Nanoscale Ferroelectric Structures: Landau Theory for the Polarization Profile in a Ferroelectric Nano-Box and its Response to an Incident Electromagnetic Field

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Abstract. The Landau-Devonshire theory of ferroelectrics to date has concentrated mainly on bulk materials, thin film geometries, spherical geometries or other, essentially one-dimensional situations . By extending such calculations to three dimensions it is possible to consider a ferroelectric in the form of a box in which the influence of all surfaces of the box are included in the theory. This influence is expected to be important as the size of the box decreases and the surface to volume ratio increases. With interest in nanoscale materials burgeoning, it is of interest to study such size effects and how they influence the distribution in a ferroelectric box. This paper will show how Landau-Devonshire theory can be applied to such a box. After showing how spontaneous polarization profiles can be calculated, an outline of how Maxwell's equations together with Landau-Khalatnikov dynamical equations can be brought in to study the interaction of the nano-box with incident electromagnetic waves.

Keywords: Ferroelectrics, nanoscale, nano-box, Landau theory, polarization, phenomenology, Euler-Lagrange minimization.
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INTRODUCTION

One of the defining characteristics of a ferroelectric is that it has a non-zero spontaneous polarization in the absence of an applied electric field provided that the temperature is lower than a certain critical temperature T_C [1]. The other defining feature is that the polarization can be reversed by applying an electric field opposing the direction of the polarization. This allows ferroelectrics to be used in random access memories. Binary information can be stored according to the polarization direction which can be switched between two states by an electric field.[2].

With the increasing miniaturization of devices it becomes important to investigate size-effects in ferroelectrics. Thin film geometries for ferroelectrics, in which one spatial dimension is confined, have been studied fairly extensively[3, 4, 5, 6, 7, 8]. In this paper a box geometry in which all three dimensions are confined will be considered. Confinement in the box means that the pairs of oppositely facing surfaces are close enough to the central region of the strip that their presence causes a non-negligible effect on the ferroelectric as a whole, so that the ferroelectrics properties are different from those of a bulk region far from any surfaces. Such effects are expected to be important at the nanoscale, and so here we refer to the boxes as ferroelectric nano-boxes.

The formalism for calculating the spontaneous polarization in the nano-box will be developed using Landau-Devonshire theory. In addition Landau-Khalatnikov equations will be introduced, which will allow the dynamic interaction of the box with incident electromagnetic waves to be studied.

A problem similar to the one of interest here, but applied to spheres and cylinders, has been dealt with by Morison's et al.[9], who have given approximate analytical solutions of the equations that define the spontaneous polarization. The work in the present paper, however, is concerned with the formalism for ferroelectric nano-boxes and does not consider approximate analytical solutions. This does not lead to equations which can be solved exactly in analytical terms, but possible numerical schemes for solving the equations are discussed.

FREE ENERGY FORMALISM

The region occupied by the interior of the ferroelectric nano-box is defined, in Cartesian coordinates, by

$$V = \left\{ \mathbf{x} \,|\, x_i \in \left(l_i^-, l_i^+ \right), i = 1,2,3 \right\}. \tag{1}$$

The sides of the box are given by $l_i = l_i^+ - l_i^-, i = 1,2,3$.

Other notation that will be useful is: $\mathbf{x} = (x_1, x_2, x_3)$, for a position in the ferroelectric crystal; $\mathbf{P} = (P_1, P_2, P_3)$, the polarization vector; $P_i = P_i(x_1, x_2, x_3)$, $i = 1,2,3$; $\mathbf{P}_{x_i} = \partial \mathbf{P} / \partial x_i$, $i = 1,2,3$.

An important quantity in Landau-Devonshire theory is the Gibbs free energy given as an expansion in powers of the polarization components that are invariant under the

symmetry operations of the symmetric ($T < T_C$) phase of the ferroelectric[10, 11]. For a cubic ferroelectric crystal (such as lead titanate) the free energy can be written as

$$\begin{aligned} f_{\text{cubic}}\big(\mathbf{x},\mathbf{P},\mathbf{P}_{x_1},\mathbf{P}_{x_2},\mathbf{P}_{x_3},\langle\mathbf{P}\rangle\big) &= \frac{1}{2}\alpha_1(T-T_C)P^2 \\ &+ \frac{1}{4}\alpha_2 P^4 + \frac{1}{6}\alpha_3 P^6 \\ &+ \frac{1}{2}\beta_2\left(P_1^2P_2^2 + P_2^2P_3^2 + P_3^2P_1^2\right) \\ &+ \frac{1}{2}\beta_3\Big(P_1^4\big(P_2^2+P_3^2\big) \\ &\qquad + P_2^4\big(P_3^2+P_1^2\big) + P_3^4\big(P_1^2+P_2^2\big)\Big) \\ &+ \frac{1}{2}\gamma_3 P_1^2P_2^2P_3^2 \\ &+ \frac{1}{2}\delta\left(\left|\frac{\partial\mathbf{P}}{\partial x_1}\right|^2 + \left|\frac{\partial\mathbf{P}}{\partial x_2}\right|^2 + \left|\frac{\partial\mathbf{P}}{\partial x_3}\right|^2\right) \\ &+ \frac{1}{2\epsilon_0\epsilon_\infty}\Big(P_1\big(P_1-\langle P_1\rangle\big) + P_2\big(P_2-\langle P_2\rangle\big) \\ &\qquad + P_3\big(P_3-\langle P_3\rangle\big)\Big). \end{aligned} \tag{2}$$

Here x_1, x_2 and x_3 are Cartesian coordinates, the polarization components are P_i, with $P^2 = P_1^2 + P_2^2 + P_3^2$; the α_i, β_i and γ_i are the terms that form the free energy for a bulk ferroelectric; the δ terms are gradient terms accounting for the change of polarization that occur near surfaces of the ferroelectric [3]; the final terms involving the P_i account for the depolarization field for the case in which the polarization has components along x_1, x_2 and x_3 [4, 5]. The α_i, β_i and γ_i coefficients are found from experimental data or in some cases may be calculated from first principles[1]; d is an extrapolation length[3], which in general can vary over the surfaces of the ferroelectric; ϵ_0 is the vacuum permittivity and ϵ_∞ accounts for the contribution of high frequency resonances to the dielectric response[12]. The notation $\mathbf{P}_{x_i}$ denotes partial derivatives of $\mathbf{P}$ with respect to x_i, and

$$\langle P_i\rangle = \frac{1}{l_i}\int_{l_i^-}^{l_i^+} P_i\,dx_i, \quad i = 1,2,3, \tag{3}$$

which is an averaged polarization, and $\langle\mathbf{P}\rangle$ is defined by

$$\langle\mathbf{P}\rangle = \big(\langle P_1\rangle,\langle P_2\rangle,\langle P_3\rangle\big). \tag{4}$$

Together with the free energy given in Eq. (1) there is also a surface energy density [1] given by

$$f_{\text{surf}}\big(\mathbf{x},\mathbf{P}\big) = \frac{\delta}{2d(\mathbf{x})}P^2(\mathbf{x}) \quad \text{for} \quad \mathbf{x}\in S, \tag{5}$$

where S is the entire surface of the ferroelectric box given by

$$\begin{aligned} S = &\\ &S_{x_1=l_1^-}\cup S_{x_{1=l_1^+}}\cup S_{x_2=l_2^-}\cup S_{x_2=l_2^+} \\ &\cup S_{x_3=l_3^-}\cup S_{x_3=l_3^+}, \end{aligned} \tag{6}$$

in which the sides of the box at $x_i = l_i^{\mp}$ are given by

$$S_{x_j=l_j^{\mp}} = \big\{\mathbf{x}\,|\,x_i = l_i^{\mp}, x_{\sigma^j(i)}\in\big[l_i^-,l_i^+\big], j=1,2\big\}, \tag{7}$$

where σ is a cyclic operator performing the operation $x_1\mapsto x_2\mapsto x_3\mapsto x_1$. From this it follows that

$$\sigma(x_i) = x_{j+1 \pmod 3}. \tag{8}$$

Also, σ^n denotes σ applied n times, and the definition of the operator is extended to when the x_i are arguments of a function h such that

$$\sigma\big(h(x_1,\ldots,x_3)\big) = h\big(\sigma(x_1),\ldots,\sigma(x_3)\big). \tag{9}$$

Using σ, Eq. (2) can be written in a shortened form that shows the cyclic patterns present in the free energy expression:

$$\begin{aligned} f_{\text{cubic}}\big(\mathbf{x},\mathbf{P},\mathbf{P}_{x_1},\mathbf{P}_{x_2},\mathbf{P}_{x_3},\langle\mathbf{P}\rangle\big) &= \alpha_1(T-T_C)P^2 \\ &+ \sum_{i=2}^{3}\frac{1}{2i}\alpha_i\big(P^2\big)^i + \frac{1}{2}\beta_2\sum_{i=0}^{2}\sigma^i\left(P_1^2P_2^2\right) \\ &+ \frac{1}{2}\beta_3\sum_{i=0}^{2}\sigma^i\Big(P_1^4\big(P_2^2+P_3^2\big)\Big) + \frac{1}{2}\gamma_3P_1^2P_2^2P_3^2 \\ &+ \frac{1}{2}\delta\sum_{i=1}^{3}\left|\frac{\partial\mathbf{P}}{\partial x_i}\right|^2 + \frac{1}{2\epsilon_0\epsilon_\infty}\sum_{i=1}^{3}P_i\big(P_i-\langle P_i\rangle\big). \end{aligned} \tag{10}$$

MINIMIZING THE FREE ENERGY FUNCTION TO OBTAIN THE SPONTANEOUS POLARIZATION

In Eq. (2), the functional dependence of the polarization enters explicitly via the first term. For a nano-box the polarization varies in all three space dimensions x_1, x_2, and x_3. So it is useful to consider the free energy for the general case in which the ferroelectric is in the region V bounded by a closed surface S. The free energy in this case is of the form

$$\begin{aligned} G = &\int_V f_{\text{cubic}}\big(\mathbf{x},\mathbf{P},\mathbf{P}_{x_1},\mathbf{P}_{x_2},\mathbf{P}_{x_3},\langle\mathbf{P}\rangle\big)\,dV \\ &+ \int_S f_{\text{surf}}\big(\mathbf{x},\mathbf{P}\big)\,dS. \end{aligned} \tag{11}$$

The spontaneous polarization distribution is that which minimizes the free energy, that is, the problem of minimizing a functional. This will be done using the classical Euler-Lagrange calculus of variations method. Applying this method[13] results in the following set differential equations for **P**:

$$\begin{aligned}
&\alpha_1(T-T_C)P_i + P_i\sum_{j=2}^{3}\alpha_j\left(P^2\right)^{j-1} \\
&+\beta_2 P_i\sum_{j=1}^{2}\sigma^j\left(P_j^2\right) \\
&+\beta_3 P_i\left[2P_i^2\sum_{j=1}^{2}\sigma^j\left(P_i^2\right)+\sum_{j=2}^{2}\sigma^j\left(P_j^4\right)\right] \\
&+\delta\nabla^2 P_i + \frac{1}{\epsilon_0\epsilon_\infty}\left(P_i-\langle P_i\rangle\right), \quad i=1,2,3, \quad (12)
\end{aligned}$$

where,

$$\nabla^2 = \frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial x_3^2}. \quad (13)$$

Assuming that $d(\mathbf{x}|_S)$ is constant over the surfaces, the boundary conditions are

$$\mp\frac{\partial P_i}{\partial x_i}+\frac{1}{d_i^{\mp}}=0\ \forall\mathbf{x}\in S_{x_i=l_j^{\mp}} \quad i=1,2,3. \quad (14)$$

The spontaneous polarization, which is a function of x_1, x_2 and x_3, is found by solving Eq. (12) subject to the boundary conditions (Eq. (14)), and the solution could be denoted $\mathbf{P}=\mathbf{P}_s$. There is no analytical solution and the equations will have to be solved numerically. Such work has yet to be done, but is in progress and will be reported in due course. However, it is likely that a multigrid numerical solution technique will be a good way to solve the equations efficiently.

DYNAMICS

Here it will be shown how the dynamic response of the ferroelectric nano-box to incident electromagnetic radiation can be calculated. The dynamic response is modeled using Landau-Khalatnikov equations[14], which are of the form[15],

$$m\frac{\partial^2 P_i}{\partial t^2}+\gamma\frac{\partial P_i}{\partial t}=-\frac{\delta G}{\delta P_i}+E_i, \quad i=1,2,3. \quad (15)$$

The δ notation on the right hand side of the equation denotes a variational derivative[13]; the incident electric field is $\mathbf{E}=(E_1,E_2,E_3)$; m and γ are mass and damping parameters, respectively. Values of these parameters can be found from experimental data[16], or in some cases from first-principles calculations[1].

To find the response of the ferroelectric nano-box to **E** it is necessary to to solve the Landau-Khalatnikov equation together with the Maxwell wave equation:

$$\frac{\partial^2 E_i}{\partial x_i^2}+\frac{\epsilon_\infty}{c^2}\frac{\partial^2 E_i}{\partial t^2}=-\frac{1}{\epsilon_0 c^2}\frac{\partial^2 P_i}{\partial x_i^2} \quad i=1,2,3. \quad (16)$$

When solving theses equations the dynamic response is written as the sum of the spontaneous polarization $\mathbf{P}_s$ and the changes to it $\mathbf{Q}(t)$ caused by the incident field **E**, that is, $\mathbf{P}(t)=\mathbf{P}_s+\mathbf{Q}(t)$. To make further progress it will first be necessary to calculate $\mathbf{P}_s$ and therefore is left for future work to be reported in due course.

AN OUTLINE OF THE EFFECTS OF STRAIN

The analysis above is suitable for free standing nano-boxes in which there are no appreciable strains other than those directed along the direction of the polarization. In Ref. [1] it is explained that strains in this direction do not change the form of the free energy. Instead they cause a change in the phenomenological values of some of the coefficients without altering the form of the free energy. To account for strains in other directions, an extension of the theory that introduces strain terms into the free energy is required. The starting point for such a development could be the consideration of unequal biaxial misfit strains. These strains could be induced in the nano-box if it were grown on a substrate that gave rise to a lattice mismatch. According to Wang and Zang[8], for a cubic film on a tetragonal substrate, the mismatch creates two components of misfit strain given by $\epsilon_{11}=(b-a_0)/b$ and $\epsilon_{22}=(c-a_0)/c$, where b and c are the substrate lattice parameters, and a_0 is the cubic cell constant of the film in the free standing paraelectric state. Here the interest is in a nano-box rather than a film, but as a first approximation these strain forms could be assumed, and in the direction normal to the substrate, would give rise to an extra term in the free energy of the form

$$\frac{s_{11}(\epsilon_{11}^2+\epsilon_{22}^2)-2s_{12}\epsilon_{11}\epsilon_{22}}{2(s_{11}^2-s_{12}^2)}. \quad (17)$$

Renormalization of some the other coefficients in the free energy would also occur—see Wang and Zhang[8] for further details. But these can be considered as modifying the phenomenological values of the affected constants. So the essential change in form of the free energy is given by the additional term in Eq. (17).

CONCLUSION

Formally, it has been shown how Landau-Devonshire theory can be used to the calculate the spontaneous polarization in a ferroelectric nano-box. In addition the equations for calculating the dynamic response to an incident electric field have been presented. This opens up a program of future research concerned with solving these equations for a given ferroelectric. The nature of the equations is such that numerical techniques will be required to solve them.

A possible way of incorporating the effects of strain into the theory has also been discussed. The substantial work required to extend this in a more general way appropriate for ferroelectric nano-boxes will also provide an interesting programme of future research activity.

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