

# Ferroelectric and Ferromagnetic Phase Field Modeling

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**Abstract** This chapter provides an introduction to phase field modeling. It is directed at the level of a graduate student with some background in mechanics. It begins with a review of the electro-statics, magneto-statics, and mechano-statics that are needed when setting up phase field models. These yield the various conservation laws that are used. After this review, thermodynamics of materials is discussed. The first law of thermodynamics is used to equate work done on a material plus heat added to the material to the increase of internal energy. This is used with the second law, a statement that irreversible processes generate entropy. This leads to fundamental relations that must be followed in postulating forms for the internal energy. The ways that internal energy is stored in a material are determined through observation. Once the mechanisms have been identified, work conjugate internal variables are introduced to enable writing a specific form for the internal energy and its derivatives. Observations are invoked once again regarding material symmetry to reduce the number of constants that must be determined when modeling a specific material.

## 1 Introduction

Phase field models are based on the idea that there is some order parameter that describes the state of the material. In a ferroelectric material the order parameter is the polarization and in a ferromagnetic material the order parameter is the magnetization. Analysis of the behavior of the material when not in an equilibrium state gives the driving force for evolution of the order parameter. This driving force is then used with

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a kinetic relation that governs its rate of change. In the case of a ferroelectric material the kinetic relation is the time dependent Ginzburg Landau equation (TDGL) and in the case of a ferromagnetic material the kinetic relation is the Landau Lifshitz Gilbert equation (LLG). Detailed attention is given to the divergence of the second order tensors that are work conjugate to the polarization and magnetization gradients, as these are less familiar than the divergence of the second order stress tensor that is work conjugate to the strain tensor. The roles in balance laws are similar. This is followed by a mathematical treatment of the development of the equations used in phase field models and an example of their implementation and use.

## 2 Maxwell's Equations and Polarization

The discussion of electro-statics presented here is largely a reduced version of that presented by Panofsky and Phillips (2005). This discussion begins with a few comments about systems of units. Although the SI (rationalized MKS) system of units has been broadly adopted, much of the magnetics literature is in CGS units or in atomic units. As discussed in the chapter by J. Schöder, not only must the units be converted to SI from CGS or atomic units, Maxwell's equations must also be modified to correspond to the different systems of units. The equations discussed in this chapter will be those that correspond to rationalized SI units.

The differential form of Maxwell's equations in SI units is represented by four equations

$$\begin{aligned}
 \nabla \cdot \mathbf{D} &= \rho_f && \text{(Gauss' law)} \\
 \nabla \cdot \mathbf{B} &= 0 && \text{(Gauss' law for magnetism)} \\
 \nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t} && \text{(Faraday's law of induction)} \\
 \nabla \times \mathbf{H} &= \mathbf{J}_f + \frac{\partial \mathbf{D}}{\partial t} && \text{(Ampere's law of induction)}
 \end{aligned} \tag{1}$$

where is  $\mathbf{D}$  the electric displacement vector,  $\rho_f$  is the free charge density,  $\mathbf{B}$  is the magnetic flux density,  $\mathbf{E}$  is the electric field,  $\mathbf{H}$  is the magnetic field,  $\mathbf{J}_f$  is the free current density, and  $t$  is time. The subscript f on the volume charge density and the current density is used to indicate that these terms are associated only with the free charge. Separately considering the motion of charges associated with dipoles (bound charge for electric dipoles and bound current for magnetic dipoles) and motion of free charge carriers that can move over longer distances (free charge) provides a simpler description of a material at larger length scales. This simplification is at the expense of having to now consider electric displacement currents associated with oscillatory motion of the bound charge (important at higher frequencies) and the magnetic field associated with contributions from internal magnetic moments associated with the bound current loops. By bound we mean localized ionic charges or localized currents associated with electron spins and orbits that are tied to specific atoms or small groups of atoms in the material. The corresponding constitutive relations are

$$\begin{aligned} \mathbf{D} &= \varepsilon_0 \mathbf{E} + \mathbf{P} \\ \mathbf{H} &= \frac{\mathbf{B}}{\mu_0} - \mathbf{M} \end{aligned} \quad (2)$$

where  $\mathbf{P}$  is the polarization, and  $\mathbf{M}$  is the magnetization,  $\varepsilon_0 = 8.85 \times 10^{-12} (F/m)$  is the permittivity of free space,  $\mu_0 = 4\pi \times 10^{-7} (N/A^2)$  is the magnetic permeability of free space.

Maxwell's equations are consistent with several observable forces.

- Coulomb's law gives the force between two charges.

$$\mathbf{F} = \frac{1}{4\pi\varepsilon_0} \frac{q_1 q_2 \mathbf{r}}{r^3} \quad (3)$$

where  $q_i$  are charges,  $\mathbf{r}$  is the position vector connecting them.

- The Lorentz force (force on a charge) in a static electric field or moving through a magnetic field is given by

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (4)$$

where  $\mathbf{v}$  is the velocity of the charge.

- A current produces an associated magnetic flux density. A magnetic flux density increment generated by a current filament of magnitude  $I$  and length  $d\mathbf{l}$  is given by the Biot-Savart law (in differential form)

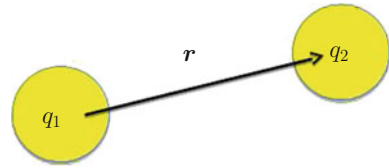
$$d\mathbf{B} = \frac{\mu_0}{4\pi} \frac{I d\mathbf{l} \times \mathbf{r}}{r^3} . \quad (5)$$

## 2.1 Electro-Statics

In the electrostatic approximation the contributions of  $\partial\mathbf{E}/\partial t$  and  $\partial\mathbf{B}/\partial t$  in Maxwell's equations are neglected. In this case, the electric field can be represented by the negative gradient of the potential established by a distribution of point charges. It has units of  $V/m$  where  $1V = 1 Nm/C$  is the work per unit charge to move the unit charge up a potential gradient. The electric field ( $N/C$ ) is the force per unit charge on a charge held stationary in a potential gradient.

Certain clusters of point charges produce electric field distributions that are relatively easy to define mathematically. These include the field of two parallel sheets of charge which produces a uniform electric field within a parallel plate capacitor, the field of two equal magnitude but opposite sign charges held a fixed distance apart to create a dipole field, and the field of certain arrangements of charges that can be represented by quadrupoles, octapoles, and higher order poles.

**Fig. 1** Two charges separated by a distance,  $r$ , experience an interaction force between them



The potential and electric field distributions in the vicinity of point charges and dipoles are of particular interest to the discussion of ferroelectric materials. The fields of higher order multi-poles fall off faster with distance than the fields of dipoles, enabling the representation of a continuum as a dipole moment density, the polarization. Although there is no point magnetic charge, from a distance the magnetic field associated with a current loop can be described by the same equations used to describe the electric dipole field. This leads to an often-used introduction of fictitious point magnetic charges to represent the magnetic field of current loops. This provides a convenient method of establishing a uniform external magnetic field when using computational methods.

**Charge as the source of electric field.** When two charges are placed a distance apart as shown in Fig. 1, they experience an interaction force. The force on charge 1 due to the presence of charge 2 is given by

$$\mathbf{F} = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2 \mathbf{r}}{r^3}. \quad (6)$$

Like charges repel and unlike charges attract.

**Electric field of a point charge.** The electric field is the force per unit charge. The electric field at charge (1) due to the presence of charge (2) is given by

$$\mathbf{E}^{(1)} = \frac{\mathbf{F}}{q_2} = \frac{q_1 \mathbf{r}}{4\pi\epsilon_0 r^3} = -\frac{q_1}{4\pi\epsilon_0} \nabla \left( \frac{1}{r} \right). \quad (7)$$

The electric field is defined as the negative gradient of the potential. This leads to the expression for the potential of a point charge,

$$\phi = \frac{q}{4\pi\epsilon_0} \left( \frac{1}{r} \right). \quad (8)$$

The gradient is most easily worked out in terms of Cartesian coordinates. As a reminder, write the distance “ $r$ ” as  $(x_i x_i)^{1/2}$  (implied summation) and the operator  $\text{dell } \nabla = \partial_k \hat{e}_k$  as (implied summation). Proficiency with this operation is important to understanding the dipole field.

**Electric field of a dipole.** Two equal charges  $q$  that are opposite in sign and held a fixed distance  $d$  apart define a dipole moment

$$\mathbf{p} = q\mathbf{d} . \quad (9)$$

The potential of a dipole is given by

$$\phi^{(2)} = \frac{1}{4\pi\epsilon_0} \frac{\mathbf{p} \cdot \mathbf{r}}{r^3} . \quad (10)$$

We can derive the expression for the potential of a dipole by differentiating the potential of a point charge with respect to the position of the charge. The definition of the derivative is also the definition of the dipole field, i.e.  $\lim_{\delta x \rightarrow 0} \frac{\phi(x + \delta x) - \phi(x)}{\Delta x}$  where  $\phi$  is the potential field of the point charge. Further differentiation leads to quadrupoles, octopoles, etc. Their fields fall off faster than  $1/r^2$  and thus can be (and are) neglected in continuum descriptions of volumes of material containing many atoms. The electric field in the vicinity of a single dipole is found by taking the negative gradient of the dipole field. This leads to

$$\mathbf{E}(\mathbf{p}) = -\frac{1}{4\pi\epsilon_0} \nabla \left( \frac{\mathbf{p} \cdot \mathbf{r}}{r^3} \right) . \quad (11)$$

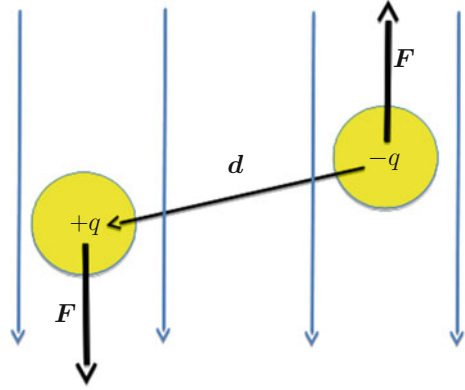
**The field of a polarization distribution.** Certain solids have naturally occurring dipoles. These are associated with a separation of positive and negative charge centers. The small length scale of the atomic dimensions associated with the dipoles makes finding the superposition of the fields of individual dipoles prohibitive in all but very small volumes, on the order of a few hundreds of lattice parameters. This leads to defining the polarization field as the average dipole moment per unit volume. The volume for defining the polarization needs to be large enough that the field fluctuations associated with individual dipoles cannot be detected and the contributions of the higher order poles can be neglected relative to the dipole field, yet small enough that gradients in the dipole fields can be neglected and the volume considered a “mathematical point”. As the discussion progresses, this volume will be made even larger such that the gradient of the polarization field can be detected when domain walls are considered. The polarization is defined as the dipole moment density

$$\mathbf{P} = \lim_{V \rightarrow 0} \frac{\mathbf{p}}{V} . \quad (12)$$

**Forces on a dipole in a uniform electric field.** An electric field produces a force per unit charge on charges in the field. A dipole consists of a positive and a negative charge with a fixed separation. If a dipole is placed in a uniform electric field, the two charges will experience equal and opposite forces as shown in Fig. 2. The force on each charge is in the opposite direction and is given by

$$\begin{aligned} \mathbf{F} &= +q\mathbf{E} \\ \mathbf{F} &= -q\mathbf{E} . \end{aligned} \quad (13)$$

**Fig. 2** A dipole placed in an electric field experiences equal magnitude and opposite sign forces on each of the charges. This results in a torque and stretching of the dipole



The resulting torque on a dipole of fixed magnitude is given by

$$\begin{aligned}\tau &= \mathbf{d} \times \mathbf{F} \\ &= \mathbf{d} \times q\mathbf{E} \\ &= \mathbf{p} \times \mathbf{E} .\end{aligned}\tag{14}$$

If the charges are connected by a spring, the dipole will rotate to align with the field and will be stretched by the field. With certain asymmetric charge distributions bound to a crystal lattice this results in an electric field producing mechanical deformation, or converse piezoelectricity. Direct piezoelectricity is when mechanically deforming the lattice changes the charge separation of the dipoles causing a polarization change or, as in the case of piezoelectric polymers like PVDF, the dipole moments remain nearly constant and the volume is decreased; again leading to a polarization change.

The potential energy of a dipole of fixed charge separation in a uniform electric field can be found by imagining the dipole being initially aligned with the field. Perform a thought experiment where a torque is physically applied to rotate the dipole against the field. The torque will start small, go through a maximum when the dipole has been rotated  $90^\circ$ , and return to zero as the rotation reaches  $180^\circ$ . The work done is the integral of the torque over the angle of rotation. This is given by

$$dW = \mathbf{p} \times \mathbf{E} d\Theta = pE \sin \Theta d\Theta .\tag{15}$$

The work per unit volume is the work required to rotate the polarization in an electric field. This gives

$$dw = -d(PE \cos \Theta) = -d(\mathbf{P} \cdot \mathbf{E}) ,\tag{16}$$

thus the potential energy of a polarized volume element in a uniform electric field is given by

$$\Psi = -\mathbf{P} \cdot \mathbf{E} .\tag{17}$$

The potential energy is at a minimum when  $\mathbf{P}$  and  $\mathbf{E}$  are aligned and at a maximum when  $\mathbf{P}$  and  $\mathbf{E}$  are at  $180^\circ$  to one another.

**Dipole-dipole interaction energy.** Two dipoles in proximity to one another interact. The electric field produced by one produces forces on the charges of the other. Panofsky and Phillips (2005) outline the calculation of the interaction energy. The result is obtained by placing one dipole,  $p_1$  in the field of another dipole,  $p_2$ . The interaction energy is

$$U_{12} = \frac{1}{4\pi\epsilon_0} \left[ \frac{\mathbf{p}_1 \cdot \mathbf{p}_2}{r^3} + 3 \frac{(\mathbf{p}_1 \cdot \mathbf{r})(\mathbf{p}_2 \cdot \mathbf{r})}{r^3} \right]. \quad (18)$$

When a solid is modeled as a continuum and the polarization of neighboring regions varies slightly, the neighboring polarization can be found from the gradient of the polarization field. The differences in neighboring polarizations interact just as the neighboring dipoles interact. The interaction energy per unit volume is expressed in terms of the polarization gradient squared in the phenomenological treatment discussed below.

**Electrical boundary conditions.** The electrical boundary conditions are found directly from Maxwell's equations. Integration of the expression

$$\nabla \cdot \mathbf{D} = \rho_f \quad (19)$$

over a volume that encloses an interface or a surface, applying the divergence theorem to convert to a surface integral, then shrinking the volume such that it closely follows a small portion of the surface leads to the statement that the jump in the normal component of electric displacement at a surface is equal to the surface charge density, i.e.

$$\|\mathbf{D} \cdot \hat{n}\| = -\omega^s. \quad (20)$$

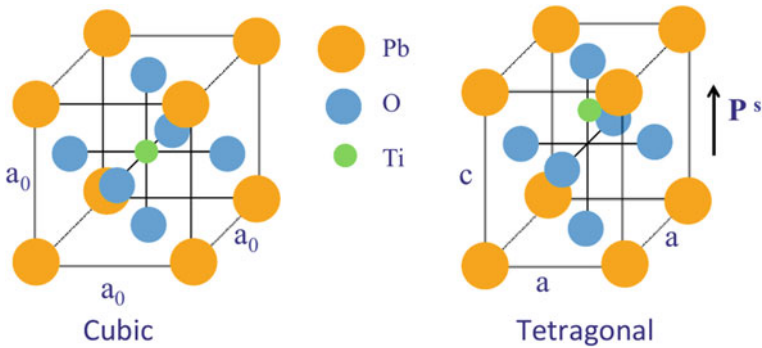
Similarly integrating using Stokes' theorem,

$$\nabla \times \mathbf{E} = 0 \quad (21)$$

indicates that the tangential component of electric field at an interface is continuous, i.e.

$$\|\mathbf{E} \cdot \hat{t}\| = 0. \quad (22)$$

**Ferroelectric materials and multi-well behavior.** Ferroelectric materials with the perovskite crystal structure have a spontaneous dipole moment per unit volume associated with the crystal structure when cooled below the Curie point. The dipole moment couples to the crystal structure in certain materials such as barium titanate and lead zirconate titanate such that it is at lower potential energy when it is aligned with certain crystallographic directions. When this spontaneous polarization occurs, a spontaneous strain simultaneously occurs. The  $ABO_3$  Perovskite crystal structure



**Fig. 3** A conceptual schematic showing the perovskite structure of lead titanate in the high temperature cubic structure (left) and the low temperature tetragonal structure (right). Note that the tetragonal structure has 6 variants with polarization along each of the six  $\langle 001 \rangle$  directions

is shown in Fig. 3. The cubic referenced unit cell shown on the left is made up of Pb (+2) ions at the corners, O (−2) ions at each face center, and Zr (+4) or Ti (+4) at the center. When cooled below the Curie temperature, the structure distorts. The figure to the right conceptually shows the spontaneous strain and the spontaneous polarization. The polarization is the result of the A and B ions shifting relative to the O ions.

In a tetragonal crystal, the spontaneous polarization lies along one of the six  $\langle 001 \rangle$  directions. The potential energy therefore has minima in these six directions. This is referred to as a crystal with a multi-well potential. An illustration of the energy wells is shown as a two dimensional plot of the potential energy as a function of the polarization in Fig. 4. Positive work must be done to rotate the polarization out of one well and negative work is done as it slides into another. Because the different energy wells have the same depth, no total work is done by changing the polarization from one well to another if the system is conservative. If the process is dissipative, positive work is done and heat is generated each time the polarization is forced to move from one well to another.

When the polarization is in a particular well and a small electric field is applied, it will change, but will not escape the well. This polarization change in response to an applied electric field contributes to the dielectric permittivity of the material. Because the polarization is the result of bound charge in the crystal structure and the bound charge is tied to the atomic structure in a piezoelectric, a change of polarization results in a change of strain. This is the converse piezoelectric effect. When a mechanical stress is applied to the lattice, the resulting strain deforms the lattice and changes the polarization. This is the direct piezoelectric effect.

There are many books describing piezoelectricity and ferroelectricity and the reader is referred to these for more information. The intent in this discussion is address how to identify the energy landscapes associated with particular crystals and to use them in the study of domain formation and domain wall motion.



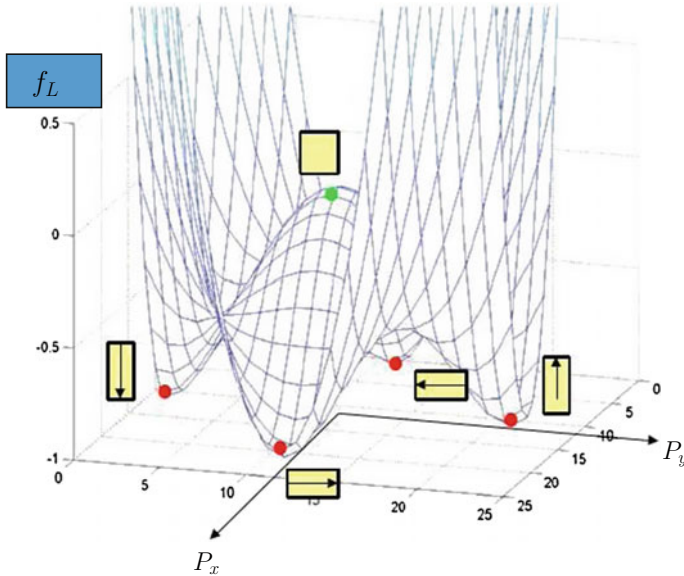


Fig. 4 Potential energy as a function of polarization in the  $x - y$  plane shows four of the energy wells of the tetragonal structure

### 3 Magnetism

When modeling quasi-static magnetic material behavior, the focus is usually on understanding the magnetic dipole, the magnetization (magnetic moment per unit volume), the boundary conditions, and the multi-well potential. In many ways, modeling ferromagnetic material behavior is similar to modeling ferroelectric material behavior. The multi-well potentials appear remarkably similar. There is a significant difference in that the time rate of change of polarization is treated as a damped viscous behavior whereas the time rate of change of magnetization is treated as a damped time rate of change of the angular momentum associated with the electron spin and orbital motion. The latter is necessary to capture effects such as ferromagnetic resonance.

There are several fundamental differences between magnetization and polarization.

- Polarization is the result of the volume average of an approximation of a particular point charge distribution, the dipole moment (bound charge). The surface boundary conditions include the possibility of coating the surface with point charges to terminate the polarization.

The source of the magnetic dipole is a small current loop (bound current) associated with electron spin and orbital motion that gives rise to a magnetic field some distance away from the loop that looks just like the field of an electric dipole. The magnetization  $\mathbf{M}$  is the magnetic moment per unit volume. The magnetic boundary conditions do not include the ability to spread magnetic charges on the surface. This

means that some magnetic field will always exit a magnetized material and re-enter elsewhere. We can, however, introduce a fictitious magnetic charge on the surface to simulate the behavior of a magnetic material in a uniform external magnetic field.

- Another difference is in the way the magnetic moment couples to the lattice. The magnetic current loop that acts as the magnetization source comes from electron spin and electron orbital motion. Many ferromagnetic materials have unfilled d-orbitals that result in a net spin associated with each atom in the lattice. The spin couples to the orbital motion, and the orbital motion couples to the lattice. This results in “easy” directions and “hard” directions for the magnetization relative to the lattice. The electric dipole can be thought of as two charges connected by a spring. The dipole can rotate and it can stretch. The magnetization, being nothing more than the effect of electron spin and orbital motion, cannot change its magnitude much and is modeled as having a fixed magnitude. Only the orientation is allowed to change. This leads to representing magnetic moment in terms of the direction cosines of the magnetization vector (normalized magnetization).

### 3.1 Magneto-Statics Review

This section provides a brief overview of the equations that govern the behavior of magnetic current loops in an applied magnetic field for the quasi-static case.

**Current loops as the source of magnetic field.** If two current loops are in proximity to one another, the current in loop 1 will exert a force on loop 2. Ampere’s law gives the magnitude of this force. In MKS units this is given by

$$\mathbf{F}_2 = \frac{\mu}{4\pi} J_1 J_2 \oint_1 \oint_2 \frac{d\mathbf{l}_2 \times (d\mathbf{l}_1 \times \mathbf{r}_{12})}{r_{12}^3} . \quad (23)$$

This can be written as the generalized Biot-Savart law,

$$\mathbf{F}_2 = J_2 \oint_2 d\mathbf{l}_2 \times \mathbf{B}_2 \quad (24)$$

where  $\mathbf{B}_2$  is the magnetic flux density at the position the force is being evaluated and is given by,

$$\mathbf{B}_2 = \frac{\mu}{4\pi} J_1 \oint_1 \frac{(d\mathbf{l}_1 \times \mathbf{r}_{12})}{r_{12}^3} \quad (\text{Weber}/m^2) . \quad (25)$$

This can also be written as volume integrals over current densities. Under near quasi-static conditions, the magnetic flux density can be written as the negative gradient of a scalar potential with some restrictions on the line integral,

$$\mathbf{B} = -\mu_0 \nabla \phi_m . \quad (26)$$

More generally,  $\mathbf{B}$  is derived from a vector potential and is given by

$$\mathbf{B} = \nabla \times \mathbf{A} \quad (27)$$

where the vector  $\mathbf{A}$  is determined from

$$\mathbf{A} = \frac{\mu_0}{4\pi} \oint \frac{\mathbf{J}}{r} dv' = \frac{\mu_0}{4\pi} J \oint \frac{d\mathbf{l}}{r} \quad (28)$$

where  $r$  points from the current point to the observation point.

In developing expressions for magnetic field within a material, the problem can be formulated in terms of magnetization (the volume average of the atomic scale current loops) if the current within the material is separated into the current loops bound to the structure (electron spin and orbital current loops or bound current), and current loops associated with electrical conduction (free current). Several types of currents exist.

1. True of free currents associated with electron transport in response to an EMF.
2. Polarization currents  $\frac{d\mathbf{P}}{dt}$ .
3. Magnetization currents  $\mathbf{j}_m$ .
4. Convective currents associated with media in motion,  $q\mathbf{v}$ .

When we consider the design of multiferroic antennas or filters, all of these must be considered and care taken to justify neglecting terms for the particular problem.

**The magnetic moment of a current loop.** The magnetic moment as a function of position relative to a uniform current density within a small volume is defined as

$$\mathbf{m} = \frac{1}{2} \int (\boldsymbol{\xi} \times \mathbf{j}_m) dV \quad (29)$$

where the  $\boldsymbol{\xi}$  are the position coordinates. If we consider the current densities as charge densities moving with a velocity  $\mathbf{v}$ , then the magnetic moment is given by

$$\mathbf{m} = \frac{1}{2} \int \rho_v (\boldsymbol{\xi} \times \mathbf{v}) dV . \quad (30)$$

Note the analogy with mechanical angular momentum,

$$\mathbf{s} = \frac{1}{2} \int \rho_m (\boldsymbol{\xi} \times \mathbf{v}) dV . \quad (31)$$

The gyromagnetic ratio is defined as the ratio of the magnetic moment to angular momentum,

$$\Gamma = \frac{\mathbf{m}}{\mathbf{s}} . \quad (32)$$

If the current is produced by an electron of mass  $m$ , and charge  $e$ , then the gyromagnetic ratio is given by

$$\Gamma = \frac{e}{2m} . \quad (33)$$

Note that any charged objects that are spinning about an axis will have a gyromagnetic ratio of

$$\Gamma = g \frac{e}{2m} . \quad (34)$$

The definition of magnetic moment becomes simpler when the current loop is so small that it is inaccessible to measurement, i.e. an electron circling an atom in its orbital. In this case the magnetic moment is given by the product of the current  $J$ , and the area of the loop  $S$ , with the direction determined by the right hand rule;

$$\mathbf{m} = JS . \quad (35)$$

The magnetization is a field quantity used in the continuum description of a ferromagnetic material. The magnetization is defined as the magnetic moment per unit volume,

$$\mathbf{M} = \frac{\mathbf{m}}{V} . \quad (36)$$

Working with the vector potential, it can be shown that the curl of the volume magnetization is equal to an equivalent current density Panofsky and Phillips (2005),

$$\mathbf{j}_m = \nabla \times \mathbf{M} . \quad (37)$$

Note that this equivalent current vanishes in regions where the magnetization is homogeneous and it represents the net current density produced in regions where the magnetization is inhomogeneous.

The descriptions of the three types of current lead to an important result. The total current density is given by

$$\mathbf{j}^{total} = \mathbf{j}^m + \mathbf{j}^P + \mathbf{j}^{true} = \nabla \times \mathbf{M} + \frac{\partial \mathbf{P}}{\partial t} + \mathbf{j}^{true} . \quad (38)$$

Charge continuity requires that

$$\nabla \cdot \mathbf{j}^{total} = -\frac{\partial \rho}{\partial t} = -\nabla \cdot \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} . \quad (39)$$

Combining these expressions gives

$$\nabla \cdot \left( \nabla \times \mathbf{M} + \frac{\partial \mathbf{D}}{\partial t} + \mathbf{j}^{true} \right) = 0 \quad (40)$$

where  $\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}$ . The solenoidal current  $\mathbf{c}$ , is given by

$$\nabla \times \mathbf{M} + \frac{\partial \mathbf{D}}{\partial t} + \mathbf{j}^{true} = \mathbf{c} = \mathbf{j}^{total} + \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t}. \quad (41)$$

The true current is associated with the motion of free charges. The total current is associated with the sum of the effects of the free and bound charges. There is also an effective current associated with the time rate of change of electric field in free space that must be included. This term is present within the free space occupied by the material and outside of the material. The solenoidal current is used with the magnetic flux density expressions. It leads to

$$\begin{aligned} \nabla \cdot \mathbf{B} &= 0 \\ \nabla \times \mathbf{B} &= \mu_0 \mathbf{c} = \mu_0 \left( \nabla \times \mathbf{M} + \frac{\partial \mathbf{D}}{\partial t} + \mathbf{j}^{true} \right). \end{aligned} \quad (42)$$

Rewriting the second equation with all of the magnetic terms on the LHS gives

$$\nabla \times (\mathbf{B} - \mu_0 \mathbf{M}) = \mu_0 \left( \frac{\partial \mathbf{D}}{\partial t} + \mathbf{j}^{true} \right). \quad (43)$$

This leads to the definition of the magnetic field as

$$\mathbf{H} = \frac{1}{\mu_0} (\mathbf{B} - \mu_0 \mathbf{M}) \quad (\text{amp turns}/m) \quad (44)$$

often written as

$$\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M}). \quad (45)$$

**Dipole character of a current loop.** Panofsky and Phillips (2005) perform a multipole expansion of the vector magnetic potential. The result is that the first term in the expansion leads to the vector potential of a magnetic dipole,  $\mathbf{m}$ . This vector potential is given by

$$\mathbf{A} = -\frac{\mu_0}{4\pi} \frac{\mathbf{m} \times \mathbf{R}}{R^3} = \frac{\mu_0}{4\pi} \mathbf{m} \times \nabla \left( \frac{1}{R} \right). \quad (46)$$

**The field of a magnetization distribution.** The magnetization is the magnetic moment per unit volume with the volume large enough that individual spins can be ignored, yet small enough that the magnetization can be defined at a point. This definition will be relaxed when larger volumes are used to capture the magnetization gradients within a domain wall.

**Torque on a current loop in a magnetic field.** The torque on a magnetic moment is given by

$$\mathbf{L} = \mathbf{m} \times \mathbf{B}. \quad (47)$$

For systems with angular momentum, the torque is equated to the time rate of change of angular momentum. This results in

$$\frac{ds}{dt} = \mathbf{m} \times \mathbf{B} = \Gamma(\mathbf{s} \times \mathbf{B}) . \quad (48)$$

If  $\mathbf{s}$  makes an angle with  $\mathbf{B}$ , then the magnetic moment will precess about  $\mathbf{B}$  with angular velocity

$$\omega = \Gamma \mathbf{B} . \quad (49)$$

**Dipole-dipole magnetic interaction energy.** Just as there is interaction energy between two electric dipoles, there is interaction energy between two magnetic moments. The equations and their derivations are similar to those for polarization and the reader is again referred to Panofsky and Phillips (2005).

**Magnetic boundary conditions.** The boundary conditions are analogous to those for polarization.  $\text{Div } \mathbf{B} = 0$  leads to

$$||\mathbf{B} \cdot \hat{\mathbf{n}}|| = 0 \quad (50)$$

and  $\nabla \times \mathbf{H} = \mathbf{J}_f$  leads to

$$||\mathbf{H} \cdot \hat{\mathbf{t}}|| = K \quad (51)$$

where  $K$  is the true surface current.

**Ferromagnetic materials and multi-well behavior.** As with ferroelectric materials, ferromagnetic crystalline materials can be described by a multi-well potential. Certain crystalline materials display a spin-orbital-lattice coupling wherein the lattice produces a torque on the magnetic moments of each atom. When the magnetic moments are aligned with the preferred lattice directions, the torque goes to zero. This defines an easy axis. In a cubic symmetry crystal there is typically an easy, an intermediate, and a hard axis. These can be in any of the  $\langle 001 \rangle$ ,  $\langle 011 \rangle$ , or  $\langle 111 \rangle$  directions. The easy, intermediate, and hard directions are identified experimentally as described by Cullity and Graham (2011) and the results are fit to even order polynomials in magnetization. The equations for the energy wells in magnetization have a form identical to the energy wells in polarization, i.e. they are expressed in terms of even order powers of magnetization.

## 4 Mechano-Statics Review

The equations of mechano-statics describe mechanical equilibrium conditions (mechanical force balance) in terms of stress, strain, and displacement. Stress is a second order tensor that describes force per unit area within a solid. Strain is a second order tensor that represents the symmetric part of the displacement gradient.

In materials that undergo small deformation, geometric effects are neglected. This is the case for most of the ferroelectric and ferromagnetic materials of interest with the exception of ferroelectric polymers. Finite deformation formulations must be used when describing a force per unit area when the area changes appreciably during deformation, and in describing the deformation gradient when there is a significant difference between the un-deformed and deformed shape. The following discussion is focused on the small deformation case that is most often used for ferroelectric and ferromagnetic materials.

**Stress and equilibrium.** Stress is a second order tensor that describes internal forces per unit area within a body. The stress tensor is written as

$$\boldsymbol{\sigma} = \sigma_{ij} \hat{e}_i \hat{e}_j \quad (52)$$

where summation over the repeated indices is implied. The system is in dynamic equilibrium when the sum of forces on a volume element is equal to its mass times its acceleration. This leads to the equilibrium equation

$$\nabla \cdot \boldsymbol{\sigma} + \mathbf{f} = \rho_m \ddot{\mathbf{u}} \quad (53)$$

where  $\mathbf{f}$  represents a vector force per unit volume,  $\ddot{\mathbf{u}}$  the acceleration and  $\rho_m$  the mass density. The components of this vector equation are

$$\sigma_{ij,j} + f_i = \rho_m \ddot{u}_i \quad (54)$$

where  $\rho_m$  is the mass density. In the absence of acceleration the system is in quasi-static equilibrium. If the externally applied body forces are also zero, the stress can be derived from a potential that ensures the equilibrium equation will be satisfied by the second order tensor identity

$$\nabla \cdot (\nabla \times \boldsymbol{\phi} \times \nabla) = 0 . \quad (55)$$

When  $\boldsymbol{\phi} = \phi_{33}(x_1, x_2) \hat{e}_3 \hat{e}_3$  we have Airy's stress function, and when the second order tensor has an off-diagonal element, we have a torsion stress function. Numerous special cases are discussed in books on the theory of elasticity.

**Strain.** Strain is the symmetric part of the displacement gradient. The displacement vector field is denoted

$$\mathbf{u}(\mathbf{x}) . \quad (56)$$

The displacement gradient is given by

$$\nabla \mathbf{u}(\mathbf{x}) = u_{i,j} \hat{e}_i \hat{e}_j . \quad (57)$$

The second order displacement gradient tensor is separated into a symmetric part (strain) and a skew symmetric part (rigid body rotation),

$$\begin{aligned}\varepsilon_{ij}\hat{e}_i\hat{e}_j &= \frac{1}{2}(u_{i,j} + u_{j,i})\hat{e}_i\hat{e}_j \\ \omega_{ij}\hat{e}_i\hat{e}_j &= \frac{1}{2}(u_{i,j} - u_{j,i})\hat{e}_i\hat{e}_j.\end{aligned}\tag{58}$$

In a material with linear constitutive behavior, the strain is proportional to the stress. This is expressed in component form as

$$\sigma_{ij} = C_{ijkl}\varepsilon_{kl} \quad \text{or} \quad \varepsilon_{kl} = S_{kl ij}\sigma_{ij}.\tag{59}$$

For historical reasons (German origin),  $C$  is called stiffness and  $S$  is called compliance.

In a common approach to 2-D elasticity problems, the equilibrium equation is satisfied by introducing a stress function. Stress is used to find strain using the constitutive law. The strain components are then integrated to find the displacement components. The six strain components are not independent. They must be derived from the gradient of a displacement field that has just three displacement components. A second order tensor identity, the compatibility condition, places a constraint on the strain components. This is given by

$$\nabla \times \varepsilon \times \nabla = 0.\tag{60}$$

The dot product and cross product operations between the unit vectors are readily expanded using the relations

$$\hat{e}_i \cdot \hat{e}_j = \delta_{ij} \quad \text{and} \quad \hat{e}_i \times \hat{e}_j = e_{ijk}\hat{e}_k\tag{61}$$

where  $\delta_{ij}$  represents the components of a unit second order tensor and  $e_{ijk}$  is the permutation symbol.

The mechanics that will be used to describe ferroelectric and ferromagnetic materials will require the definitions of stress and strain as well as the constitutive law, but will not make much use of the various available closed form solutions. The approach will be computational, where the partial differential equations and boundary conditions are identified and numerical methods are used to solve them.

**Mechanical boundary conditions.** The stress tensor just beneath a surface is related to the traction vector on that surface by the relation

$$\boldsymbol{\sigma} \cdot \hat{n} = \mathbf{t},\tag{62}$$

with components

$$\sigma_{ij}\hat{n}_j = t_i.\tag{63}$$

Either the traction or the displacement can be prescribed on the surface.



## 5 Thermodynamics of Ferroelectric and Ferromagnetic Materials

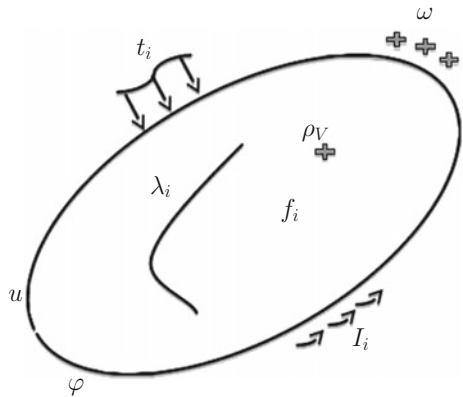
The approach to describing ferroelectric and ferromagnetic material behavior will use the first and second laws of thermodynamics. The first law is a conservation of energy statement that includes thermal, mechanical, electrical, magnetic and internal energy. It is therefore a balance law wherein the energy added to a body, in the form of work performed on the body by external generalized set of forces and heat added and/or generated in the body, is stored within that body in the form of internal and kinetic energy. The second law says something about the conversion of mechanical, electrical, or magnetic energy to thermal energy. No energy is lost in this process, but some of the work is converted to heat in an irreversible process. Next, we focus on the phase-field modeling of ferroelectric and ferromagnetic and multiferroic materials.

### 5.1 Ferroelectric Materials: External Mechanical, Electrical Work; and Heat Addition

The description of material behavior within a thermodynamic framework begins with a description of all of the ways work can be done on the material through external surface and body forces. This work will be added to the description of the heat that can be added to the body and equated to the change of internal energy. The relations are formulated in a rate form. Figure 5 shows a body under general mechanical and electrical loading, including internal material interfaces.

Assessing the external mechanical work done on a material requires identifying the distributed forces on the surface of the body, the traction vector, and the associated displacements. It also requires the identification of any externally applied distributed body forces that act on displacements of the body elements. The work done by surface

**Fig. 5** A body subjected to mechanical, electrical, and magnetic boundary conditions



tractions ( $N/m^2$ ) on a displacement increment (in this case the instantaneous power) is found by integrating the traction vector and displacement rate over the surface and the body forces over the volume as:

$$\dot{W}^M = \int_S t_i \dot{u}_i dS + \int_V f_i \dot{u}_i dV . \quad (64)$$

When surface and volume free charge densities are considered, the electrical work done must be evaluated by integrating over the surface such that:

$$\dot{W}^E = \int_\tau \varphi \dot{\omega}_s d\Gamma + \int_V \varphi \dot{\rho}_v dV . \quad (65)$$

Note here that the volume charge is a free charge distribution not equal to the bounded charge related to the polarization. Typically, in the treatment of ferroelectrics as insulators this volume charge is equal to zero unless an external charge distribution is considered.

Lastly, the thermal energy added to a body by heat transfer from the surrounding environment can be evaluated as the sum of the heat transferred to the volume (a material in a microwave oven is a good example) plus the heat transferred across the surface of the body by heat flux. The rate of heat addition is given by

$$\dot{\Theta} = \int_\Gamma \dot{r} dV - \int_{\partial\Gamma} \dot{q}_i n_i dS \quad (66)$$

where  $\dot{r}$  is the rate at which heat is generated within the volume from an external source (to be distinguished from heat generated by an internal dissipative process), and  $\dot{q}_i$  are components of the outward heat flux vector (heat leaving per unit area per unit time). The minus sign is to account for the heat entering the body. The expression for energy balance is thus

$$\dot{W}^M + \dot{W}^E + \dot{\Theta} = \dot{K} + \dot{U} \quad (67)$$

where each of the terms on the left hand side (LHS) of the equation represents work done on the body or heat added to the body, the LHS is a sum of all energy transferred to the body; and the terms on the right hand side (RHS) represent where this energy is going. The first term on the RHS is the rate of increase of kinetic energy of the body and the second term on the RHS is the increase of internal energy of the body. Note that the long wavelength assumption has been applied, which allows for the quasi-static decoupling of the electromagnetic fields. That is under quasi-static electrical behavior the effect of a changing electric field generating a magnetic field can be ignored and quasi-stationary magnetic fields have been assumed such that the radiation fields can be neglected.

Combining the expressions for mechanical, and electrical work gives

$$\begin{aligned} & \int_S t_i \dot{u}_i dS + \int_V f_i \dot{u}_i dV + \int_S \varphi \dot{\omega}_s dS + \int_V \varphi \dot{\rho}_\nu dV + \int_V \dot{r} dV \\ & - \int_S \dot{q}_i n_i dS = \frac{d}{dt} \int_V \frac{1}{2} \rho \dot{u}_j \dot{u}_j dV + \int_V \rho \dot{e} dV . \end{aligned} \quad (68)$$

Using the definition of traction and surface charge the surface integrals on the LHS can be written as

$$\begin{aligned} & \int_S \sigma_{ij} n_j \dot{u}_i dS + \int_V f_i \dot{u}_i dV - \int_S \varphi \dot{D}_j n_j dS + \int_V \varphi \dot{\rho}_\nu dV + \int_V \dot{r} dV \\ & - \int_S \dot{q}_i n_i dS = \frac{d}{dt} \int_V \frac{1}{2} \rho \dot{u}_j \dot{u}_j dV + \int_V \rho \dot{e} dV \end{aligned} \quad (69)$$

which, using the divergence theorem, becomes

$$\begin{aligned} & \int_V (\sigma_{ij} \dot{u}_i)_{,j} dV + \int_V f_i \dot{u}_i dV - \int_V (\varphi \dot{D}_j)_{,j} dV + \int_V \varphi \dot{\rho}_\nu dV \\ & + \int_V \dot{r} dV - \int_V \dot{q}_{j,j} dV = \frac{d}{dt} \int_V \frac{1}{2} \rho \dot{u}_j \dot{u}_j dV + \int_V \rho \dot{e} dV . \end{aligned} \quad (70)$$

The partial derivatives are now expanded, it is noted that the stress does no work on the rigid body rotations (symmetric times anti-symmetric matrices give zero), and the terms are grouped.

$$\begin{aligned} & \int_V (\sigma_{ij,j} \dot{u}_i + \sigma_{ij} \dot{\varepsilon}_{ij}) dV + \int_V f_i \dot{u}_i dV - \int_V (\varphi_{,j} \dot{D}_j + \varphi \dot{D}_{j,j}) dV \\ & + \int_V \varphi \dot{\rho}_\nu dV + \int_V \dot{r} dV - \int_V \dot{q}_{j,j} dV \\ & = \frac{d}{dt} \int_V \frac{1}{2} \rho \dot{u}_j \dot{u}_j dV + \int_V \rho \dot{e} dV . \end{aligned} \quad (71)$$

Noting that  $\sigma_{ij,j} + f_i = \frac{d}{dt} (\frac{1}{2} \rho_m \dot{u}_m \dot{u}_j)$  and  $D_{j,j} - \rho_\nu = 0$  and  $E_i = -\phi_{,i}$  the result is

$$\int_V \sigma_{ij} \dot{\varepsilon}_{ij} dV + \int_V E_j \dot{D}_j dV + \int_V \dot{r} dV - \int_V \dot{q}_{j,j} dV = \int_V \rho \dot{e} dV . \quad (72)$$

This is our desired expression for the rate of change of the internal energy. Note that up to this point along with the first law of thermodynamics we have used expressions of mechanical equilibrium and the Gauss equation and linear kinematics. Given a static domain structure, the solution of a boundary value problem within the context of linear piezoelectricity requires the introduction of the appropriate boundary conditions along with the constitutive equations required to connect the field quantities satisfying the fundamental balance laws (mechanical stress and electric field) to the kinematical fields describing the configuration of the body. The constitutive equation describing the material behavior can be derived through invoking a free energy that depends on the configurational quantities, the strain and the electric displacements in this case, through thermodynamic considerations.

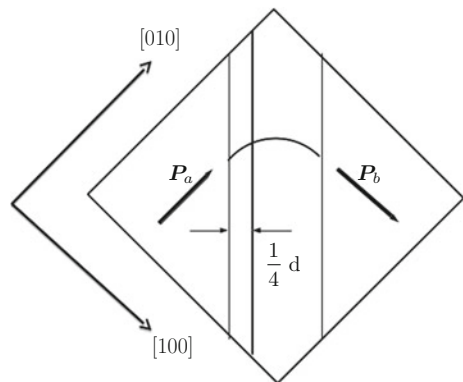
However in this chapter we are not only interested in the distribution of the fields, but also in how these fields cause the domain structure to evolve. Thus at this point we introduce the notion of internal surfaces separating uniform domain structure in the material, which are related to the polarization (or magnetization for ferromagnetic materials) variable. The free energy of the material has to be able to represent the spatial distribution and evolution of these internal interfaces within the ferroelectric crystal and hence depend on the order parameter identifying the phases. The natural order parameter for the ferroelectric domain structure is the polarization vector. The relationship between the polarization vector, the electric displacement and the electric field is given by  $D_i = P_i + \epsilon_0 E_i$ , where  $\epsilon_0$  is the permittivity of free space.

## 5.2 Balance Laws for Internal Fields

Just as we have balance laws for stress, electric field, and magnetic field; we can apply the concept of equilibrium on an internal surface in the material and have balance laws for the polarization and magnetization variables. These will first be written as an equilibrium equation, and then be modified to give a balance when there is a viscous force present that introduces damping proportional to polarization or magnetization rate. Polarization will be addressed first. The magnetization case is trickier when there is magnetization evolution present because of the angular momentum leading to precession.

Consider a volume element where the volume has been taken small enough that the electric dipole behavior of the element can be represented by the average polarization multiplied by the volume; but the neighboring elements can have small differences in polarization that give rise to interaction energy. This effect will be proportional to the polarization gradient that is present between neighboring elements. Lets consider the 2-D case of a 90 degree domain wall as an example. This is shown in Fig. 6. The polarization must rotate 90° across this domain wall and be in equilibrium at each

**Fig. 6** A domain wall is a diffuse interface separating regions of uniform polarization (or magnetization). Within the wall there is a gradient in the order parameter



point within the wall. The first generalized forces to consider are those produced by the crystal structure on the polarization that tend to align the polarization with the crystal structure. This generalized force is the effective electric field. To the left and right of the wall, the polarization is in equilibrium with this force. Right at the center of the wall the polarization is also in equilibrium with this force, although it is in a metastable equilibrium state. At the  $\frac{1}{4}$  and  $\frac{3}{4}$  points through the wall, the polarization is not in equilibrium with the effective electric field. At the  $\frac{1}{4}$  point the effective field is driving the polarization to rotate to the left to align with the polarization to the left, and at the  $\frac{3}{4}$  point the effective field is driving the polarization to rotate to the right to align with the polarization to the right. There must be another source of effective field that can hold the polarization in an equilibrium position that is mis-aligned with the local effective field. This is the result of divergence of the polarization gradient. The effect is easily understood in terms of the interaction energy of two dipoles. Neighboring dipoles interact through their dipole fields. When they are held a fixed distance apart, they are in a low energy state when they are aligned head to tail. If one is rotated, the energy goes up. The energy is reduced if the polarization is rotated back into alignment. Consider a small volume element with average polarization  $\mathbf{P}(\mathbf{x})$ . The forces acting on this polarization are the effective field and the gradient relative to neighboring elements. The element size in this continuum approximation must be selected such that when the nearest neighbor elements are used to compute the gradient effects, a good approximation of the interaction energy is obtained. In the 2-D case being considered, the polarization is only changing in the  $x$ -direction. The force on the dipole is taken to be proportional to the polarization gradient in each direction. This force is given by the change of gradient in that direction, i.e. the gradient is

$$\nabla \mathbf{P}(\mathbf{x}) = P_{i,j} \hat{e}_i \hat{e}_j \quad (73)$$

where the gradient represents the rate of change of polarization with position. The rate of change of polarization in a particular direction is found by taking the dot product of the gradient with a unit normal in that direction. This gives

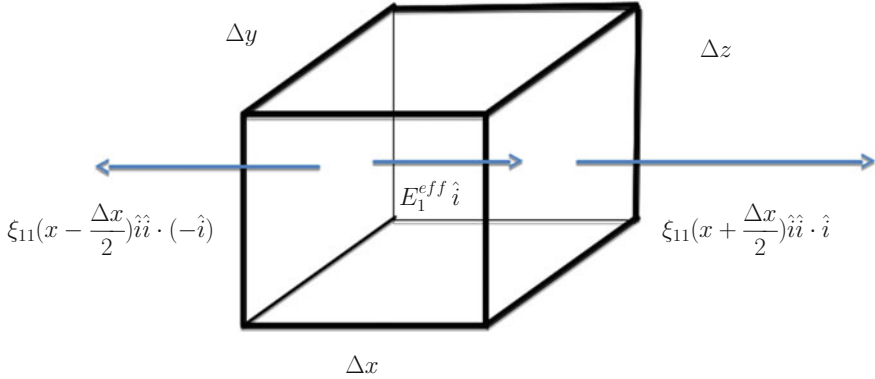
$$\nabla \mathbf{P}(\mathbf{x}) \cdot \hat{n} = P_{i,j} \hat{e}_i \hat{e}_j n_j . \quad (74)$$

The generalized force associated with the polarization gradient is given by

$$\boldsymbol{\xi} = \mathbf{G} \cdot \cdot \nabla \mathbf{P}(\mathbf{x}) \quad \text{or} \quad \xi_{ij} = G_{ijkl} P_{k,l} \quad (75)$$

and the force or the generalized traction vector in a particular direction is given by

$$\boldsymbol{\lambda} = \boldsymbol{\xi} \cdot \hat{n} = \mathbf{G} \cdot \cdot \nabla \mathbf{P}(\mathbf{x}) \cdot \hat{n} . \quad (76)$$



**Fig. 7** A volume element used to describe the balance of generalized forces acting on the polarization (or magnetization) within

The fourth order  $\mathbf{G}$  tensor will have cubic symmetry of the cubic phase and will be most easily presented in terms of a coordinate system aligned with the crystallographic directions. Note that in our example the coordinate system has been rotated  $45^\circ$  and thus the  $\mathbf{G}$ -matrix would have to be rotated.

Lets perform a balance of the generalized forces acting on a volume element in which the polarization is in equilibrium with the effective field and the polarization gradient. The volume element is shown in Fig. 7.

The generalized forces in this force balance are the fields that put torque on the dipole moment per unit volume within the element, the polarization. They therefore must have units that will contract with polarization and when multiplied by the volume or area will give work. The effective field has units of volts/meter. Contract with polarization ( $C/m^2$ ) and multiply by the volume ( $m^3$ ) and the result is  $(N - m)$ . The effective field associated with the gradient has units of volts  $(N - m/C)$ . This is multiplied by area ( $m^2$ ) and polarization ( $C/m^2$ ) to get work  $(N - m)$ .

The term  $\xi_{11}$  is related to the polarization gradient by

$$\xi_{11} = G_{1111} P_{1,1} . \quad (77)$$

Note that this is not the only non-zero component, but it is the only one being addressed in this 1-D force balance example. The force balance becomes

$$\xi_{11} \left( x + \frac{\Delta x}{2} \right) \Delta y \Delta z - \xi_{11} \left( x - \frac{\Delta x}{2} \right) \Delta y \Delta z + E_1^{\text{eff}} \Delta x \Delta y \Delta z = 0 \quad (78)$$

leading to

$$\frac{\xi_{11} \left( x + \frac{\Delta x}{2} \right) - \xi_{11} \left( x - \frac{\Delta x}{2} \right)}{\Delta x} + E_1^{\text{eff}} = 0 \quad (79)$$

or

$$\xi_{11,1} + E_1^{\text{eff}} = 0 . \quad (80)$$

The same force balance can be performed with the possibility of polarization gradients in each direction. This leads to

$$\nabla \cdot \boldsymbol{\xi} + \mathbf{E}^{\text{eff}} = 0 . \quad (81)$$

If there is an externally applied electric field, this will also put an effective body force on the polarization in the element. This can be added by superposition to obtain

$$\nabla \cdot \boldsymbol{\xi} + \mathbf{E}^{\text{eff}} + \mathbf{E}^{\text{ext}} = 0 . \quad (82)$$

This set of generalized forces acts on the polarization. If the polarization is not in equilibrium with the generalized forces, there will be a driving force for it to change and a kinetic law needs to be added. An assumption that this polarization change is governed by a viscous type behavior is typically made such that the rate of change of polarization is proportional to the driving force leading to:

$$\nabla \cdot \boldsymbol{\xi} + \mathbf{E}^{\text{eff}} + \mathbf{E}^{\text{ext}} = \beta \cdot \dot{\mathbf{P}} . \quad (83)$$

This result is the generalized form of the TDGL equation developed by Su and Landis using the micro-force balance approach of Gurtin. In their analysis (discussed next) the force balance for the polarization internal variable along with mechanical equilibrium and Gauss law is adopted a priori and the dissipative, viscous term follows as a restriction of the second law of thermodynamics for non-equilibrium processes along with the restriction of the constitutive equations. Although most points of the analysis are described next, the interested reader should refer to the original text for the full formal approach.

### ***5.3 Phase-Field Model of Ferroelectrics; Dissipative Evolution of Domains; Second Law of Thermodynamics***

The phase-field modeling approach has been used successfully to study several different features of ferroelectric domain switching behavior including the structure of domain walls Cao and Cross (1991), switching of polycrystals and single crystals Choudhury et al. (2005); Zhang and Bhattacharya (2005), the interactions of domain walls with charge defects Su and Landis (2007) and dislocations Kontsos and Landis (2009), domain switching Song et al. (2007) and nucleation and growth near crack tips Li and Landis (2011). Su and Landis (2007), working along the lines of Fried and Gurtin (1993, 1994); Gurtin (1996), developed a continuum mechanics, non-equilibrium, thermodynamic framework that distinguishes the fundamental balance laws which are universal from the material constitutive response.

In the phase field setting we are interested in how the electromechanical fields can cause the domain structure to evolve through the dissipative motion of internal material interfaces separating uniform domain structure. Given that position and evolution of the internal interface is now part of the solution and the free energy is permitted to depend on polarization, the internal micro-forces introduced that are work-conjugate to the order parameter have to satisfy their own balance equation. However in order to account for the internal dissipation in the material along with the  $\xi_{ij}$  tensor we introduce a micro-force vector  $\pi_i$  akin to  $\mathbf{E}^{\text{eff}}$  which can be thought as the equilibrium internal force. The integral balance of this set of configurational forces,

$$\nabla \cdot \boldsymbol{\xi} + \boldsymbol{\pi} = 0. \quad (84)$$

The work associated with this set of internal micro-forces is then written as:

$$\int_S \lambda_i \dot{P}_i dS = \int_S \xi_{ji} n_j \dot{P}_i dS. \quad (85)$$

Here note that anticipating the dissipative nature of domain wall motion, the internal micro-force vector  $\pi_i$  enters the balance of the micro-forces but does not contribute to the external power. With this addition the first law of thermodynamics accounting for the thermal, electromechanical and domain wall energy conversion of the continuum is given as:

$$\begin{aligned} & \int_S \sigma_{ij} n_j \dot{u}_i dS + \int_V f_i \dot{u}_i dV + \int_S \xi_{ji} n_j \dot{P}_i dS - \int_S \varphi \dot{D}_j n_j dS \\ & + \int_V \varphi \dot{\rho}_v dV + \int_V \dot{r} dV - \int_S \dot{q}_i n_i dS = \frac{d}{dt} \int_V \frac{1}{2} \rho \dot{u}_j \dot{u}_j dV + \int_V \rho \dot{e} dV. \end{aligned} \quad (86)$$

Using the traction and surface charge definition equations and applying the divergence theorem and eliminating terms that satisfy the balance laws we are left with the rate of change of internal energy as:

$$\dot{U} = \sigma_{ij} \dot{\epsilon}_{ij} + E_i \dot{D}_i - \pi_i \dot{P}_i + \xi_{ij} \dot{P}_{i,j} - q_{i,i} + r. \quad (87)$$

The constraint of the second law of thermodynamics in the entropy production is given through the pointwise local Clausius-Duhem dissipation inequality as

$$\frac{\dot{q}_i T_{,i}}{T} - \dot{q}_{i,i} \leq T \dot{S} \quad (88)$$

where  $S$  is the total entropy and  $T$  the absolute temperature. Using the equation of rate of change of internal energy to eliminate the divergence of the heat flux vector we have

$$T \dot{S} \geq \dot{U} - \sigma_{ij} \dot{\epsilon}_{ij} - E_i \dot{D}_i + \pi_i \dot{P}_i - \xi_{ij} \dot{P}_{i,j} - r + \frac{\dot{q}_i T_{,i}}{T}. \quad (89)$$



In terms of the free energy  $\psi$  the second law can be written as

$$\dot{\psi} \leq \sigma_{ij} \dot{\varepsilon}_{ij} + E_i \dot{D}_i - \pi_i \dot{P}_i + \xi_{ij} \dot{P}_{i,j} + r - \frac{\dot{q}_i T_{,i}}{T} - \dot{T} S. \quad (90)$$

To simplify calculation let's restrict the problem to spatially homogeneous, temperature independent microstructural evolution, below the Curie temperature. Therefore under isothermal conditions, the dissipation inequality reads

$$\dot{\psi} \leq \sigma_{ij} \dot{\varepsilon}_{ij} + E_i \dot{D}_i - \pi_i \dot{P}_i + \xi_{ij} \dot{P}_{i,j}. \quad (91)$$

Concluding the thermodynamics based formulation of the constitutive equations, we need to specify the independent state variables on which the thermodynamic functional and the thermodynamic conjugate forces, i.e. stresses, electric field micro-force tensor and internal micro-force vector can depend on.

For isothermal behavior, below the Curie temperature the thermodynamic functional is the Helmholtz free energy and the independent configurational/state variables are components of strain, electric displacement, polarization vector, polarization vector gradients and time rate. The constitutive response is written as

$$\psi = \psi(\varepsilon_{ij}, D_i, P_i, P_{i,j}, \dot{P}_i). \quad (92)$$

Then using the above functional form of the Helmholtz free energy we have:

$$\begin{aligned} & \frac{\partial \psi}{\partial \varepsilon_{ij}} \dot{\varepsilon}_{ij} + \frac{\partial \psi}{\partial D_i} \dot{D}_i + \frac{\partial \psi}{\partial P_i} \dot{P}_i + \frac{\partial \psi}{\partial P_{i,j}} \dot{P}_{i,j} + \frac{\partial \psi}{\partial \dot{P}_i} \ddot{P}_i \\ & \leq \sigma_{ij} \dot{\varepsilon}_{ij} + E_i \dot{D}_i - \pi_i \dot{P}_i + \xi_{ij} \dot{P}_{i,j} \end{aligned} \quad (93)$$

or equivalently:

$$\begin{aligned} & \left( \sigma_{ij} - \frac{\partial \psi}{\partial \varepsilon_{ij}} \right) \dot{\varepsilon}_{ij} + \left( E_i - \frac{\partial \psi}{\partial D_i} \right) \dot{D}_i \\ & - \left( \pi_i + \frac{\partial \psi}{\partial P_i} \right) \dot{P}_i + \left( \xi_{ij} - \frac{\partial \psi}{\partial P_{i,j}} \right) \dot{P}_{i,j} - \frac{\partial \psi}{\partial \dot{P}_i} \ddot{P}_i \geq 0. \end{aligned} \quad (94)$$

The above inequality must hold for any permissible thermodynamic process for arbitrary levels of  $\dot{\varepsilon}_{ij}, \dot{D}_i, \dot{P}_i, \dot{P}_{i,j}, \ddot{P}_i$  through the appropriate control of the external sources. A way not to violate the inequality for arbitrary combination of  $\dot{\varepsilon}_{ij}, \dot{D}_i, \dot{P}_i, \dot{P}_{i,j}, \ddot{P}_i$  is to set the coefficients of  $\dot{\varepsilon}_{ij}, \dot{D}_i, \dot{P}_i, \dot{P}_{i,j}, \ddot{P}_i$  equal to zero and ensure that the term

$$\left( \pi_i + \frac{\partial \psi}{\partial P_i} \right) \dot{P}_i \leq 0. \quad (95)$$

Therefore we have

$$\frac{\partial \psi}{\partial \dot{P}_i} = 0 \rightarrow \psi = \psi(\varepsilon_{ij}, D_i, P_i, P_{i,j}) \quad (96)$$

and

$$\sigma_{ij} = \frac{\partial \psi}{\partial \varepsilon_{ij}}, \quad E_i = \frac{\partial \psi}{\partial D_i}, \quad \xi_{ij} = \frac{\partial \psi}{\partial P_{i,j}}. \quad (97)$$

Finally setting internal micro-force equal to

$$\pi_i = -\frac{\partial \psi}{\partial P_i} - \beta_{ij} \dot{P}_j \quad (98)$$

the inequality is satisfied for any level of  $\dot{P}_i$  and for  $\beta_{ij}$  positive definite. For a cubic high temperature phase the tensor  $\beta_{ij}$  is usually taken to be  $\beta_{ij} = \beta \delta_{ij}$  where  $\beta > 0$ . Substitution of the definitions of internal micro-force vector and tensor into the micro-force balance yields a generalized form of the Ginzburg-Landau equation governing the evolution of the material polarization in a ferroelectric material as:

$$\left( \frac{\partial \psi}{\partial P_{i,j}} \right)_{,j} - \frac{\partial \psi}{\partial P_i} + \gamma_i = \beta_{ij} \dot{P}_j. \quad (99)$$

The first term can be understood by considering three dipoles in a row. If the center one is vertical, the one to the left tilts left, and the one to the right tilts right by an equal but opposite angle, the dipoles on either side will put equal and opposite forces on the dipole in the middle. This corresponds to a polarization gradient with zero divergence. If the left dipole is vertical, the center dipole is vertical and the one on the right is tilted, there will be unequal forces on the center dipole such that the center dipole will want to tilt to make the polarization gradient divergence free. The second term in this expression is the effective electric field. This term includes all of the various torques and stretches the lattice puts on a particular volume with polarization. The third term represents external forces that drive changes of polarization, possibly an externally applied electric field. The term on the RHS is the kinetic (viscous) response of the polarization. It governs the rate at which the polarization will respond to the net effective electric field at a point in the solid.

## 5.4 Internal Energy

The next question to be addressed is how energy can be stored in ferroelectric and ferromagnetic materials. We have already seen that if we place an electric dipole in a uniform electric field, the dipole will experience a torque. If the dipole orientation is held in place by some kind of internal spring (atomic bonds of the lattice), then the spring will be stretched and the internal energy will go up. This suggests we need a way to describe these spring forces in terms of the lattice behavior. The same argument arises with respect to the storage of magnetic energy. The stored magnetic energy must be the result of winding up some kind of spring when the magnetic

moment is torqued. Several means of storing energy in a lattice are identified and these are used as variables in our formulation.

**Independent variables associated with internal energy and associated work-conjugate forces.**

- Temperature (average stretch or torsion of the springs associated with vibration amplitude),

The temperature of a material is a function of lattice vibrations. It is the work conjugate variable to entropy and plays the role of a generalized force. The work conjugate pair is thus

$$(T, S) . \quad (100)$$

- Elastic strain (stretch of the springs by mechanical force),

The elastic strain is that fraction of the symmetric part of the displacement gradient that is induced by mechanical forces. It does not include thermal strain, electrostrictive strain, or magnetostrictive strain. The work conjugate pair for the internal energy is given by

$$(\sigma, \varepsilon^{el}) . \quad (101)$$

- Polarization (stretch or rotation of a dipole),

When the polarization is in a uniform electric field and is rotated against that electric field, the field will produce a restoring torque on that polarization. Within the material there are a number of sources of torque on the polarization. These include externally applied electric field, the combined fields produced by all other dipoles in the material (also expressed as combined fields of all other polarizations associated with small volume elements), and changes of the polarization gradient with position (the divergence of the polarization gradient applies a torque to the local polarization, an effect associated with a length scale for the particular set of internal generalized forces). The work conjugate pair associated with internal energy density for this term is the effective electric field and the polarization,

$$(\mathbf{E}^{\text{eff}}, \mathbf{P}) . \quad (102)$$

- Electric displacement (this term must be included to account for free space contribution),

Any time there is an electric field present, there will be a polarization of free space. This term is the component associated with the permittivity of free space. The work conjugate pair representing the polarization of free space is given by

$$(\mathbf{E}, \mathbf{P}^{FS}) \text{ or } (\mathbf{E}, (\mathbf{D} - \mathbf{P})) . \quad (103)$$

- Polarization gradient (interaction energy of mis-aligned dipoles),

The divergence of the polarization gradient makes a contribution to the effective electric field. It can be easier to keep this as a separate term rather than to combine it with the effective electric field. The work conjugate variables associated with the

polarization gradient are a second order tensor with units of volts and the gradient of polarization,

$$(\xi, \nabla P) . \quad (104)$$

### 5.5 Series Expansions for the Energy Functions

The expression for internal energy indicates that the internal energy is a function of each of the independent variables. At this point the function is unknown, but a well behaved function can be approximated using a Taylor's series expansion. As mentioned, internal energy is also stored in polarization gradients. The electric displacement density is written as

$$D_i = \varepsilon_o E_i + P_i = P_i^{FS} + P_i \quad (105)$$

giving

$$U = U(\varepsilon_{ij}, P_i^{FS}, P_i, P_{i,j}) \quad \text{and} \quad \psi = \psi(\varepsilon_{ij}, P_i^{FS}, P_i, P_{i,j}) . \quad (106)$$

The series expansion will give the energy relative to a reference state. Many of the ferroelectric materials of interest have the perovskite structure. This structure is cubic in the parent phase and experiences spontaneous polarization when cooled below the Curie point. The reference energy state will be taken as a cubic state at a given temperature. This will be a metastable state when below the Curie point, but maintains all of the cubic symmetry. If the temperature is held constant, the Helmholtz energy density can be expanded about the cubic state to obtain

$$\begin{aligned} \Delta\psi(\varepsilon_{ij}, P_i, P_i^{FS}, P_{i,j}) = & \\ & \frac{\partial\psi}{\partial\varepsilon_{ij}} \Big|_{P,T} \Delta\varepsilon_{ij} + \frac{\partial\psi}{\partial P_k} \Big|_{\varepsilon,T} \Delta P_k + \frac{\partial\psi}{\partial P_k^{FS}} \Big|_{\varepsilon,T} \Delta P_k^{FS} + \frac{\partial\psi}{\partial P_{i,j}} \Big|_{\varepsilon,T} \Delta P_{i,j} \\ & \frac{1}{2!} \left( \frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial\varepsilon_{kl}} \Big|_{\varepsilon,T} \Delta\varepsilon_{ij}\Delta\varepsilon_{kl} + 2 \frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial P_k} \Delta\varepsilon_{ij}\Delta P_k \right. \\ & \left. + \frac{\partial^2\psi}{\partial P_k\partial P_l} \Big|_{\varepsilon,T} \Delta P_k\Delta P_l + \frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial P_k^{FS}} \Big|_{\varepsilon,T} \Delta\varepsilon_{ij}\Delta P_k^{FS} + \dots \right) \\ & + \frac{1}{3!} \left( \frac{\partial^3\psi}{\partial\varepsilon_{ij}\partial\varepsilon_{kl}\partial\varepsilon_{mn}} \Delta\varepsilon_{ij}\Delta\varepsilon_{kl}\Delta\varepsilon_{mn} \right. \\ & + 3 \frac{\partial^3\psi}{\partial\varepsilon_{ij}\partial\varepsilon_{kl}\partial P_k} \Delta\varepsilon_{ij}\Delta\varepsilon_{kl}\Delta P_k + 3 \frac{\partial^3\psi}{\partial\varepsilon_{ij}\partial P_k\partial P_l} \Delta\varepsilon_{ij}\Delta P_k\Delta P_l \\ & \left. + \frac{\partial^3\psi}{\partial P_k\partial P_l\partial P_s} \Delta P_k\Delta P_l\Delta P_s + \dots \right) + \dots \end{aligned} \quad (107)$$

We can eliminate a number of terms by making some observations about the symmetry of the energy function.

1. There can be no linear terms. That is because the system is in a cubic state with symmetry in all directions about this state. A positive polarization change should give the same effect on energy as a negative polarization change. This eliminated the linear terms in the series.
2. The free space polarization is only a quadratic term that gives rise to the linear contribution of electric field to electric displacement. The time rate of change of this term gives the displacement current correction of free space. This term is not coupled to other terms.
3. The polarization gradient term is associated with dipole-dipole interactions. It will be taken as a quadratic term only. This term could be coupled to other terms, requiring higher order contributions. But for now it will be taken as quadratic.
4. Constant temperature will be assumed. In general, temperature dependence needs to be included. The temperature coupling terms are used to model Curie-Weiss behavior.
5. Making all measurements relative to the cubic configuration where the strain and polarization are zero enables dropping all of the deltas.

This simplified system will be considered as a means of presenting the approach. With these restrictions, the Helmholtz energy can be expressed as

$$\begin{aligned}
\Delta\psi(\varepsilon_{ij}, P_i, P_i^{FS}, P_{i,j}) \approx & \\
\frac{1}{2!} \left( \frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial\varepsilon_{kl}} \Big|_{\varepsilon,T} \varepsilon_{ij}\varepsilon_{kl} + 2 \frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial P_k} \Delta\varepsilon_{ij} P_k + \frac{\partial^2\psi}{\partial P_k \partial P_l} \Big|_{\varepsilon,T} P_k P_l \right. & \\
+ \frac{\partial^2\psi}{\partial P_j^{FS} \partial P_k^{FS}} \Big|_{\varepsilon,T} P_j^{FS} P_k^{FS} + \left. \frac{\partial^2\psi}{\partial P_{k,r} \partial P_{l,s}} \Big|_{\varepsilon,T} P_{k,r} P_{l,s} \right) & \quad (108) \\
+ \frac{1}{3!} \left( \frac{\partial^3\psi}{\partial\varepsilon_{ij}\partial\varepsilon_{kl}\partial\varepsilon_{mn}} \varepsilon_{ij}\varepsilon_{kl}\varepsilon_{mn} + 3 \frac{\partial^3\psi}{\partial\varepsilon_{ij}\partial\varepsilon_{kl}\partial P_k} \varepsilon_{ij}\varepsilon_{kl} P_k \right. & \\
+ 3 \frac{\partial^3\psi}{\partial\varepsilon_{ij}\partial P_k \partial P_l} \varepsilon_{ij} P_k P_l + \left. \frac{\partial^3\psi}{\partial P_k \partial P_l \partial P_s} P_k P_l P_s + \dots \right) + \dots &
\end{aligned}$$

Note that all partial derivatives are taken with all other independent variables fixed. This was explicitly denoted in the second terms but from here forward will not be indicated.

The energy function is a perfect differential such that

$$\begin{aligned}
d\psi &= \frac{\partial\psi}{\partial\varepsilon_{ij}} d\varepsilon_{ij} + \frac{\partial\psi}{\partial P_i} dP_i + \frac{\partial\psi}{\partial P_i^{FS}} dP_i^{FS} + \frac{\partial\psi}{\partial P_{i,j}} dP_{i,j} \\
&= \sigma_{ij} d\varepsilon_{ij} + E_i dP_i + E_i dP_i^{FS} + \xi_{ij} dP_{i,j}
\end{aligned} \quad (109)$$

where  $P_i^{FS} = \varepsilon_0 E_i$  is notation used for convenience so as not to introduce both polarization and electric field as independent variables. This expression leads to the coupled constitutive behavior. Taking the partial derivatives of the energy function leads to

$$\begin{aligned} \sigma_{ij} = \frac{\partial \psi}{\partial \varepsilon_{ij}} \approx & \frac{1}{2!} \left( 2 \frac{\partial^2 \psi}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} \Big|_{P,T} \varepsilon_{kl} + 2 \frac{\partial^2 \psi}{\partial \varepsilon_{ij} \partial P_k} P_k \right) \\ & + \frac{1}{3!} \left( 3 \frac{\partial^3 \psi}{\partial \varepsilon_{ij} \partial \varepsilon_{kl} \partial \varepsilon_{mn}} \varepsilon_{kl} \varepsilon_{mn} + 6 \frac{\partial^3 \psi}{\partial \varepsilon_{ij} \partial \varepsilon_{kl} \partial P_k} \varepsilon_{kl} P_k \right. \\ & \left. + 3 \frac{\partial^3 \psi}{\partial \varepsilon_{ij} \partial P_k \partial P_l} P_k P_l \right) + \dots \end{aligned} \quad (110)$$

$$\begin{aligned} E_k = \frac{\partial \psi}{\partial P_k} \approx & \frac{1}{2!} \left( 2 \frac{\partial^2 \psi}{\partial \varepsilon_{ij} \partial P_k} \varepsilon_{ij} + 2 \frac{\partial^2 \psi}{\partial P_k \partial P_l} \Big|_{\varepsilon,T} P_l \right) \\ & + \frac{1}{3!} \left( 3 \frac{\partial^3 \psi}{\partial \varepsilon_{ij} \partial \varepsilon_{kl} \partial P_k} \varepsilon_{ij} \varepsilon_{kl} + 6 \frac{\partial^3 \psi}{\partial \varepsilon_{ij} \partial P_k \partial P_l} \varepsilon_{ij} P_l \right. \\ & \left. + 3 \frac{\partial^3 \psi}{\partial P_k \partial P_l \partial P_s} P_l P_s + \dots \right) + \dots \end{aligned} \quad (111)$$

$$\xi_{kr} = \frac{\partial \psi}{\partial P_{k,r}} \approx \frac{\partial^2 \psi}{\partial P_{k,r} \partial P_{l,s}} \Big|_{\varepsilon,T} P_{l,s} . \quad (112)$$

With the polarization fixed, a tensile strain should be associated with a tensile stress and a compressive strain with a compressive stress. The first term in the stress equation is the linear elastic stiffness. If the strain is held fixed and the polarization changed, coupling between the polarization and strain should give rise to stress. This is the second term in the stress equation. The term in strain squared provides a correction for a non-linear stiffness. This will be taken as zero. At this point the higher order terms in stress are dropped. This requires that the same terms be removed from the electric field equation. The result is

$$\begin{aligned} \sigma_{ij} &= C_{ijkl}^{P,T} \varepsilon_{kl} + \frac{1}{2} Q_{ijkl}^{\varepsilon,T} P_k P_l \\ E_k &= \kappa_{kl}^{\varepsilon,T} P_l + Q_{ijkl}^{\varepsilon,T} \varepsilon_{ij} P_l \\ \xi_{kr} &= G_{krls} P_{l,s} \end{aligned} \quad (113)$$

and the energy function is written as

$$\begin{aligned} \Delta\psi(\varepsilon_{ij}, P_i, P_i^{FS}, P_{i,j}) = & \frac{1}{2} \left( C_{ijkl}^{P,T} \varepsilon_{ij} \varepsilon_{kl} + \kappa_{kl}^{\varepsilon,T} P_k P_l \right. \\ & \left. + \frac{1}{\varepsilon_0} P_j^{FS} P_j^{FS} + G_{krls}^{\varepsilon,T} P_{k,r} P_{l,s} \right) \\ & + \frac{1}{2} (Q_{ijkl}^{\varepsilon,T} \varepsilon_{ij} P_k P_l) + \dots \end{aligned} \quad (114)$$

Higher order terms than 3rd order are still needed to be able to generate a multi-well energy function in polarization. This requires additional even order terms in  $\mathbf{P}$  (4th, 6th, 8th, etc.). The easy way to visualize this is to consider a quadratic polynomial with a negative coefficient and a quartic polynomial with a positive coefficient. Add the two together and the resulting function will initially be negative, the slope will be zero at the bottom of the well, then the function will go positive. Lets add some even order terms in polarization. Remember that these are just the last terms in the 4th, 6th, etc. order terms in the Taylor's series expansion.

$$\begin{aligned} \Delta\psi(\varepsilon_{ij}, P_i, P_i^{FS}, P_{i,j}) = & \frac{1}{2} \left( C_{ijkl}^{P,T} \varepsilon_{ij} \varepsilon_{kl} + \kappa_{kl}^{\varepsilon,T} P_k P_l \right. \\ & \left. + \frac{1}{\varepsilon_0} P_j^{FS} P_j^{FS} + G_{krls}^{\varepsilon,T} P_{k,r} P_{l,s} \right) \\ & + \frac{1}{2} (Q_{ijkl}^{\varepsilon,T} \varepsilon_{ij} P_k P_l) \\ & + \frac{1}{4!} (\kappa_{klmn}^{\varepsilon,T} P_k P_l P_m P_n) \\ & + \frac{1}{6!} (\kappa_{klmnr}^{\varepsilon,T} P_k P_l P_m P_n P_r P_s) + \dots \end{aligned} \quad (115)$$

This energy function can be further modified with additional terms to better represent ferroelectric crystals. For example, the fourth order elasticity tensor must have cubic symmetry with this energy function regardless of the polarization, but a real material has spontaneous polarization and will display an elastic symmetry when the polarization is fixed at the spontaneous polarization value that may have tetragonal, orthorhombic, or rhombohedral symmetry. In this case a higher order term should be kept that represents the elastic constant dependence on polarization, i.e.

$$\frac{\partial^3 \psi}{\partial \varepsilon_{ij} \partial \varepsilon_{kl} \partial P_m} \varepsilon_{ij} \varepsilon_{kl} P_m \quad (116)$$

which leads to an elasticity tensor that is a function of polarization,

$$C_{ijkl}^{P,T} + \frac{\partial C_{ijkl}^{P,T}}{\partial P_m} P_m \quad (117)$$

The same can be done for the quadratic electrostrictive stress tensor that has cubic symmetry in this formulation. Just add the higher order dependence on polarization to enable matching the lower symmetry piezoelectric constants associated with the polarization induced tetragonal, orthorhombic, or rhombohedral symmetry.

In conclusion, for a relatively accurate representation of material properties the general form of the free energy must contain a sufficient number of parameters to allow for independent fitting of the spontaneous polarization, spontaneous strain, dielectric permittivity, piezoelectric coefficients and the elastic properties near the zero stress and zero electric field free spontaneous polarization and strain states. To accomplish this task, Su and Landis (2007) introduced the following form for the free energy to fit the material parameters to the tetragonal single crystal properties of Barium Titanate.

$$\begin{aligned}
\psi(\varepsilon_{ij}, P_i, P_{i,j}, D_i) = & \frac{1}{2} a_{ijkl} P_{i,j} P_{k,l} + \frac{1}{2} \bar{a}_{ij} P_i P_j \\
& + \frac{1}{2} \underline{\bar{a}}_{ijkl} P_i P_j P_k P_l \\
& + \frac{1}{2} \underline{\underline{\bar{a}}}_{ijklmn} P_i P_j P_k P_l P_m P_n \\
& + \frac{1}{8} \underline{\underline{\underline{\bar{a}}}}_{ijklmnr s} P_i P_j P_k P_l P_m P_n P_r P_s \\
& + b_{ijkl} \varepsilon_{ij} P_k P_l \\
& + \frac{1}{2} c_{ijkl} \varepsilon_{ij} \varepsilon_{kl} + f_{ijklmn} \varepsilon_{ij} \varepsilon_{kl} P_m P_n \\
& + g_{ijklmn} \varepsilon_{ij} P_k P_l P_m P_n \\
& - \frac{1}{2\varepsilon_0} (D_i - P_i)(D_i - P_i) .
\end{aligned} \tag{118}$$

The first term of the free energy penalizes large gradients of polarization and gives domain walls thickness and energy within the model. The four terms on the second and third lines are used to create the non-convex energy landscape of the free energy with minima located at the spontaneous polarization states. The four terms on the fourth line are then used to fit the material's spontaneous strain along with the dielectric, elastic and piezoelectric properties about the spontaneous state. The final term represents the energy stored within the free space occupied by the material. The eighth rank term on the third line was introduced in order to allow for adjustments of the dielectric properties and the energy barriers for 90 switching Zhang and Bhat-tacharya (2005). The sixth rank terms introduced on the fourth line allow us to fit the elastic, piezoelectric and dielectric properties of the low symmetry phase at the spontaneous state. Without these terms the elastic properties of the material arise only from the  $c_{ijkl}$  tensor, which must have the symmetry of the high temperature phase. With regard to the piezoelectric coefficients,  $b_{ijkl}$  is used to fit the spontaneous strain components associated with the stress and electric field free spontaneous polarization



state and by introducing the  $f_{ijklmn}$  and  $g_{ijklmn}$  tensors the full tetragonal structure of the piezoelectric tensor can be matched.

## 5.6 Phase-Field Modeling of Ferromagnetics

Following the same approach as in the case of ferroelectric materials, ferromagnetic materials are analyzed in terms of micro-forces associated with the magnetization order parameter. Within the micro-magneto-mechanical approach taken here the free energy of the material under consideration depends on the magnetization and its gradients. The relationship between the magnetization components, the magnetic field and the magnetic induction is given as:

$$B_i = \mu_0(M_i + H_i) \quad (119)$$

where  $\mu_0$  is the permittivity of free space. Following Landis, Landis (2008) a micro-force system is introduced, work conjugate to the dependent variable introduced. Specifically, let  $\zeta_{ij}$  be a micro-force tensor such that  $\zeta_{ijn_j}\dot{M}_i$  is the power expended on a surface by neighboring configurations, an internal micro-force vector  $\pi_i$  such that  $\pi_i\dot{M}_i$  is the power expended by the material internally and accounts for any dissipation as in the case of ferroelectrics. Then the angular momentum balance, stating that rate of change of angular momentum associated with changes in magnetization equals the torque associated with the moment of the magnetization and the micro-forces) reads as:

$$\frac{1}{\mu_0} \left( \int_S \varepsilon_{ijk} M_j \zeta_{lk} n_l dS + \int_V \varepsilon_{ijk} M_j \pi_k dV \right) = \frac{1}{\gamma_0} \int_V \dot{M}_i dV \quad (120)$$

where  $\gamma_0 = 2.21 \times 10^5$  m/As is the gyromagnetic ratio of the electron spin. Applying the divergence theorem on the first term, leads to an equivalent local form of the angular momentum balance given as:

$$\varepsilon_{ijk} M_{j,l} \zeta_{lk} + \varepsilon_{ijk} M_j (\zeta_{lk,l} + \pi_k) = \frac{\mu_0}{\gamma_0} \dot{M}_i . \quad (121)$$

Taking the cross product of the third equation with the magnetization we have:

$$\begin{aligned} (\varepsilon_{jmn} M_{m,p} \zeta_{pn} + \varepsilon_{jmn} M_m (\zeta_{pn,p} + \pi_n)) \varepsilon_{ijk} M_k &= \frac{\mu_0}{\gamma_0} \varepsilon_{ijk} M_k \dot{M}_j \Rightarrow \\ \varepsilon_{jki} M_k \varepsilon_{jmn} M_{m,p} \zeta_{pn} + \varepsilon_{jki} M_k \varepsilon_{jmn} M_n (\zeta_{pn,p} + \pi_n) &= \frac{\mu_0}{\gamma_0} \varepsilon_{ijk} M_k \dot{M}_j \Rightarrow \\ \varepsilon_{jki} M_k \varepsilon_{jmn} M_{m,p} \zeta_{pn} + (\delta_{km} \delta_{in} - \delta_{kn} \delta_{im}) M_k M_m (\zeta_{pn,p} + \pi) &= \frac{\mu_0}{\gamma_0} \varepsilon_{ijk} M_j \dot{M}_k \Rightarrow \\ \varepsilon_{jki} M_k \varepsilon_{jmn} M_{m,p} \zeta_{pn} + M_k M_k (\zeta_{pi,p} + \pi_i) - M_k M_i (\zeta_{pk,p} + \pi_k) &= \frac{\mu_0}{\gamma_0} \varepsilon_{ijk} M_j \dot{M}_k . \end{aligned} \quad (122)$$

Note that the angular momentum balance does not provide any information for the changes along the magnetization axis. However it is assumed that the magnetization magnitude changes under balance of micro-force in the magnetization direction at every point in time and in shorter time than magnetization rotation. Mathematically then we have that:

$$M_k(\zeta_{lk,l} + \pi_k) = 0. \quad (123)$$

Therefore substituting the above result in the momentum balance and noting that  $M^2 = M_k M_k$  we have:

$$(\zeta_{pi,p} + \pi_i) = \frac{\mu_0}{M^2 \gamma_0} \varepsilon_{ijk} M_j \dot{M}_k - \frac{1}{M^2} \varepsilon_{jki} \varepsilon_{jmn} M_{m,p} \zeta_{pn} M_k. \quad (124)$$

Next consider the free energy of the material and the free space depending on strain, magnetic induction, the magnetization order parameter and time and spatial derivatives as:

$$\psi = \psi(\varepsilon_{ij}, B_i, M_i, M_{i,j}, \dot{M}_i). \quad (125)$$

Also all field quantities are allowed to depend on the same set of independent variables. The energy balance is then written as

$$\begin{aligned} \int_V \dot{U} dV + \frac{d}{dt} \int_V \rho \dot{u}_i \dot{u}_i dV &= \int_V (b_i \dot{u}_i + J_i \dot{A}_i) dV \\ &+ \int_S (t_i \dot{u}_i + K_i \dot{A}_i + \zeta_{ijn} \dot{M}_i) dS \\ &+ \int_V r dV + \int_S -q_i n_i dS \end{aligned} \quad (126)$$

where  $U$  is the internal energy density,  $q_i$  are the components of the outward heat flux vector per unit area and  $r$  is the supply of heat per unit volume from external source. Also where  $J_i$  and  $K_i$  are the components of the volume and surface current density respectively and  $A_i$  is a magnetic vector potential arising from  $B_{i,i} = 0 \rightarrow B_i = \varepsilon_{ijk} A_{k,j}$ . Next, applying the divergence theorem on the surface integral term and substituting the balance equations the local equivalent form can be written as:

$$\begin{aligned} \dot{U} &= \sigma_{ij} \dot{\varepsilon}_{i,j} + \dot{B}_i H_i + \zeta_{ji} \dot{M}_{i,j} \\ &+ \left( \frac{1}{M^2} \frac{\mu_0}{\gamma_0} \varepsilon_{ijk} M_j \dot{M}_k - \frac{1}{M^2} \varepsilon_{ijk} \varepsilon_{jmn} M_{m,p} \zeta_{pn} M_k - \pi_i \right) \dot{M}_i \\ &+ r - q_{i,i}. \end{aligned} \quad (127)$$

The constraint of the second law of thermodynamics in the entropy production is given through the pointwise local Clausius-Duhem dissipation inequality as:

$$\frac{\dot{q}_i T_{,i}}{T} - \dot{q}_{i,i} \leq T \dot{S}. \quad (128)$$

Eliminating the divergence of the heat flux vector we have

$$T\dot{S} \geq \frac{q_i T_{,i}}{T} + \dot{e} - \sigma_{ij}\dot{\varepsilon}_{ij} - \dot{B}_i H_i - \zeta_{ji}\dot{M}_{i,j} - r - \left( \frac{1}{M^2} \frac{\mu_0}{\gamma_0} \varepsilon_{ijk} M_j \dot{M}_k - \frac{1}{M^2} \varepsilon_{ijk} \varepsilon_{jmn} M_{m,p} \zeta_{pn} M_k - \pi_i \right) \dot{M}_i. \quad (129)$$

In terms of the free energy  $\psi = U - \theta s \rightarrow \dot{\psi} = \dot{U} - \dot{\theta} s - \theta \dot{s} \Rightarrow \dot{U} - \theta \dot{s} = \dot{\psi} + \dot{\theta} s$  the second law can be written as

$$\dot{\psi} + \dot{T} S - \frac{\dot{q}_i T_{,i}}{T} - \sigma_{ij}\dot{\varepsilon}_{ij} - \dot{B}_i H_i - \zeta_{ji}\dot{M}_{i,j} - r - \left( \frac{1}{M^2} \frac{\mu_0}{\gamma_0} \varepsilon_{ijk} M_j \dot{M}_k - \frac{1}{M^2} \varepsilon_{ijk} \varepsilon_{jmn} M_{m,p} \zeta_{pn} M_k - \pi_i \right) \dot{M}_i \leq 0. \quad (130)$$

Finally, under isothermal conditions and using the definition of the free energy and for an arbitrary volume element the pointwise form of the above the inequality can be written as:

$$\left( \frac{\partial \psi}{\partial \varepsilon_{ij}} - \sigma_{ij} \right) \dot{\varepsilon}_{ij} + \left( \frac{\partial \psi}{\partial B_i} - H_i \right) \dot{B}_i + \left( \frac{\partial \psi}{\partial M_{i,j}} - \zeta_{ji} \right) \dot{M}_{i,j} + \frac{\partial \psi}{\partial \dot{M}_i} \ddot{M}_i + \left( \frac{\partial \psi}{\partial M_i} + \frac{1}{M^2} \varepsilon_{ijk} \varepsilon_{jmn} M_{m,p} \zeta_{pn} M_k + \pi_i \right) \dot{M}_i \leq 0. \quad (131)$$

Linearity in  $\dot{\varepsilon}_{ij}$ ,  $\dot{B}_i$ ,  $\dot{M}_i$ ,  $\dot{M}_{i,j}$ ,  $\ddot{M}_i$  implies that:

$$\frac{\partial \psi}{\partial \dot{M}_i} = 0 \rightarrow \psi \neq \psi(\dot{M}_i), \quad \frac{\partial \psi}{\partial \varepsilon_{ij}} = \sigma_{ij}, \quad \frac{\partial \psi}{\partial B_i} = H_i, \quad \frac{\partial \psi}{\partial M_{i,j}} = \zeta_{ji} \quad (132)$$

and

$$\left( \frac{\partial \psi}{\partial M_i} + \frac{1}{M^2} \varepsilon_{ijk} \varepsilon_{jmn} M_{m,p} \zeta_{pn} M_k + \pi_i \right) \dot{M}_i \leq 0 \rightarrow \pi_i = - \left( \frac{\partial \psi}{\partial M_i} + \frac{1}{M^2} \varepsilon_{ijk} \varepsilon_{jmn} M_{m,p} \zeta_{pn} M_k \right) - \beta \dot{M}_i. \quad (133)$$

Substituting the above result for the form of the internal micro-force vector in the balance of angular momentum we have:

$$\begin{aligned} (\zeta_{pi,p} + \pi_i) &= \frac{\mu_0}{M^2 \gamma_0} \varepsilon_{ijk} M_j \dot{M}_k - \frac{1}{M^2} \varepsilon_{jki} \varepsilon_{jmn} M_{m,p} \zeta_{pn} M_k \\ \Rightarrow \frac{1}{\mu_0} \left( \zeta_{pi,p} - \frac{\partial \psi}{\partial M_i} \right) &= \beta \dot{M}_i + \frac{1}{M^2 \gamma_0} \varepsilon_{ijk} M_j \dot{M}_k. \end{aligned} \quad (134)$$

The resulting equation is a generalized form of the Landau-Lifshitz-Gilbert equation describing the micromagnetic dynamics. Following Landis (2008), recognizing that

$$H_i^{\text{eff}} = \frac{1}{\mu_0} \left( \zeta_{pi,p} - \frac{\partial \psi}{\partial M_i} \right) \quad (135)$$

and taking the cross product of the equation with the magnetization vector we have:

$$\mathbf{M} \times (\mathbf{H}^{\text{eff}} - \beta \dot{\mathbf{M}}) = \frac{1}{\gamma_0 M^2} \mathbf{M} \times (\mathbf{M} \times \dot{\mathbf{M}}) . \quad (136)$$

As the magnitude of the magnetization vector approaches the saturation value of magnetization,  $M \rightarrow M_s$  we have

$$\mathbf{M} \times (\mathbf{H}^{\text{eff}} - \beta \dot{\mathbf{M}}) = \frac{1}{\gamma_0} \dot{\mathbf{M}} \quad (137)$$

where the viscous parameter  $\beta$  is related to the Gilbert damping parameter as

$$\beta = \frac{\alpha}{\gamma_0 M_s} . \quad (138)$$

An apparent advantage of using the generalized Landau-Lifshitz-Gilbert equation that results from the micro-force analysis is that the restriction of the value of the magnetization magnitude to be close to the saturation magnetization value can be applied directly without the use of special techniques to ensure the constraint in a numerical setting. Landis introduced an energy penalty term for deviations of the magnetization magnitude from the saturation value in the Helmholtz free energy of the ferromagnetic material of the form:

$$\psi_{\text{constraint}} = \frac{\mu_0(1 + \chi)}{2\chi} (M - M_s)^2 . \quad (139)$$

As the magnetic susceptibility  $\chi \rightarrow 0$  the constraint  $M = M_s$  is enforced. A general form of the free energy for ferromagnetic materials can be written as

$$\begin{aligned} \psi(\varepsilon_{ij}, M_i, M_{i,j}, B_j) = & \frac{1}{2} A_{ijkl} M_{i,j} M_{k,l} + K_{ijkl} M_i M_j M_k M_l \\ & + \bar{K}_{ijklmn} M_i M_j M_k M_l M_m M_n \\ & + \frac{1}{2} c_{ijkl} (\varepsilon_{ij} - \varepsilon_{ij}^0) (\varepsilon_{kl} - \varepsilon_{kl}^0) \\ & + \frac{\mu_0(1 + \chi)}{2\chi} (M - M_s)^2 \\ & - \frac{1}{2\mu_0} B_i B_i - M_i B_i . \end{aligned} \quad (140)$$

The first term in the free energy expansion is the exchange energy between magnetic spins that penalizes large gradients of magnetization and gives the magnetic domain walls the thickness and the corresponding energy in the theory. The second and third terms are used to fit the magnetocrystalline anisotropy associated with the symmetry required for different materials that creates the energy wells for easy directions of magnetization. The next terms describe the energy associated with the elastic and magnetostrictive strain and the energy penalty that accounts for deviations of the magnetization magnitude from the saturation magnetization respectively. The last two terms are magnetostatic energy associated with the free energy.

## 5.7 Finite Element Implementation

To summarize, the governing equations for ferroelectric materials are

$$\begin{aligned} D_{i,i} &= 0 & \text{in } V \\ D_i n_i &= -\omega & \text{on } S \\ E_i &= -\phi_{,i} \end{aligned} \quad (141)$$

for the electrical fields,

$$\begin{aligned} \sigma_{ij,j} &= \rho \ddot{u}_i & \text{in } V \\ \sigma_{ij} n_j &= t_i & \text{on } S \\ \varepsilon_{ij} &= \frac{1}{2}(u_{i,j} + u_{j,i}) \end{aligned} \quad (142)$$

for the mechanical fields, and for the internal forces associated with the polarization

$$\begin{aligned} \xi_{ji,j} - \frac{\partial \psi}{\partial P_i} &= \beta \dot{P}_i & \text{in } V \\ \xi_{ij} n_j &= \lambda_i & \text{on } S. \end{aligned} \quad (143)$$

The relationship between the electric displacement, electric field and polarization vectors  $D_i = \varepsilon_0 E_i + P_i$ . Let  $\delta P_i$ ,  $\delta \phi$ ,  $\delta u_i$  be test functions. Then multiplying the equations with the test functions and integrating over the volume we have:

$$\int_V \left( \xi_{ij,j} - \frac{\partial \psi}{\partial P_i} - \beta \dot{P}_i \right) \delta P_i dV + \int_V D_{i,i} \delta \phi dV + \int_V \sigma_{ij,j} \delta u_i dV = 0. \quad (144)$$

Applying the divergence theorem and taking into account kinematics and boundary charge and traction definition we have:

$$\begin{aligned} & \int_V \left( \beta \dot{P}_i \delta P_i + \frac{\partial \psi}{\partial P_i} \delta P_i + \xi_{ji} \delta P_{i,j} \right) dV \\ & + \int_V \sigma_{ij} \delta \varepsilon_{ij} dV - \int_V D_i \delta E_i dV = \int_S t_i \delta u_i - \omega \delta \phi + \xi_{ij} n_j \delta P_i dS. \end{aligned} \quad (145)$$

The above equation implies that the components of mechanical displacement, electric polarization and the electric potential are used as nodal degrees of freedom. Defining the array of degrees of freedom as  $\mathbf{d}$  each of the field quantities is interpolated from the nodal quantities with the same set of shape functions such that

$$\{ u_i \ \phi \ P_i \}^T = [N]\{d\}. \quad (146)$$

We note that even though polarization gradient appears in the free energy, the shape function matrix  $N$  must meet only the requirements for standard  $C^0$  continuous elements. This is due to the fact that both electric field and polarization can be taken as independent variables. Therefore, the polarization components take the same status as mechanical displacement and electric potential and the polarization gradient takes the same status as strain and electric field. If, for example, the electric field were the order parameter, then higher order elements would be required in the formulation. Hence, the displacements, electric potential and polarization components are approximated by continuous functions throughout the mesh, but strains, electric fields, and polarization gradients will have jumps in certain components along element boundaries. The stress, electric displacement and micro-forces are computed as

$$\sigma_{ij} = \frac{\partial h}{\partial \varepsilon_{ij}}, \quad D_i = -\frac{\partial h}{\partial E_i}, \quad \xi_{ji} = \frac{\partial h}{\partial P_{i,j}} \quad (147)$$

where  $h(\varepsilon_{ij}, P_i, P_{i,j}, E_i) = \psi(\varepsilon_{ij}, P_i, P_{i,j}, D_i) - E_i D_i$  is the enthalpy of the material is used in order to accommodate the electric potential as a degree of freedom. The discretized formulas for the polarization rates and the basic solution fields during a given time step are as follows:

$$\dot{P}_i = \frac{P_i^{t+\Delta t} - P_i^t}{\Delta t} \quad \text{and} \quad d_i = d_i^{t+\Delta t}. \quad (148)$$

Here, the superscript indicates the time step at which the field is evaluated which result in the first order accurate backward Euler scheme that allows for enhanced numerical stability with larger time increments. Then given a known set of nodal degrees of freedom at time  $t$ , a set of nonlinear algebraic equations results for the nodal degrees of freedom at  $t + \Delta t$  that can be written in the form

$$\mathbf{B}(\mathbf{d}^{t+\Delta t}) = \mathbf{F}. \quad (149)$$

These equations can be solved incrementally with the Newton-Raphson method.

$$\left. \frac{\partial \mathbf{B}}{\partial \mathbf{d}} \right|_{\mathbf{d}_i^{t+\Delta t}} \Delta \mathbf{d}_i = \mathbf{F} - \mathbf{B}(\mathbf{d}_i^{t+\Delta t}) \quad (150)$$

where  $i$  is the current step counter in the Newton-Raphson sequence and  $\Delta \mathbf{d}_i$  is the increment computed for  $\mathbf{d}_i^{t+\Delta t}$  such that  $\mathbf{d}_i^{t+\Delta t} = \mathbf{d}_{i-1}^{t+\Delta t} + \Delta \mathbf{d}_i$ . The Newton-

Raphson procedure is carried out until a suitable level of convergence is obtained yielding a solution for the displacement, electric potential, and polarization fields. Note that the viscous parameter  $\beta$  should be equal to zero for equilibrium domain structure solution. However, in practice we usually need to allow the domain structure to evolve along non-equilibrium paths so this parameter is used as a free numerical parameter to drive the solution and is gradually reduced and set to zero at equilibrium. Similarly, the governing equations for ferromagnetic materials are

$$\begin{aligned} B_{i,i} &= 0 & \text{in } V \\ \varepsilon_{ijk} H_{j,k} &= J_i & \text{in } V \\ \varepsilon_{ijk} H_j n_k &= K_i & \text{in } S \end{aligned} \quad (151)$$

for the magnetic fields, where  $J_i$  and  $K_i$  are the volume and surface current density respectively and  $\varepsilon_{ijk}$  stands for the permutation symbol.

$$\begin{aligned} \sigma_{ij,j} &= \rho \ddot{u}_i & \text{in } V \\ \sigma_{ij} n_j &= t_i & \text{on } S \\ \varepsilon_{ij} &= \frac{1}{2}(u_{i,j} + u_{j,i}) \end{aligned} \quad (152)$$

for the mechanical fields, and for the internal forces associated with the magnetization

$$\frac{1}{\mu_0} \left( \zeta_{pi,p} - \frac{\partial \psi}{\partial M_i} \right) = \frac{\alpha}{\gamma_0 M_S} \dot{M}_i + \frac{1}{M_S^2 \gamma_0} \varepsilon_{ijk} M_j \dot{M}_k \quad \text{in } V. \quad (153)$$

The relationship between the magnetic induction, magnetic field and magnetization vector is  $B_i = \mu_0(H_i + M_i)$ . Neglecting inertial terms and considering zero volume and surface current densities, the magnetic field can be written in terms of a scalar magnetic potential as  $H_i = -\phi_{,i}^M$  and a variational form is then written as

$$\begin{aligned} & \int_V \sigma_{ij} \delta \varepsilon_{ij} dV - \int_V B_i \delta H_i dV \\ & + \int_V \left( \frac{\alpha}{\gamma_0 M_S} \dot{M}_i + \frac{\partial \psi}{\partial M_i} + \frac{1}{\gamma M_S^2} \varepsilon_{ijk} \dot{M}_j M_k \right) \delta M_i dV \\ & + \int_V \zeta_{ji} \delta M_{i,j} dV = \int_S t_i \delta u_i + \zeta_{ij} n_j \delta M_i dS. \end{aligned} \quad (154)$$

The above equation implies that the components of mechanical displacement, magnetization and the magnetic potential are used as nodal degrees of freedom and the nodal quantities with the same set of shape functions such that

$$\{ u_i \ \phi^M \ M_i \}^T = [N] \{d\} \quad (155)$$

where the shape function matrix  $N$  must meet the requirements for standard  $C^0$  continuous elements. In this case, the magnetization components take the same status as mechanical displacement and magnetic potential and the magnetization gradient takes the same status as strain and magnetic field. The stress, magnetic induction and micro-forces are computed as

$$\sigma_{ij} = \frac{\partial h}{\partial \varepsilon_{ij}}, \quad B_i = -\frac{\partial h}{\partial H_i}, \quad \zeta_{ji} = \frac{\partial h}{\partial M_{i,j}} \quad (156)$$

where  $h(\varepsilon_{ij}, M_i, M_{i,j}, H_i) = \psi(\varepsilon_{ij}, M_i, M_{i,j}, B_i) - B_i H_i$  is the enthalpy of the material is used in order to accommodate the magnetic potential as a degree of freedom. The resulting nonlinear problem can be solved using the Newton-Raphson method as in the case of ferroelectrics. For an equilibrium domain structure the parameter  $\alpha$  can either be used as a free parameter to drive the numerical solution or taken to corresponding values of the Gilbert damping constant for a realistic representation of the micromagnetic dynamics.

## 5.8 Example of Strain-Mediated Multiferroic Phase-Field Modeling

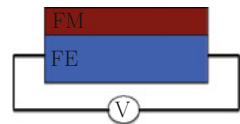
The above formulation of the phase field method for ferroelectric and ferromagnetic materials can be extended to the case of strain mediated multiferroic composites. This is demonstrated through an example case study as follows. Consider a ferroelectric and a ferromagnetic static domain structure as shown in the Fig. 8 where the ferroelectric and the ferromagnetic materials share an interface at the common boundary.

Then given a static domain structure the free energy of the system can be written as

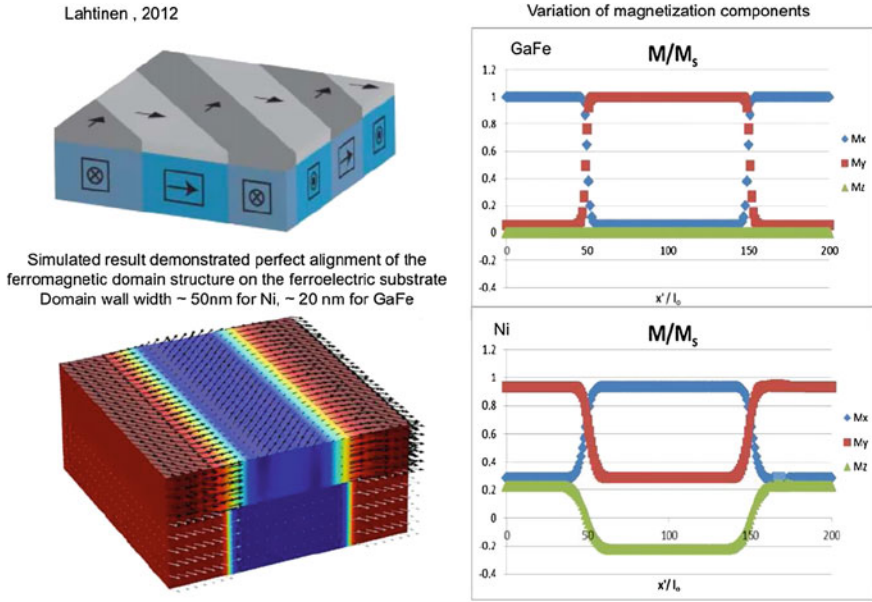
$$\begin{aligned} \psi^{FE/M} = & \int_{V^{FE}} \psi^{FE}(\varepsilon_{ij}, D_i, P_i, P_{i,j}) \\ & + \int_{V^{FM}} \psi^{FM}(\varepsilon_{ij}, B_i, M_i, M_{i,j}) dV \end{aligned} \quad (157)$$

where  $V^{FE}$  and  $V^{FM}$  corresponds to the volume of the ferroelectric and ferromagnetic part respectively. In the strain-mediated approach the total strain is written as the sum of the elastic and electrostrictive/magnetostrictive strain as

**Fig. 8** Schematic of strain-mediated ferroelectric (FE) and ferromagnetic (FM) heterostructures







$$\varepsilon_{ij} = \varepsilon_{ij}^{el} + \varepsilon_{ij}^0 = \varepsilon_{ij}^{el} + A Q_{ijkl} P_k P_l + (1 - A) \lambda_{ijkl} M_k M_l \quad (158)$$

where the parameter  $A$  takes the value 1 in the ferroelectric volume and 0 in the ferromagnetic. A variational form for the coupled problem is then written as:

$$\begin{aligned} & \int_{V_{FE}} \left( \xi_{ji,j} - \frac{\partial \psi}{\partial P_i} - \beta \dot{P}_i \right) \delta P_i dV + \int_{V_{FE}} D_{i,i} \delta \phi dV \\ & + \int_{V_{FE} \& V_{FM}} \sigma_{ij,j} \delta u_i dV + \int_{V_{FM}} B_{i,i} \delta \phi_i^M dV \\ & + \int_{V_{FM}} \left( \zeta_{ji,j} - \frac{\partial \psi}{\partial M_i} - \frac{\alpha \mu_0}{\gamma_0 M_S} \dot{M}_i - \frac{\mu_0}{\gamma_0 M_S^2} \varepsilon_{ijk} \dot{M}_j M_k \right) \delta M_i = 0. \end{aligned} \quad (159)$$

The finite element formulation described above is used to simulate the experimental results of Lahtinen et al. (2012) who demonstrated full imprinting of ferroelastic  $\text{BaTiO}_3$  domains into CoFe during thin film growth (Fig. 9).

We first apply appropriate periodic boundary conditions based on the spontaneous strains and polarization distribution to allow for the formation of an equilibrium  $90^\circ$  domain pattern using the phase field formulation described above. The energy function and the parameters correspond to barium titanate and are taken from Su and Landis. Once the equilibrium periodic domain pattern of the ferroelectric substrate is obtained we consider a random thin ferromagnetic layer and allow for the evolution

of the ferromagnetic domain structure using the multiferroic formulation. Evolution of the domain pattern towards minimizing the energy of the system results in full imprinting of the ferroelectric domain structure explained by strain transfer at the heterostructure interface. The ferroelastic strains of the ferroelectric substrate interact with the magnetoelastic anisotropy of the ferromagnetic material via the inverse magnetostriction effect. Two ferromagnetic materials of different magnetic anisotropies are considered. The resulting domain imprinting is demonstrated in the Figure for Gallium Ferrite (GaFe) and Nickel (Ni).

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