Nanoscale Ferroelectric Films, Strips and Boxes

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Additional information is available at the end of the chapter

1. Introduction

A major characteristic of ferroelectric materials is that they posses a non-zero polarization in the absence of any applied electric field provided that the temperature is below a certain critical temperature[1]; in the literature this is often called a spontaneous polarization, or an equilibrium polarization. Another important defining characteristic is that this polarization can be reversed by applying an electric field. This is the basis of a useful application of ferroelectrics in which binary information can be stored according to the polarization direction which can be switched between two states by an electric field. For example, a thin film of ferroelectric can be switched to different states at different regions by suitably patterned electrodes, thus creating a ferroelectric random access memory[2].

With the increasing miniaturization of devices it becomes important to investigate size-effects in ferroelectrics. Thin film geometries are of interest in which one spatial dimension is confined, as well as strip geometries in which two-dimensions are confined, and, what here we will call box geometry in which all three dimensions are confined. By confinement we mean that surfaces of the ferroelectric that intersect on at least one line going through the central region of the ferroelectric are sufficiently close to this region to make their presence cause a non-negligible effect on the ferroelectric as a whole so that the behaviour is different from what would be expected in a bulk region far from any surface. The geometries chosen are typical of the sort that can be fabricated in micro or nanoelectronics and fit conveniently into a Cartesian coordinate system.

The aim of this chapter is to show how the equilibrium polarization can be calculated in general for a confined volume of ferroelectric and this is applied to the three aforementioned geometries. In fact such calculations for thin films are well established[3–7]; here they are included with the other geometries, which are not so well studied, for completeness, and because they fit logical into the theoretical framework to be presented. A general problem of a similar nature to the one of interest here, but applied to spheres and cylinders has been considered by Morison's et al.[8]. This work employed approximate analytical solutions to the problem of calculating the polarization and avoided a full three-dimensional application of the general theory.

$T > T_C$ $T < T_C$

Paraelectric phase   Ferroelectric phase
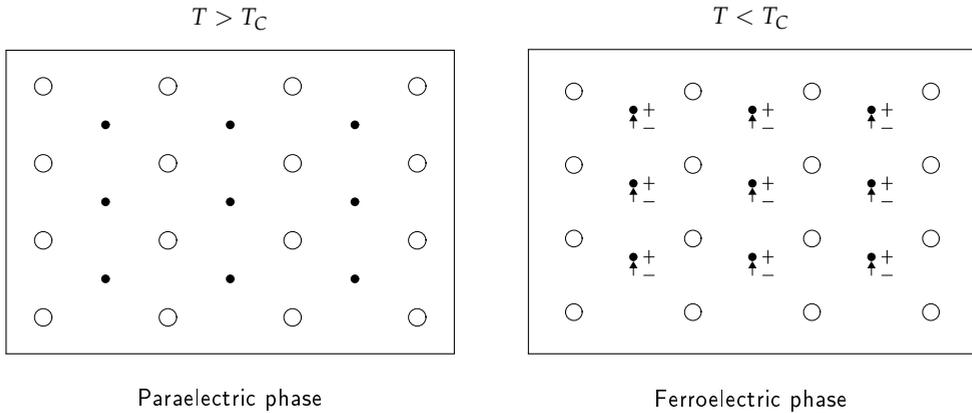
Figure 1. A two-dimensional representation of how a crystal structure changes symmetry when passing between the paraelectric ($T > T_C$) and ferroelectric ($T < T_C$) phases

2. Foundations of the Landau-Devonshire theory of ferroelectrics

2.1. Bulk ferroelectrics

Since Landau-Devonshire theory is the theoretical basis for the work in this chapter it will be introduced here. Further details can be found elsewhere such as in Refs. [1, 9, 10]. In this section we consider the case of a bulk ferroelectric; the effect of surfaces will be introduced after that.

It is common to state that the starting point for Landau-Devonshire theory is the free energy per unit volume of a bulk ferroelectric expressed as an expansion in powers of the polarization P. The observed equilibrium polarization P_0 is then given by the value of P that minimizes the free energy. Here, however, following Strukov and Lenanyuk[10], we outline how this expansion comes from a statistical thermodynamic treatment involving an incomplete Gibbs potential, since this gives more insight into the theory. First a few more details about the nature of ferroelectrics.

When a ferroelectric crystal is above the critical temperature T_C there is no spontaneous polarization; this is the paraelectric or high symmetry phase in which the crystal structure is of higher symmetry than the ferroelectric phase below T_C since the appearance of the spontaneous polarization lowers the symmetry, as is evident from the two-dimensional representation in Fig. 1. Thus we see that during the transition from the paraelectric to ferroelectric state, a structural phase transition occurs. A consequence of this is that as the temperature approaches T_C the structure becomes easy to distort giving rise to anomalous peaks in some of the properties such as the dielectric function ϵ, as illustrated in Fig. 2. In fact, in the ferroelectric phase, a crystal may have different domains such that the polarization in adjacent domains is not in the same direction[9], however it is possible to produce single-domain crystals—by cooling through T_C in the presence of an electric field in one of the possible polarization directions for instance—and that is what we consider here.
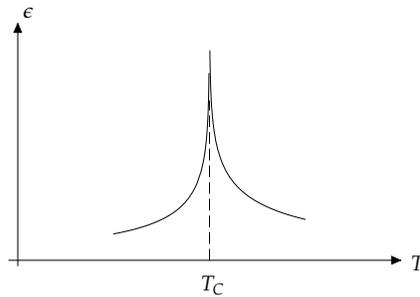
Figure 2. A peak in the dielectric function ϵ occurs as $T \to T_C$.

In the simplest case, then, a ferroelectric phase transition can be described by a single parameter that in Fig. 1 would be describable by the displacement of the sublattice from its central position. Since the paraelectric phase is of higher symmetry than the ferroelectric phase we can consider it to be more orderly and so the parameter is sometimes referred to as an order parameter. Actually the atoms are ions with charge and the corner-atom lattice would have a charge opposite to that of the interior sub-lattice. From the macroscopic point of view the corner atoms can be considered to produce a focus of charge at the center of each rectangle of opposite sign to the atoms that are displaced during the phase transition (see Fig. 1 where the centers of positive and negative charge are marked for the ferroelectric phase). For this reason the order parameter is often taken to be the polarization, which is the dipole moment per unit volume. For the time being, however, we will stay with the displacement representation of the order parameter as this is more directly related to the structural transition. If the displacement is denoted by η then it is clear that in the ferroelectric phase $\eta \neq 0$ and in the paraelectric phase $\eta = 0$.

The description above implies that each center ion is displaced in the same direction and this is the case for what are termed displacive ferroelectrics. There is another possibility, however, in which the displacement is not the same for every unit cell. For example, in some cells the displacement could be up while in others it could be down. Macroscopically ferroelectric and paraelectric phases can still result but now the ferroelectric phase occurs when statistically there are more displaced in one direction than in the other; and the paraelectric phase corresponds to the number of atoms displaced upwards is statistically equal to the number displaced downwards. In this case the ferroelectric is called an order-disorder ferroelectric. In terms of the macroscopic crystal symmetry however displacive and order-disorder ferroelectrics are equivalent and both can be described in general by Landau-Devonshire theory. The crystal structure of order-disorder ferroelectrics tends to be more complicated than for the displacive type[9, 10].

The basis of the Landau-Devonshire theory is that in the phase transition the ferroelectric phase may be represented by a distorted symmetrical phase. As outlined above this is a macroscopic view and the theory is phenomenological, as will be brought out further below. It turns out that the symmetry elements lost by the crystal at the transition temperature is sufficient information for a description of the anomalies of practically all of the thermodynamic properties of the crystal[10].

To make further progress consider the crystal as a system of N interacting particles with potential energy $U(\mathbf{r}_1, \ldots, \mathbf{r}_N)$. According to Gibbs[11, Chapter 8], the equilibrium thermodynamic potential at pressure p and temperature T associated with the potential energy of interaction of the particles is given by

$$\Phi(p, T) = -k_B T \ln Z, \tag{1}$$

where k_B is Boltzmann's constant and

$$Z = \int_{-\infty}^{\infty} \exp\left[-U(\mathbf{r}_1, \ldots, \mathbf{r}_N) / (k_B T)\right] \prod_i d\mathbf{r}_i. \tag{2}$$

The expression for Z in Eq. (2) comes from the probability that the value of the radius vector of the first particle lies between $\mathbf{r}_1$ and $\mathbf{r}_1 + d\mathbf{r}_1$ and similarly for the other vectors, being given by

$$dw = C \exp\left[-U(\mathbf{r}_1, \ldots, \mathbf{r}_N) / (k_B T)\right] \prod_i d\mathbf{r}_i. \tag{3}$$

Since integration of all of the variables must yield unity, $C = 1/Z$. The probability distribution can therefore be written as

$$dw = \exp\left\{\left[\Phi(p, T) - U(\mathbf{r}_1, \ldots, \mathbf{r}_N)\right] / (k_B T)\right\} \prod_i d\mathbf{r}_i. \tag{4}$$

A Gibbs thermodynamic potential for nonequilibrium states can also be formulated by using a larger number of variables than only p and T. The new variables are introduced via a linear transformation:

$$\mathbf{r}_1, \ldots, \mathbf{r}_N \rightarrow \xi_1, \ldots, \xi_{3N}. \tag{5}$$

We choose one of these variables to be η, which describes the nonequilibrium state of interest as explained above, by setting $\xi_1 = \eta$. Now

$$dw = \exp\left\{\left[\Phi(p, T) - U(\eta, \xi_2 \ldots, \xi_{3N})\right] / (k_B T)\right\} d\eta \, d\xi_2 \cdots \xi_{3N}, \tag{6}$$

the probability that the variables will lie in the ranges η to $\eta + d\eta$, ξ_2 to $\xi_2 + d\xi_2$, and so on. Focusing on the variable of interest η the probability of finding the system in a state in which this variable is in the range $\eta + d\eta$ is

$$dw(\eta) = d\eta \int_{-\infty}^{\infty} \exp\{[\Phi(p,T) - U(\eta,\xi_2,\ldots,\xi_{3N})]/(k_BT)\}d\xi_2 \cdots \xi_{3N}. \tag{7}$$

The thermodynamic potential is now also a function of η, and we write

$$\Phi(p,T,\eta) = -k_BT\ln\int_{-\infty}^{\infty}\exp\{[-U(\eta,\xi_2,\ldots,\xi_{3N})]/(k_BT)\}d\xi_2\cdots\xi_{3N}, \tag{8}$$

and

$$dw(\eta) = \exp\{[\Phi(p,T) - \Phi(p,T,\eta)]/(k_BT)\}d\eta. \tag{9}$$

Here it can be seen that the value of η that minimizes $\Phi(p,T,\eta)$ will maximize the distribution function and so this value corresponds to the equilibrium value of η. If $\Phi(p,T,\eta)$ is known, the usual equilibrium function $\Phi(p,T)$ can be found, using Eq. (9), from

$$\Phi(p,T) = -k_BT\ln\int_{-\infty}^{\infty}\exp\{[-\Phi(\eta)]/(k_BT)\}d\eta. \tag{10}$$

Now, let the equilibrium value of η be η_0—which corresponds to the minimum value of $\Phi(p,T,\eta)$—and expand $\Phi(p,T,\eta)$ in a series about the point $\eta = \eta_0$:

$$\Phi(p,T,\eta) = \Phi(p,T,\eta_0) + \Delta\Phi(p,T,\eta-\eta_0) = \Phi(p,T,\eta_0) + \frac{1}{2}A(p,T)(\eta-\eta_0)^2 + \cdots. \tag{11}$$

Using Eq. (10), $\Phi(p,T)$ can be written as

$$\Phi(p,T) = \Phi(p,T,\eta_0) - k_BT\ln\int_{-\infty}^{\infty}\exp\{[-\Delta\Phi(p,T,\eta-\eta_0)]/(k_BT)\}d\eta. \tag{12}$$

In Eq. (12) the first term is the minimum of the potential as a function of p, T and η, and we are interested in the minimizing value $\eta = \eta_0$ for given values of p and T. The second term is the contribution to the thermodynamic potential of fluctuations in η with order of magnitude given by the thermal energy per degree of freedom $K_BT/2$. However since we are dealing with a large number of particles in a macroscopic sample ($\sim 10^{23}$) the fluctuations are very small and the second term can be neglected to give

$$\Phi(p,T) = \Phi(p,T,\eta_0). \tag{13}$$

Note that if the total number of degrees of freedom (left unintegrated as the single degree η was) required to describe the system is comparable to N, then the neglect of the second term is no longer valid and Eq. (10) must be used in place of Eq. (13). We will not be concerned with such situations here, but very close to the transition temperature the Landau-Devonshire theory breaks down and the fluctuations must be considered, which can be done with the aid of Eq. (10), as discussed in Ref. [10].

In general thermodynamic functions which contain extra variables that remain unintegrated as η was above, are nonequilibrium thermodynamic functions known as incomplete functions. The general form is

$$\Phi(p, T, \eta_1, \eta_2, \ldots, \eta_n) = \Phi_0(p, T) + \Phi_1(p, T, \eta_1, \eta_2, \ldots, \eta_n). \tag{14}$$

The equilibrium values of the η_i are found by minimizing $\Phi(p, T, \eta_1, \eta_2, \ldots, \eta_n)$ according to

$$\frac{\partial \Phi}{\partial \eta_1} = 0, \ldots, \frac{\partial \Phi}{\partial \eta_n} = 0, \tag{15}$$

which determine a set of minimizing values $\eta_{oi}(p, T)$. Substituting these values into Eq. (14) determines the equilibrium thermodynamic function

$$\Phi(p, T) = \Phi_0(p, T) + \Phi_1(p, T, \eta_{01}, \eta_{02}, \ldots, \eta_{0n}). \tag{16}$$

This does not take fluctuations of the η_{0i} into account but the corresponding error will be small provided that $n \ll 3N$.

Although we are only considering a ferroelectric phase transition of the simplest type describable by introducing a single extra variable η into the thermodynamic potential the general form shows how to treat more complicated cases for which the polarization may occur in more ways than along one line, as we will see later. Polarization in three-dimensionss can be treated with three parameters, η_1 to η_3.

Returning to a one-component case we now show how the form of the thermodynamic potential can be worked out. As explained, in a ferroelectric phase transition we are dealing with displacements of certain atoms or groups of atoms; the structure of the nonsymmetric phase can be obtained from the structure of the symmetric phase by small displacements. Although the same lowering of symmetry in a phase transition can occur with different types of ordering implying that the choice of the order parameter is ambiguous, it turns out that the character of the anomalies of the physical properties in the transitions can be elucidated for any particular relationship between the order parameter and the displacements as long at the appearance of the order parameter leads to a symmetry change corresponding to that of the crystal's[10, 12].

In view of this we can take the order parameter as the extra variable of the incomplete thermodynamic potential. The phase transition can then be described at a given pressure if $\Phi(p, T, \eta)$ has a minimum at $\eta = 0$ in the symmetric phase ($T > T_C$), and at least two
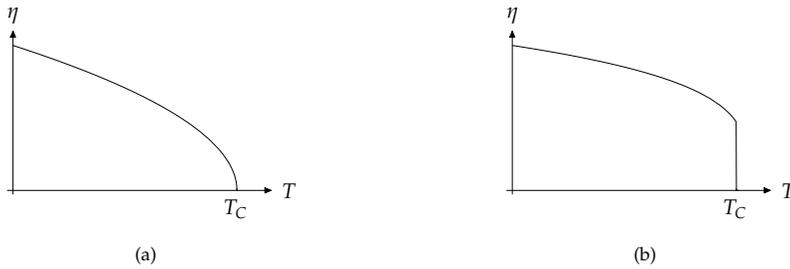
Figure 3. (a) Second order phase transition in which the order parameter decreases continuously to zero. (b) First order phase transition in which the order parameter displays a discontinuity. There is a continuous decrease in η before, which means that it is a first-order transition close to a second order transition. at $T = T_C$.

minima[1] at $\eta \neq 0$ in the nonsymmetric phase ($T < T_C$). The function $\Phi(p, T, \eta)$ must be consistent with this as T changes through the transition temperature so that it is determined for both the symmetric and nonsymmetric phases. These requirements place restrictions on the dependence of the potential Φ on η: Φ is a scalar function characterizing the physical properties of ferroelectric crystals, and as such must be invariant under any symmetry operations on the symmetric phase consistent with the crystal symmetry of this phase.

Before exploring further the form of Φ that describes the phase transition the difference between first and second order phase changes will be discussed. In a second order transition η decreases continuously to zero as the temperature is lowered through T_C; in a first order transition, on the other hand, there is a discontinuous jump of η to zero at $T = T_C$. Both situations are illustrated in Fig. 3. The first order transition shown in this figure is in fact close to a second order transition and so there is a continuous decrease in η before the jump and the jump is not very large. Crystals can exhibit first or second order transitions depending on the crystal structure[9, 10]. Either case can be treated by Landau-Devonshire theory, as long as the first order case is close to a second order transition. Turning back now to the development of an expression for Φ, we see that in the vicinity of a second order transition it is permissible to deal only with small lattice distortions, that is, small η. Hence the thermodynamic potential can be expanded into a series in η, with p and T treated as parameters, and we obtain

$$\Phi(p, T, \eta) = \Phi(p, T, 0) + \Phi'(p, T, 0)\eta + \frac{1}{2}\Phi'(p, T, 0)\eta^2 + \cdots . \tag{17}$$

To represent a given crystal this expression must be invariant under symmetry operations that correspond to the symmetry elements of the crystal. A ferroelectric phase transition resulting in a spontaneous polarization occurs as long as the order parameter transforms as a vector component. Only crystal symmetries for which this is true are ferroelectric and then the order parameter can be considered to be equivalent to a component of the spontaneous polarization (this point is discussed in more detail in Refs.[9, 10, 12]).

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[1] Part of the definition of a ferroelectric is that it has a reversible polarization in the nonsymmetric phase so that at least two minimum are required; otherwise the reverse direction would not be an equilibrium state.

$2/m$	1	2	m	$\bar{1}$
$\eta = P$	P	P	$-P$	$-P$

Table 1. Transformation of the order parameter
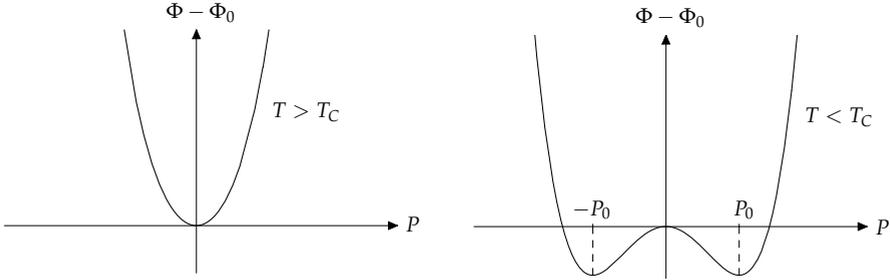
Figure 4. The form of $\Phi - \Phi_0$ that satisfies the basic requirements for a ferroelectric phase transition. When $T > T_C$ there is single minimum at $P = 0$ and there is no spontaneous polarization; for $T < T_C$ a spontaneous polarization can exist at one of the minima at $P = \pm P_0$.

To make further progress we consider a definite example of a symmetry which allows the order parameter to transform as a vector and so corresponds to a polarization having a single component; to reflect this correspondence we also make the notation change $\eta \to P$ where P is the polarization component.[2]   Consider a second-order phase transition such that the change into the ferroelectric state at the critical temperature is accompanied by a symmetry change from the group $2/m$ (symmetry elements: 1, $\bar{1}$, m, 2) to 2 (symmetry elements: 1, 2). The ferroelectric triglycine sulphate shows this symmetry change during its phase transition[13, 14]. During the transition to the nonsymmetric phase the crystal loses the inversion center and the plane of symmetry, $\bar{1}$ and m. These disappearing symmetry elements correspond to the symmetry operations that reverse the sign of the order parameter $\eta = P$, as is shown in Table 1. Since Φ must be invariant under any transformations of the symmetrical phase it is clear from this that it cannot include terms linear in P or odd powers of P, since such terms would be changed by the operations m and $\bar{1}$.

Therefore the first $\eta = P$ dependent term in Eq. (17) will be of the form $A(p,T)P^2$. For simplicity we now assume that the pressure is at some fixed value and discuss the temperature dependence. The expression for Φ must reflect the fact that at $T > T_C$ there is a minimum at $P = 0$ so that the equilibrium state (represented by the minimum) is one in which $P = 0$, and when $T < T_C$ there will be two minima for which $P \neq 0$ so that the possible equilibrium states occur at nonzero values of P. This is satisfied if $A(T)$ passes continuously from $A(T < T_C) < 0$ to $A(T > T_C) > 0$ when $T > T_C$, with $A(T = T_C) = 0$, provided that the next allowable term $B(T)P^4$ (remembering that odd terms have the wrong symmetry) is included with $B(T) > 0$, as can be seen from Fig. 4. This results in a thermodynamic potential of the form

$$\Phi = \Phi_0 + A(T)P^2 + B(T)P^4. \tag{18}$$

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[2] The general case in which the polarization has three components would be covered by three order parameters and the correspondence would be $(\eta_1 \to P_1, \eta_2 \to P_2, \eta_3 \to P_3)$, with $\mathbf{P} = (P_1, P_2, P_3)$.

Generally the exact form of the temperature dependence may be difficult to find. However near the phase transition temperature a series expansion in powers of $T - T_C$ (at a given pressure) can be used to give

$$A(T) = A(T_C) + A_1(T - T_C)A_2(T - T_C)^2 + \cdots \qquad (19)$$

$$B(T) = B(T_C) + B_1(T - T_C)B_2(T - T_C)^2 + \cdots . \qquad (20)$$

Taking into account the above mentioned properties: $A(T_C) = 0$ and $B(T_C) > 0$, the simplest forms retaining the essential non-zero first terms gives

$$A(T) = A_1(T - T_C) = \frac{1}{2}a(T - T_C) \qquad (21)$$

$$B(T) = B(T_C) = \frac{1}{4}b. \qquad (22)$$

The numerical factors are introduced for convenience, as will be clear shortly. We thus obtain, for a given pressure,

$$\Phi(T, P) = \Phi_0(T) + \frac{1}{2}a(T - T_C)P^2 + \frac{1}{4}bP^4. \qquad (23)$$

Usually it is sufficient to consider the energy due to the presence of the spontaneous polarization per unit volume (we are dealing with a bulk sample assumed uniform of the crystal volume) so that it is convenient to write, for a volume v of ferroelectric,

$$F = \frac{\Phi(T, P) - \Phi_0(T)}{v} = \frac{1}{2}\alpha(T - T_C)P^2 + \frac{1}{4}\beta P^4, \qquad (24)$$

where $\alpha = a/v > 0$, $\beta = b/v > 0$, and we refer to F as the Gibbs free energy density.

The equilibrium polarization P_0 is now found by minimizing F from the conditions

$$\frac{\partial F}{\partial P} = 0, \quad \text{and} \quad \frac{\partial^2 F}{\partial P^2} > 0.$$

From this we find

$$P_0^2 = \begin{cases} 0 & \text{for } T > T_C, \\ -\frac{\alpha(T - T_C)}{\beta} & \text{for } T < T_C. \end{cases} \qquad (25)$$

Here we see that it is necessary to differentiate to find P_0 which explains why the numerical coefficients $1/2$ and $1/4$ were introduced into the expansion of the thermodynamic potential.

The form of F in Eq. (24) is sufficient to describe a second order phase transition since $P_0 \to 0$ continuously as $T \to T_C$. For second order transitions in which there is a discontinuous jump, Eq. (24) is insufficient. However a first-order transitions near to a second-order transition the
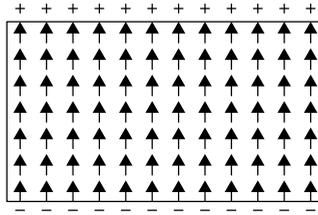
Figure 5. A component of polarization that is directed along a normal to the plane of the film when $T < T_C$. The resulting surface charges with opposite sides having signs of opposite charge, creates an electric field which in the opposite direction to the polarization.

phase change can be described by adding a further term in P^6 (a term in P^5, since it is an odd power, does not fulfill the symmetry requirements) which results in an energy density given by

$$F = \frac{1}{2}\alpha(T - T_C)P^2 + \frac{1}{4}\beta P^4 + \frac{1}{6}\gamma P^6. \tag{26}$$

But, whereas $\beta > 0$ for a second order transition, for F to exhibit a discontinuous jump it is necessary to choose $\beta < 0$ with $\gamma > 0$. More on this can be found in Lines and Glass[9].

We have thus shown in some detail how it is that a relatively simple free energy expression can account for the main characteristics of a ferroelectric, with the observed equilibrium polarization found by minimizing the free energy. Other terms can be added to the free energy to account for various external influences. For example an external electric field with component E along the direction of polarization can be accounted by first substituting the equilibrium polarization P_0 into F and adding a term EP_0. The corresponding susceptibility is then given by $\chi = \frac{\partial^2 F}{\partial E^2}$.

Note that Landau-Devonshire theory is a phenomenological theory of the macroscopic properties of the ferroelectric: the coefficients, α, β, etc., are not derivable from it; instead they must be found from experiment, or, in some cases, can be found from first-principle calculations[1].

2.2. Extension to thin films

Here a free-standing thin film is considered. If the equilibrium polarization below T_C has a component that is aligned with a normal to the plane of the film, then depolarization effects due to the space charge that appears at the surfaces, as illustrated in Fig. 5, must be taken into account. At first we avoid this complication by assuming a polarization that is in-plane. Also to remain with a one dimensional treatment for now we assume that this this is along the x direction of a Cartesian coordinate system and that the plane surfaces of the film are normal to the z axis at $z = 0$ and $z = L$, where L is the thickness of the film. The effect of the surfaces is such that the polarization near them may differ from the bulk value. For the case just described this implies that $P = P(z)$. It can be shown[1, 3, 15] that this can be accounted for in the free energy by adding surface terms involving P^2 integrated over the surfaces, and a gradient term $|dp/dz|$. The free energy is now given by

$$G = \left(\iint dxdy \right) \int_0^L f(P, dP/dz) \, dz + \frac{1}{2} \frac{D}{d} \left(\iint dx\,dy \right) \left[P^2(0) + P^2(L) \right], \qquad (27)$$

in which

$$f(P, dP/dz) = \frac{1}{2} AP^2 + \frac{1}{4} BP^4 + \frac{1}{6} CP^6 + \frac{1}{2} D \left(\frac{dP}{dz} \right)^2, \qquad (28)$$

the temperature dependence is in A through $A = a(T - T_C)$, and the integrals over x and y are factored out of the three dimensional integral over a volume of the film because P does not vary in these directions. Thus any surface area can be chosen to integrate over so that, if this areas is S, then $\iint dxdy = S$, and we can write a free energy per unit area as

$$F = \frac{G}{S} = \int_0^L dz \left[\frac{1}{2} AP^2 + \frac{1}{4} BP^4 + \frac{1}{6} CP^6 + \frac{1}{2} D \left(\frac{dP}{dz} \right)^2 \right] + \frac{1}{2} D \left[\frac{P^2(0)}{d} + \frac{P^2(L)}{d} \right]. \qquad (29)$$

Here since the film is free standing with identical surface properties for both surfaces the surface terms at $z = 0$ and $z = L$ involve the same factor, $1/d$, which simplifies the problem. If the film was not free standing, with for example, one surface an interface with a substrate, then this could be modeled by introducing different factors[6] so that the last term in square brackets in Eq. (29) would be replaced by $P(0)/d_1 + P(L)/d_2$.

The equilibrium polarization is still the P that minimizes F, but now the problem is to find the function $P(z) = P_0(z)$ that minimizes F rather than a finite set of values. So we are dealing with the minimization of a functional and the classical methods from the calculus of variations[16, Chapter 4] may be used, which cast the problem into the form of a differential equation known as the Euler-Lagrange equation and the function that minimizes F is the solution to this equation for a set of boundary conditions that also need to be specified. In this case, as will be shown below the boundary conditions used are implicit in Eq. (29) and are equivalent to allowing the polarization to be free at the film surfaces rather than fixed. More details on the method for the general three dimensional case are given in Section 4. Here we simply state that the classical methods lead to the following Euler-Lagrange equation and boundary conditions for the equilibrium polarization in the film:
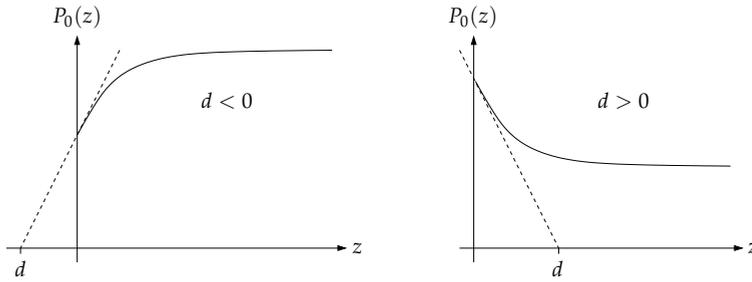
$$D \frac{d^2 P_0}{dz^2} - AP_0 - BP_0^3 - CP_0^5 = 0. \qquad (30)$$

With boundary conditions

$$\frac{dP_0}{dz} - \frac{1}{d} P_0 = 0, \quad \text{at } z = 0, \qquad (31)$$

and

$$\frac{dP_0}{dz} + \frac{1}{d} P_0 = 0, \quad \text{at } z = L. \qquad (32)$$

Figure 6. The extrapolation length d for one of the film surfaces at $z = 0$. For $d < 0$ the polarization turns down as the surface is approached; for $d > 0$ it turns up; this is also true for the surface at $z = L$ (not shown). Here the extrapolated gradient line crosses the z-axis at $z = 0 + d$; for the surface at $z = L$ it would cross at $z = L + d$.

It can be seen from the boundary conditions that d can be interpreted as an extrapolation length, as illustrated in Fig. 6. For $d < 0$ the polarization turns upwards as it approaches a surface; for $d > 0$ it turns down as a surface is approached.

Now the task is to solve the differential equation—Eq. (30) which is nonlinear—subject to the boundary conditions. For first order transitions in which $C \neq 0$ the equation must be solved numerically[17, 18]. However, for the simpler case of second-order transitions ($C = 0$) even though the equation is still nonlinear, an analytical solution can be found in terms of elliptic functions[3, 19, 20] and is given by

$$P_0(z) = P_1 \, \text{sn} \left[K(\lambda) - \frac{z - L/2}{\zeta}, \lambda \right], \quad \text{for } d < 0, \tag{33}$$

where sn is the Jacobian elliptic function with modulus $\lambda = P_1/P_2$, $K(\lambda)$ is the complete elliptic integral of the first kind (see Ref. [21] for more on elliptic functions and integrals),

$$P_1^2 = -\frac{A}{B} - \sqrt{\frac{A^2}{B^2} - \frac{4G}{B}}, \tag{34}$$

$$P_2^2 = -\frac{A}{B} + \sqrt{\frac{A^2}{B^2} - \frac{4G}{B}}, \tag{35}$$

$$\zeta = \frac{1}{P_2} \sqrt{\frac{2D}{B}}, \tag{36}$$

and G is found by substituting it into the boundary conditions and solving the resulting transcendental equations numerically.

A plot of the polarization profile according to Eq. (33) is given in Fig. 7 for parameter values given in the figure caption. The polarization throughout the film decreases continuously to zero as the temperature increases and approaches T_C. So there are two states: a ferroelectric state below T_C for which there is a polarization everywhere in the film and a paraelectric state above T_C for which the polarization is zero everywhere.

$P_0(z/\zeta_1)/P_{0\infty}$
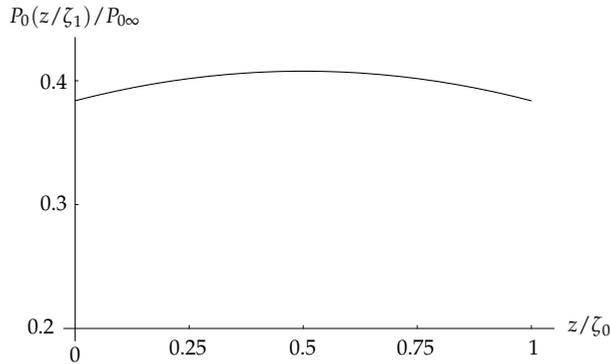
Figure 7. Polarization in a thin film plotted from Eq. (33) and the boundary conditions in Eqs. (31) and (32). Dimensionless variables and parameters used are: $P_{0\infty} = (aT_C/B)^{1/2}$ (the spontaneous polarization for a bulk ferroelectric), $\zeta_0 = [2D/(aT_C)]^{1/2}$, $\zeta_1 = P_{0\infty}/P_2$ (P_2 is given by Eq. (35)), $\Delta T' = (T - T_C)/T_C = -0.4$, $L' = L/\zeta_0 = 1$, $d' = 4L'$, $G' = 4GB/(a/T_C)^2 = 0.105$ (found from the boundary conditions).

The case $d > 0$ is complicated by the appearance of a surface term between T_C and a lower temperature T_{C0} for which the regions near the film surfaces have a spontaneous polarization but the polarization in the interior is still zero. Only below T_{C0} is there a nonzero polarization in the interior of the film. The form of the solution, although still expressible in terms of an elliptic function is somewhat different for the surface state, as is discussed elsewhere[3, 19, 20]

The above was for in-plane polarization which, as has been explained, avoids the need to consider a depolarization field induced by the polarization. In general, however, there may be an out-of-plane component that would give rise to a depolarization field. Theoretical descriptions of the depolarization field have been considered by several authors[5, 7, 22, 23]. For the case in which there are no free charges at the surfaces it can be shown[5, 22] from Maxwell's equations that a term

$$\frac{1}{2\epsilon_0\epsilon_\infty}\Big[P\big(P - \langle P\rangle\big)\Big] \tag{37}$$

added to the energy density in Eq. (28) accounts for the effect of the depolarization field provided that P is now taken to be directed along a normal to the plane of the the film (as it is in Fig. 5). In Eq. (37) ϵ_0 is the permittivity of free space and ϵ_∞ is the background dielectric constant of the film[5, 24], and

$$\langle P\rangle = \frac{1}{L}\int_0^L P\,dz, \tag{38}$$

which is the average value of $P(z)$ in the film.

3. The free energy density appropriate for a three-dimensional treatment of a ferroelectric crystal

The general form of the free energy density for the interior of a ferroelectric crystal in three-dimensions can be written as series expansion in components of the polarization,

together with terms taking into account the influence of surfaces and depolarization fields. The region occupied by the interior of the ferroelectric (the surface energy will appear later as a surface energy density integrated over the surface), is taken to be the interior of a rectangular box defined by

$$V = \{\mathbf{x} \mid x_i \in (l_i^-, l_i^+), i = 1, 2, 3\}, \tag{39}$$

so that the sides of the box are given by $l_i = l_i^+ - l_i^-$, $i = 1, 2, 3$. Extending the formalism in the previous sections to three dimensions, the energy density can be written

$$f\left(\mathbf{x}, \mathbf{P}, \mathbf{P}_{x_1}, \mathbf{P}_{x_2}, \mathbf{P}_{x_3}, \langle \mathbf{P} \rangle\right) = f_{\text{series}}\left(\mathbf{x}, \mathbf{P}\right) + f_{\text{grad}}\left(\mathbf{x}, \mathbf{P}_{x_1}, \mathbf{P}_{x_2}, \mathbf{P}_{x_3}\right) + f_{\text{dep}}\left(\mathbf{x}, \mathbf{P}, \langle \mathbf{P} \rangle\right) \tag{40}$$

The notation used for the arguments, which will be useful when applying calculus of variations methods in the next section, is as follows: $\mathbf{x} = (x_1, x_2, x_3)$, for a position in the crystal in Cartesian coordinates; $\mathbf{P} = (P_1, P_2, P_3)$, the polarization vector; $P_i = P_i(x_1, x_2, x_3)$, $i = 1, 2, 3$; $\mathbf{P}_{x_i} = \partial\mathbf{P}/\partial x_i$, $i = 1, 2, 3$, and the averages vector is $\langle \mathbf{P} \rangle = (\langle P_1 \rangle, \langle P_2 \rangle, \langle P_3 \rangle)$ in which

$$\langle P_i \rangle = \frac{1}{l_i} \int_{l_i^-}^{l_i^+} P_i \, dx_i. \tag{41}$$

The terms on the right of Eq. (40) are given next. The first of these terms f_{series} is the series expansion part of the free energy (due to the polarization, without a constant first term) in terms of the components of the polarization. A general series expansion in these terms can be written as

$$f_{\text{series}}\left(\mathbf{x}, \mathbf{P}\right) = \sum_{i=1}^{\infty} \frac{1}{i} \left(\sum_{\alpha_1 \geqslant \cdots \geqslant \alpha_i} A_{\alpha_1 \cdots \alpha_i} P_{\alpha_1} \cdots P_{\alpha_i} \right). \tag{42}$$

Here each α_i runs from x_1 to x_3 and the notation $\alpha_1 \cdots \alpha_i$ indicates that all permutations of $P_{\alpha_1} \cdots P_{\alpha_i}$ of the ith term, which would otherwise appear as separate, have already been summed: the inequalities insure that only one permutation is present for the ith term with coefficient $A_{\alpha_1 \cdots \alpha_i}$. However in practice, depending on the crystal symmetry, terms which are not separately invariant under the symmetry transformations of the symmetry group of the crystal, will not appear.

The term f_{grad}, a gradient term, is given by

$$f_{\text{grad}}\left(\mathbf{x}, \mathbf{P}_{x_1}, \mathbf{P}_{x_2}, \mathbf{P}_{x_3}\right) = \frac{1}{2}\delta\left[|\boldsymbol{\nabla}P_1|^2 + |\boldsymbol{\nabla}P_2|^2 + |\boldsymbol{\nabla}P_3|^2\right] = \frac{1}{2}\delta\left[\left|\frac{\partial\mathbf{P}}{\partial x_1}\right|^2 + \left|\frac{\partial\mathbf{P}}{\partial x_2}\right|^2 + \left|\frac{\partial\mathbf{P}}{\partial x_3}\right|^2\right]. \tag{43}$$

It is easy to show that $\frac{1}{2}\delta\left[|\boldsymbol{\nabla}P_1|^2 + |\boldsymbol{\nabla}P_2|^2 + |\boldsymbol{\nabla}P_3|^2\right]$ is equal to the right hand side of Eq. (43). Both forms are shown so that it can be seen that f_{grad} involves gradient terms. However the other form is sometimes convenient to work with. Note that in general there are other symmetry allowed terms such as $\left[\left|\frac{\partial\mathbf{P}}{\partial x_1}\right|^2\left|\frac{\partial\mathbf{P}}{\partial x_2}\right|^2\right]$. However usually such terms are ignored

– a practice which will be followed here. Nonetheless, in the future it may be interesting to study such terms to extended the formalism given here.

Finally f_{dep} is the term due to the depolarization field for the general case in which the polarization has components along x_1, x_2 and x_3. It is given by

$$f_{\text{dep}}(\mathbf{x}, \mathbf{P}, \langle \mathbf{P} \rangle) = \frac{1}{2\epsilon_0 \epsilon_\infty} \Big[P_1 (P_1 - \langle P_1 \rangle) + P_2 (P_2 - \langle P_2 \rangle) + P_3 (P_3 - \langle P_3 \rangle) \Big]. \tag{44}$$

Having dealt with the energy density for the interior of the ferroelectric the remaining energy density is the surface energy density at any point on the surface of the ferroelectric. This will be proportional to P^2, where $P = |\mathbf{P}|$ and, as will be evident below, it is convenient to write it as

$$f_{\text{surf}}(\mathbf{x}, \mathbf{P}) = \frac{\delta}{2d(\mathbf{x})} P^2(\mathbf{x}) \quad \text{for} \quad \mathbf{x} \in S, \tag{45}$$

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

$$S = S_{x_1 = l_1^-} \cup S_{x_1 = l_1^+} \cup S_{x_2 = l_2^-} \cup S_{x_2 = l_2^+} \cup S_{x_3 = l_3^-} \cup S_{x_3 = l_3^+} \tag{46}$$

where the sides of the box at $x_i = l_i^\mp$ are given by

$$S_{x_j = l_j^\mp} = \big\{ \mathbf{x} \,|\, x_i = l_i^\mp, x_{\sigma^j(i)} \in [l_i^-, l_i^+], j = 1, 2 \big\}, \tag{47}$$

where we have introduced the cyclic operator σ which performs the operation $x_1 \mapsto x_2 \mapsto x_3 \mapsto x_1$, so that

$$\sigma(x_i) = x_{j+1 \pmod 3}, \tag{48}$$

also σ applied n times where $n \geqslant 0$ is denoted by σ^n, and the definition of the operator is extended to when the x_i are arguments of a function h such that

$$\sigma \big(h(x_1, \ldots, x_3) \big) = h \big(\sigma(x_1), \ldots, \sigma(x_3) \big). \tag{49}$$

It is easy to see that many of the terms in the free energy can be written in a shortened form with this notation because successive terms can often be generated by cyclic permutations of a starting term; later this operator notation will be useful when the free energy for the box is inserted into the Euler-Lagrange equations in Section 5.

Showing the form of the free energy densities for the ferroelectric box helps pave a way for dealing with the general problem of finding the minimum of the free energy density for an arbitrary volume of ferroelectric, which will be discussed next.

4. The calculus of variations applied to the polarization of a ferroelectric of arbitrary shape in three dimensions

The next step towards working out the equilibrium polarization for ferroelectric boxes and strips—an extension of the theory for thin films—is to work out in general the free energy for an arbitrary volume of ferroelectric. The minimization of this, as for the thin film, involves the minimization of a functional, which involves the calculus of variations and will be dealt with using classical methods.

It can be seen from the previous section that the general form of the free energy for a ferroelectric in the region V in $\mathbb{R}^3$ bounded by the closed surface S is given by

$$G = \int_V f\left(\mathbf{x}, \mathbf{P}, \mathbf{P}_{x_1}, \mathbf{P}_{x_2}, \mathbf{P}_{x_3}, \langle \mathbf{P} \rangle\right) dV + \int_S f_{\text{surf}}\left(\mathbf{x}, \mathbf{P}\right) dS. \tag{50}$$

Here G depends on whatever function $\mathbf{P}$ is, so the domain of G is a function space and the equilibrium polarization distribution is that function $\mathbf{P}_0$ in the space which minimizes G. At this point certain boundary conditions could be imposed on $\mathbf{P}$ according to the physical situation. For a ferroelectric crystal no such conditions are imposed which implies that $\mathbf{P}$ is free at the boundaries. However natural boundary conditions (that do not fix $\mathbf{P}$) will emerge from the minimization as we will see.

The minimization of the functional G in Eq. (50) will be carried out using a classical technique due to Euler[16] which involves considering a variation around $\mathbf{P}_0 = (P_{01}, P_{02}, P_{03})$ in function space. To this end we write

$$\mathbf{P}(\mathbf{x}) = \mathbf{P}_0(\mathbf{x}) + \epsilon \boldsymbol{\eta}(\mathbf{x}), \tag{51}$$

in which ϵ is a variable parameter and $\boldsymbol{\eta} = (\eta_1, \eta_2, \eta_3)$ is an arbitrary vector function. G can now be expressed as

$$G(\epsilon) = \int_V f\left(\mathbf{x}, \mathbf{P}_0 + \epsilon \boldsymbol{\eta}, \mathbf{P}_{0x_1} + \epsilon \boldsymbol{\eta}_{x_1}, \mathbf{P}_{0x_2} + \epsilon \boldsymbol{\eta}_{x_2}, \mathbf{P}_{0x_3} + \epsilon \boldsymbol{\eta}_{x_3}, \langle \mathbf{P}_0 + \epsilon \boldsymbol{\eta} \rangle\right), \tag{52}$$

where

$$\mathbf{P}_{0x_i} = \frac{\partial \mathbf{P}_0}{\partial x_i}. \tag{53}$$

The key idea for finding the minimizing function $\mathbf{P}_0$ is that a necessary condition for its existence is

$$\left. \frac{dG}{d\epsilon} \right|_{\epsilon=0} = 0.$$

Applying this condition to Eq. (52), and using the chain rule when differentiating the integrands, we find

$$\frac{dG}{d\epsilon}\bigg|_{\epsilon=0} = \int_V \left\{ (\boldsymbol{\nabla}_{\mathbf{P}_0} f) \cdot \boldsymbol{\eta} + \left(\boldsymbol{\nabla}_{\mathbf{P}_{0x_1}} f \right) \cdot \boldsymbol{\eta}_{x_1} + \left(\boldsymbol{\nabla}_{\mathbf{P}_{0x_2}} f \right) \cdot \boldsymbol{\eta}_{x_2} + \left(\boldsymbol{\nabla}_{\mathbf{P}_{0x_3}} f \right) \cdot \boldsymbol{\eta}_{x_3} \right.$$
$$\left. + \left(\boldsymbol{\nabla}_{\langle \mathbf{P}_0 \rangle} f \right) \cdot \langle \boldsymbol{\eta} \rangle \right\} dV + \int_S (\boldsymbol{\nabla}_{\mathbf{P}_0} f_{\text{surf}}) \cdot \boldsymbol{\eta} \, dS = 0, \quad (54)$$

in which the notation

$$(\boldsymbol{\nabla}_{\mathbf{A}} f) \cdot \mathbf{B} = \frac{\partial f}{\partial A_1} B_1 + \frac{\partial f}{\partial A_2} B_2 + \frac{\partial f}{\partial A_3} B_3 \qquad (55)$$

has been introduced.

If all terms in the integrands in Eq. (54) could be written as a dot product with $\boldsymbol{\eta}$, as is the case for the first and last terms on the right of Eq. (54), then $\boldsymbol{\eta}$ would appear as a single factor in the volume and surface integrands. Eq. (54) could then be written in the form $\int_V \boldsymbol{\eta} \cdot \boldsymbol{\Lambda}_1 + \int_S \boldsymbol{\eta} \cdot \boldsymbol{\Lambda}_2$, where $\boldsymbol{\Lambda}_1$ and $\boldsymbol{\Lambda}_2$ do not involve $\boldsymbol{\eta}$. As shown below, the Euler-Lagrange equations and boundary conditions will then follow by setting $\boldsymbol{\Lambda}_1 = \boldsymbol{\Lambda}_2 = 0$, which will satisfy Eq. (54). Therefore we now proceed to express Eq. (54) in the $\boldsymbol{\eta}$ factored form.

To facilitate this we start by writing Eq. (54) as

$$\frac{dG}{d\epsilon}\bigg|_{\epsilon=0} = \int_V \left\{ (\boldsymbol{\nabla}_{\mathbf{P}_0} f) \cdot \boldsymbol{\eta} + \mathcal{I}_1 + \mathcal{I}_2 \right\} dV + \int_S (\boldsymbol{\nabla}_{\mathbf{P}_0} f_{\text{surf}}) \cdot \boldsymbol{\eta} \, dS = 0, \qquad (56)$$

where

$$\mathcal{I}_1 = \left(\boldsymbol{\nabla}_{\mathbf{P}_{0x_1}} f \right) \cdot \boldsymbol{\eta}_{x_1} + \left(\boldsymbol{\nabla}_{\mathbf{P}_{0x_2}} f \right) \cdot \boldsymbol{\eta}_{x_2} + \left(\boldsymbol{\nabla}_{\mathbf{P}_{0x_3}} f \right) \cdot \boldsymbol{\eta}_{x_3}, \qquad (57)$$

$$\mathcal{I}_2 = \left(\boldsymbol{\nabla}_{\langle \mathbf{P}_0 \rangle} f \right) \cdot \langle \boldsymbol{\eta} \rangle. \qquad (58)$$

Now we want to find $\boldsymbol{\Lambda}_1$ and $\boldsymbol{\Lambda}_2$ such that $\mathcal{I}_1 = \boldsymbol{\eta} \cdot \boldsymbol{\Lambda}_1$ and $\mathcal{I}_2 = \boldsymbol{\eta} \cdot \boldsymbol{\Lambda}_2$.

Starting with $\mathcal{I}_1$, by expanding the dot products and re-grouping the terms, it is easy to show that it can be rewritten as

$$\mathcal{I}_1 = (\boldsymbol{\nabla}_{P_{o1}\mathbf{x}} f) \cdot (\boldsymbol{\nabla} \eta_1) + (\boldsymbol{\nabla}_{P_{o2}\mathbf{x}} f) \cdot (\boldsymbol{\nabla} \eta_2) + (\boldsymbol{\nabla}_{P_{o3}\mathbf{x}} f) \cdot (\boldsymbol{\nabla} \eta_3), \qquad (59)$$

in which the following notation has been used:

$$\boldsymbol{\nabla} \mathbf{A} = \left(\frac{\partial A_1}{\partial x_1}, \frac{\partial A_2}{\partial x_2}, \frac{\partial A_3}{\partial x_3} \right) = \frac{\partial A_1}{\partial x_1} \hat{\mathbf{x}}_1 + \frac{\partial A_2}{\partial x_2} \hat{\mathbf{x}}_2 + \frac{\partial A_3}{\partial x_3} \hat{\mathbf{x}}_3, \qquad (60)$$

the normal gradient operation, where $\hat{\mathbf{x}}_i$, $i = 1, 2, 3$, are unit vectors along the corresponding x_i axes of a Cartesian coordinate system. Also,

$$\nabla_{A_{ix}} = \left(\frac{\partial}{\partial A_{ix_1}}, \frac{\partial}{\partial A_{ix_2}}, \frac{\partial}{\partial A_{ix_3}} \right), \tag{61}$$

with $A_{ix_j} = \partial A_i / \partial x_j$.

Now, we utilize the vector identity

$$(\nabla \phi) \cdot \mathbf{A} \equiv \nabla \cdot (\phi \mathbf{A}) - \phi \left(\nabla \cdot \mathbf{A} \right), \tag{62}$$

together with the divergence theorem

$$\int_V \nabla \cdot \mathbf{A} \, dV = \oint_S \mathbf{A} \cdot (\hat{\mathbf{n}} \, dS), \tag{63}$$

where at each point on the surface S, $\hat{\mathbf{n}} = \hat{\mathbf{n}}(\mathbf{x}|_S)$ is a unit normal vector directed outwards (from the enclosed volume). Using Eqs. (62) and (63), it follows that

$$\int_V \mathcal{I}_1 \, dV = - \int_V \boldsymbol{\eta} \cdot \left[\sum_{i=1}^3 \nabla \cdot \left(\nabla_{P_{0i}\mathbf{x}} f \right) \hat{\mathbf{x}}_i \right] dV + \int_S \boldsymbol{\eta} \cdot \left[\sum_{i=1}^3 \left\{ \left(\nabla_{P_{0i}\mathbf{x}} f \right) \cdot \hat{\mathbf{n}} \right\} \hat{\mathbf{x}}_i \right] dS. \tag{64}$$

Next the $\mathcal{I}_2$ term is dealt with. But here is is better to look at it together with the integral from the outset, by considering

$$\int_V \mathcal{I}_2 \, dV = \int_V \left(\nabla_{\langle \mathbf{P}_0 \rangle} f \right) \cdot \langle \boldsymbol{\eta} \rangle \, dV = \int_V \left(\sum_{i=1}^3 \frac{\partial f}{\partial \langle P_i \rangle} \langle \eta_1 \rangle \right) dV. \tag{65}$$

The reason for considering $\mathcal{I}_2$ inside the integral is that, remembering that $\langle \eta_i \rangle$ is proportional to $\int_{l_i^-}^{l_i^+} \eta_i \, dx_i$, Eq. (65) can be written as

$$\int_V \mathcal{I}_2 \, dV = \int_V \left(\sum_{i=1}^3 \eta_i \left\langle \frac{\partial f}{\partial P_{0i}} \right\rangle \right) dV = \int_V \boldsymbol{\eta} \cdot \left\langle \nabla_{\langle \mathbf{P}_0 \rangle} f \right\rangle dV, \tag{66}$$

by changing the order of integration. In doing this we have used the fact that $dV \equiv dx_1 dx_2 dx_3$ and $\int_V \equiv \int_{x_1} \int_{x_2} \int_{x_3}$.

The goal of factoring out $\boldsymbol{\eta}$ involving a dot product has now been achieved and Eq. (54) can be written, using Eqs. (64) and (66), as

$$\int_V \boldsymbol{\eta} \cdot \left[\boldsymbol{\nabla}_{\mathbf{P}_0} f - \sum_{i=1}^{3} \boldsymbol{\nabla} \cdot \left(\boldsymbol{\nabla}_{P_{0i}\mathbf{x}} f \right) \hat{\mathbf{x}}_i + \left\langle \boldsymbol{\nabla}_{\langle \mathbf{P}_0 \rangle} f \right\rangle \right] dV$$

$$+ \int_S \boldsymbol{\eta} \cdot \left[\sum_{i=1}^{3} \left\{ \left(\boldsymbol{\nabla}_{P_{0i}\mathbf{x}} f \right) \cdot \hat{\mathbf{n}} \right\} \hat{\mathbf{x}}_i + \boldsymbol{\nabla}_{\mathbf{P}_0} f_{\text{surf}} \right] dS = 0. \quad (67)$$

However, at first we consider a restricted function space such that $\boldsymbol{\eta}$ is zero on S; then the surface integral in Eq. (67) vanishes resulting in

$$\int_V \boldsymbol{\eta} \cdot \left[\boldsymbol{\nabla}_{\mathbf{P}_0} f - \sum_{i=1}^{3} \boldsymbol{\nabla} \cdot \left(\boldsymbol{\nabla}_{P_{0i}\mathbf{x}} f \right) \hat{\mathbf{x}}_i + \left\langle \boldsymbol{\nabla}_{\langle \mathbf{P}_0 \rangle} f \right\rangle \right] dV = 0. \quad (68)$$

For this to be zero for any $\boldsymbol{\eta}$ in the restricted space, it follows from the lemma of du Bois-Reymond[25], that

$$\boldsymbol{\nabla}_{\mathbf{P}_0} f - \sum_{i=1}^{3} \boldsymbol{\nabla} \cdot \left(\boldsymbol{\nabla}_{P_{0i}\mathbf{x}} f \right) \hat{\mathbf{x}}_i + \left\langle \boldsymbol{\nabla}_{\langle \mathbf{P}_0 \rangle} f \right\rangle = 0, \quad (69)$$

which can be rewritten as

$$\frac{\partial f}{\partial P_{0i}} - \boldsymbol{\nabla} \cdot \left(\boldsymbol{\nabla}_{P_{0i}\mathbf{x}} f \right) + \left\langle \frac{\partial f}{\partial \langle P_{0i} \rangle} \right\rangle = 0, \quad i = 1, 2, 3. \quad (70)$$

These form the Euler-Lagrange equations that we seek. It is clear that the lifting of the restriction on $\boldsymbol{\eta}$ so that it is not necessarily zero on S, means that the Euler-Lagrange equations still result from Eq. (67), provided the lemma of du Bois-Reymond is applied to the surface integral term. This implies the boundary conditions

$$\left(\boldsymbol{\nabla}_{P_{i}\mathbf{x}} f \right) \cdot \hat{\mathbf{n}} + \frac{\partial f_{\text{surf}}}{\partial P_i} \quad \text{on } S, \quad i = 1, 2, 3. \quad (71)$$

For any i the first term is a natural boundary condition arising from the minimization (not a prescribed condition), and the second term is due to the surface energy.

Thus we have shown that the equilibrium polarization for a ferroelectric of arbitrary shape in the region V is found by solving the Euler-Lagrange equations in Eq. (70), subject to the boundary conditions in Eq. (71). This formulation can be applied to finding the polarization in ferroelectrics with the geometries, box, strip and film, as will be shown in the next section for the case of a ferroelectric exhibiting a symmetric phase of cubic symmetry.
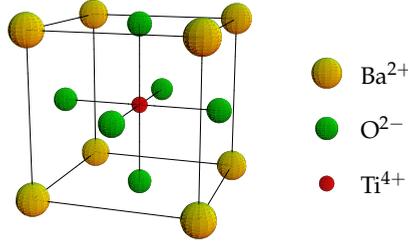
Figure 8. A structural unit for barium titanate, BaTiO$_3$.

5. The equilibrium Polarization in ferroelectric boxes, strips and films for cubic symmetry

Cubic symmetry is chosen because it is the symmetry of the popular perovskite ferroelectrics such as barium titanate (BaTiO$_3$) and lead titanate (PbTiO$_3$). A structural unit for barium titanate is represented in Fig. 8

The interest is in nanoscale boxes, strips and films. The formalism itself could easily be applied to thicker films, however for confinement in the nanoscale (in all three dimensions for boxes, in two dimensions in strips and in one for films) it is expected that the influence of the change in the polarization as it approaches a surface will have a more significant effect that at lager scales where the bulk properties would be more dominant, and so is sometimes referred to as a size effect.

5.1. Polarization for a ferroelectric nano-box

For a cubic crystal only those terms in f given by Eq. (40) that are invariant under the symmetry 16 operations of the cubic symmetry group[26] are allowed.[3] It can be shown[10, 12] that these are given by

$$
\begin{aligned}
f_{\text{cubic}}\left(\mathbf{x}, \mathbf{P}, \mathbf{P}_{x_1}, \mathbf{P}_{x_2}, \mathbf{P}_{x_3}, \langle \mathbf{P} \rangle\right) &= \alpha_1(T - T_C)P^2 + \sum_{i=2}^{3} \frac{1}{2i}\alpha_i\left(P^2\right)^i \\
&+ \frac{1}{2}\beta_2 \sum_{i=0}^{2} \sigma^i\left(P_1^2 P_2^2\right) + \frac{1}{2}\beta_3 \sum_{i=0}^{2} \sigma^i\left(P_1^4\left(P_2^2 + P_3^2\right)\right) + \frac{1}{2}\gamma_3 P_1^2 P_2^2 P_3^2 \\
&+ \frac{1}{2}\delta \sum_{i=1}^{3}\left|\frac{\partial \mathbf{P}}{\partial x_i}\right|^2 + \frac{1}{2\epsilon_0\epsilon_\infty} \sum_{i=1}^{3} P_i\left(P_i - \langle P_i \rangle\right), \quad (72)
\end{aligned}
$$

where the cyclic operator defined by Eqs. (48) and (49) is being used and, to lighten the notation a little we make the replacement $\mathbf{P}_0 \to \mathbf{P} \Rightarrow P_{oi} \to P_i$, although the subscript that distinguishes the equilibrium polarization from the general function space remains implied.

---

[3] The operations are: 1, $\bar{1}$, 4, 4^{-1}, $\bar{4}$, $\bar{4}^{-1}$, 2′, 2″, 2_x, 2_y, 2_z, m_1, m_2, m_3, m_4, m_5.

The Euler-Lagrange equations that need to be solved to find the equilibrium polarization in the nano-box are then found from Eq. (70) with $f = f_{\text{cubic}}$. The steps will not be shown here but the cyclic operator can make the working easier and it is straightforward to show that the required Euler-Lagrange equations are given by

$$\alpha_1(T - T_C)P_i + P_i \sum_{j=2}^{3} \alpha_j (P^2)^{j-1} + \beta_2 P_i \sum_{j=1}^{2} \sigma^j (P_j^2)$$

$$+ \beta_3 P_i \left[2P_i^2 \sum_{j=1}^{2} \sigma^j (P_i^2) + \sum_{j=2}^{2} \sigma^j (P_j^4) \right] + \delta \nabla^2 P_i + \frac{1}{\epsilon_0 \epsilon_\infty} (P_i - \langle P_i \rangle), \quad i = 1, 2, 3. \quad (73)$$

The surface term is given by Eq. (45), but here we assume that $d(\mathbf{x}|_S)$ is constant over each surface of the box. The boundary conditions in Eq. (71) can then be shown to reduce to

$$\mp \frac{\partial P_i}{\partial x_i} + \frac{1}{d_i^{\mp}} = 0 \; \forall \mathbf{x} \in S_{x_i = l_j^{\mp}} \quad i = 1, 2, 3. \tag{74}$$

For a free standing box it is reasonable to have $d_i^{\mp} = d \; \forall i = 1, 2, 3$.

The solution of Eqs. (73) and (74) has not yet been obtained but progress is being made on it and will be reported later. Eq. (73) is a nonlinear partial differential equation, and as such it is unlikely that an analytical solution can be found. Instead, a numerical approach or an approximate solution using trial functions with adjustable parameters could be employed. The box geometry is likely to be amenable to a finite difference numerical solution. Dealing with a simpler symmetry such as that discussed in the introduction would make the problem less computationally intensive but still not amenable to an analytical solution, as will now be discussed.

If Eq. (72) were reduced to a simpler form by putting $\alpha_3 = \beta_2 = \beta_3 = \gamma_3 = 0$, neglecting the depolarization terms, and arranging for the polarization to be aligned along only one coordinate axis; the problem would then be something like a three-dimensional form of the thin-film case discussed in Section 2.2. It might then be tempting to try a separation of variables approach to solving the Euler-Lagrange equations with the hope that the solution would be of the form $P(x_1)P(x_2)P(x_3)$ in which each factor is a solution of the form of the thin film solution given in Section 2.2. However any attempt to do this would fail to produce an exact solution to the three-dimensional problem due to the nonlinearity of a term cubic in the polarization. However it might be useful to treat $P(x_1)P(x_2)P(x_3)$ as an approximate function and introduce into it some variable parameters that could be optimized to find the best approximation. This idea is currently being explored but as yet there are no final conclusions.

5.2. Polarization for a ferroelectric nano-strip

The case of a strip in which confinement along two of the axes can be thought of as a special case of the box in which one side, l_1 say, approaches infinity such that $\mathbf{P}(\mathbf{x}) = \mathbf{P}(x_1, x_2, x_3) \rightarrow$

$P(x_2, x_3)$, and is constant with respect to x_3 since the boundaries in this direction have no influence, which also implies that the depolarization terms only involve $\langle \mathbf{P} \rangle = (\langle P_2 \rangle, \langle P_3 \rangle)$.

Now the relevant quantity is a free energy density per unit length, since for a section of the strip between $x_1 = 0$ and $x_1 = l_1'$ the free energy is

$$G = \int_0^{l_1'} dx_1 \int_A f\left(\mathbf{x}, \mathbf{P}, \mathbf{P}_{x_2}, \mathbf{P}_{x_3}, \langle \mathbf{P} \rangle\right) dA + \int_0^{l_1'} dx_1 \int_\Gamma f_{\text{surf}}(\mathbf{x}, \mathbf{P}) d\Gamma, \tag{75}$$

leading to an energy density

$$F = \frac{G}{l_1'} = \int_A f\left(\mathbf{x}, \mathbf{P}, \mathbf{P}_{x_2}, \mathbf{P}_{x_3}, \langle \mathbf{P} \rangle\right) dA + \int_\Gamma f_{\text{surf}}(\mathbf{x}, \mathbf{P}) d\Gamma, \tag{76}$$

where $\int_\Gamma$ is a line integral around the path Γ that traces a rectangular cross section of the strip normal to x_1, $\int_A \equiv \int_{l_2^-}^{l_2^+} \int_{l_3^-}^{l_3^+}$, and $dA = dx_2 dx_3$.

For $f = f_{\text{cubic}}$ (Eq. (72)), the Euler-Lagrange equations are similar to Eq. (73) but P_1 is constant, and so $\nabla^2 = \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2}$, and the depolarization term for $i = 1$ reduces to zero. Also the boundary conditions are given by Eq. (74), but with $i = 2, 3$. The solution is again best approached by numerical or other approximate methods. Work on this is in progress.

The comments made in at the end of the previous section for the ferroelectric nano-box with regard to simplifying it to a three dimensional form of the problem in Section 2.2 also apply here: for the same reason it is not possible to express an exact solution of the form $P(x_2)P(x_3)$, where P has the form of the solution given in Section 2.2. Again it may be possible to utilize such a solution as an approximate function. This needs to be investigated further.

5.3. Polarization for a ferroelectric nano-film

For a film confined in the x_3 direction, a similar argument to the one given for a nano-strip yields $\mathbf{P} = \mathbf{P}(x_3)$, $\langle \mathbf{P} \rangle = \langle P_3 \rangle \hat{\mathbf{x}}_3$, and a free energy density

$$F = \frac{G}{l_1' l_2'} = \int_{l_3^-}^{l_3^+} f\left(x_3, \mathbf{P}, \mathbf{P}_{x_3}, \langle P_3 \rangle\right) dx_3. \tag{77}$$

With $f = f_{\text{cubic}}$ given by Eq. (72), the Euler-Lagrange equations again take the form of Eq. (73); now with P_1 and P_2 constant so that the depolarization terms reduce to zero for $i = 1, 2$, and $\nabla^2 \to \frac{\partial^2}{\partial x_3^2}$. The boundary conditions are given by Eq. (74), with $i = 3$ and $\frac{\partial}{\partial x_3} \to \frac{d}{dx_3}$. An analytical solution, even for this one-dimensional case is still not likely to exist unless f is reduced to the simpler higher symmetry form for second order transitions and in-plane polarization discussed in Section 2.2. However it is amenable to numerical solution or other approximate methods. A similar thin film problem, but involving strain in the ferroelectric as well, which we do no consider, has been solved numerically using a finite difference method by Wang and Zhang[7].

6. Conclusion

The foundations of Landau-Devonshire theory have been introduced and it has been used to develop a general formulation for the calculation of the spontaneous polarization in a ferroelectric nano-box which is confined to the nanoscale in all three dimensions, and for which the influence of the surfaces is expected to be more pronounced than for large scales. From the formalism for the box calculations it has been shown how to deal with a nano-strip which is confined to the nanoscale in two dimensions and to a nano-film with such confinement in only one dimension. The thin film case has been fairly well studied, but much less work has been done on the other geometries, box and strip. Such work is timely given the increasing use of nanoscale structures in electronic devices which include ferroelectric materials, for example ferroelectric random access memories.

A particular example of how the formalism can applied to a ferroelectric crystal of cubic symmetry has been given for all three geometries. Many ferroelectric materials have this symmetry. However the general formalism presented is not restricted to this symmetry, any symmetry can be handled through knowledge of which terms in the free energy needed to be dropped, the criterion being that only terms invariant under the symmetry operations of the symmetry group are allowed.

Future work will involve investigating the numerical or approximate function solutions to the Euler-Lagrange equations which need to be solved in order to be able to plot the spontaneous polarization. Such work is in progress and will be reported in due course.

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