqrt{\frac{\alpha_{33}}{-\alpha_3}} \sqrt{1 + k_{A3}^2 K(k_{A3})} \\
    &\approx \pm \sqrt{\frac{\pi k_0}{\eta} \frac{1}{l} \sqrt{l^2 - l_c^2}} (62)
\end{align*}
\]

FIG. 7. Inhomogeneous susceptibility dependence on the coordinate \( \xi_3/(2K(m)) \) = \( z_1/l_{A3} \) for different \( m_3 \) values for \( \chi_S = 2\chi_t \) (a and b) and for \( \chi_S = 0 \) (c).
\[ \omega_{1,2}^2 = \frac{1}{2(\eta_{A_z} - \eta_{B_x})^2} \left\{ -\frac{8\pi^2}{l^2}(\eta_{A_z} + \eta_{B_x}) + \frac{4\pi}{l} \sqrt{\frac{4\pi^2}{l^2}(\eta_{A_z} + \eta_{B_x})^2 - 4 \left( \frac{\pi^2}{l^2} - k^2 \right) (\eta_{A_z} - \eta_{B_x})^2} \right\} \] (63)

We have dropped the minus sign before the square root in Eq.(63) because \( \omega_{1,2} > 0 \). It is seen that when \( k^2 = \frac{\pi^2}{l^2} \) then \( \omega_{1,2} = 0 \), similar to the isotropic case. Thus this noteworthy aspect of the dispersion law is conserved for the general anisotropic case. We plot the general dependence in Fig.10. Although the qualitative features of the \( \omega(k) \) law for the isotropic case are preserved in the anisotropic case, there are peculiarities at large \( k \) in the anisotropic case: we determine \( \omega \sim \sqrt{k} \) rather than linear dependence in the isotropic case (compare Figs.10a and 9a) and there is a different thickness dependence, with a small decrease of \( \omega(l) \) at large \( l \) (compare Figs. 10b and 9b).

![Fig. 8](image)

FIG. 8. Temperature dependence of the dielectric susceptibility in units of \( \chi_1 = 1/(\alpha_0 B_0 \tau_0) \), for \( \chi_2 = 0 \) (a) at \( T \leq T_{B_0}^D \) using Eq.(40) (solid line) and Curie-Weiss law (dashed line) for \( l_B = 2l_B^D \) and (b) in the entire temperature range using Eq.(40) \( (T < T_{B_0}^D) \) and Eq.(48) \( (T > T_{B_0}^D) \) for different \( c_B^D \) values and for \( l_B = 2l_B^D \) (solid line: \( 1/c_B^D = 2c_B \); dashed line: \( 1/c_B^D = c_B/2 \)) and \( l_B = 3l_B^D \) (dot-dashed line : \( 1/c_B^D = 2c_B \); dotted line: \( 1/c_B^D = c_B/2 \)).

![Fig. 9](image)

FIG. 9. Nonlinear wave dispersion law for a multilayer in the isotropic case as a function of (a) the wave vector and (b) the film thickness. The dashed line is \( \omega = k \eta^{-1/2} \).

IV. DISCUSSION. GIANT DIELECTRIC RESPONSE OF FERROELECTRIC THIN FILM MULTILAYERS.

Let us begin with the comparison of the calculated and the observed dielectric susceptibility. The susceptibility was recently measured \( \chi \) in superlattices consisting of ferroelectric PbTiO\(_3\) and paraelectric Pb\(_{1-x}\)La\(_x\)TiO\(_3\) \( (x = 0.28 - PLT) \) grown on (100)-oriented SrTiO\(_3\) single crystal substrates. Three superlattices of PT/PLT with modulation wavelengths of 100 A\(^\circ\) (sample S-40), 400 A\(^\circ\) (sample S-10), 2000 A\(^\circ\) (sample S-2) were studied. In each superlattice the PT and PLT layers were of equal thickness, and the total thickness was 4000 A\(^\circ\). The authors observed a Debye-like frequency dispersion of the real and imaginary parts of the dielectric susceptibility \( \varepsilon_{xx} \) for the samples S-10 and S-2 in which the value of the real part of the dielectric susceptibility at low frequency approached 420000 and 350000 respectively at \( T \approx 50^\circ C \). A significant increase in the susceptibility with tempera-
ture was observed in sample S-10. We present this temperature dependence by the full circles in Fig.11, where the solid line represents the C-W law given by Eq.(43) with $c_B = 7 \cdot 10^6 K$, and $T_cB(S-10) = 533K$. The independence of $c_B$ on layer thickness (see Eq.(43)) makes it possible to obtain the transition temperature for specimen S-2: $T_cB(S-2) = 575K$. Taking the ratio of these $T_cB$ values and using Eq.(30) for S-10 and S-2 leads to the critical thickness $l_{B0} = 55A$. This value is larger than the layer thickness ($l_B = 50A$) in S-40 specimen, which is why no ferroelectric phase transition was observed for this multilayer. Thus the value reported for S-40, $\varepsilon''_{xx} \simeq 750$ at $T \approx 50^\circ C$, represents the contribution from the paraelectric phases of both the PT and PLT layers. This value is several orders of magnitude smaller than the values measured in the ferroelectric phase for S-10 and S-2. The contribution from the PT-layers in the paraelectric phase of the S-40 sample, where $T_cB \approx 0$ (see Eq.(30) at $l_B \approx l_{B0}$) can be written as $\varepsilon''_{xx} = 4\pi c_{BP}/T$, where $c_{BP} = c_B^0$ in accordance with Eq.(48). Keeping in mind that $\varepsilon''_{xx}(PT) < 750$, we can conclude that the C-W constant in Eq.(48) $c_{BP} < 2 \cdot 10^4$. Therefore the dielectric susceptibility in the paraelectric phase of the thin film is much smaller than in the ferroelectric phase. This is contrary to what is observed in bulk ferroelectrics. On the other hand this gives support to the supposition that the contribution of the permittivity from the PLT paraelectric phase to the giant value observed in S-10 and S-2 is negligibly small in comparison with the contribution from the PT layers. Estimation of the transition temperature for a thick layer, $T_cB_{cl}$, with the help of Eq.(30) and the values determined above for $T_cB$ leads to $T_cB_{cl} = 580K$. This value is smaller than that for bulk PbTiO$_3$: $T_cB_{cl} = 763K$. This would seem to favor compressive strain in the layer, i.e. $X < 0$ in Eq.(9b) because $Q_{B11}^B + Q_{B12}^B > 0$ for PbTiO$_3$. Note, that the $T_cB$ and $c_B$ values were obtained assuming the temperature dependence of the low frequency (1 kHz) dielectric permittivity is close to the static one. Calculation of the static susceptibility via the maximum value of $\varepsilon''_{xx}$ measured at $T = 50^\circ C$ [7] has shown that the low frequency $\varepsilon''_{xx}$ was in fact close to the static value.

![Graph](image1)

**FIG. 10.** Nonlinear wave dispersion law for a multilayer in the anisotropic case at $\eta_{Bx} = 0.2$, $\eta_{Bz} = 0.25$ (1); $\eta_{Ax} = 0.2$, $\eta_{Az} = 2$ (2) as a function of (a) the wave vector and (b) the film thickness.

**V. CONCLUSION**

The model used for the calculations was a multilayer consisting of alternating layers of two different ferroelectric materials for which the interfaces between the layers were abrupt and the polarization at these interfaces was taken to be zero. The interaction between the polarization in different layers was neglected because of the rapid decay of this interaction with distance [8] and because of the zero polarization at the interfaces. The production of sharp interfaces in multilayer structures is now possible using the most recent oxide thin film deposition techniques as has been demonstrated in [6]. Our independent layer model produces results that are in agreement with published results [5,6,9] for both multilayers and for single thin films. In addition, this model should also be valid for bulk materials in which polarization gradients are present and thus rendering calculations in the mean field approximation meaningless.

We have shown that the inhomogeneous polarization in the multilayers is at the origin of the inhomogeneous static dielectric susceptibility. We have determined the differential equation for the susceptibility and, from its solution, we show that the conventional way of calculating the susceptibility as the second derivative of the free energy [11] is approximately valid only for thick films with small polarization inhomogeneity. The results related to the consideration of renormalization of the free energy coefficients by homogeneous stresses in the film, to the criteria of “a/c”, “c/a” or “a/a” domains structure as well as to thickness induced ferroelectric phase transition can be applied both to multilayers and, after some transformations, to single thin films on substrates. Several results are valid mainly for ferroelectric thin film multilayers. In particular, the results obtained for the nonlinear polarization waves and for the dispersion law exhibiting a critical wave vector or, equivalently, a criti-
cal thickness, reflect the characteristic peculiarities of the dynamic properties of thin film multilayers.

The calculations of the inhomogeneous susceptibilities in the form of Eq.(42) can be valid only for multilayers. Therefore the calculated divergence of $\chi$ at the thickness induced ferroelectric phase transition temperature may be the exclusive feature of ferroelectric thin film multilayers. Because of the technical difficulties in producing and studying ferroelectric thin film multilayers are more involved than for those of single films or bulk materials, experimental results are still somewhat restricted to just a few different series of superlattices. The theoretical calculations of multilayer structures performed in this work are quite complex even for the relatively simple independent layer model. This model corresponds fairly closely to that of [12] where, for the case of weak coupling at the interfaces, they also find the most interesting physical phenomenon in the layers: a thickness induced ferroelectric phase transition. Our results are in agreement with the numerical solutions in Ref. [12]. We are now extending our calculations to obtain the static and dynamic dielectric susceptibilities over a wide temperature region, including the response of the ferroelectric phase for different orientations of an external electric field. A more general model should take into account the interfaces where gradients in the mechanical stress can appear. Thus the calculations will increase in complexity since the equilibrium stresses must then be calculated on the basis of the entire Euler-Lagrange equation (7b) rather than by the simple differentiation of the free energy with respect to stress that we have used above. Nevertheless even with the increased computational complexity, further theoretical, as well as experimental, investigation of ferroelectric multilayers, including those with finite interfaces and with more than two layers in a modulation period, would seem to be extremely desirable both for basic science and potential applications.

FIG. 11. Temperature dependence of the dielectric permittivity of a PT-PLT multilayer. Solid line: theory; Full circles: experiment [7].

VI. APPENDICES

A. Appendix 1

Since the free energy density $f_B(P_{Bz})$ and $f_B(P_{Bx})$ as well as $P_{Bz}$ and $P_{Bx}$ can be obtained from one another by substitution of their parameters (see Eq.(5a) $A \to B$ and (5b), Eq.(23) with (28a)) we shall perform a detailed calculation of $F_B(P_{Bz})$ and then obtain $F_B(P_{Bx})$ by this substitution.

To calculate $F_B(P_{Bz})$ we can take into account the first integral for $P_{Bz}$ (the step going from Eq.(14) to Eq.(15) with $A \to B$). In view of this first integral we can substitute the derivative for powers of $P_{Bz}$ in Eq.(5a) (again with $A \to B$) and obtain

$$f_B(P_{Bz}) = 2\beta_{33}\left(\frac{dP_{Bz}}{dz}\right) + CBz$$  (A1.1a)

$$CBz = b_3P_{Bz}^2 + b_{33}P_{Bz}^4$$  (A1.1b)

We determine the derivative to be:

$$\frac{dP_{Bz}}{dz} = P_{Bz m} = \frac{-b_3}{\beta_{33}} \frac{1}{1 + k_{Bz}^2} \text{cn}(u_z) \text{dn}(u_z)$$  (A1.2)

$$u_z = \sqrt{\frac{b_3}{\beta_{33}} \frac{z + L/2 - (2j + 1)L_B}{1 + k_{Bz}^2}}$$

where $\text{cn}(u)$ and $\text{dn}(u)$ are elliptic functions (see e.g. [19]). With respect to (A1) and (A2) the free energy $F_B(P_{Bz})$ can be written as

$$F_B(P_{Bz}) = \frac{1}{L} \sum_{j=0}^{N} \int_{-L/2 + (2j + 1)L_B}^{L/2 + (2j + 1)L_B} dz \left(cBz - \frac{2b_3}{1 + k_{Bz}^2} \text{cn}^2(u_z) \text{dn}^2(u_z)\right) =$$

$$= \frac{l_B}{l_A + l_B} \left(cBz - \frac{2b_3}{1 + k_{Bz}^2} \frac{1}{\sqrt{1 + k_{Bz}^2}} \times \int_{0}^{\sqrt{1 + k_{Bz}^2}} \text{cn}^2(u) \text{dn}^2(u) du \right)$$

Since $l_{Bz} = 2\sqrt{1 + k_{Bz}^2}K(k_{Bz})$ (see Eq.(25) with $A \to B$) the last integral in (A3) has the form

$$I = \int_{0}^{2K(k_{Bz})} \text{cn}^2(u) \text{dn}^2(u) du$$  (A1.4)

We will now calculate the integral (A4) (see [20])
where

\[ I = 2 \int_0^{2K(k_{Bz})} (1 - \sin^2 u)(1 - k_{Bz} \sin^2 u) \, du = \]

\[ = 2 \left\{ K(k_{Bz}) - (1 + k_{Bz}^2) I_1 + k_{Bz}^3 I_2 \right\}, \quad (A1.5) \]

where

\[ I_1 = \int_0^{2K(k_{Bz})} \sin^2 u \, du, \]

\[ I_2 = \int_0^{2K(k_{Bz})} \sin^4 u \, du = \]

\[ \frac{1}{3k_{Bz}^2} \text{cn}(u) \, \text{dn}(u) \, \text{sn}(u) \bigg|_0^{K(k_{Bz})} + \]

\[ \frac{2}{3} \frac{(1 + k_{Bz}^2)}{k_{Bz}^2} \int_0^{K(k_{Bz})} \sin^2 u \, du - \frac{1}{3k_{Bz}^2} K(k_{Bz}). \quad (A1.6) \]

Since \( \text{cn}(K) = \text{sn}(0) = 0 \), we obtain

\[ I_2 = -\frac{1}{3k_{Bz}^2} K(k_{Bz}) + \frac{2}{3} \frac{(1 + k_{Bz}^2)}{k_{Bz}^2} I_1 \quad (A1.7) \]

We calculate \( I_1 \):

\[ I_1 = \frac{1}{k_{Bz}^2} \left\{ u - E(\text{am}(u), k_{Bz}) \right\} \bigg|_0^{K(k_{Bz})} = \]

\[ = \frac{1}{k_{Bz}^2} \left\{ K(k_{Bz}) - E(\pi/2, k_{Bz}) \right\} = \]

\[ = \frac{1}{k_{Bz}^2} \left\{ k_{Bz} - E(k_{Bz}) \right\}, \quad (A1.8) \]

where \( E(k_{Bz}) = \int_0^{\pi/2} \sqrt{1 - k_{Bz}^2 \sin^2 \theta} \, d\theta \) is complete elliptic integral of the second kind.

Taking into consideration (A1.5), (A1.7), and (A1.8), the integral (A1.4) can be rewritten as

\[ I = \frac{2}{3} \left[ 2K(k_{Bz}) - \frac{(1 + k_{Bz}^2)}{k_{Bz}^2} (K(k_{Bz}) - E(k_{Bz})) \right] \quad (A1.9) \]

Substitution of (A1.9) and (A1.1a) into (A1.3) gives

\[ F_B(P_{Bz}) = \frac{l_B P_{Bzm}^2}{l_A + l_B} \left\{ b_3 + b_{33} P_{Bzm}^2 - \right. \]

\[ - \frac{b_3}{(1 + k_{Bz}^2)K(k_{Bz})} \times \]

\[ \times \left[ 2K(k_{Bz}) - \frac{1 + k_{Bz}^2}{k_{Bz}^2} (K(k_{Bz}) - E(k_{Bz})) \right] \right\} \quad (A1.10) \]

To express (A1.10) in terms of the parameter \( k_{Bz} \) and the coefficients \( b_3, b_{33} \) we first substitute \( P_{Bzm}^2 / P_{Bz0}^2 = 2k_{Bz}^2 / (1 + k_{Bz}^2) \) (see Eq.(19)) and then we take into account that \( P_{Bz0} = -b_3 / (2b_{33}) \). Thus we have

\[ F_B(P_{Bz}) = -\frac{l_B}{l_A + l_B} \frac{b_3^2}{b_{33} (1 + k_{Bz}^2)^2/3} \times \]

\[ \times \left\{ k_{Bz}^2/2 + 1 - (1 + k_{Bz}^2) E(k_{Bz}) / K(k_{Bz}) \right\} \quad (A1.11) \]

and \( F_B(P_{Bz}) \) can be obtained from (A1.11) by substituting \( k_{Bz} \) for \( k_{Bz} \), \( b_1 \) and \( b_{11} \) for \( b_3 \) and \( b_{33} \) respectively.

This gives the inequality (32) and the function (33).

### B. Appendix 2

Let’s consider the solution of Eq.(37b) for the dielectric susceptibility:

\[ \frac{d^2 \chi(\xi)}{d\xi^2} + (1 + m - 6m \sin^2(\xi, m)) \chi(\xi) = -2(1 + m)\chi_1, \]

(A2.1)

with the boundary conditions

\[ \chi(\xi = 0) = \chi(\xi = 2K(m)) = \chi_s \quad (A2.2) \]

Here for the sake of simplicity we have omitted all subscripts and have denoted \( m = k_{Bz}^2 \). In accordance with the theory of linear differential equations we have to solve the homogeneous part of equation (A2.1), which is a particular case of the Lamé equation \[ 24,25 \]. A solution of the homogeneous equation is the following \[ 25 \]:

\[ \chi_1(\xi) = C_1 \text{cn}(\xi, m) \, \text{dn}(\xi, m), \quad (A2.3) \]

A second solution can be easily obtained by varying the constant \( C_1 \) and it has the form:

\[ \chi_2(\xi) = C_2 \text{cn}(\xi, m) \, \text{dn}(\xi, m) \int_0^\xi \frac{d\zeta}{\text{cn}^2(\zeta, m) \, \text{dn}^2(\zeta, m)}. \]

(A2.4)

The particular solution of the inhomogeneous equation (A2.1) can be obtained by varying the constants \( C_1 \) and \( C_2 \) in the sum of the solutions (A2.3) and (A2.4). This procedure leads to:

\[ \chi_i(\xi) = -2(1 + m)\chi_1 \, \text{cn}(\xi, m) \, \text{dn}(\xi, m) \times \]

\[ \times \int_0^\xi \frac{\text{sn}(\zeta, m) \, d\zeta}{\text{cn}^2(\zeta, m) \, \text{dn}^2(\zeta, m)}. \quad (A2.5) \]

After substitution of the variable \( \zeta \) by \( \varphi = \text{am}(\xi) \), this integral has the form \( I_{i1} = \int_0^{\text{am}(\xi)} (1 - \sin(\varphi)^2)^{-1}(1 - m \sin(\varphi)^2)^{-\frac{3}{2}} \). The integral \( I_{i1} \) can be put in standard
form (see [19]), and its substitution into Eq. (A2.4) gives us the direct form of the second fundamental solution of the equation (A2.1):

\[
\chi_2(\xi) = \left( \xi - \frac{1 + m}{1 - m} E(\text{am}(\xi), m) \right) \text{cn}(\xi, m) \text{dn}(\xi, m) + \\
+ \frac{\text{sn}(\xi, m)(\text{cn}^2(\xi, m) + m^2 \text{dn}^2(\xi, m))}{1 + m}.
\]  
(A2.6)

The integral in the expression (A2.5) can be reduced, by the substitution \( t = \text{cn}(\xi, m) \), to which can be found in various sources [21]. Then Eq. (A2.5) can be rewritten as

\[
\chi_i(\xi) = 2\chi_t \left( \frac{1 + m}{1 - m} \right) \left( (1 + m) \text{cn}(\xi, m) \text{dn}(\xi, m) + \\
+ 2m \text{sn}^2(\xi, m) - (1 + m) \right)
\]  
(A2.7)

Finally the complete solution of Eq. (A2.1) has the following form:

\[
\chi(\xi) = C_1\chi_1(\xi) + C_2\chi_2(\xi) + \chi_i(\xi)
\]  
(A2.8)

where the constants \( C_1, C_2 \) are determined from the boundary conditions (A2.2). When using the properties of elliptic functions [19], the constants \( C_1, C_2 \) can be found to have the form:

\[
C_1 = \chi_S,
\]  
(A2.9)

\[
C_2 = \frac{(1 - m)^2 \chi_S + 2\chi_t(1 + m)^2}{(1 + m)E(m) - (1 - m)K(m)} \left( \frac{1}{1 - m} \right).
\]

Substitution of (A2.3), (A2.6), (A2.7) and (A2.9) in (A2.8) gives us the expression (38).

C. Appendix 3

We will calculate the susceptibility from Eq. (39d) where, for the sake of simplicity, we have omitted all subscripts and have denoted \( m = k_B^2/t \):

\[
\chi(m) = \frac{1}{2K(m)} \int_0^{2K(m)} \chi(\xi, m) d\xi
\]  
(A3.1)

using Eq. (38) for \( \chi(\xi, m) \). It is convenient to divide the integral in the expression (A3.1) into the following three parts:

\[
\int_0^{2K(m)} \chi_1(\xi) d\xi = \int_0^{2K(m)} \text{cn}(\xi) \text{dn}(\xi) d\xi = \text{sn}(\xi) \big|_0^{2K(m)} = 0,
\]  
(A3.2a)

\[
\int_0^{2K(m)} \chi_2(\xi) d\xi = \int_0^{2K(m)} \frac{1 + m}{1 - m} E(\text{am}(\xi), m) \text{cn}(\xi, m) \text{dn}(\xi, m) + \\
+ \frac{\text{sn}(\xi, m)(\text{cn}^2(\xi, m) + m^2 \text{dn}^2(\xi, m))}{1 + m}.
\]

E. Case 1: \( m \to 1 \) (thick film limit).

When we expand the elliptic functions as a series about \( \mu = (1 - m) \to 0 \) we obtain:

\[
K(\mu) = \frac{\pi}{2} \left( 1 + \frac{1}{4} \mu + \frac{9}{64} \mu^2 + \ldots \right)
\]
(E4.1)

\[
E(\mu) = \frac{\pi}{2} \left( 1 - \frac{1}{4} \mu - \frac{3}{64} \mu^2 + \ldots \right)
\]
(A4.1)

and using the Legendre relation [19]

\[
E(m)K(1 - m) + E(1 - m)K(m) - K(m)K(1 - m) = \frac{\pi}{2}
\]

we find that:

\[
(1 + m)E(m) - (1 - m)K(m) = 2 - \frac{3}{2} \mu + \frac{3}{32} \mu^2 - \frac{3}{8} \mu^2 K(m) + \ldots
\]  
(A4.2a)

and

\[
2E(m) - (1 - m)K(m) = 2 - \frac{1}{2} \mu - \frac{5}{32} \mu^2 + \frac{1}{8} \mu^2 K(m) + \ldots
\]  
(A4.2b)
After substituting Eqs. (A4.2a) and (A4.2b) into the expression (A3.3) and keeping in mind that $K(m) \to \infty$ as $m \to 1$ we find the following limiting expression:

$$\chi(m \to 1) = \left( \chi_t + \left( \chi_s + \frac{3}{4} \chi_t \right) \frac{1}{K(m)} \right) \left( 1 - \frac{1 - m}{2} \right) \to \chi_t$$

(A4.3)

F. Case 2: $m \to 0$ (paraelectric thin film limit).

For $m \to 0$ the thickness of the layer tends to the critical value $l_{xx} = \pi$ at which the transition to the paraelectric phase occurs. Since at $m \to 0$, $K(m) \to (\pi/2)(1 + m/4)$ and $E(m) \to (\pi/2)(1 - m/4)$ (which can be seen from the integrals of Eqs. (24) and (A1.8)), we obtain from Eq.(A3.3):

$$\chi(m \to 0) \approx (\chi_s + 2\chi_t) \frac{8}{3\pi^2 m}$$

(A4.4)

which coincides with Eq.(41).

G. Appendix 5

Let us find the approximate dependence of the susceptibility (A3.3) on temperature. Only the dimensionless thickness $l_{Bz}$ depends on temperature in our theory (see Eq.(29)):

$$l_{Bz} = \sqrt{\frac{\alpha^0_B (T_B^{cl} - T)}{\beta_{44}}}$$

(A5.1)

In the vicinity of the thickness induced transition temperature $T = T_{cl}(l_{Bz} = \pi)$ the expression (A5.1) can be rewritten as:

$$l_{Bz} \approx \pi \left( \frac{1}{2} + \frac{l_{B0}^2 T_{cl} - T}{T_B^{cl}} \right)$$

(A5.2)

where $l_{B0}$ and $T_{cl}$ are given by Eq.(30).

On the other hand it follows from the expansion of Eq.(25) at $m_1 \to 0$ that:

$$l_{Bz} = 2\sqrt{1 + m_1 K(m_1)} \approx \pi \left( 1 + \frac{3}{4} m_1 \right)$$

$$m_1 \approx \frac{4}{3} \left( \frac{l_{Bz}}{\pi} - 1 \right)$$

(A5.3)

Substitution of Eq.(A5.2) into Eq.(A5.3) yields

$$m_1 \approx \frac{2 l_{B0}^2 T_{cl}^{B} - T}{3 l_{B0}^2 T_{cl}^{B} - T_{cl}^{B}}$$

(A5.4)

From this temperature dependence of $m_1$ we can find from Eq.(A4.4) the susceptibility $\chi_{xx}$ as a function of temperature. In order to obtain the temperature dependence of the susceptibility we have to choose a specific susceptibility $\chi_s(T)$ at the interface. We considered two forms for $\chi_s$ on temperature and obtained the corresponding formulae for $\chi_{xx}(T)$:

$$\chi_s = const$$

$\chi_{xx}(T) \approx \left( 4\chi_s \frac{\beta_{44}}{T_B^{cl}} + \frac{2}{\pi^2} \right) \frac{1}{\alpha^0_B (T_{cl}^{B} - T)}$ (A5.5a)

$$\chi_s = \frac{\alpha}{4\alpha^0_B (T_B^{cl} - T)}$$

(A5.5b)

Under the assumption $\chi_s = 0$, Eqs.(A5.5a) and (A5.5b) lead us to Eq.(43).

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[1] H. T. Grahn, Semiconductor superlattices: Growth and Electronic Properties (World Scientific, Singapore, 1995).
[2] T. Shinjo and T. Takada, Metallic Superlattices: Artificially Structured Materials (Elsevier, New York, 1987).
[3] M. G. Cottam, Linear and Nonlinear Spin Waves in Magnetic Films and Superlattices (World Scientific, Singapore, 1994).
[4] I. Bozovic, Superconducting Superlattices and Multilayers (SPIE, Bellingam, 1994)
[5] S. L. Swartz and V. E. Wood, Condensed Matter News, 1, N 5, 4 (1992).
[6] H. Tabata and T. Kawai, Appl. Phys. Lett., 70, 321 (1997).
[7] Y. Kim, R. A. Gerhardt and A. Erbil, Phys. Rev. B, 55, 8766 (1997).
[8] E. D. Specht, H.-M. Christen, D. P. Norton and L. A. Boatner, Phys. Rev. Lett., 80, 4317 (1998).
[9] J. C. Jiang, X. Q. Pan, W. Tian, C.D. Theis and D. Schlom, Appl. Phys. Lett., 74, 2851 (1999).
[10] F. Le Marrec, R. Farhi, M. El. Marssi, J. L. Dellis, M. G. Karkut and D. Ariosa (Phys. Rev. B, to be published).
[11] Bai Shaoping Li, J. A. Eastman, J. M. Vetrone, R. E. Newnham and L. E. Cross, Phil. Mag. B, 76, 47 (1997).
[12] B. D. Qu, W. L. Zhong and R. H. Prince, Phys. Rev. B, 55, 11218 (1997).
[13] See, for example, J. Mathews and J. L. Walker, Mathematical methods of physics (W. A. Benjamin, New York, 1965).
[14] W. D. Nix, Metallurgical Transactions, 20A, 2217 (1989).
[15] G. A. Rossetti, Jr., L. E. Cross and K. Kushida, Appl. Phys. Lett., 59, 2524 (1991).
[16] N. A. Pertsev, A. G. Zembilgotov and A. K. Tagantsev, Phys. Rev. Lett., 80, 1988 (1998).
[17] J. S. Speck and W. Pompe, J. Appl. Phys., 76, 466 (1994).
[18] D. R. Tilley, Ferroelectric Thin Films (Gordon and Breach, Amsterdam, 1996) p.11.
[19] M. Abramowitz and A. Stegun, Handbook of Mathematical Functions (Dover Publications Inc., N.Y.).
[20] E. Yahneke, F. Emde and P. Losch, Tables of Higher Functions (McGraw-Hill, N. Y., 1960).
[21] I. S. Gradshteyn and I. M. Ryzhik, Tables of Integrals, Series and Products (Academic Press, New York, 1965).
[22] Y. Ishibashi, H. Orihara and D. R. Tilley, J. Phys. Soc. Jap., 67, 3292 (1998).
[23] Y. G. Wang, W. L. Zhong and P. L. Zhang, Phys. Rev. B, 51, 5311 (1995).
[24] E. Whittaker and G. Watson, A course of modern analysis (Cambridge University Press, 1958).
[25] A. Erdelyi, Higher Transcendental Functions (McGraw Hill, N. Y., 1953).
[26] V. G. Vaks, Vvedenie v microscopicheskuyu teoriyu segmentoelektrikov (Moscow, Nauka, 1973).
[27] see for example V. L. Ginzburg, JETF, 19, 36 (1949); UFN, 38, 490 (1949); FTT, 2, 2031 (1960).
[28] see for example A. M. Kosevich and A. S. Kovalev, Introduction to nonlinear physical mechanics (Naukova Dumka, Kiev, 1989).
[29] A. P. Prudnikov, Yu. A. Bruchkov and O. I. Marichev, Integrals and Series, 3, (Moscow, Nauka, 1986).