

A Landau Primer for Ferroelectrics

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1 Introduction

Based solely on symmetry considerations, Landau theory can provide a reliable description of a system's equilibrium behavior near a phase transition. This phenomenological approach relates measurable quantities to one another using a minimum set of input parameters that can be determined either by comparison to experiment or from first-principles approaches. Landau theory (LT) can therefore serve as a conceptual bridge between microscopic models and observed macroscopic phenomena. Because it assumes spatial averaging of all local fluctuations, LT is particularly well-suited to systems with long-range interactions such as superconductors and ferroelectrics. In this chapter we hope to give the curious reader a self-contained contemporary presentation of the application of Landau theory to ferroelectrics, including references to more extensive treatments for those who wish more detail [1, 2, 3, 4, 5, 6]. We begin by developing LT for homogenous bulk ferroelectrics, and then consider the finite-size (thin film) case [7] within the related Landau-Ginzburg (LG) approach. Next we discuss the treatment of inhomogeneity within this framework. We end with a number of open questions for future pursuits.

Let us begin by stating in general terms what Landau theory is and then subsequently what it is not. In a nutshell, Landau theory is a symmetry-based analysis of equilibrium behavior near a phase transition. In his classic 1937 papers, Landau [8] notes that a system cannot change smoothly between two phases of different symmetry; the continuous path that a system can take between liquid and gaseous states around a first-order critical point is only possible because there is no symmetry change involved. Furthermore, because the thermodynamic states of two phases that are symmetrically distinct must be the same at their shared transition line, the symmetry of one phase must be higher than that of the other. Landau then characterizes the transition in terms of an order parameter, a physical entity that is zero in the high-symmetry (disordered) phase, and changes continuously to a finite value once the symmetry is lowered; for the case of the paraelectric-ferroelectric transition [9, 10],

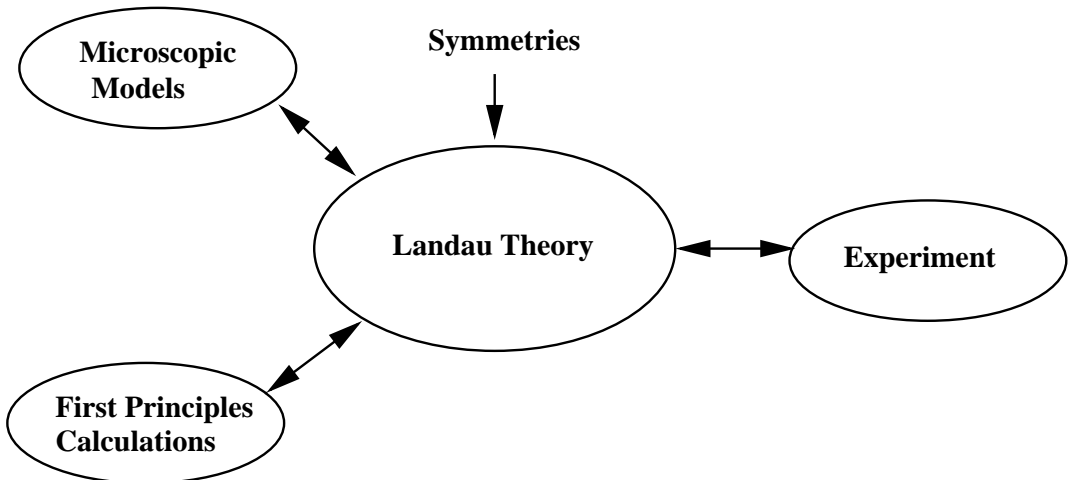


Figure 1: Schematic of relationship of Landau theory and first principles calculations, microscopic models and experiment in the vicinity of a phase transition

this order parameter is the polarization P . The free energy, \mathcal{F} , in the vicinity of the transition is then expanded as a power series of the order parameter ($\mathcal{F}(P)$) where only symmetry-compatible terms are retained. The state of the system is then found by minimizing this free energy $\mathcal{F}(P)$ with respect to P to obtain P_0 , and specific thermodynamic functions are subsequently computed by differentiating \mathcal{F} accordingly. As an aside, we note that if the order parameter is multicomponent, then the Landau free energy is constructed from all scalar terms consistent with the system's symmetries that are powers and scalar products of the order parameter components. Here, for simplicity, we'll consider a scalar order parameter (P) unless otherwise specified.

The appeal of the Landau approach is that it is a straightforward phenomenology for linking measurable thermodynamic quantities in the vicinity of a phase transition. However it is only as good as its input parameters, the coefficients of the series expansion terms in $\mathcal{F}(P)$, which can be determined from experiment or from first principles calculations. We emphasize that Landau theory is strictly a macroscopic approach and thus it cannot describe any microscopic physics (e.g. atomic displacements etc.) associated with the phase transition. In its simplest rendition, the order parameter (e.g. P) is considered to be completely uniform.

A central ansatz of the Landau approach is that the free energy can be represented as a series expansion of the order parameter in the vicinity of the transition. At first glance, it may be surprising that singular behavior associated with a transition can emerge from such a regular expansion. This occurs because the value of the order parameter that minimizes the free energy (e.g. P_0) is itself a singular function of the

Phenomenology	Ferroelectric (near T_c)
Landau - Devonshire Theory (Uniform Polarization)	Poled Bulk System
Landau-Ginzburg Theory (Polarization with Spatial Gradient)	Bulk System
Landau-Ginzburg Theory with Boundary Conditions	Film

Table 1: Phenomenologies and Relevant Ferroelectric Systems (close to T_c)

expansion coefficients which are temperature-dependent. However, more generally we expect that this power-law form of \mathcal{F} may not be valid very close to the transition. Furthermore Landau theory is based on the premise that local fluctuations in the order parameter are small, whereas we expect that this will not be the case in the immediate vicinity of the transition.

So when does Landau theory break down? Levanyuk and Ginzburg have developed [12, 13] a criterion which uses Landau theory to estimate its own demise. More specifically, they argue that for LT to be valid, fluctuations of the order parameter must be small compared to the order parameter itself when both are coarse-grained over a volume determined by the correlation length.. We shall present a detailed version of their argument once we introduce a specific Landau free energy. Qualitatively their criterion suggests that LT works well when the coordination number is high, which can be achieved either by large dimensionality or by long-range interactions. Since significant dipolar interactions are present in ferroelectrics, does this mean that Landau theory is always valid in these systems? It is certainly very useful in ferroelectrics but we emphasize that the angular dependence of the dipolar forces leads to non-Landau behavior very close to the transition, though this region is usually practically unobservable (we will be more specific later). Indeed historically the theoretical

study of a simplified version of this problem, the uniaxial dipolar model, yielded the first predictions of logarithmic corrections to Landau exponents [15]. Detailed measurements confirmed these quantitative results in appropriate experimental systems [16], and this set of findings served as an important benchmark in the development of the renormalization group method.

Many readers may have encountered the phenomenology of Landau theory in the context of magnetism, and thus it is worth contrasting its application there and in ferroelectrics (and we encourage the interested reader to pursue more on this subject in the chapter by N. Spaldin). First and perhaps foremost, the couplings in a ferromagnet are predominantly short-range, since interactions between magnetic dipoles are essentially negligible. More specifically we note that the interaction energy between two magnetic dipoles, each of magnitude one Bohr magneton, at a distance r is

$$F_M = \frac{\mu_o \mu_B}{4\pi r^3} \approx \frac{\alpha^2}{4\pi} \left(\frac{a_B}{r} \right)^3 \quad (1)$$

where $a_B = 0.05$ nm and $\alpha \approx \frac{1}{137}$, and we are working in atomic units. By contrast, for an electrical dipole of magnitude $p = e\Delta a_B$, the dipolar interaction force is

$$F_D = \frac{p^2}{8\pi\epsilon_o r^3} \approx \frac{\Delta^2}{4\pi} \left(\frac{a_B}{r} \right)^3 \quad (2)$$

where the parameter $\Delta \approx 1$ is determined by examining atomic displacements and transverse effective charges [14]. The ratio of the ferroelectric to the ferromagnetic dipolar forces is then of order $\frac{\Delta^2}{\alpha^2} \approx (137)^2$, so clearly long-range interactions are more significant in ferroelectrics than in generic magnetic systems. Thus LT is more reliable for a broader temperature region in these electric dipolar systems than in their magnetic counterparts, though it can provide guiding information in both cases. In conventional ferromagnets magnetic dipolar interactions play a role in the determination of domain structures, whereas in ferroelectrics the analogous dipolar couplings are important at essentially all length-scales.

Screening represents a second qualitative distinction between ferroelectric and ferromagnetic systems. This phenomenon is due to the presence of free charges that effectively reduce local fields; it does not have a magnetic analogue due to the absence of free magnetic monopoles. Indeed this simple fact about screening has been used to explain why magnetism was known in ancient times but ferroelectricity is a relatively modern discovery [4]. The surface of a ferroelectric crystal attracts free charge from its environment to neutralize the effective surface charge that results from the polarization discontinuity; this partially accounts for the historical name “pyroelectric” to describe transient fields that were observed upon changes in temperature. Screening effects are particularly pronounced in ultrathin ferroelectric films, [17, 18, 19, 20, 21, 22] where internal electric fields generated by the ferroelectric

dipoles are large enough to produce both electronic and ionic currents. These processes contribute to fatigue, to “imprint” and to the memory of domain patterns stored over time [7]. A detailed understanding of these screening processes, particularly near metal-ferroelectric interfaces in thin-film devices, requires knowledge of metal-induced gap states and charge compensation processes. Since these are local effects, they can be captured within a Landau-Ginzburg framework and this physics will be discussed later in the chapter.

The third major difference between LT treatments of ferroelectricity and ferromagnetism arises from the strong coupling between the polarization and the lattice, a feature which is usually not very important in the magnetic case. Ferroelectric dipoles are generated by the displacement of atoms, and thus on a local scale there is strong spatial anisotropy. Many magnets retain continuous spin symmetry (e.g. xy or Heisenberg), and thus have low barriers associated with the reorientation of the magnetization. By contrast in ferroelectrics domain walls, discontinuities in the polarization direction, are roughly a few lattice constants in contrast to the mesoscopic length-scale associated with their magnetic counterparts. In general the development of a macroscopic polarization in a ferroelectric will be accompanied by a macroscopic strain, and thus ferroelectricity and ferroelasticity are closely related phenomena. Indeed if this strain is suppressed, the transition temperature and even its order can be modified. Elastic degrees of freedom thus must be represented in a LT for most ferroelectrics.

Let us now turn to a general outline of this chapter. We will begin with a discussion of the homogenous Landau theory for bulk ferroelectrics with spatially-uniform polarizations, reviewing first- and second-order transitions and the dielectric response. Next we allow the polarization to vary with position within a bulk sample, and discuss Landau-Ginzburg theory and correlation functions. Surface boundary conditions, corresponding to the situation for thin films, are then added and the resulting polarization profile is discussed. Here screening effects, depolarization fields and strain will be important. The enigmatic extrapolation length, borrowed from the literature on surface superconductivity [23], will be described with remarks about its underlying physical meaning. Then we’ll switch to a treatment of inhomogenous systems in the bulk, where strain effects and domain formation become very important. We end with a number of open questions for further exploration. For example, is LT appropriate when both long-range strain and Coulomb interactions are present? How can we begin to treat the ever-important question of dynamics of domain motion within this framework? Landau-Ginzburg theory is certainly only useful when its constructing assumptions and its input parameters are appropriate; if so, it is a fairly powerful approach, based almost solely on symmetry, to yield important information about measurable quantities in the vicinity of a phase transition. In this chapter we emphasize the underlying philosophy and methodology of this phenomenology, pointing

the interested reader to detailed discussions of successful applications to particular materials including $SrTiO_3$ [24], $BaTiO_3$ [25] and $PbZr_{1-x}Ti_xO_3$ [26]; towards this more pragmatic end, an Appendix of Landau parameter sets for specific common ferroelectric systems is included for easy reference.

2 Landau-Devonshire Theory

2.1 General Phenomenology

To our knowledge, Landau’s symmetry-based treatment of phase transitions [1, 8] was first applied to the case of ferroelectrics by Devonshire [10], and in this section we will discuss this Landau-Devonshire theory that is appropriate for bulk systems with spatially uniform polarization. In general, the thermodynamic state of any system in equilibrium can be completely specified by the values of specific variables; for bulk ferroelectrics these include the temperature (T), the polarization (P), the electric field (E), the strain (η), and the stress (σ). Usually we apply electric fields E and elastic stresses σ externally, so we can regard the polarization and the strain as “internal” or dependent variables. A fundamental postulate of thermodynamics applied to a ferroelectric is that its free energy \mathcal{F} can be generally expressed as a function of ten variables (three components of polarization, six components of the stress tensor, and finally one of temperature). Our goal here is to write down an *ansatz* for this free energy, using symmetry arguments whenever possible to pare down the number of terms. The second important thermodynamic principle that we will also employ is that the values of the dependent variables in thermal equilibrium are obtained at the free energy minimum when the free energy is optimized.

We make the key approximation that in the vicinity of a phase transition we can expand the free energy in powers of the dependent variables with coefficients that can be fit to experiment or gleaned from microscopic calculations. In the best case, we may be able to truncate this series with only a few terms. In order to be more specific, let us take a simple example where we expand the free energy in terms of a single component of the polarization; for the moment we ignore the strain field, an assumption which might be appropriate for a uniaxial ferroelectric. We shall choose the origin of energy for the free unpolarized, unstrained crystal to be zero, and hence we write

$$\mathcal{F}_P = \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 - EP \quad (3)$$

where we have truncated the power series at the sixth term, and a , b and c are coefficients that will be discussed in more detail shortly. Here we will use the notational convention that \mathcal{F} and $F = \int dV \mathcal{F}$ refer to the free energy density and the total

free energy respectively. The equilibrium configuration is determined by finding the minima of \mathcal{F}_P , where we shall have

$$\frac{\partial \mathcal{F}_P}{\partial P} = 0 \quad . \quad (4)$$

This equation gives us an expression for the electric field E as a function of the polarization

$$E = aP + bP^3 + cP^4 \quad (5)$$

Thus we can determine the linear dielectric susceptibility above the transition by differentiating this equation with respect to P and then setting $P = 0$ to obtain

$$\chi = \frac{P}{E} = \frac{1}{a}. \quad (6)$$

In the Landau-Devonshire theory it is assumed that around the Curie point ($T \sim T_0$)

$$a = a_0(T - T_0) \quad (7)$$

and the other coefficients in the free energy expansion are independent of temperature. Combining the last two equations, we find an expression for the dielectric stiffness

$$\kappa = \frac{1}{\chi} = a_0(T - T_0) \quad (8)$$

which captures the Curie-Weiss behavior (in χ) observed in most ferroelectrics for $T > T_0$; this provides additional support for the linear temperature ansatz for a . For the sake of completeness, we note that the temperature T_0 where a changes sign is close but not exactly coincident with the Curie temperature, as we shall discuss shortly.

If we include the linear temperature-dependence of a , we have the general expression for the free energy

$$\mathcal{F}_P = \frac{1}{2}a_0(T - T_0)P^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 - EP \quad (9)$$

where, to our knowledge, a_0 and c are both positive in all known ferroelectrics [3, 4]. Figure 2 shows the free energy as a function of polarization in the paraelectric ($T \gg T_0$) and the ferroelectric ($T \ll T_0$) phases. How this free energy transforms between these two configurations will be determined by the sign of the coefficient b ; as we shall see shortly, its sign will determine the nature of the paraelectric-ferroelectric transition, and whether the polarization at $T < T_0$ develops continuously or discontinuously.

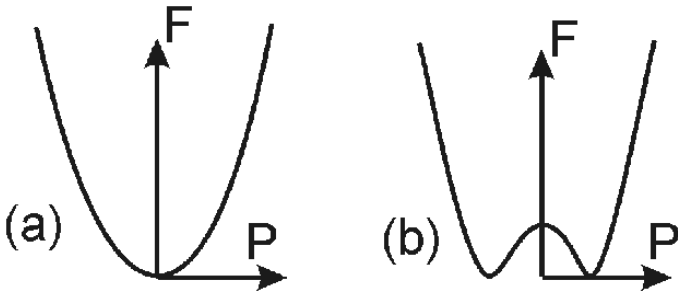


Figure 2: Free energy as a function of polarization for (a) a paraelectric material, and for (b) a ferroelectric material

2.2 Second-Order (Continuous) Transition

If $b > 0$, then a second-order transition occurs at $T = T_0$, and the free energy will evolve continuously as a function of decreasing temperature from the first schematic ($P = 0$) in Fig 2 to the second, that has minima at finite polarizations $P = \pm P_0$. The spontaneous polarization can be estimated by setting $E = 0$ in (5); since all the coefficients are positive, we will only retain the two lowest-order terms. The result is

$$P_0 = \left\{ \frac{a_0}{b} (T_0 - T) \right\}^{\frac{1}{2}} \quad (10)$$

where we see that the spontaneous polarization P_s will increase with decreasing temperature from the point $T = T_0$. We note that if we determine the dielectric stiffness below the transition ($T < T_0$) then we find

$$\kappa = 2a_0(T_0 - T) \quad (11)$$

which is to be compared with (8), its value just above T_0 ; perusal of these two expressions suggests that κ vanishes at $T = T_0$ and that consequently the dielectric susceptibility diverges. In practice, the latter achieves large but finite values in real materials where this expression is appropriate [3, 4]. We can now also solve for the discontinuity in the specific heat at the transition; using $P = 0$ for $T > T_0$ and (10) for $T < T_0$, we determine

$$\Delta C_v = C_v(T = T_0^+) - C_v(T = T_0^-) \quad (12)$$

where $C_v \equiv -T \frac{\partial^2 \mathcal{F}_P}{\partial T^2}$ to obtain

$$\Delta C_v = \frac{a_0^2 T_0}{2b} \quad (13)$$

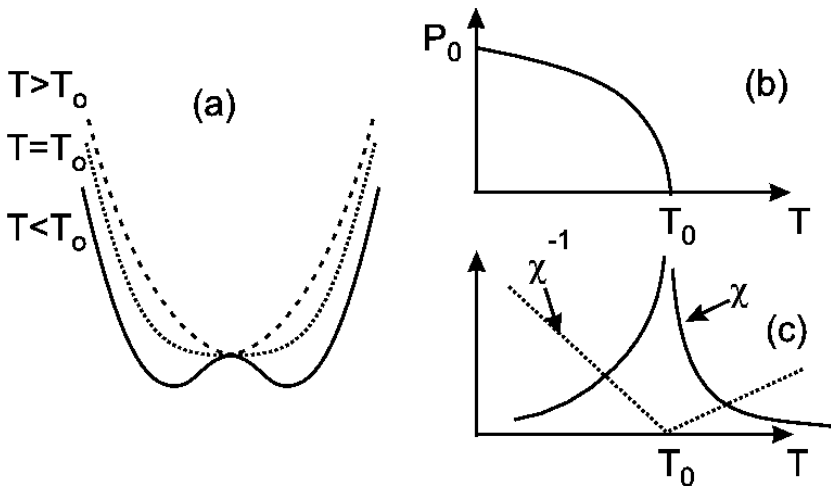


Figure 3: Second order phase transition. (a) Free energy as a function of the polarization at $T > T_0$, $T = T_0$, and $T < T_0$; (b) Spontaneous polarization $P_0(T)$ as a function of temperature (c) The susceptibility χ and its inverse, where $\chi = \partial P / \partial E|_{P_0}$ is evaluated at the equilibrium polarization $P_0(T)$

for the Landau expression for this quantity. Schematics associated with this second-order phase transition as described by Landau-Devonshire theory are displayed in Fig. 3.

2.3 First-Order (Discontinuous) Transition

Logically (and practically as it turns out), we should also consider the case of $b < 0$ (while c remains positive). This is sketched in Fig. 4.

With the negative quartic coefficient, it should be clear that even if $T > T_0$ (such that the quadratic coefficient is positive) the free energy may have a subsidiary minimum at non-zero P . As a is reduced, which corresponds physically to the reduction of the temperature, this minimum will drop in energy below that of the unpolarized state, and so will be the thermodynamically favored configuration. The temperature at which this happens is, by definition, the Curie temperature T_c which however now exceeds T_0 . At any temperature between T_c and T_0 the unpolarized phase exists as a local minimum of the free energy. The most important feature of this phase transition is that the order parameter jumps discontinuously to zero at T_c . This type of phase transition is usually called a first-order or discontinuous transition, of which solid-liquid transitions are common examples.

The procedure for finding the spontaneous polarization and the linear dielectric susceptibility is conceptually the same as before, but now one cannot neglect the

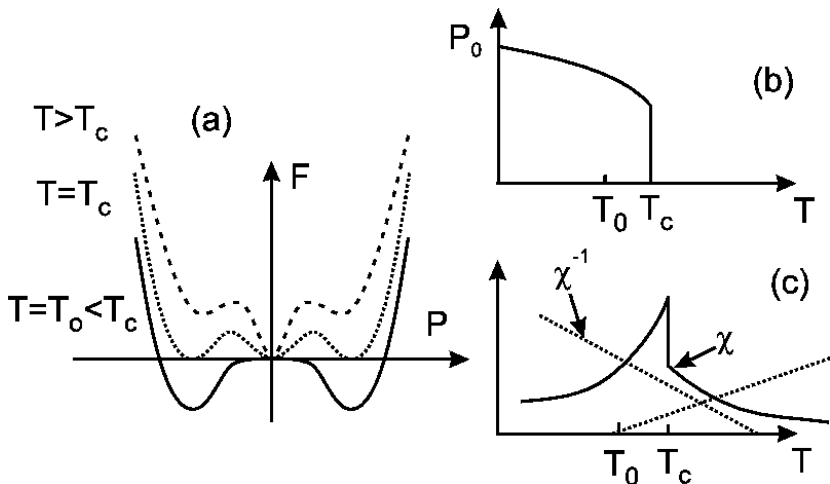


Figure 4: First order phase transition. a) Free energy as a function of the polarization at $T > T_c$, $T = T_c$, and $T = T_0 < T_c$; (b) Spontaneous polarization $P_0(T)$ as a function of temperature (c) Susceptibility χ .

quartic and sixth order terms. Qualitatively we then find a dielectric stiffness (inverse of the linear susceptibility) that does not vanish at T_0 , corresponding to the finite jump in both the susceptibility and the spontaneous polarization at the transition. Schematics of the free energy, the spontaneous polarization, the dielectric stiffness and the linear susceptibility are shown in Fig. 4. We note that at $T = T_c$ the three minima are energetically degenerate. As a result, the system's behavior at $T = T_c$ will depend on whether it is approaching T_c from lower or higher temperatures. More specifically, the system will be in one of the two finite polarization ($P \neq 0$) minima if it is heated from an initial low temperature $T_i < T_c$, whereas it will be in a paraelectric state ($P = 0$) if the initial temperature is high ($T_i > T_c$). Indeed the phenomenon of thermal hysteresis, where the transition temperature depends on whether the sample is heated or cooled, is prevalent in a number of first-order ferroelectrics including barium titanate [3]. We emphasize that it is only for $T_0 < T_c$ that the ferroelectric minima are thermodynamically favorable.

In a ferroelectric below T_0 there are (at least) two minima of the free energy, corresponding to spontaneous polarizations of different spatial orientations. The barrier between these minima means that a small electric field will not immediately switch the polarization. We note that the Landau-Devonshire theory described here predicts hysteresis [3, 4], shown schematically in Figure 5, in the ideal (and fictitious) case where all the dipoles have to be overturned together to switch from one polarization orientation to the other.

We note that for ferroelectrics with either continuous or discontinuous transitions,

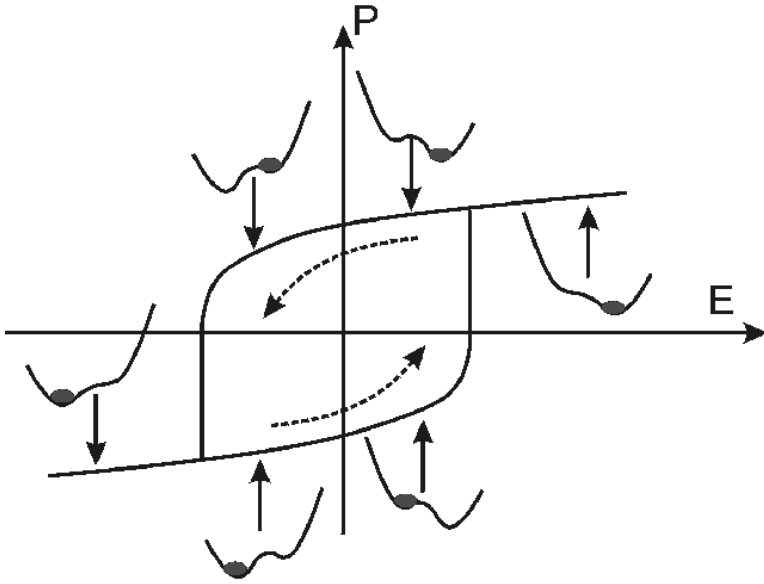


Figure 5: Schematic picture of hysteresis in an idealized ferroelectric

values of the Landau coefficients can be determined by comparing experimental measurements of κ and P_s to the Landau-Devonshire expressions; such parameter sets for a number of commonly studied materials are included in an Appendix at the end of this chapter.

2.4 Coupling to strain

An important feature of ferroelectric materials is their great sensitivity to elastic stress. In order to understand why this is so, we can again take recourse to Landau theory by adding in strain dependent terms to (9). The strain in a solid is measured by how the displacement \vec{u} of a point in the solid varies with position \vec{r} , and since this is the dependence of a vector upon a vector, the answer is a tensor: the strain is usually defined as

$$\eta_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial r_j} + \frac{\partial u_j}{\partial r_i} \right) \quad (14)$$

where here i, j indicate the x, y, z components of the vectors. η is therefore a 3x3 symmetric matrix, with six independent components. In materials that are cubic (or nearly so) there will be three independent components to the strain: the volume strain (uniform in all three directions and two kinds of shear).

In general, the polarization will couple to one or more types of strain, and specif-

ically which ones can generally be seen by inspection. Consider a cubic crystal (e.g. $BaTiO_3$) that undergoes a ferroelectric phase transition to a state where the polarization can point along one of the six orthogonal cubic directions. Now it is clear that there is a special axis (one of the six directions after the symmetry has been broken) and so it would no longer be expected that the crystal as a whole will remain cubic — one expects a distortion into a tetragonal crystal, which can be described by a tetragonal strain η . The fact that the lowest order coupling allowed in this case is of the form ηP^2 (and not, for example, ηP or $\eta^2 P$) is of course a matter of symmetry.

For a uniaxial ferroelectric, the leading order terms will be of the following form

$$\mathcal{F}_\eta = \frac{1}{2}K\eta^2 + Q\eta P^2 + \dots - \eta\sigma \quad , \quad (15)$$

Here η is (a component of) the strain field, and the first term represents Hooke's law, namely that the elastic energy stored in a solid is quadratically dependent on the distortion, so K is (one of) the elastic constant(s). The second term is a coupling between the elastic strain and the polarization; the fact that this is linear in the strain and quadratic in the polarization depends on the special symmetry of the transition. While this is the leading term in pseudocubic materials, there are other materials (e.g. KH_2PO_4) where the symmetry is lower, and the coupling can be of the form ηP — linear in both strain and polarization. Materials with a linear relation between stress and polarization are called piezoelectric.

Using the free energy, which now consists of the terms in (9) and (15), $\mathcal{F} = \mathcal{F}_P + \mathcal{F}_s$, we can now determine the properties in equilibrium by minimizing with respect to both P and η , viz

$$\frac{\partial \mathcal{F}(P, \eta)}{\partial P} = \frac{\partial \mathcal{F}(P, \eta)}{\partial \eta} = 0 \quad (16)$$

Let us take the second of these equations first:

$$\frac{\partial \mathcal{F}(P, \eta)}{\partial \eta} = K\eta + QP^2 - \sigma \quad (17)$$

There are a few different limits to look at. Firstly, note that if the polarization is zero, we get Hooke's law $\eta = \sigma/K$. The second — apparently trivial case — is when a stress is applied to force the strain to be exactly zero at all times. This is not as absurd as it seems, because often crystals can be considered to be clamped by their surroundings so that no strain is allowed at all. One common situation is of a thin epitaxial film which is forced to have the lattice constants matched to the substrate, and is free to relax only in the third direction. In the case of perfect “clamping” $\eta = 0$, and the free energy is just as before.

The third case to consider is when no external stresses are applied ($\sigma = 0$), and we then have

$$\eta = -\frac{QP^2}{K} \quad (18)$$

so that a spontaneous (tetragonal strain) occurs proportional to the square of the polarization. Notice now that we can substitute for the strain as a function of polarization, and we have a free energy

$$\mathcal{F}(P, \eta(P)) = \frac{1}{2}aP^2 + \frac{1}{4}(b - 2Q^2/K)P^4 + \frac{1}{6}cP^6 + \dots - EP \quad (19)$$

In comparison with the clamped system, the only change is to reduce the quartic coefficient (notice that the result is independent of the sign of Q). This means that in the case of an already first-order transition ($b < 0$) the transition is driven even more strongly first order, and T_0 is raised. In many ferroelectrics, the effects of clamping can be large - shifting the transition temperature by tens of Kelvin, and even changing the order of the transition. If $2Q^2/K > b > 0$, a first-order transition becomes second-order in a clamped system where the strain is allowed to relax; this is the case [3] in $BaTiO_3$.

Application of external hydrostatic pressure leads to a shift [27] in T_0 whose sign is determined by that of the volume expansion coefficient; a reduced lattice constant is accompanied by a reduction in T_0 , consistent with measurements where similar effects have been achieved by chemical substitution [27]. The effect of biaxial stress, where the crystal contracts along two axes and expands along the third, on T_0 was also studied both theoretically and experimentally [28]; enhancement of T_0 was predicted and observed in barium titanate crystals [28]. We shall see shortly that this effect is even more dramatic in thin films where such elastic effects occur at the interface to the substrate.

2.5 Domains

So far we have pretended that the polarization in a ferroelectric can be treated as entirely uniform, and this is far from the case. There are many reasons for the existence of domains, including non-uniform strain, microscopic defects, and the thermal and electrical history of the sample. But even in an ideal crystal, domains are to be expected for energetic reasons associated with electrostatics.

The macroscopic bulk polarization is produced by a displacement of positive charge relative to negative charge; at the surface of the sample there must then be a net charge density of opposite signs on the opposite sides of the crystal (Fig. 6). Any inhomogeneity in the polarization acts like a charge density - and in particular

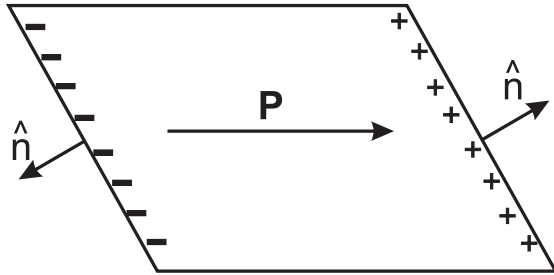


Figure 6: Surface charge density generated by a bulk polarization at an interface

the discontinuity in the polarization at an interface or boundary acts like a surface charge, as can be seen by the following elementary electrostatic argument.

The potential $V(\vec{r})$ induced by a dipole \vec{p} at the origin is

$$V(\vec{r}) = -\frac{1}{4\pi\epsilon_o} \vec{p} \cdot \vec{\nabla} \left(\frac{1}{r} \right) , \quad (20)$$

and thus the potential due to a distributed polarization $\vec{P}(\vec{r})$ in a volume τ bounded by a surface \vec{S} is

$$V(\vec{r}) = \frac{1}{4\pi\epsilon_o} \int_{\tau} d\vec{r}' \vec{P}(\vec{r}') \cdot \vec{\nabla}_{\vec{r}'} \left(\frac{1}{|\vec{r} - \vec{r}'|} \right) . \quad (21)$$

Using the product rule: $\vec{\nabla} \cdot (\vec{A}f) = f\vec{\nabla} \cdot \vec{A} + \vec{A} \cdot \vec{\nabla} f$, we have

$$V(\vec{r}) = \frac{1}{4\pi\epsilon_o} \int_{\tau} d\vec{r}' \left[-\frac{\vec{\nabla} \cdot \vec{P}(\vec{r}')}{|\vec{r} - \vec{r}'|} + \vec{\nabla} \cdot \left(\frac{\vec{P}(\vec{r}')}{|\vec{r} - \vec{r}'|} \right) \right] , \quad (22)$$

$$= \frac{1}{4\pi\epsilon_o} \left[-\int_{\tau} d\vec{r}' \frac{\vec{\nabla} \cdot \vec{P}(\vec{r}')}{|\vec{r} - \vec{r}'|} + \int_{\vec{S}} \frac{d\vec{S} \cdot \vec{P}(\vec{r}')}{|\vec{r} - \vec{r}'|} \right] , \quad (23)$$

where the last manipulation uses the divergence theorem leading to a surface integral.

The potential appears to be generated by a distributed bulk charge density

$$\rho(\vec{r}) = -\vec{\nabla} \cdot \vec{P}(\vec{r}) \quad (24)$$

as well as a surface charge density

$$\sigma = \vec{P} \cdot \hat{n} \quad (25)$$

where \hat{n} is the vector normal to the boundary surface \vec{S} . Occasionally, some books that like to make arbitrary distinctions between “bound” and “free” charge will call

the charges generated by an inhomogeneous polarization “fictitious”. These charges are fictitious only in the sense that they are conserved - namely if we begin with an electrically neutral system and create a polarization density from it by moving the electrons relative to the ions, the integral of the polarization charge (over the whole system) must vanish. They are in all other respects quite real. The surface charges generate electric fields, both internal and external to the sample, and the fields themselves store energy - just as in a capacitor. In an approximation where the polarization \vec{P} is assumed to be homogeneous within a domain, and changing abruptly at surfaces or interfaces, only the surface term survives.

The system will minimize its energy by eliminating – as far as is possible – the surface charges, and in a thin film for example this makes clear that the preferred orientation of the polarization will be in the plane of the film, rather than pointing perpendicular to the film. If one has a crystal that is thick in all dimensions, another situation is preferable – to introduce domains where the polarization is oriented to be always parallel to the crystal surface. Such a situation can of course only be achieved by introducing domain walls into the bulk, and this will produce polarization charges unless the walls are appropriately oriented.

The interface charge density between two neighbouring domains is, by extension of the formula at a free surface,

$$\sigma = (\vec{P}_1 - \vec{P}_2) \cdot \hat{n} \quad (26)$$

where \vec{P}_1, \vec{P}_2 are the polarizations of the two domains, and \hat{n} is a unit vector normal to the interface. The two cases when the surface charge will exactly vanish are when the polarizations are antiparallel to each other, and parallel to the domain wall (called a 180° domain wall), or when the domain wall bisects the angle between two domains pointing head-to-tail. Because we are often dealing with nearly cubic crystals where the possible polarizations are at 90° to each other, the latter is often termed a 90° domain wall. Both of these wall types are illustrated in the sketch Fig. 7, which is the ideal configuration of the polarization in a “bar” of ferroelectric single crystal — and which bears obvious comparison to the ideal magnetic configuration in a single crystal bar magnet, that may be familiar to some.

The presence of domain walls involves other energy costs. Firstly, the domain wall is microscopically different from the bulk, and the energy gain of forming the polarized ground state has been lost. Secondly, the polarization is coupled to elastic strain – as we saw above – and we must also make sure that the strain fields are compatible. There is no difficulty with a 180° domain wall, but a 90° domain wall produces problems, and the “ideal” configuration of Fig. 7 is by no means ideal in terms of the strain fields. The existence of domains in a sample automatically generates inhomogeneities in the strain which interact in complex ways.

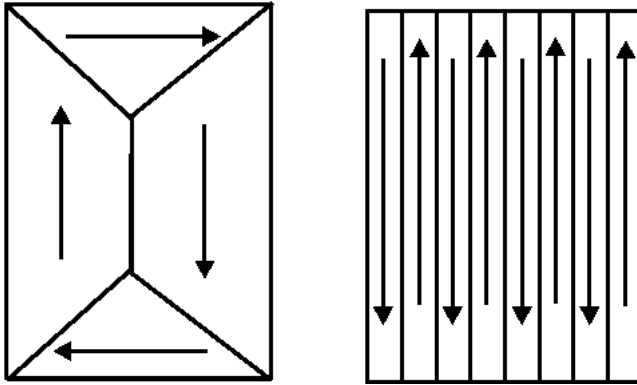


Figure 7: Ideal domain configuration in a single crystal of cubic ferroelectric material, where the coupling to strain is negligible. On the right is the configuration adopted when strain effects are important.

Some contemplation of the two-dimensional pictures above makes it evident that only certain kinds of domain structures are allowed, unless dislocations, cracks, or voids are introduced into the crystal. The moment we have inhomogeneous strain, we must remember to maintain the condition that the displacement field $\vec{u}(\vec{r})$ must be *continuous*; however, the free energy depends only on the strains η , which are derivatives of \vec{u} (see Eq. (14)). Imposing the continuity constraint gives rise to the additional (St Venant) compatibility conditions on the strain fields [29]

$$\vec{\nabla} \times (\vec{\nabla} \times \eta) = 0, \quad (27)$$

which formally reduces the number of independent strain components. When dealing with the allowed arrangements of domains of (locally) homogeneous strain (except at the boundary), the application of condition Eq. (27) (typically by taking a line-integral around the intersection of three domains) determines the legality of various domain arrangements in two and three dimensions.

This condition can also be used to integrate out a single component of the strain, at the expense of introducing long-range forces[30], and this approach can then be used to support calculations and simulations of domain structures in two [31] and three [32] dimensions. This methodology is now quite far advanced in understanding ferroelastic effects on domain structures in martensites [33] though it has not yet been combined with simulations of both the elastic and the ferroelectric order parameter.

There is another feature of ferroelectric domain walls which is not shared by magnetic domains. As far as we are aware, magnetic monopoles do not exist, and therefore the (fictitious in the sense of conserved) magnetic charges that are generated on magnetic boundaries cannot be screened. In ferroelectrics, the surface polarization

charges can be, and are, screened by real electrical charges – from impurities, defects, and migrating ions for example. The motion of charged species (on a fairly slow time scale) to domain walls then provides a mechanism for memory and associated physical phenomena.

This brief introduction to domain structure highlights several issues. The first is that we need to extend the Landau-Devonshire theory of a uniform ferroelectric to incorporate non-uniform polarization. This we do by a parameterization of the free energy now including terms in powers of gradients - this is Ginzburg-Landau theory, introduced in the next section. Secondly, we noted that the geometry of the sample influences the domain structure, and in particular that there is potentially antagonism between the strain fields and electric fields introduced by the domain structure. The final major point is to note that the effect of inhomogeneities in ferroelectrics is to introduce *long-range* forces, from either charge inhomogeneity or strain fields. It is these two phenomena that complicate a local description of the ferroelectric free energy.

3 Landau-Ginzburg Theory

3.1 General Considerations

The Landau-Devonshire theory that we discussed in the previous Section is well-suited for the description of a *poled* bulk ferroelectric near its transition (T_0) with a polarization for $T < T_0$ that is spatially uniform. However we also offered physical motivation for treating spatially nonuniform polarization in unpoled bulk ferroelectrics, and this will be the subject of our treatment in this Section. Generally speaking, Landau-Ginzburg (LG) theory incorporates small spatial variations of the order parameter (here the polarization) within the phenomenological Landau-Devonshire theory with assumptions used originally by Ornstein-Zernike; there fluctuations of the order parameter at different wavevectors are assumed uncorrelated and thus independent.

Let us now discuss specifics of this Landau-Ginzburg approach. Slow variations in the direction of the polarization lead to an additional contribution in the free energy density ($\Delta\mathcal{F}_{LG}$) that is proportional to $|\nabla P|^2$. Though here, as before, we restrict our discussion to the case of a single-component order parameter, we note that this specific quadratic form of $\Delta\mathcal{F}_{LG}$ is valid for more general vector order parameters based on symmetry considerations [1, 2]. Let us return to the scalar order parameter. Then if we define a polarization density $P(\vec{r})$ where \vec{r} is a d -dimensional spatial vector, then to lowest order the Landau-Ginzburg free energy is

$$F = a_0(T - T_0) \int d^d\vec{r} \{P(\vec{r})\}^2 + \gamma \int d^d\vec{r} \{\nabla P(\vec{r})\}^2 \quad (28)$$

where the second term is simply the leading contribution in an expansion of polarization-polarization interactions that estimates the additional free energy cost if the polarizations at different spatial positions are not parallel. Using the fact that the polarization is real (i.e. $P^*(\vec{q}) = P(-\vec{q})$), then we can perform a standard Fourier transform to rewrite the Landau-Ginzburg free energy as

$$F = \int \frac{d^d \vec{k}}{(2\pi)^d} (a_0(T - T_0) + \gamma k^2) |P(\vec{k})|^2. \quad (29)$$

We note that here we have two quadratic degrees of freedom; by the equipartition theorem we can then write

$$(a_0(T - T_0) + \gamma k^2) |P(\vec{k})|^2 = k_B T \quad (30)$$

where k_B is the Boltzmann constant.

3.2 The Polarization Correlation Function

We are now in a position to determine the static two-site polarization correlation function

$$g(\vec{r}) = \langle P(\vec{r}) P(\vec{0}) \rangle - \langle P(\vec{0}) \rangle^2 \quad (31)$$

which is a measure of the fluctuations of the polarization. We note that in ferroelectrics such quantities can be measured with diffuse X-ray scattering [4, 34]. Taking a Fourier transform of $g(\vec{r})$ above in the paraelectric phase (where $\langle P(\vec{0}) \rangle = 0$) and assuming that the different wavevector modes are uncorrelated, we obtain

$$g(\vec{q}) = \langle |P(\vec{q})|^2 \rangle \quad (32)$$

which then, combined with the expression in (30), yields

$$g(\vec{q}) = \frac{k_B T}{a_0(T - T_0) + \gamma q^2} \quad (33)$$

as the expression for the Fourier transform of the correlation function. Now we simply take the inverse transform to find

$$g(\vec{r}) \sim \frac{k_B T}{\gamma} \frac{e^{-r/\xi}}{r^{d-2}} \quad T \neq T_0 \quad (34)$$

and

$$g(\vec{r}) \sim \frac{k_B T}{\gamma} \frac{1}{r^{d-2}} \quad T = T_0 \quad (35)$$

where the correlation length is

$$\xi = \sqrt{\frac{\gamma}{a_0|T - T_0|}} = \sqrt{\frac{\gamma}{a_0 T_0}} \sqrt{\frac{T_0}{|T - T_0|}} \equiv \xi_0 |t|^{-1/2}. \quad (36)$$

and $t = \frac{T - T_0}{T_0}$ is the reduced temperature. Physically for $T > T_0$ this correlation length, ξ , corresponds to the length-scale over which the polarization exists; it diverges at $T = T_0$, and for $T < T_0$ it is associated with the length-scale over which P varies from its equilibrium value. We note that the polarization correlation function is exponentially decreasing above the transition, but has a dimensionally-dependent power-law form when $T \sim T_0$. As a final note to this subsection, we remark that the dimensions of γ and $a_0(T - T_0)$ are $\frac{E}{P^2 L}$ and $\frac{E}{P^2 L^3}$ respectively, so that $[\xi_0] = \sqrt{L^2} = L$ as expected.

3.3 The Levanyuk-Ginzburg Criterion

How reliable is this Landau-Ginzburg theory, and when is it no longer valid? The LG approach is a long-wavelength description of a system near a phase transition, where its modes are coarse-grained on scales of order the correlation length ξ . The resulting effective free energy density is written as an expansion of the order parameter (e.g. P) averaged over a volume Ω_ξ determined by ξ . When are the fluctuations of the order parameter, averaged over the correlation volume Ω_ξ , small in comparison with its coarse-grained average? The answer, relevant for the validity of this long-wavelength approach, is dependent on system dimensionality. We have just seen that the LG approach yields a two-site correlation function, a measure of the order parameter fluctuations, that increases dramatically at $T \sim T_0$; it is therefore clear that in the immediate vicinity of T_0 the LG expansion is no longer valid. So how close can we get to the transition itself before this approach no longer works?

As it turns out, we can use Landau-Ginzburg theory itself to determine its own fallibility [12, 13]. Before we present this argument, let us return to Landau-Devonshire theory and look at its predictions for behavior near the phase transition. We recall the expression for the free energy

$$\mathcal{F}_P = \frac{1}{2}a_0(T - T_0)P^2 + \frac{1}{4}bP^4 - EP \quad (37)$$

which we have truncated at quartic order. The equilibrium value of the polarization corresponds to a free energy minimum

$$\frac{\partial \mathcal{F}_P}{\partial P} = a_0(T - T_0)P + bP^3 = 0 \quad (38)$$

which yields (for $T < T_0$)

$$P = \sqrt{\frac{a_0(T_0 - T)}{b}} \sim (-t)^{1/2}. \quad (39)$$

whereas $P = 0$ in the paraelectric phase. The form of the free energy, (37), combined with these results for the polarization imply that the associated specific heat, $C_v = -T \frac{\partial^2 F}{\partial T^2}$, has a discontinuity at the transition so that the mean-field exponent α is zero (i.e. $C_v \sim |t|^0$).

Equipped with this information, we are now ready to determine the condition for when Landau-Ginzburg theory breaks down. Basically this occurs when the fluctuation free energy associated with a typical fluctuation of order the correlation length is comparable to the total free energy. The fluctuation free energy per unit volume can be estimated as

$$\mathcal{F}_{fluct} \sim \frac{kT}{\xi^d} \sim |t|^{\nu d} \quad (40)$$

where we have used $\xi \sim |t|^{-\nu}$. We have defined the specific heat, $C_v \sim |t|^{-\alpha}$ so that two integrations yield $\mathcal{F} \sim |t|^{2-\alpha}$. Thus for a consistent theory, for $t \rightarrow 0$, we must have

$$d^* > \frac{2 - \alpha}{\nu}. \quad (41)$$

Inputting the mean-field values ($\alpha = 0$ and $\nu = 1/2$), we get

$$d^* > 4 \quad (42)$$

which indicates that above the upper critical dimension, $d^* = 4$, the LG approach is valid. We note that the value of d^* depends on the form of the Landau expansion and can be different for systems with different underlying symmetries [35].

This calculation indicates that for real materials in $d < 4$, the Landau-Ginzburg approach breaks down close to the phase transition...but how close? Intuitively it seems that the larger the number of neighbors the better it does, which suggests that it works better for systems with long-range forces. Let us use what we have learned to put this speculation on firmer footing, and here we follow the original Levanyuk-Ginzburg reasoning [12, 13]. For $T < T_0$ let us argue that coarse-grained fluctuations in the polarization must be small in comparison with the average polarization itself; this translates into the condition

$$g(\vec{r}) \ll P^2 \quad (43)$$

where $|r| \sim \xi$. Using our previous results in (34) with $d = 3$ and (39), we can rewrite this expression as

$$\frac{k_B T_0}{\gamma \xi(T)} \ll \frac{a_0(T - T_0)}{b} \quad (44)$$

which, when using specific expressions for $\xi(T)$ and C_v in (36) and (13), results in the standard form of the Levanyuk-Ginzburg criterion

$$\mathcal{A} \frac{1}{(\Delta C_v)^2 \xi_0^6} \ll |t| \quad (45)$$

where \mathcal{A} is a constant that is unimportant for our present purposes; here the key point is that the range of the interaction, ξ_0 , plays an important role in determining the validity of the mean-field theory. More specifically, the Levanyuk-Ginzburg temperature, determined by the expression in (45), is inversely proportional to the *sixth* power of the range of the interaction, and thus Landau-Ginzburg theory should be quite reliable in the vicinity of the paraelectric-ferroelectric transition. We note that if we generalize the condition (43) to d -dimensions then, using (35) with $|r| \sim \xi$ and (39), we obtain

$$\mathcal{B} |t|^{\frac{d-2}{2}} << |t|^1 \quad (46)$$

which is satisfied for $d > d^* = 4$ for arbitrarily small $|t|$ where \mathcal{B} is a constant. We have thus recovered the same result that we obtained earlier in this section, namely that Landau-Ginzburg theory is exact for dimensions greater $d > 4$ for the ferroelectrics under consideration. Here we remark that the angular-dependence of the dipolar interactions has not been considered here, and it is indeed this feature that leads to logarithmic corrections to mean-field exponents in certain experimentally observable (i.e. $d = 3$) cases [15]. We note that here we have referred to this condition as the Levanyuk-Ginzburg criterion (rather than simply that due to Ginzburg) since we have learned [36] that Levanyuk, a student of Ginzburg's, derived this condition independently of his advisor and indeed published the result in a sole author publication [12] a year before Ginzburg's paper appeared [13].

3.4 Displacive and order-disorder transitions

The Levanyuk-Ginzburg criterion indicates the validity of the mean-field approach to the transition, but more fundamental in many practical senses is the validity of the continuum approximation underlying the LG theory. A continuum theory is of course good close enough to a second order critical point since the diverging correlation length ξ is much larger than the interatomic spacing — this is the condition that coarse graining works. But *far* from the transition — either well above T_c or well below it — this condition will not necessarily hold.

If one takes the Landau theory literally as a description of the phase transition and its dynamics, the order parameter vanishes uniformly everywhere above the transition temperature. Equivalently one would say that the lattice displacements corresponding to the electronic polarization are equally uniform - and zero above T_c , finite below.

Such a type of transition is termed *displacive*. A contrasting limit for an ordering transition is that of local moment magnetism [37], wherein the magnetic moment on an atom persists above T_{curie} but the long-range order is destroyed. In the case of a ferroelectric (or other structural transition), this limit is described as an *order-disorder* transition, where the local symmetry-breaking distortions are present in every unit cell above T_c , but are randomly oriented at high temperatures, so there is no net polarization. Any real material will of course lie somewhere along the spectrum between these two limits.

We have argued above that one reason for the practical usefulness of the LG approach is that there are intrinsic interactions (elastic and charge) that are long-range, and these induce a long correlation length. But there are also conditions related to the underlying microscopic drivers for ferroelectricity that are ineluctably electronic in nature. Although in this chapter we are largely avoiding microscopic theory here we engage in a short digression on the topic of *electronic ferroelectricity*, which has some relevance to the issue.

Spontaneous development of a ferroelectric moment is always associated with a (broken symmetry) atomic displacement, and often this is pictured as an essentially rigid displacement of charge. But of course the driving force for ferroelectricity arises from interactions in the electron system, so a completely rigid displacement of ions is not to be expected. One may study this even in linear response theory - how much charge redistribution is produced by a small displacement of the ion - or equivalently how large an electrical dipole is produced by a particular phonon displacement. Phonons in solids can be separated into acoustic and optical branches, where the eigenmodes of the latter describe the relative motion of different ionic species against each other. One may quantify the electronic rigidity for an optic mode by a number known as the transverse electric charge Z_T^* [14], which measures (to linear order) the average electrical dipole moment per unit cell p generated by the corresponding relative ionic displacement u (taken to be the same in every cell), viz.

$$p = Z_T^* e u \quad (47)$$

where e is the electron charge. There is a different value of effective charge Z_T^* for each optical mode (and it may be zero if the displacement preserves inversion symmetry); even a non-ferro-electric crystal will usually have dipole-active modes. A simple case is just that of the rocksalt structure, where the optical eigenmode is a displacement of the two sublattices relative to each other. The effective charge can be straightforwardly measured by the optical response of an infra-red active phonon. The connection to ferroelectricity is that if such a phonon goes “soft” and acquires a finite frozen amplitude u_0 , then $Z_T^* e u_0$ is the approximate magnitude (to linear order) of the ferroelectric moment per unit cell. This is the classic soft mode theory of ferroelectric instability [38, 39, 40].

In the context of the Landau theory, this relates the polarization to the atomic motion. In a rigid ion picture, one expects Z_T^* to reflect the charge on the ion, but it is in fact not uncommon to measure effective charges that are quite large: for example [41] in the rocksalt structure IV-VI compounds (Z_T^* values in brackets) PbS (4.8), PbSe (5.8), PbTe (6.5), SnTe (8.1), GeTe (11), where a rigid ion viewpoint would lead one to expect $Z_T^* \leq 2$. Only the last two of these materials (which are the least ionic in the Pauling sense!) become ferroelectric at low temperature. What these large numbers represent physically is of course that as the nuclei are displaced the electron distribution sloshes from one side of the ion to another, with the electrons moving much further than the nuclei themselves. This large amplification of motion happens in electronically driven transitions of the Peierls type [42]; it can also happen in cases of electronically-driven spontaneous symmetry breaking where the Coulomb interaction favours the breaking of spontaneous orbital symmetry [43, 44].

In these cases, the large induced polarization arises because of a broken orbital symmetry. Whatever the underlying model, in what one can see in the not entirely formal limit of a ferroelectric that has $Z_T^* \rightarrow \infty$, the transition is indeed electronic in nature. Moreover it corresponds in that case to a metal-insulator transition as well, where the distortion leads to the opening of a small electronic energy gap 2Δ in the spectrum. Such transitions are in fact charge density wave instabilities in disguise, where the broken symmetry happens also to break inversion symmetry, and the CDW onset is also that of ferroelectricity. The driving force for these transitions is the opening (or increase of) an electronic gap at the fermi energy (for a review, see [45]).

Suppose for a moment that we can ignore the lattice dynamical effects on this transition, we can then estimate the transition temperature and correlation length in a weak coupling limit, which is well-known to be mathematically just like the Bardeen-Cooper-Schrieffer theory of superconductivity [46, 47, 48]:

$$T_c^{MF} \propto \Delta \simeq W e^{-1/\lambda} \quad (48)$$

$$\frac{\xi_0}{a} \simeq \frac{W}{\Delta} \quad (49)$$

where W is the electronic bandwidth, a the lattice constant, and $\lambda \ll 1$ the effective dimensionless interaction strength (scaled by the electronic bandwidth), which must be small for this kind of theory to be appropriate. In weak coupling, the gap and transition temperature are small (in comparison to the electronic bandwidth) and the correlation length ξ_0 is long.

Now we consider the effect of the coupling to the lattice, and in particular we must take account of dynamical phonons. Provided $k_B T_c^{MF}$ is much smaller than a characteristic phonon energy $\hbar\omega_D$, there will be no appreciable fluctuations of dynamical

modes until one is at a temperature very close to the transition, so the mean-field theory is rather good as an estimate of the transition temperature. And moreover, even above T_c the dynamical modes are weakly excited so there are few thermal fluctuations of the lattice. All that remains is just the (small, in this case) mean-field lattice distortion that smoothly vanishes at T_c . We see that the condition for the displacive limit is that of *ultra-weak* coupling, namely that

$$\frac{\hbar\omega_D}{W} \gg e^{-1/\lambda} . \quad (50)$$

However, if this condition is violated, thermal fluctuations of dynamical modes will become important, and the extra entropy associated with the lattice distortions will drive a transition to the paraelectric phase at a temperature well below the mean-field one [49]. Here we now crossover to the “order-disorder” regime of the transition, and we remark that (as commonly observed in CDW transitions) this crossover happens when λ is still very small, since typically the electronic bandwidth is two to three orders of magnitude larger than a typical phonon energy.

Thus we see that there are two potentially quite distinct reasons to stabilise the displacive picture. One is the coupling to elastic strain, and the presence of long-range forces, about which we will have more to say later. This is important in all classes of ferroelectrics. A second type is where the transition is predominantly driven by electronic redistribution of states near the fermi level of a metal or narrow-gap semiconductor, and furthermore the displacive limit obtains only when the coupling is very weak, so that electronic gaps are small in comparison to the Debye frequency. These CDW-like systems are rare as classic ferroelectrics, (except maybe for SnTe, which has a transition near 40K and shows the classic soft-mode behavior[50]), but they are probably quite common in small-moment ferroelectrics where the ferroelectricity is an “accidental” adjunct to a charge-ordering transition. Such is potentially the case in charge-ordered manganites, for example [51].

3.5 Recent Developments in Bulk Ferroelectricity

Landau-Devonshire theory has been successful at reproducing the observed phase behavior in simple ferroelectric compounds (e.g. $BaTiO_3$ and $PbTiO_3$) and these results are described in many textbooks [3, 4, 5]. Recently it was shown [52] that the standard sixth-order free energy expansion can not account for an observed phase where the polarization is not symmetry-restricted to an axis. More specifically, a monoclinic phase was observed in PZT for a given temperature and compositional range [53], that did not emerge from a standard Landau-Devonshire (sixth-order) treatment [54]. However this phase did emerge in the observed parameter regime from simulations [55] based on a first-principles effective Hamiltonian approach [56];

this result suggested that no additional physics (or specifically instabilities) were necessary for its description. An eighth-order expansion of the free energy yielded the observed monoclinic phase [52] where it was argued that the higher-order terms might be generated by disorder-averaging. This analysis will be relevant for other ferroelectric phases where the polarization is constrained to a symmetry plane.

In the Introduction we alluded to a link between first-principles calculations and Landau theory, and here we discuss it more specifically. In the last two decades, there has been great progress in the collective understanding of atomic-scale ferroelectricity through detailed density-functional theory investigations. We refer the interested reader to two recent reviews [57, 58] and other chapters in this book for more information about these developments. First principles effective Hamiltonians, based on these first-principles approaches with reduced degrees of freedom, have been analyzed by statistical methods to explore the finite-temperature behavior of ferroelectrics. In particular such an effective Hamiltonian approach was very successful in reproducing the known phase behavior [59] of $BaTiO_3$. More recently the compatibility of this particular Hamiltonian and the Landau-Devonshire theory of $BaTiO_3$ was demonstrated [60] in a careful Monte Carlo study of the order-parameter configuration space. Thus first-principles density functional calculations, via an effective Hamiltonian, can provide the input coefficients for Landau-Ginzburg theory; this bridging of theoretical methods is crucial for studying phenomena on many length-scales in ferroelectrics.

In this Chapter, we focus primarily on the thermodynamic description of ferroelectrics using Landau-Ginzburg theory. However the resulting free energy can be incorporated into a treatment of thermally activated dynamical processes, specifically the determination of nucleation rates [61]. We note in passing that the coupling between the polarization and the long-range elastic degrees of freedom in bulk materials implies that nucleation of new ferroelectric regions must be a cooperative effect in that these events cannot occur completely independently. Dynamical studies of field-quenched $BaTiO_3$ crystals provide experimental support for this statement [62]. This observed behavior can be qualitatively described by a modified time-dependent Landau analysis with simple feedback to account for the strain-mediation between growing regions [63].

In concluding our discussion on bulk ferroelectricity, we note that there was much work done in this field in the former Soviet Union that was not communicated to the West. This situation was recently summarized by Ginzburg [64], and we point the interested reader to these thought-provoking reminiscences.

4 Reduced Size and Other Boundary Effects

4.1 General Discussion

Ferroelectric materials are very sensitive to electromechanical boundary conditions due to the long-range nature of their underlying electrostatic interactions and to the strong coupling between the polarization and the strain [7, 57, 58]. Thus the influence of surfaces and other boundary conditions on their collective behavior is very pronounced [65]. Furthermore there are numerous ways in which the external environment, via applied boundary conditions, can alter ferroelectric behavior; examples include electric fields due to surface charges and homogeneous misfit strains. Finally there is a significant commercial impetus to use ferroelectrics for portable high-density data storage; for such increasingly miniaturized applications, key size-dependent effects must be understood and modeled in order to optimize design [7, 66]. Typically the fabricated structures will be of linear dimension 10 nanometer - 1 micron, length-scales that are not accessible to purely atomistic methods. However such approaches can be used towards determining the effects of local variations (e.g. compositions, strains, displacements) in conjunction with specific boundary conditions; the results could then be incorporated into a bridging phenomenological theory that spans physics on longer length-scales to enable direct comparison with experimental observation.

In this section we summarize key features of Landau-Ginzburg approaches to ferroelectrics with specific boundary conditions, focusing on the well-studied case of planar geometries. We begin with semi-infinite ferroelectrics with a free surface, a case that can be easily generalized to a free-standing thin film. Because of reduced coordination number at a free surface compared to the bulk, we expect the average polarization to display altered behavior at the boundary which could lead to changes in its overall thermodynamic behavior [67, 68]. We observe how this need for a specific boundary condition emerges technically from a Landau-Ginzburg approach of the bulk and the surface free energies. We also discuss the necessary assumptions underlying the emergence of the so-called extrapolation length from such a treatment and suggest a test for this often-used (but rarely justified) approach [70]. If the polarization is normal to the free surface of the ferroelectric film, a geometry that is often used in practice, then depolarization effects must be included and this is the topic of the next subsection. Next we turn to epitaxial misfit strain, and how it can be turned to dramatically increase the spontaneous polarization of a ferroelectric film beyond that in the bulk. We end with a discussion of inhomogeneous strain and polarization configurations, a more recent area of investigation that is of particular relevance to three-dimensional ferroelectric nanostructures [69].

4.2 The Polarization at the Boundary

The presence of the Ginzburg term, $|\vec{\nabla}P|^2$, in the Landau-Ginzburg free energy implies that a boundary condition is necessary to solve the second-order differential equation that results from the minimization procedure. Let us consider a semi-infinite ferroelectric with a second-order phase transition. We begin by considering the bulk free energy, including the new gradient term, of this system

$$\mathcal{F}_{bulk}^{LG} = \int dV \left[\gamma |\vec{\nabla}P|^2 - \frac{a}{2}|P|^2 + \frac{b}{4}|P|^4 \right] \quad (51)$$

such that $a > 0$ (implying $T < T_0$). We note that we can use the divergence theorem to split the gradient term in (51) into a surface and a volume integral

$$\int dV (\vec{\nabla}P \vec{\nabla}P) = \int dV [\vec{\nabla}(P \vec{\nabla}P) - (P \nabla^2 P)] = \int dS (\hat{n} \cdot \vec{\nabla}P)P - \int dV (P \nabla^2 P) \quad (52)$$

where \hat{n} is the normal unit vector to the surface. Borrowing from analogous studies of superconducting [47] and magnetic [71, 72] films, we argue that there is a “surface tension” contribution so that the full free energy ($\mathcal{F} = \mathcal{F}_{bulk}^{LG} + \mathcal{F}_{stension}$) is now a sum of interior and surface contributions, $\mathcal{F} = \mathcal{F}_{interior} + \mathcal{F}_{surface}$, where

$$\mathcal{F}_{interior} = \int dV \left[-\gamma P \nabla^2 P - \frac{a}{2}|P|^2 + \frac{b}{4}|P|^4 \right] \quad (53)$$

and

$$\mathcal{F}_{surface} = \int dS \left[\gamma (\hat{n} \cdot \vec{\nabla}P)P + \frac{\alpha(T - T^*)}{2}|P|^2 + \frac{\beta}{4}|P|^4 \right]. \quad (54)$$

We note that this form of the “surface tension” free energy contribution assumes that there exists a temperature T^* , not necessarily equal to the bulk transition temperature T_0 , where the surface becomes ferroelectric; here the coefficients α and β are usually considered to be thickness-independent with $\beta \ll \alpha$ [47, 67].

If we vary the free energy density with respect to δP , we obtain

$$\delta \mathcal{F} = \int dV \left[-\gamma \nabla^2 P - a|P| + b|P|^3 \right] (\delta P) + \int dS \left[\gamma (\hat{n} \cdot \vec{\nabla}P) + \alpha(T - T^*)|P| \right] (\delta P). \quad (55)$$

In bulk systems the surface integral in (55) is often neglected, either due to periodic boundary conditions or due to the absence of variation in P on very long length-scales. However this approach cannot be justified for finite-size systems.

For simplicity, let us restrict our attention here to the case where the polarization is only z -dependent, the surface defined as $z = 0$, and the sample occupies the space

$z > 0$. Then the stationary condition for the total free energy to a small variation $\delta P(z)$ leads to the second-order differential equation

$$-\gamma \frac{d^2 P}{dz^2} - aP + bP^3 = 0 \quad (56)$$

together with the boundary condition

$$\gamma \frac{dP}{dz} + \alpha(T - T^*)P = 0|_{z \rightarrow 0^+} \quad (57)$$

at the surface. We can rewrite the boundary condition as

$$\frac{dP}{dz} = -\frac{P}{\delta}|_{z \rightarrow 0^+} \quad (58)$$

which results in

$$P = P(0)e^{-\frac{z}{\delta}}|_{z \rightarrow 0^+} \quad (59)$$

with

$$\delta = \frac{\gamma}{\alpha(T - T^*)} \quad (60)$$

where we note that the dimensions of γ and $\alpha(T - T^*)$ are $\frac{E}{P^2 L}$ and $\frac{E}{P^2 L^2}$ respectively so that $[\delta] = L$ and δ is the so-called extrapolation length; here $P(0)$, the polarization at the surface, must be determined by an electrical boundary condition. We remark that we must obtain

$$|\delta| > \xi_0 \quad (61)$$

in order for this calculation to be self-consistent, where ξ_0 is the length-scale over which the polarization has spatial variation in the bulk. We see that δ is temperature-dependent, and its sign is determined by the relative values of T^* and T . For example if, as we have assumed above, $T < T_0$, and $T_0 < T^*$, then $(T - T^*) < 0$ and $\delta < 0$. In this case, the surface becomes ferroelectric at a temperature higher than that in the bulk, so the polarization at the surface increases as indicated in (59). By contrast, it will decrease at the boundary if $T_0 > T^*$. This approach has been generalized to ferroelectric films [23, 70, 73] with the appropriate boundary conditions at the surfaces/interfaces. The solution of (56) and the film analogues of (59) leads to a thickness-dependent critical temperature that is qualitatively similar to that observed [23, 70, 73]. It can also be extended to the case where the bulk material has a first-order transition [74]; now higher-order terms in the Landau-Ginzburg free energy must be retained. Another generalization is to superlattices with alternating films of two different materials [73, 75].

The scheme that we have just outlined assumes implicitly that the free energy of interest can be clearly separated into two distinct parts, $\mathcal{F}_{interior}$ and $\mathcal{F}_{surface}$, that

have the similar algebraic structures but different transition temperatures. More specifically, there must be a distinct separation of length-scales associated with the surface and the interior; this requirement translates into the inequality

$$\xi_0 < |\delta| < L \quad (62)$$

where $L \gg 1$ is the lateral dimension of the sample. To our knowledge, there is no direct experimental confirmation of the extrapolation length, though it may be indirectly accessible via x-ray diffraction [76] and far-infrared. We note that there is some suggestion [78] that the Landau coefficients for thin films may have some thickness-dependence that is not included in this standard treatment. Another complementary approach is to assume a spatially varying transition temperature in the finite-size ferroelectric [79]. This might be a productive way of incorporating known imperfections into the phenomenological theory. Finally we remind the reader that the Landau-Ginzburg approach assumes that the free energy can be expressed as a polynomial expansion of the average polarization; as finite-size effects become increasingly important such coarse-graining may no longer be possible. The possible breakdown of this free energy ansatz should be checked explicitly with first-principles methods for a variety of sizes and geometries.

4.3 Depolarization Effects

So far we have discussed finite-size planar ferroelectrics where the polarization has been parallel to the surfaces of interest. Now we switch to a geometry where the polarization is normal to the boundary, as displayed in Fig. 8. Physically we expect a build-up of free surface charge which, if uncompensated, results in a depolarizing electric field E_d . It is then energetically difficult for the sample to sustain its uniform polarization, and phases with ferroelectric domains often result. Since, as we shall see shortly, the depolarization field increases with decreasing film thickness [17, 18, 19], its importance increases with reduced size and it must be incorporated in the phenomenological description of such finite-size ferroelectric systems.

In practice these depolarization effects can be significantly reduced by the presence of metal electrodes that provide charge compensation at the ferroelectric boundaries. We now develop an expression for the Landau-Ginzburg free energy of a short-circuited ferroelectric capacitor that consists of a ferroelectric film bracketed by two metal electrodes (see Fig. 8). For pedagogical simplicity, we'll consider the short-circuited case ($V_{ext} = 0$) where the length-scale of the electrodes is significantly larger than that of the film ($L \gg d$; $L \rightarrow \infty$), which is in turn greater than the screening length (λ) in the electrodes; succinctly our operating condition is then $L \gg d \gg \lambda$ and a schematic of this situation is displayed in Fig. 8. We will also assume that

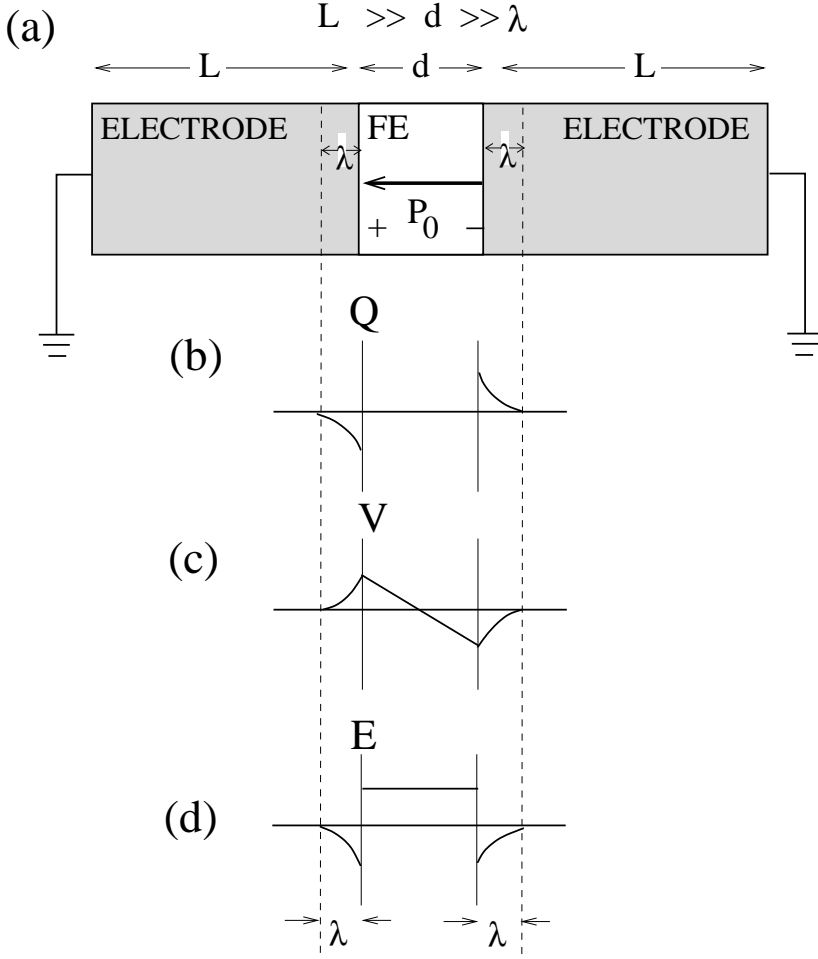


Figure 8: **a)** Schematic of short-circuited ferroelectric capacitor with $L \gg d \gg \lambda$ and accompanying plots of the spatial distribution of **b)** the charge Q , **c)** the potential V and **d)** the depolarization field E . Note that the charge distribution in **b)** would simply be δ -functions at the film-electrode interfaces for perfect electrodes; then V and E would simply be constant and zero.

the polarization gradient is negligible at the ferroelectric-electrode interfaces, namely that $\frac{dP}{dz} = 0|_{z=\pm\frac{d}{2}}$, which implies that the inverse extrapolation length in (58) is zero (e.g. $\delta \rightarrow \infty$). We note that calculations in this simplified parameter regime yield results that are compatible with experiment [19, 22]. The interested reader is referred to more complex treatments of the depolarization field for other parameter specifications [80].

Let us consider the zero-potential (short-circuited) ferroelectric capacitor shown schematically in Fig. 8 a). The spontaneous polarization is displayed. In an idealized system with perfect metal plates, there would be complete charge compensation at the electrode-ferroelectric interface and thus no depolarization field in the film. However in realistic electrodes, screening charge resides within a small but nonzero distance from the ferroelectric boundary (cf. Fig. 8 b). For a short-circuited ferroelectric capacitor, this spatial charge distribution leads to an associated voltage drop in the electrodes and a compensating depolarization potential across the film (cf. Fig. 8 c). There is therefore an accompanying depolarization field which, in the case of uniform polarization, will simply scale inversely with film thickness (Fig. 8). Intuitively we expect the presence of this depolarization field to suppress ferroelectricity since it is antiparallel to the polarization.

More formally we follow previous treatments [80] in the specific limit $L \gg d \gg \lambda$ to derive the total Landau free energy of the ferroelectric capacitor; this free energy has two contributions

$$F = F_e + F_f \quad (63)$$

where F_e and F_f are associated with the electrodes and the film respectively. We assume that the charge density at each ferroelectric-electrode interface takes the simple Thomas-Fermi form $\rho(z) = \frac{Q}{\lambda} e^{-\frac{z}{\lambda}}$ where λ is a screening length [81]. Then, solving for the free energy associated with the field inside each electrode, we find that

$$F_e = \frac{\lambda Q^2}{2\epsilon_0\epsilon_e} \quad (64)$$

where ϵ_e and ϵ_0 are the permittivities of the electrodes and of free space respectively. We note that the choice of ϵ_e , a quantity usually defined in the long-wavelength limit [82], is tricky since it enters this treatment via a boundary condition at the ferroelectric-electrode interface, and we refer the interested reader to two distinct approaches to this issue [22, 80] where comparisons with experiment are made.

Next we turn to the free energy in the film, which has the form

$$F_f = \int_{-d/2}^{d/2} \left\{ \mathcal{F}_P - \frac{1}{2} E_d(z) P(z) \right\} dz \quad (65)$$

where $E_d(z)$ is the depolarization field and the second term in (65) above represents its self-energy (and hence the factor of $\frac{1}{2}$ [67]). Using the fact that there is no free charge

in the ferroelectric, we write the depolarization field in the form $E_d(z) = E_0 - \frac{P(z)}{\epsilon_0}$ where by continuity at the interface $E_0 = E(\pm \frac{d}{2}) = \frac{Q}{\epsilon_0}$. Now we need to find E_0 in terms of $P(z)$ since we do not know Q . Use of the short-circuit condition leads to the expression

$$E_0 = \frac{1}{\epsilon_0(2\lambda + d)} \int_{-\frac{d}{2}}^{+\frac{d}{2}} P(z) dz \quad (66)$$

which can then be inputted into the expressions (64) and (65) for F_e and F_f respectively. We note that for P uniform and $\lambda \ll d$, the depolarization field takes the form

$$E_d = E_0 - \frac{P}{\epsilon_0} = \frac{P}{\epsilon_0} \left\{ \frac{1}{1 + \frac{2\lambda}{d}} - 1 \right\} \sim \frac{2P\lambda}{\epsilon_0 d} \quad (67)$$

which varies inversely with the film thickness (d) and vanishes in the case of perfect electrodes ($\lambda = 0$); we note that a similar result for E_d is found by introducing an air gap of thickness λ between the film and perfect electrodes [22, 84] thereby displacing the compensating charge from the ferroelectric interface.

The Landau free energy for the ferroelectric capacitor then is

$$F = \left(\int_{-\frac{d}{2}}^{+\frac{d}{2}} \mathcal{F}_P dz \right) + \Delta F \quad (68)$$

where

$$\Delta F = \int_{-\frac{d}{2}}^{+\frac{d}{2}} \frac{P^2(z)}{2\epsilon_0} dz - \frac{1}{2\epsilon_0 d (1 + \frac{2\lambda}{d})} \left\{ 1 - \frac{\lambda}{\epsilon_e d (1 + \frac{2\lambda}{d})} \right\} \left[\int_{-\frac{d}{2}}^{+\frac{d}{2}} P(z) dz \right]^2 \quad (69)$$

where we reiterate that this free energy is for the limits $L \gg d \gg \lambda$ where $L \rightarrow \infty$ and $\delta \rightarrow \infty$. We see from (69) that if P is uniform and $\lambda = 0$, then $\Delta F = 0$. However if $P = P(z)$, ΔF is finite even for perfect electrodes [67]. For uniform P and finite λ where $\frac{2\lambda}{d} \ll 1$, (69) yields

$$\frac{\Delta F}{d} \sim \frac{P^2}{2\epsilon_0} \left[\frac{\lambda}{\epsilon_e d} \right] \quad (70)$$

which contributes to the coefficient of the quadratic term in the overall free energy density. As a result, the expression for the film's transition temperature T^* is

$$\frac{1}{2} a_0 (T^* - T_0) + \frac{\lambda}{2\epsilon_e \epsilon_o d} = 0 \quad (71)$$

which leads to

$$T^* = T_0 - \frac{\lambda}{\epsilon_0 \epsilon_e d a_0} \quad (72)$$

that is shifted from its bulk value (T_0) by a term due to the depolarization field; we note that when $2\lambda \sim d$, a more complicated expression results [83] that suggests that there exists a minimum thickness d_{min} below which ferroelectricity is unstable [17, 18, 73]. For a given material, characterized by a_0 and T_0 , this minimum thickness can be tuned by the choice of electrodes [20, 21, 22] whose relevant characteristics enter d_{min} via λ and ϵ_e . However recent experiments [85, 86, 87] indicate the presence of ferroelectricity below this minimum cutoff, which may be consistent with theoretical expectations for a polydomain ferroelectric state [88]. Naturally the depolarization effects will be significantly reduced if the ferroelectric film is treated as a semiconductor [89] rather than as an insulator. Before closing this section, we note that recently the dielectric properties of ferroelectric-paraelectric multilayers have also been studied within this type of thermodynamic approach, and it has been found that there exists a critical paraelectric film thickness such that ferroelectricity is completely suppressed due to interlayer electrostatic interactions [90]. We emphasize that the Landau-Ginzburg approach presented to this point has assumed a single-domain (homogeneous) ferroelectric phase, and its generalization to include inhomogeneous effects will be discussed later in this chapter.

4.4 Misfit Epitaxial Strain

The thermodynamic behavior of a ferroelectric film is also sensitive to mechanical boundary conditions due to the strong coupling between the polarization and the strain. Application of pressure, both hydrostatic [27] and biaxial [28], is known to affect the transition temperature of bulk perovskite ferroelectrics. More recently homogeneous epitaxial strain associated with substrate-film lattice mismatch has been included in a Landau free energy [91]; this approach results in strain-induced shifts in the transition temperature and the spontaneous polarization whose signs depends on details of specific elastic compliances and electrostrictive constants. Furthermore, theoretical studies [91, 92, 93, 94] of temperature-misfit strain phase diagrams indicate that there are observable “epitaxial phases” that would not be stable in the bulk. Indeed the effects of homogeneous misfit strain have been characterized and controlled to such a degree that $BaTiO_3$ films have been strain-engineered so that their observed spontaneous polarization is more than twice that in the bulk [96]. Furthermore room-temperature ferroelectricity has been observed in strained $SrTiO_3$ films [24], where we note that bulk $SrTiO_3$ remains paraelectric down to the lowest observable temperatures [97].

Let us be more specific. In the phenomenological treatment of epitaxially strained ferroelectric films grown on thick substrates [91, 92], the finite-size ferroelectric is approached as a bulk material with homogeneous elastic terms constrained to match

the substrate lattice conditions. Here it is implicit that

$$L \gg d_c > d > \xi_0 \quad (73)$$

where L and d are the substrate and the film thicknesses respectively, ξ_0 is the correlation length and d_c is the critical film thickness above which elastic defects appear; d_c varies roughly as the inverse of the lattice mismatch and is usually approximately $10nm$ [96]. With this set of modelling assumptions, the in-plane strains, η_1 , η_2 and η_6 (here we follow the conventional Voigt notation) are constant throughout the film thickness and are completely controlled by the substrate-film lattice mismatch. The associated stresses σ_1 , σ_2 and σ_6 are finite but not fixed. By contrast,

$$\sigma_3 = \sigma_4 = \sigma_5 = 0 \quad (74)$$

since there are no tractions acting on the top film surface. For the special case of a (001) ferroelectric film grown on a cubic paraelectric substrate

$$\eta_1 = \eta_2 = \bar{\eta} = \frac{a - a_0}{a} \quad (75)$$

where a and a_0 are the constrained and the free film lattice constants respectively. For this simple case of cubic symmetry $\eta_6 = 0$ since the angle between the two lattice vectors remains unchanged ($\theta = \frac{\pi}{2}$). (74) and (75) represent mixed mechanical boundary conditions associated with two-dimensional clamping, and the standard elastic free energy $\mathcal{F}(P, \sigma)$ cannot be used to find the equilibrium properties of these systems [28, 91]. Instead a Legendre transformation to a modified thermodynamic potential

$$\tilde{\mathcal{F}} = \mathcal{F} + \eta_1 \sigma_1 + \eta_2 \sigma_2 + \eta_6 \sigma_6 \quad (76)$$

must be performed in order to study the equilibrium properties of this constrained film.

For pedagogical simplicity, we consider a uniaxial ferroelectric where P is the polarization in the z-direction. The free energy, with condition (74), of a cubic ferroelectric is [98]

$$\mathcal{F} = \mathcal{F}_P - \frac{1}{2}s_{11}(\sigma_1^2 + \sigma_2^2) - Q_{12}\{(\sigma_1 + \sigma_2)P^2\} - s_{12}\sigma_1\sigma_2 - \frac{1}{2}s_{44}\sigma_6^2 \quad (77)$$

where Q_{ij} and s_{ij} are the electrostrictive constants and the elastic compliances at constant polarization respectively. Using $\frac{\partial \mathcal{F}}{\partial \sigma_i} = -\eta_i$, and solving for $\sigma_1 = \sigma_2 = \bar{\sigma}$ (in this special case $\sigma_6 = 0$), we find that

$$\tilde{\mathcal{F}} = \frac{\bar{\eta}^2}{s_{11} + s_{12}} + \frac{1}{2}\tilde{a}P^2 + \frac{1}{4}\tilde{b}P^4 + \frac{1}{6}cP^6 \quad (78)$$

where

$$\tilde{a} = a - \frac{4\bar{\eta}Q_{12}}{s_{11} + s_{12}} \quad (79)$$

and

$$\tilde{b} = b + \frac{4Q_{12}^2}{s_{11} + s_{12}} \quad (80)$$

so that the coefficients of both the quadratic and the quartic polarization terms in the Landau free energy are renormalized. This has important implications for the thermodynamic properties of the thin film; more specifically it means that its transition temperature is shifted from the bulk value (T_0)

$$T^* = T_0 + \frac{4\bar{\eta}Q_{12}}{a(s_{11} + s_{12})} \quad (81)$$

as is its spontaneous polarization (please see the discussion preceding (10)) due to the in-plane straining of the film by the compressive substrate. The signs of these shifts will be determined by the relative signs and magnitudes of Q_{12} , s_{11} and s_{12} . We note that such misfit epitaxial strain can change the nature of the transition from first- to second-order ($b < 0$ but $\tilde{b} > 0$) For ferroelectric films with multicomponent polarization and with different orientations, this approach yields a temperature-strain phase diagram with equilibrium phases that are not stable in a mechanically-free bulk sample [91, 92, 93, 94, 95]. The resulting low-temperature phase diagrams are very sensitive to the Landau coefficients, particularly for increasing misfit strain; here the phenomenological approach is nicely complemented by first-principles studies that can resolve uncertainties associated with these input parameters [94]. This combined phenomenological-first principles approach has been very successful in explaining the phase behavior of epitaxially strained films and we refer the interested reader to a sample of recent experimental papers in this field [96, 99, 100, 101, 102]. For ultrathin ferroelectric films with biaxial compressive strain at the substrate interface, the competition between elastic and surface effects has also been considered [103]. In particular we note that if we do include a gradient (Ginzburg) term to the free energy then the epitaxial strain leads to a modified correlation length

$$\tilde{\xi} = \sqrt{\frac{\gamma}{\tilde{a}}} \quad (82)$$

where $\xi = \sqrt{\frac{\gamma}{a}}$ is that associated with the bulk material that is mechanically free [103]. Similar mechanical boundary conditions have also been studied in epitaxially-strained superlattices [104]. We note that recently a combined numerical-thermodynamic approach resulted in generalized temperature-strain phase diagrams for thin ferroelectric films that include multidomain phases [105] inaccessible by the approaches described here that assume homogenous polarization.

4.5 Inhomogeneous Effects

In the previous discussion, we assume that the energy cost of uniformly straining the film to lattice-match the substrate is significantly less than that associated with other strain relaxation mechanisms; these include the creation of elastic dislocations, polydomain formation and even multiphase coexistence which are all inhomogeneous in nature. We expect elastic homogeneity for films thinner than a critical thickness ($d < d_c$), where d_c scales (roughly) inversely with the lattice mismatch [96]. Typically such coherent epitaxially strained films have thicknesses $d \sim 10 \text{ nm}$, though film growth parameters can be tuned to achieve $d \sim 50 \text{ nm}$ by kinetically suppressing other elastic relaxation processes [96]. However the physics of thicker ferroelectric films, particularly those used in current applications ($d \sim 120 \text{ nm}$) [58], does include inhomogeneous effects and next we review aspects of this topic within a phenomenological framework.

The misfit epitaxial strain decreases roughly exponentially [106, 107, 108] with distance ($\eta(z) \sim \eta_0 e^{-\frac{z}{\lambda}}$) from the film-substrate interface with a “strain depth” of approximately $\lambda \sim 300 \text{ nm}$ and thus is negligible for $d \gg \lambda$. In films of thickness $d_c < d < \lambda$, elastic defects often form to accommodate film-substrate lattice mismatch. While permitting the film’s lattice constants to relax, these defects do generate inhomogeneous strains which couple to the film’s polarization and therefore affect its ferroelectric properties. We note that compositional and thermal gradients can also produce such inhomogeneities [109]. Here we will focus on such elastic effects. Indeed the epitaxial phenomenological treatment can be generalized to include isotropic inhomogeneous strain due to such lattice defects [110]; this results in further contributions to the coefficients of both P^2 and P^4 in the free energy, and thus to a defect-induced change in the transition temperature qualitatively consistent with experiment [110].

The broadening of the dielectric peak in ferroelectric films with decreasing thickness has been observed by several groups [108, 111, 112, 113]. In bulk systems, such behavior is often attributed to disorder and/or low-dimensional effects [114] but these explanations are not appropriate to ferroelectric films due to the underlying long-range interactions. Indeed we expect these dipolar systems to be more sensitive to electromechanical boundary conditions than to local fluctuations. This qualitative idea has been confirmed by measurements on ferroelectric free-standing lamellae of sharp dielectric peaks, strongly indicating that it is due to substrate-related effects most probably associated with interfacial lattice mismatch [115].

Recent experiments on the flexoelectric coupling between strain gradients and the polarization indicate that these effects could be important in thin films [116, 117]. Theoretically it has been shown that this flexoelectric effect is enhanced in high-permittivity materials such as ferroelectrics [118] where the coupling is maximized near the dielectric peak. This flexoelectric coupling has been incorporated into a

Landau-Ginzburg framework with the goal of studying its effect on the thermodynamic properties of epitaxially strained ferroelectric films [119]. The strain gradient contribution, $\Delta_{FC} = \gamma \frac{d\eta(z)}{dz}$, couples to the polarization in the free energy, acting as an effective field, so that the equation for the spontaneous polarization

$$\tilde{a}P + \tilde{b}P^3 = \Delta_{FC}|_{P=P_0} \quad (83)$$

can only have finite solutions, even in the absence of an external electric field ($E = 0$); here \tilde{a} and \tilde{b} are the Landau coefficients that have been renormalized by epitaxial strain. As a result the inverse dielectric susceptibility

$$\chi^{-1} = 3\tilde{b}P_0^2 + \tilde{a} \quad (84)$$

can never be zero, so the standard singularity in χ is replaced by a broadened peak. Similarly the temperature scale associated with the onset of reversible polarization is distinct from that of the maximum of χ . This approach also yields a polarization that increases with decreasing film thickness despite the associated reduction and broadening of the dielectric peak; these seemingly contradictory features are consistent with known experiment [119].

We have just seen that the presence of strain gradients via the flexoelectric effect leads to the broadening of the dielectric peak in ferroelectric films. This phenomena can be generalized to consider other effective fields that couple linearly to the polarization [120]; possible origins of this effective field include asymmetric electrodes, compositional and temperature gradients as well as the stress profiles already considered. Qualitatively the effects on the dielectric response will be the same, though naturally quantitative differences will depend on the physical origin of the effective field.

Inhomogeneities, particularly strain and temperature gradients, can also lead to multidomain formation [122] as an overall energy reduction mechanism; this behavior has been observed in relatively thick ($d \sim 500 \text{ nm}$) films [123]. The competition between different strain relaxation processes including domain formation and misfit dislocation has been studied theoretically [124, 125]. Within the framework of a Landau-Ginzburg theory, the development of domain structure has been addressed [88, 121, 122]; qualitatively this is done by seeking polarization solutions of the form

$$P = P_0 + \delta P_k(z)e^{ikx} \quad (85)$$

where $\delta P_k(z) \ll P_0$. Such a treatment in nearly cubic ferroelectrics indicates that a multidomain state may well be stable down to atomic film thicknesses, length-scales well below the previous estimates that only described single-domain ferroelectricity [88]. The time evolution of the polarization and therefore the resulting domain

structures can also be obtained by numerical studies of the time-dependent Landau-Ginzburg equations[126]; such phase-field studies predict specific domain morphologies [25, 26, 127, 128] for epitaxial thin films of a variety of materials including $PbZr_{1-x}Ti_xO_3$, $SrTiO_3$ and $BaTiO_3$. We note that inhomogeneities in multicomponent ferroelectrics may also lead to multiphase coexistence [125, 129, 130, 131], particularly in the region of a first-order phase transition.

5 Summary and (Some) Open Questions

At this point we have discussed the main features associated with ferroelectrics that have been addressed within a phenomenological Landau-Ginzburg theory. Due to their underlying long-range interactions, we have learned that bulk ferroelectrics are well described within this framework; for the same reason, their finite-size counterparts are very sensitive to electromechanical boundary conditions including surface charge and misfit epitaxial strain. Inhomogeneous effects, particularly strain gradients, have also been discussed. We have now worked our way to the present and naturally there remain a number of challenges that can be addressed within this framework. Let us discuss a few of these:

(i) Strain-gradients and finite-size effects in novel nanogeometries

Three-dimensional ferroelectric nanogeometries are being explored as key components in competitive high-density data storage devices [132]. The complexity of their topologies and their boundary conditions tends to favor inhomogeneous polarization and strain configurations (e.g. [133, 134]) which remain largely unstudied, particularly from a phenomenological standpoint. For example, the energetics associated with the formation of misfit dislocations in ferroelectrics with curved topologies is known to be different than those in planar structures [135], and the associated strain gradients could lead to complex three-dimensional polarization patterns.

(ii) Multiferroics

There exist a number of materials that display both long-range ferroelectricity and incommensurate magnetic order [136] and we refer the interested reader to the chapter by N. Spaldin on this topic. Landau treatments [137, 138] for this class of materials have provided symmetry-based arguments for the type of underlying interactions that must be present at the microscopic level; furthermore the couplings between ferroelectric and magnetic order parameters can be studied in nanostructured electromagnets [139]. Detailed interplay between microscopic and phenomenological models should provide guidance on material parameters necessary to enhance the magnetoelectric couplings, particularly at room temperature for device applications.

(iii) Dynamics

The dynamical dielectric response of ferroelectrics should be accessible via time-

dependent Landau-Ginzburg theory, similar to studies performed with this method in ferroelastics (e.g. [31]). More generally a detailed phenomenological study of domain nucleation [140], domain motion (and domain interlocking [141]) could be particularly useful for the characterization of switching properties of thin-films [142]. Also glassy behavior has been observed in a number of ferroelectric relaxor materials [143], and a phenomenological model of these relaxational dynamics should be feasible.

(iv) Possible Breakdown of Landau-Ginzburg theory

Landau-Ginzburg theory may well break down in ultrasmall ferroelectric structures where the necessary averaging of the order parameter (i.e. the polarization) is no longer possible. Also it remains a challenge to see how this highly local approach can be used to described nonlocal elastic and Coulomb effects, particularly vis a vis domain formation and energetics.

(v) Quantum Critical Fluctuations

The paraelectric-ferroelectric transition in the limit $T \rightarrow 0$ may well be a textbook candidate [144, 145, 146] for quantum critical behavior [147]. Though some theoretical predictions [148] exist, logarithmic corrections to mean-field (Landau) scaling should be both theoretically and experimentally accessible and have yet to be explored. As in the classical case [15], ferroelectric materials may well provide the setting for the first detailed study of criticality at a quantum phase transition.

These are only some of the many outstanding challenges that the Landau-Ginzburg theory of ferroelectrics still has to address. Most generally, it can provide a solid bridge between the physics on atomistic scales and macroscopic measurable quantities, particularly in finite-size ferroelectrics where electromechanical boundary conditions are crucial and therefore the physics spans many length-scales. In closing, we invite the (hopefully still) curious reader to partake in these and other adventures with this phenomenological approach to ferroelectric materials.

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References

- [1] L.D. Landau and E.M. Lifshitz, *Statistical Physics*, (Pergamon Press, Oxford 1959).
- [2] J.-C. Toledano and P. Toledano, *Landau Theory of Phase Transitions* (World Scientific, Singapore, 1987).
- [3] E. Fatuzzo and W.M. Mertz, *Ferroelectricity* (North-Holland, Amsterdam, 1967).
- [4] M.E. Lines and A.M. Glass, *Principles and Applications of Ferroelectrics and Related Materials*, (Oxford University Press, Oxford, 1977).
- [5] F. Jona and G. Shirane, *Ferroelectric Crystals*, (Dover, NY, 1993).
- [6] B.A. Strukov and A.P. Levanyuk, *Ferroelectric Phenomena in Crystals*, (Springer, Berlin, 1998).
- [7] J.F. Scott, *Ferroelectric Memories*, Springer Series in Advanced Microelectronics, Vol. 3 (Springer, Berlin, 2000).
- [8] L.D. Landau, *Phys. Z. Sowjun.* **11**, 26 , 545 (1937); *Zh. Eksp. Teor. Fiz.* **7** 627 (1937); English translation in *Collected Papers of L.D. Landau*, ed. D. ter Haar (Pergamon Press, Oxford, 1965).
- [9] H. Mueller, *Phys Rev* **57**, 829 (1940); *Phys. Rev.* **58**, 565.
- [10] A.F. Devonshire, *Phil. Mag.* **40**, 1040 (1949); *ibid* **42**, 1065 (1951); *Adv. Phys.* **3**, 85 (1954).
- [11] V.L. Ginzburg, *Zh. Eksp. Teor. Fiz.* **15**, 739 (1945); *ibid* **19**, 36 (1949).
- [12] A.P. Levanyuk, *Sov. Phys. JETP* **36**, 571 (1959).
- [13] V.L. Ginzburg, *Fiz. tverd. Tela* **2** 2031 (1960); English translation in *Sov. Phys.-Solid State* **2**, 1824 (1960).
- [14] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, (Clarendon Press, Oxford, 1954)
- [15] A.I. Larkin and D.E. Khmel'nitskii, *Zh. eksp. teor. Fiz.* **55**, 2345 (1968); *ibid* **56**, 2087 (1969); English translations *Sov. Phys.-JETP* **28**, 1245 (1969) and *ibid* **29**, 1123 (1969).
- [16] G. Ahlers et al., *Phys. Rev. Lett.* **34**, 1227 (1975).

- [17] I.P. Batra and B.D. Silverman, *Solid State Communications* **11** 291 (1972).
- [18] R. Mehta, B. Silverman and J.T. Jacobs, *J. Appl. Phys.* **44**, 3379 (1973).
- [19] P. Wurfel and I.P. Batra, *Phys. Rev. B* **8**, 5126 (1973).
- [20] Ph. Ghosez and K.M. Rabe, *Appl. Phys. Lett.* **76** 2767 (2000).
- [21] J. Junquera and P. Ghosez *Nature* **422**, 506 (2003).
- [22] M. Dawber, P. Chandra, P.B. Littlewood and J.F. Scott, *J. Phys: Cond. Mat.* **15**, L393 (2003).
- [23] D.R. Tilley and B. Zeks, *Solid State Commun.* **49** 823 (1984).
- [24] J.H. Haeni et al, *Science* **430** 758 (2004); Y.L. Li et al, *Phys Rev. B* **73** 184112 (2006).
- [25] Y.L. Li et al, *J. Appl. Phys.* **98** 064101 (2005); Y.L. Li et al, *Appl. Phys.* **88** 072905 (2006).
- [26] Y.L. Li et al, *J. Appl. Phys.* **97** 034112 (2005).
- [27] W. Merz, *Phys. Rev. B* **77**, 52 (1950).
- [28] P.W. Forsbergh *Phys. Rev. B* **93**, 686 (1954).
- [29] E. A. H. Love, *A Treatise on the Mathematical Theory of Elasticity* (Dover, New York, 1944), p. 49.
- [30] S. Kartha, J.A. Krumhansl, J.P. Sethna, and L.K. Wickham, *Phys. Rev. B* **52**, 803 (1995).
- [31] S. R. Shenoy, T. Lookman, A. Saxena, and A. R. Bishop, *Phys. Rev. B* **60**, R12537 (1999).
- [32] K. . Rasmussen, T. Lookman, A. Saxena, A. R. Bishop, and R. C. Albers, *Phys. Rev. B* **87**, 55704 (2001).
- [33] T. Lookman, S.R. Shenoy, K.O. Rasmussen, A. Saxena, and A.R. Bishop, *Phys. Rev. B* **67**, 24114 (2003).
- [34] Y. Fujii and Y. Yamada *J. Phys. Soc. Japan* **30**, 1676 (1971).
- [35] J. Als-Nielsen and R. Birgeneau *Am. J. of Physics*, **45**, 554 (1977).

- [36] D. Khmel'nitskii and J.F. Scott, private communication.
- [37] e.g. R.M. White and T.H. Geballe, *Long-Range Order in Solids* (Academic Press, New York, 1979).
- [38] W. Cochran, *Adv. Phys.* **9**, 387 (1960).
- [39] R.A. Cowley, *Phys. Rev. Lett.* **9**, 159 (1962).
- [40] A.D. Bruce and R.A. Cowley *Structural Phase Transitions* (London: Taylor and Francis), (1981).
- [41] E. Burstein, A. Pinczuk, and R.F. Wallace, *Proceedings of the Conference on the Physics of Metals and Narrow Gap Semiconductors*, ed. D.L. Carter and R.T. Bate, (Pergamon, NY), 251-272 (1970).
- [42] P.B. Littlewood and V. Heine, *J. Phys C: Solid St. Phys.*, **12**, 4431; P.B. Littlewood, . *ibid.*, 4441.
- [43] T. Portengen, Th. Ostreich and L. J. Sham, *Phys. Rev. Lett.* **76**, 3384 (1996); *Phys. Rev. B* **54**, 17452 (1996).
- [44] C. D. Batista and A. A. Aligia, *Phys. Rev. Lett.* **92**, 246405 (2004); *Phys. Rev. B* **71**, 125110 (2005).
- [45] G. Gruner, *Density Waves in Solids* (Addison-Wesley, 1994).
- [46] *Theory of Superconductivity* (Benjamin, Reading, 1964).
- [47] P.G. deGennes, *Superconductivity of Metals and Alloys* (Benjamin, New York, 1966).
- [48] M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1975).
- [49] W. L. McMillan, *Phys. Rev. B* **16**, 643 (1977)
- [50] R.A. Cowley, *Physica A* **232**, 585 (1996).
- [51] D.V. Efremov, J van den Brink, and D.I. Khomskii, *Nature Materials* **3**, 853 (2004).
- [52] D. Vanderbilt and M.H. Cohen, *Phys. Rev. B* **63**, 094108 (2001).
- [53] B. Noheda et al., *Appl. Phys. Lett.* **74**, 2059 (1999).

- [54] M.J. Haun et al., *Ferroelectrics* **99** 13 (1989).
- [55] L. Bellaiche, A. Garcia and D. Vanderbilt, *Phys. Rev. B* **52**, 6301 (1995).
- [56] W. Zhong, D. Vanderbilt and K.M. Rabe, *Phys. Rev. B* **52**, 6301 (1995).
- [57] C.H. Ahn, K.M. Rabe and J.-M. Triscone, *Science* **303**, 488 (2004)
- [58] M. Dawber, K.M. Rabe and J.F. Scott, *Rev. Mod. Phys.* **77**, 1083 (2005).
- [59] W. Zhong, D. Vanderbilt and K.M. Rabe, *Phys. Rev. Lett.* **73**, 1861 (1994); *Phys. Rev. B* **52**, 6301 (1995).
- [60] J. Iniguez et al., *Phys. Rev. B* **63**, 144103 (2001).
- [61] J.S. Langer, *Ann. Phys. (NY)* **54**, 258 (1969).
- [62] D.B. McWhan et al., *J. Phys. C* **18**, L307 (1985); D.A. Neumann et al., *Phys. Rev. B* **32**, 1866 (1985).
- [63] P.B. Littlewood and P. Chandra, *Phys. Rev. Lett.* **57** 2415 (1986); P. Chandra, *Phys. Rev. A* **39** 3672 (1989).
- [64] V.L. Ginzburg, *Physics-Uspekii* **44**, 1037 (2001).
- [65] S.P. Li et al. *Phys. Lett.* **212** 341 (1996); S.P. Li et al. *Jap. J Appl Phys.* **36** 5169 (1997).
- [66] O. Auciello, J.F. Scott and R. Ramesh, *Physics Today* **51**, 22 - 27 (1998).
- [67] R. Kretschmer and K. Binder, *Phys. Rev. B* **20**, 1065 (1979); K. Binder, *Ferroelectrics* **35**, 99 (1981).
- [68] T.C. Lubensky and M.H. Rubin, *Phys. Rev. B* **12**, 3885 (1975).
- [69] J.F. Scott, *J. Phys. Cond. Mat* **18** R361 (2006).
- [70] L-H Ong, J. Osman and D.R. Tilley, *Phys. Rev. B* **63**, 144109 (2001).
- [71] M.I. Kaganov and A.N. Omelyandchouk, *Zh. Eksp. Teor. Fiz.* **61**, 1679 (1971) [*Sov. Phys. JETP* **34**, 895 (1972)].
- [72] K. Binder and P.C. Hohenberg, *Phys. Rev. B* **6**, 3461 (1979).
- [73] D.R. Tilley in *Ferroelectric Thin Films: Synthesis and Basic Properties* eds. C. Paz de Araujo, J.F. Scott and G.W. Taylor, (Gordon and Breach, Amsterdam, 1996) pp. 11 - 46.

- [74] J.F. Scott et al., *Physica B* **150**, 160 (1988).
- [75] D.R. Tilley, *Solid State Comm.* **65**, 657 (1988).
- [76] K. Ishikawa and T. Uemori, *Phys. Rev B* **60** 11841 (1999).
- [77] K.-H. Chew et al., *Integr. Ferr.* **23**, 161 (1999).
- [78] C. Basceri et al., *J. Appl. Phys.* **82**, 2497 (1997).
- [79] T. Li and W. Cao, *Phys. Rev. B* **66**, 24102 (2002).
- [80] D.L. Tilley in *Ferroelectric Ceramics*, eds. N. Setter and E.L. Colla (Birkhauser Verlag, Basel, 1993) pp. 163-184.
- [81] C. Kittel, *Introduction to Solid State Physics* (J. Wiley and Sons, New York 1976).
- [82] N.W. Ashcroft and N.D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, New York, 1976).
- [83] D.L. Tilley, *Ferroelectrics* **134**, 313 (1992).
- [84] A.M. Bratkovsky and A.P. Levanyuk, *Phys. Rev. B.* **63**, 132103 (2001).
- [85] D.D. Fong et al., *Science* **304**, 1650 (2004).
- [86] D.D. Fong et al., *Phys. Rev. B* **71** 144112 (2005).
- [87] Y.S. Kim et al., *Appl. Phys. Lett.* **86**, 102907 (2005).
- [88] A.M. Bratkovsky and A.P. Levanyuk, [cond-mat/0601484](#).
- [89] Y. Watanabe, *Phys. Rev. B* **57** 789 (1998).
- [90] A.L. Roytburd et al., *Appl. Phys. Lett.* **87** 72909 (2005).
- [91] N.A. Pertsev, A.G. Zembilgotov and A.K. Tagantsev, *Phys. Rev. Lett.* **80**, 1988 (1998).
- [92] N.A. Pertsev, A.G. Zembilgotov and A.K. Tagantsev, *Ferroelectrics* **223** 79 (1999).
- [93] Z.-G. Ban and S.P. Alpay, *J.of Appl. Phys* **91** 9288 (2002).
- [94] O. Dieguez et al. *Phys. Rev. B* **69**, 212101 (2004); O. Dieguez et al., *Phys. Rev. B* **72** 144101 (2005).

- [95] A.K. Tagantsev et al., *Phys. Rev. B* **65**, 012104 (2002).
- [96] K. Choi et al, *Science* **306** 1005 (2004).
- [97] K.A. Muller and H. Burkard, *Phys. Rev. B* **19** 3593 (1979).
- [98] M.J. Haun et al., *J. Appl. Phys.***62**, 3331 (1987).
- [99] X.M. Lu et al., *Phys. Rev. B* **72**, 212103 (2005).
- [100] A.K. Soh et al., *J. of the Amer. Cer. Soc.* **89** 652 (2006).
- [101] S. Rios et al., *J. of Appl. Phys.***99**, 24107 (2006).
- [102] S.K. Choi et al., *Appl. Phys. Lett.* **88**, 52901 (2006).
- [103] A.G. Zembilgotov et al., *J. of Appl. Phys.* **91**, 2247 (2002).
- [104] J.B. Neaton and K.M. Rabe, *Appl. Phys. Lett.* **82**, 1586 (2003); K. Johnston et al., *Phys. Rev. B* **71**, 100103 (2005); S.M. Nakhmanson et al. *Appl. Phys. Lett.* **87**, 102906 (2005).
- [105] Y.L. Li et al. *Appl. Phys. Let.* **83** 1608 (2003); Y.L. Li and L.Q. Chen *Appl. Phys. Let.* **88** 72905 (2006).
- [106] J.W. Matthews and A.E. Blackeslee, *J. Cryst. Growth* **27**, 118 (1974).
- [107] H.J. Kim et al., *Appl. Phys. Lett.* **78** 1724 (2001).
- [108] L.J. Sinnamon et al., *Appl. Phys. Lett.* **81**, 703 (2002).
- [109] Z.G. Ban et al., *Phys. Rev. B* **67**, 184104 (2003).
- [110] D. Balzar et al., *Phys. Rev. B* **70**, 92103 (2004).
- [111] T.M. Shaw et al., *Appl. Phys. Lett.* **75**, 2129 (1999).
- [112] C.B. Parker et al., *Appl. Phys. Lett.***81**, 340 (2002).
- [113] A. Lookman et al., *J. Appl. Phys.* **96**, 555 (2004).
- [114] J. Cardy, *Scaling and Renormalization in Statistical Physics* (Cambridge University Press, Cambridge, 1996).
- [115] M.M. Saad et al., *J. Phys. C* **16** L451 (2004).

- [116] W. Ma and L.E. Cross, *Appl. Phys. Lett.* **79** 4420 (2001); *ibid* **81** 3440 (2002); *ibid* **82** 3293 (2003); *ibid* **86** 72905 (2005).
- [117] A. Gruverman et al. *Appl. Phys. Lett.* **83**, 728 (2003).
- [118] A. Tagantsev, *Phys. Rev. B* **34** 5883 (1986); A. Tagantsev *Phase Transitions* **35** 119 (1991).
- [119] G. Catalan et al., *J. Phys. Cond. Mat.* **16**, 2253 (2004); G. Catalan et al., *Phys. Rev. B* **72** 020102 (2005).
- [120] A.M. Bratkovsky and A.P. Levanyuk, *Phys. Rev. Lett.* **94**, 107601 (2005).
- [121] Y.G. Wang et al., *Phys. Rev. B* **51** 5311 (1995).
- [122] A.M. Bratkovsky and A.P. Levanyuk, *Phys. Rev. Lett.* **1**, 43177 (2000); A.M. Bratkovsky and A.P. Levanyuk, *Phys. Rev B* **66**, 184109 (2002).
- [123] A.L. Roytburd et al., *J. Appl. Phys.* **89**, 553 (2001).
- [124] J.S. Speck and W. Pompe *J. Appl. Phys.* **7**, 466 (1994).
- [125] J. Slutsker and A.L. Roytburd *Ferroelectrics* **222** 365 (1999).
- [126] L.Q. Chen and J. Shen, *Comput. Phys. Commun.* **108**, 147 (1998).
- [127] Y.L. Li et al., *Phys. Rev. B* **73** 184112 (2006).
- [128] Y.U. Wang et al. *Acta Mat.* **52** 81 (2004).
- [129] S.Semenovskaya and A.G. Khachaturyan, *Acta Mat.* **45** 4367 (1997).
- [130] A. Roytburd and J. Slutsker, *Acta Materialia* **50**, 1809 (2002).
- [131] Y.L. Li et al., *Appl. Phys. Lett.* **88** 072905 (2006).
- [132] Y. Arimoto and H. Ishiwara, *MRS Bulletin* **29**, 823 (2004).
- [133] J.F. Scott, *Nature* **4** 13 (2005).
- [134] H.X. Fu et al, *Phys. Rev. Let.* **91**, 257601 (2003); I.I. Naumov et al., *Nature* **432** 737 (2004).
- [135] M.Y. Gutkin et al., *J. Phys. Cond. Mat.* **12**, 5391 (2000); A.G. Sherman and M.Y. Gutkin, *Phys. Stat. Sol.* **184**, 485 (2001); M.Y. Gutkin et al., *J. Phys. Cond. Mat.* **15** 3539 (2003).

- [136] D.I. Khomskii, [cond-mat/0601696](#).
- [137] G. Lawes et al, *Phys. Rev. Let.* **95**, 87205 (2005); A.B. Harris and G. Lawes, [cond-mat/0508617](#).
- [138] M. Mostovoy, *Phys. Rev. Let.* **96**, 67601 (2006).
- [139] H. Zheng et al., *Science* **303** 661 (2004).
- [140] C.S. Ganpule et al., *Appl. Phys. Lett.* **77** 3275 (2000).
- [141] A. Krishnan et al., *Integ. Ferroelectrics* **43** 31 (2002).
- [142] J. Fousek and L.E. Cross *Ferroelectrics* **293** 43 (2003).
- [143] E.V. Colla et al., *Phys. Rev. Let.* **85** 3033 (2000); E.V. Colla et al., *Phys. Rev. B* **63** 134107 (2001).
- [144] D.E. Grupp and A.M. Goldman, *Science* **276**, 382 (1997).
- [145] P. Coleman, [cond-mat/0512463](#); S.E. Rowley et al, unpublished.
- [146] J.F. Scott et al., *J. Phys. Cond. Mat.* **18** L205 (2006).
- [147] S. Sachdev *Quantum Phase Transitions* (Cambridge University Press, Cambridge, 1999).
- [148] R. Roussev and A.J. Millis, *Phys. Rev. B* **67**, 014105 (2003).