A Phenomenological Constitutive Theory for Ferroelasticity

Next we move away from linear response. We have spent several qualitative lectures on the behaviors of various "smart" materials in an effort to link the microstructural evolution mechanisms to the macroscopically observed behaviors. In the following we will attempt to develop a mathematical structure that can be applied, usually within the finite element method, to solve boundary value problems. For the sake of simplicity we will stick to the purely mechanical case of a ferroelastic description of twinning and detwinning. It is useful to define the type of problem we are interested in investigating. Let's say we have some structure with a characteristic dimension of centimeters or more, like a compact tension specimen. Grain sizes are in the micron to tens of microns regime, and domain structures are of that scale or smaller. The point of this discussion is that if we want to do a finite element calculation is a reasonable amount of time on a compact tension specimen then we are not going to be able to track every domain wall or twin boundary, and we are not even going to be able to track what is going on from grain to grain. So our constitutive law is going to have to attempt to describe what is going on in a collection of grains. Our "material point" is actually some representative volume of the material. This should not cause you too much consternation, as this is exactly what is done for polycrystalline metal plasticity, and we will use the same mathematical structure.

We are trying to model an irreversible process, so we will need to introduce a set of internal variables that will enable us to determine the state of the material. Strictly speaking, the full set of internal variables would be the locations of all of the domain walls or twin boundaries in the material. As we alluded to previously such a task would be for all intents and purposes impossible. It can be argues that the smallest set of internal variables needed to describe a ferroelastic material is the remanent (plastic) strain. Formally we will write our free energy as,

$$\psi = \psi(\varepsilon_{ij}, \varepsilon^r_{ij}) = \tfrac{1}{2} c_{ijkl}(\varepsilon_{ij} - \varepsilon^r_{ij})(\varepsilon_{kl} - \varepsilon^r_{kl}) + \psi^r(\varepsilon^r_{ij})$$

An analysis of the second law yields,

$$\sigma_{ji} = \frac{\partial \psi}{\partial \varepsilon_{ij}} = c_{ijkl}(\varepsilon_{kl} - \varepsilon^r_{kl}) \quad \text{and} \quad \left(\sigma_{ij} - \frac{\partial \psi^r}{\partial \varepsilon^r_{ij}}\right)\dot{\varepsilon}^r_{ij} \geq 0$$

Note that the original free energy functional was constructed with the desired form for the elastic stress-strain behavior in mind. Also note that we have assumed that the elastic properties c_{ijkl} are not dependent on our internal variables ε^r_{ij}. This assumption is a simplification for ferroelastic twinning and detwinning because in general the elastic properties at the lattice level are anisotropic and any texture that is induced by remanent straining will lead to elastic properties that are dependent on the orientation

of that texture and the magnitude of the remanent strain. Note that an initially isotropic texture (i.e. distribution of variant orientations) will have isotropic elastic properties. Again, we will neglect this feature of the problem for now as it is less important for ferroelastic materials than it is for ferroelectric materials.

The second law now identifies a driving force that is work/dissipation conjugate to the rate of change (or increment in the rate independent case) of the internal variables. Following the terminology of kinematic hardening plasticity, the term $\partial\psi / \partial\varepsilon^r_{ij} \equiv \sigma^B_{ij}$ is called the back stress. Note that the inclusion of $\psi^r(\varepsilon^r_{ij})$ in the Helmholtz free energy indicates a non-standard contribution to the stored energy in the material. Recall that we have simplified our description of the internal state of the material considerably and have "swept the specifics of the domain microstructure under the rug". Well, that bump under the rug is essentially the energy due to residual stress associated with the incompatibilities that arise during remanent straining. The specifics of these internal stresses depend on the geometric structure of the domains, which we have decided to ignore, so at best we can only account for this energy contribution in a phenomenological way. But that is the physical motivation for this term.

Next, we will assume that there is some region within the driving force space, which we will call $\hat{\sigma}_{ij} \equiv \sigma_{ij} - \sigma^B_{ij}$, where the material responds in a linear elastic manner and the increments of remanent strain are zero. In plasticity the boundary of this surface is called the yield surface, and for ferroelasticity this is sometimes referred to as the switching surface. So, for states of the driving force that are within the surface we have $\dot{\varepsilon}^r_{ij} = 0$, and then switching is possible for states of the driving force on the surface given by the equation,

$$\Phi(\hat{\sigma}_{ij}, \varepsilon^r_{ij}) = 0$$

Note that we have explicitly listed the potential dependence on the internal variable. For a specific material description this dependence may or may not exist. Before we discuss a specific form for the switching surface let's first discuss the implications of another widely used postulate. Specifically we will assume that the material abides by the postulate of maximum dissipation. Before stating this postulate I will note that this is not a requirement of the laws of thermodynamics, but rather is something extra. I will not get into the details, but there are some very nice fundamental arguments showing that many mechanisms of quasi-static deformation lead to this postulate. For our purposes we will take it as an assumption. So let's state the postulate.

Postulate of Maximum Dissipation – For a given remanent increment, $\dot{\varepsilon}^r_{ij}$, the state of the driving force, $\hat{\sigma}_{ij}$, that satisfies the switching criterion, $\Phi(\hat{\sigma}_{ij},\varepsilon^r_{ij}) = 0$, and causes the increment $\dot{\varepsilon}^r_{ij}$, is the one that maximizes the dissipation $\hat{\sigma}_{ij}\dot{\varepsilon}^r_{ij}$.

Let's now consider the implications of this postulate. To do this we need to maximize $\hat{\sigma}_{ij}\dot{\varepsilon}^r_{ij}$ with respect to $\hat{\sigma}_{ij}$, subject to the constraint $\Phi(\hat{\sigma}_{ij},\varepsilon^r_{ij}) = 0$. This is accomplished by introducing the Lagrange multiplier λ and solving,

$$\frac{\partial}{\partial\hat{\sigma}_{ij}}\left(\hat{\sigma}_{kl}\dot{\varepsilon}^r_{kl} - \lambda\Phi\right) = 0$$

$$\rightarrow \dot{\varepsilon}^r_{ij} = \lambda\frac{\partial\Phi}{\partial\hat{\sigma}_{ij}}$$

This equation is the *flow rule* for the remanent strain increment. What this equation states is that the increment of remanent strain is normal to the point on the switching surface at $\Phi(\hat{\sigma}_{ij},\varepsilon^r_{ij}) = 0$. In general, the flow rule is introduced through a plastic potential that is not necessarily equivalent to Φ. However, the postulate of maximum dissipation implies that the plastic potential is Φ, and the flow rule is called an *associated flow rule* (i.e. the flow rule is "associated" with the switching surface). Next, we also need to consider the conditions for this increment to be a maximum, and not a minimum or a saddle point. This will be a maximum if the Hessian

$$\frac{\partial}{\partial\hat{\sigma}_{ij}\,\partial\hat{\sigma}_{kl}}\left(\hat{\sigma}_{mn}\dot{\varepsilon}^r_{mn} - \lambda\Phi\right)$$

is negative definite. This implies that $-\lambda\dfrac{\partial\Phi}{\partial\hat{\sigma}_{ij}\partial\hat{\sigma}_{kl}}$ is negative definite, or if we take λ to only be a positive multiplier then $\dfrac{\partial\Phi}{\partial\hat{\sigma}_{ij}\partial\hat{\sigma}_{kl}}$ must be positive definite. Let's consider the geometrical implications of this condition. First, take a driving force $\hat{\sigma}_{ij}$ that satisfies $\Phi = 0$ and consider other nearby driving forces that lie on the tangent plane to Φ at that point. Note that in order to satisfy the second law, and assuming that λ is a positive multiplier, the switching surface must enclose the origin in driving force space, so without loss of generality we can always assume that $\Phi < 0$ inside the switching surface and $\Phi > 0$ outside the switching surface. For our nearby driving force state on the tangent plane we have,

$$\Phi(\hat{\sigma}_{ij} + d\hat{\sigma}_{ij}, \varepsilon^r_{ij}) = \Phi(\hat{\sigma}_{ij}, \varepsilon^r_{ij}) + \frac{\partial \Phi}{\partial \hat{\sigma}_{ij}} d\hat{\sigma}_{ij} + \frac{1}{2} \frac{\partial^2 \Phi}{\partial \hat{\sigma}_{ij} \partial \hat{\sigma}_{kl}} d\hat{\sigma}_{ij} d\hat{\sigma}_{kl} + O(d\hat{\sigma}_{ij} d\hat{\sigma}_{kl} d\hat{\sigma}_{mn})$$

Now, since our original state $\hat{\sigma}_{ij}$ is on the switching surface, we have $\Phi(\hat{\sigma}_{ij}, \varepsilon^r_{ij}) = 0$. Also, since the driving force increment $d\hat{\sigma}_{ij}$ is in the tangent plane and $\dfrac{\partial \Phi}{\partial \hat{\sigma}_{ij}}$ is normal to the tangent plane, the second term in the series is also zero. Finally, since the postulate of maximum dissipation implies that the Hessian is positive definite and neglecting the higher order terms we have,

$$\Phi(\hat{\sigma}_{ij} + d\hat{\sigma}_{ij}, \varepsilon^r_{ij}) = \frac{1}{2} \frac{\partial^2 \Phi}{\partial \hat{\sigma}_{ij} \partial \hat{\sigma}_{kl}} d\hat{\sigma}_{ij} d\hat{\sigma}_{kl} \geq 0$$

What this tells us is that for nearby driving force states on the tangent plane to $\Phi(\hat{\sigma}_{ij}, \varepsilon^r_{ij}) = 0$, $\Phi > 0$. So this means that the points on the tangent plane are *outside* of the switching surface. Since this argument applies to all of the points on the switching surface, it implies that the switching surface must be convex, i.e. all tangent planes lie to the outside of the surface.

So to recap, the postulate of maximum dissipation implies that there is an associated flow rule such that the increments of the internal variables are normal to the switching surface in driving force space, and that the switching surface is convex in driving force space. There is another way to mathematically state the requirements of the maximum dissipation postulate that is useful for bounding proofs in plasticity. Let's go through the proof.

Given: $\dot{\varepsilon}^r_{ij} = \lambda \dfrac{\partial \Phi}{\partial \hat{\sigma}_{ij}}$, $\quad \Phi(\hat{\sigma}_{ij}, \varepsilon^r_{ij}) = 0 \quad$ and $\quad \dfrac{\partial \Phi}{\partial \hat{\sigma}_{ij} \partial \hat{\sigma}_{kl}}$ positive definite

Show: $(\hat{\sigma}_{ij} - \hat{\sigma}^*_{ij}) \dot{\varepsilon}^r_{ij} \geq 0$ for any $\hat{\sigma}^*_{ij}$ on or within the switching surface, i.e. $\Phi(\hat{\sigma}^*_{ij}, \varepsilon^r_{ij}) \leq 0$, with $\hat{\sigma}_{ij}$ being the driving force state that causes $\dot{\varepsilon}^r_{ij}$.

To demonstrate our assertion we first define the driving force increment $d\hat{\sigma}_{ij}$ to be an infinitesimal driving force increment in the same direction as $\hat{\sigma}^*_{ij} - \hat{\sigma}_{ij}$. Then we must have $(\hat{\sigma}_{ij} - \hat{\sigma}^*_{ij}) \dot{\varepsilon}^r_{ij} \geq 0$ if $d\hat{\sigma}_{ij} \dot{\varepsilon}^r_{ij} \leq 0$. Next, due to the convexity of the switching surface, if $\Phi(\hat{\sigma}^*_{ij}, \varepsilon^r_{ij}) \leq 0$ then $\Phi(\hat{\sigma}_{ij} + d\hat{\sigma}_{ij}, \varepsilon^r_{ij}) \leq 0$. Now, expand this incremental state in a Taylor series,

$$\Phi(\hat{\sigma}_{ij}+d\hat{\sigma}_{ij},\varepsilon^r_{ij})=\Phi(\hat{\sigma}_{ij},\varepsilon^r_{ij})+\frac{\partial\Phi}{\partial\hat{\sigma}_{ij}}d\hat{\sigma}_{ij}+O(d\hat{\sigma}_{ij}d\hat{\sigma}_{kl})\le 0$$

Using $\Phi(\hat{\sigma}_{ij},\varepsilon^r_{ij})=0$ and $\dot{\varepsilon}^r_{ij}=\lambda\dfrac{\partial\Phi}{\partial\hat{\sigma}_{ij}}$ this implies that

$$\frac{1}{\lambda}\dot{\varepsilon}^r_{ij}d\hat{\sigma}_{ij}\le 0 \quad\rightarrow\quad d\hat{\sigma}_{ij}\dot{\varepsilon}^r_{ij}\le 0 \quad\rightarrow\quad (\hat{\sigma}_{ij}-\hat{\sigma}^*_{ij})\dot{\varepsilon}^r_{ij}\ge 0$$

So $(\hat{\sigma}_{ij}-\hat{\sigma}^*_{ij})\dot{\varepsilon}^r_{ij}\ge 0$ is simply another way to mathematically state the consequences of the maximum dissipation postulate.

These are a few nice general principals that help us to constrain our constitutive theory in a more restrictive manner than the second law does. However, we still need more specifics in order to model a particular material. Note that when dealing with transformations from one martensite variant to another martensite variant there can be no remanent volume change because the size and shapes of the variants are identical but their orientation differs. So if there is no volumetric remanent strain increment then, assuming and associated flow rule, the hydrostatic part of the driving force cannot contribute to the switching surface. This is in direct accord with the assumptions of metal plasticity. This implies that the switching surface must be in terms of the deviator of the driving force,

$$\hat{s}_{ij}=\hat{\sigma}_{ij}-\tfrac{1}{3}\hat{\sigma}_{kk}\delta_{ij}$$

Then, if the material is initially isotropic, in this case we are referring to plastic isotropy, then the switching surface can only depend on the invariants of $\hat{s}_{ij}$, which are $\hat{s}_{kk}=0$, $\hat{s}_{ij}\hat{s}_{ij}$, and $\hat{s}_{ij}\hat{s}_{jk}\hat{s}_{ki}$. In general the size and shape of the switching surface would have to be measured experimentally. For illustrative purposes we will make the simple assumption consistent with J_2-flow theory in plasticity that the switching functional can be written as,

$$\Phi=\tfrac{3}{2}\hat{s}_{ij}\hat{s}_{ij}-\sigma_0^2$$

where σ_0 is the uniaxial switching strength, which is the stress in uniaxial tension or compression where switching commences. Then the flow rule is written as,

$$\dot{\varepsilon}^r_{ij}=\lambda\frac{\partial\Phi}{\partial\hat{\sigma}_{ij}}=\lambda\frac{\partial\Phi}{\partial\hat{s}_{kl}}\frac{\partial\hat{s}_{kl}}{\partial\hat{\sigma}_{ij}}=3\lambda\hat{s}_{kl}(\delta_{ik}\delta_{jl}-\tfrac{1}{3}\delta_{kl}\delta_{im}\delta_{jm})=3\lambda\hat{s}_{ij}-\lambda\hat{s}_{kk}\delta_{ij}=3\lambda\hat{s}_{ij}$$

The one last piece of the framework that is required is the specification of the remanent potential $\psi^r(\varepsilon^r_{ij})$. Again, if the material is initially isotropic with regard to its texture, then the remanent potential can only depend on the invariants of the remanent strain. Even though the remanent strain has no volumetric part it is still useful to formally define and use the remanent strain deviator $e^r_{ij} = \varepsilon^r_{ij} - \frac{1}{3}\varepsilon^r_{kk}\delta_{ij}$. Then the remanent potential can be written in terms of the following two invariants,

$$J^e_2 = \left(\tfrac{2}{3} e^r_{ij} e^r_{ij}\right)^{1/2} \quad \text{and} \quad J^e_3 = \left(\tfrac{4}{3} e^r_{ij} e^r_{jk} e^r_{ki}\right)^{1/3}$$

With these invariants J^e_2 can be regarded as the "magnitude" of the strain, and the ratio J^e_3 / J^e_2 can be thought of as the "direction" or "type" of strain, with $J^e_3 / J^e_2 = 1$ being a uniaxial volume conserving extension, $J^e_3 / J^e_2 = -1$ a uniaxial volume conserving contraction, and $J^e_3 / J^e_2 = 0$ being a pure shear remanent strain. All other strain "types" lie in the region $-1 \le J^e_3 / J^e_2 \le 1$. With ferroelastic materials one of the required features of the remanent potential is that is must enforce the remanent strain saturation conditions. This implies that when the remanent strain state gets close to a saturated state the remanent potential must increase rapidly. Furthermore, the saturation state most like depends on the remanent strain "type" such that this state is dependent on the ratio J^e_3 / J^e_2. Specifically, in tetragonal materials where the c-axis of the unit cell is longer than the a-axes, the saturated remanent strain in tension is greater than the saturated remanent strain in compression. So in general, for an isotropic material, we would have $\psi^r = \psi^r(J^e_2, J^e_3)$.

For a material that is elastically and initially remanently isotropic the four components of our constitutive law are,

Elasticity: $\sigma_{ij} = (\frac{2}{3}\mu + \lambda_e)\delta_{ij}\varepsilon_{kk} + 2\mu(e_{ij} - \varepsilon^r_{ij})$ where $e_{ij} = \varepsilon_{ij} - \frac{1}{3}\varepsilon_{kk}\delta_{ij}$

Switching surface: $\Phi = \frac{3}{2}\hat{s}_{ij}\hat{s}_{ij} - \sigma_0^2 \le 0$ where $\hat{\sigma}_{ij} = \sigma_{ij} - \sigma^B_{ij}$ and $\hat{s}_{ij} = \hat{\sigma}_{ij} - \frac{1}{3}\hat{\sigma}_{kk}\delta_{ij}$

Flow rule: $\dot{\varepsilon}^r_{ij} = 3\lambda\hat{s}_{ij}$ with $\lambda \ge 0$ if $\Phi = 0$ and $\lambda = 0$ if $\Phi < 0$

Hardening law: $\sigma^B_{ij} = \dfrac{\partial \psi^r}{\partial \varepsilon^r_{ij}}$

From these considerations we can construct the forward tangent moduli for a material undergoing remanent straining. First consider the consistency condition,

$$\dot{\Phi} = 0 \quad \rightarrow \quad 3(s_{ij} - s^B_{ij})(\dot{s}_{ij} - \dot{s}^B_{ij}) = 0$$

Elasticity then implies that $\dot{s}_{ij} = 2\mu(\dot{e}_{ij} - \dot{\varepsilon}^r_{ij})$, which with the consistency condition and the hardening law give,

$$3(s_{ij} - s^B_{ij})\left(2\mu\dot{e}_{ij} - 2\mu\dot{\varepsilon}^r_{ij} - \underbrace{\frac{\partial s^B_{ij}}{\partial \varepsilon^r_{kl}}}_{H_{ijkl}}\dot{\varepsilon}^r_{kl}\right) = 0$$

The flow rule then yields,

$$6\mu(s_{ij} - s^B_{ij})\dot{e}_{ij} - 18\mu\lambda\underbrace{(s_{ij} - s^B_{ij})(s_{ij} - s^B_{ij})}_{\frac{2}{3}\sigma_0^2} - 9(s_{ij} - s^B_{ij})H_{ijkl}\lambda(s_{kl} - s^B_{kl}) = 0$$

Solving for λ gives,

$$\lambda = \frac{2\mu\hat{s}_{ij}\dot{e}_{ij}}{4\mu\sigma_0^2 + 3\hat{s}_{pq}H_{pqrs}\hat{s}_{rs}} \quad \rightarrow \quad \dot{\varepsilon}^r_{ij} = \frac{6\mu\hat{s}_{ij}\hat{s}_{kl}\dot{e}_{kl}}{4\mu\sigma_0^2 + 3\hat{s}_{pq}H_{pqrs}\hat{s}_{rs}}$$

Then, going back to the incremental elasticity relationships, we have,

$$\dot{\sigma}_{ij} = (2\mu + \lambda_e)\delta_{ij}\dot{\varepsilon}_{kk} + 2\mu\left(\dot{e}_{ij} - \frac{6\mu\hat{s}_{ij}\hat{s}_{kl}\dot{e}_{kl}}{4\mu\sigma_0^2 + 3\hat{s}_{pq}H_{pqrs}\hat{s}_{rs}}\right)$$

This is simply the incremental stress-strain behavior for a material point that is in the process of switching. Note that this is called the *forward tangent* description and is not the best approach to use for numerical methods. Let's take a closer look at how such constitutive laws would be implemented in the finite element method.

First let's start with the principle of virtual work.

$$\int_V \sigma_{ij}\,\delta\varepsilon_{ij}\,dV = \int_V b_i\,\delta u_i\,dV + \int_S T_i\,\delta u_i\,dS$$

In general we will be solving a non-linear irreversible problem so we will have to solve this problem both incrementally (due to the irreversibility) and iteratively (due to the non-linearity) in time. Imagine that we have some load history given to use and that at some point in time we know the solution that satisfies the weak form of equilibrium given by the principle of virtual work. In other words, we know σ^t_{ij}, u^t_i, and $\varepsilon^{r,t}_{ij}$ for the load history that is currently at b^t_i and T^t_i. Our goal is to determine $\sigma^{t+\Delta t}_{ij}$, $u^{t+\Delta t}_i$, and $\varepsilon^{r,t+\Delta t}_{ij}$ for the new state of loading $b^{t+\Delta t}_i$ and $T^{t+\Delta t}_i$ given what we already know at time t. Since our constitutive law is nonlinear we will have to do this using an iterative

scheme, and the Newton-Raphson method is usually the best procedure for this task. Let's define σ_{ij}^{I} as the Ith estimate of $\sigma_{ij}^{t+\Delta t}$. Then once we have found a converged solution we will set $\sigma_{ij}^{I} \rightarrow \sigma_{ij}^{t+\Delta t}$. The Newton-Raphson form of the principle of virtual work then looks like,

$$\int_V d\sigma_{ij}\,\delta\varepsilon_{ij}\,dV = \int_V b_i^{t+\Delta t}\,\delta u_i\,dV + \int_S T_i^{t+\Delta t}\,\delta u_i\,dS - \int_V \sigma_{ij}^{I}\,\delta\varepsilon_{ij}\,dV$$

To first order, the stress change $d\sigma_{ij}$ is related to the strain change $d\varepsilon_{ij}$ as,

$$d\sigma_{ij} = c_{ijkl}^{BE} d\varepsilon_{kl}$$

Where c_{ijkl}^{BE} is the tangent modulus that is consistent with the backward Euler constitutive integration routine that will be used to solve the constitutive model. This then leads to the following form of the PVW,

$$\int_V \delta\varepsilon_{ij} c_{ijkl}^{BE}\,d\varepsilon_{kl}\,dV = \int_V b_i^{t+\Delta t}\,\delta u_i\,dV + \int_S T_i^{t+\Delta t}\,\delta u_i\,dS - \int_V \sigma_{ij}^{I}\,\delta\varepsilon_{ij}\,dV$$

Which ultimately leads to the finite element equations,

$$[K^{tan}]\{du_N\} = \{F^{res}\}$$

where $[K^{tan}]$ is the tangent stiffness matrix, $\{du_N\}$ is the vector of nodal displacement changes such that $\{u_N^{I+1}\} = \{u_N^{I}\} + \{du_N\}$, and $\{F^{res}\}$ is the unbalanced nodal force vector. Given this new approximation for $\{u_N^{I+1}\}$ the strain at any integration station ε_{ij}^{I+1} can be obtained from the finite element interpolation. With ε_{ij}^{I+1} in hand, it is the job of the constitutive law to provide σ_{ij}^{I+1} and c_{ijkl}^{BE} at each integration station to be used within the next Newton-Raphson step for the finite element method.

Let's now consider how to compute σ_{ij}^{I+1} and c_{ijkl}^{BE}. I have alluded to the fact that we will be using a backward Euler integration routine. This integration method satisfies our constitutive equations at the *end* of the step. This means that the elasticity relations and the switching conditions will be met exactly, but the flow rule will only be satisfied to first order. The quantities that we know at this stage and that will be used in our routine are, ε_{ij}^{I+1} and $\varepsilon_{ij}^{r,t}$. We need to use these to determine σ_{ij}^{I+1} and c_{ijkl}^{BE}. The equations that we need to solve are,

$$\sigma_{ij}^{I+1} = (\lambda_e + \tfrac{2}{3}\mu)\delta_{ij}\varepsilon_{kk}^{I+1} + 2\mu(e_{ij}^{I+1} - \varepsilon_{ij}^{r,t} - \Delta\varepsilon_{ij}^{r}) \rightarrow s_{ij}^{I+1} = 2\mu(e_{ij}^{I+1} - \varepsilon_{ij}^{r,t} - \Delta\varepsilon_{ij}^{r})$$

$$\Delta\varepsilon_{ij}^{r} = 3\lambda(s_{ij}^{I+1} - s_{ij}^{B})$$

$\frac{3}{2}(s_{ij}^{I+1}-s_{ij}^{B})(s_{ij}^{I+1}-s_{ij}^{B})-\sigma_0^2=0$

To solve these equations first dot the flow rule equation with itself,

$$\Delta\varepsilon_{ij}^{r}\Delta\varepsilon_{ij}^{r}=9\lambda^2\underbrace{(s_{ij}^{I+1}-s_{ij}^{B})(s_{ij}^{I+1}-s_{ij}^{B})}_{\frac{2}{3}\sigma_0^2}$$

Now, use the switching criterion and solve for the multiplier λ.

$$\lambda=\frac{\sqrt{\Delta\varepsilon_{ij}^{r}\Delta\varepsilon_{ij}^{r}}}{\sqrt{6}\sigma_0}$$

Placing this result and the elasticity equations into the flow rule gives us the nonlinear equations that must be solved for $\Delta\varepsilon_{ij}^{r}$.

$$\Delta\varepsilon_{ij}^{r}=\frac{3\sqrt{\Delta\varepsilon_{pq}^{r}\Delta\varepsilon_{pq}^{r}}}{\sqrt{6}\sigma_0}\Big[2\mu(e_{ij}^{I+1}-\varepsilon_{ij}^{r,t}-\Delta\varepsilon_{ij}^{r})-s_{ij}^{B}\Big]$$

This set of nonlinear equations is then solved using the Newton-Raphson method as follows.

$$\Delta\varepsilon_{ij}^{r,i}-\frac{3\sqrt{\Delta\varepsilon_{pq}^{r,i}\Delta\varepsilon_{pq}^{r,i}}}{\sqrt{6}\sigma_0}\Big[2\mu(e_{ij}^{I+1}-\varepsilon_{ij}^{r,t}-\Delta\varepsilon_{ij}^{r,i})-s_{ij}^{B,i}\Big]=f_{ij}^{i}$$

Here the superscript i represents the quantity at the ith iteration. The update to $\Delta\varepsilon_{ij}^{r}$ is determined from the solution to the linear equations,

$$J_{ijkl}\partial\varepsilon_{kl}^{r}=-f_{ij}^{i}\quad\text{with}\quad\Delta\varepsilon_{ij}^{r,i+1}=\Delta\varepsilon_{ij}^{r,i}+\partial\varepsilon_{ij}^{r}$$

J_{ijkl} is the Jacobian matrix which is determined by differentiating the nonlinear equations that we are solving with respect to $\Delta\varepsilon_{kl}^{r}$. Therefore,

$$J_{ijkl}=\delta_{ik}\delta_{jl}-\frac{3\Delta\varepsilon_{kl}^{r,i}}{\sqrt{6}\sigma_0\sqrt{\Delta\varepsilon_{pq}^{r,i}\Delta\varepsilon_{pq}^{r,i}}}\Big[2\mu(e_{ij}^{I+1}-\varepsilon_{ij}^{r,t}-\Delta\varepsilon_{ij}^{r,i})-s_{ij}^{B,i}\Big]+\frac{3\sqrt{\Delta\varepsilon_{pq}^{r,i}\Delta\varepsilon_{pq}^{r,i}}}{\sqrt{6}\sigma_0}\Big(2\mu\delta_{ik}\delta_{jl}+H_{ijkl}\Big)$$

with $H_{ijkl}=\left.\dfrac{\partial^2\psi^r}{\partial\varepsilon_{ij}^{r}\partial\varepsilon_{kl}^{r}}\right|_{\varepsilon_{ij}^{r,t}+\Delta\varepsilon_{ij}^{r,i}}$ and $s_{ij}^{B,i}=\left.\dfrac{\partial\psi^r}{\partial\varepsilon_{ij}^{r}}\right|_{\varepsilon_{ij}^{r,t}+\Delta\varepsilon_{ij}^{r,i}}$

When these equations are solved we will have $f_{ij}^{i} = 0$, $\Delta\varepsilon_{ij}^{r,i} \to \Delta\varepsilon_{ij}^{r}$, and then $s_{ij}^{I+1} = 2\mu(e_{ij}^{I+1} - \varepsilon_{ij}^{r,t} - \Delta\varepsilon_{ij}^{r})$. So we have accomplished one of our tasks for the finite element method, the determination of σ_{ij}^{I+1}. Note that the hydrostatic part of the stress is simply, $\sigma_{kk}^{I+1} = (3\lambda_{e} + 2\mu)\varepsilon_{kk}^{I+1}$. Next we must also determine the tangent moduli for the finite element scheme. To do this, we need to find how the solutions to our constitutive equations vary if we vary the strain. Taking these variations at the end of our converged Newton-Raphson iterations for the constitutive solution yields,

$$d\varepsilon_{ij}^{r} - \frac{3\Delta\varepsilon_{mn}^{r} d\varepsilon_{mn}^{r}}{\sqrt{6}\sigma_{0}\sqrt{\Delta\varepsilon_{pq}^{r}\Delta\varepsilon_{pq}^{r}}}\left(s_{ij}^{I+1} - s_{ij}^{B}\right) - \frac{3\sqrt{\Delta\varepsilon_{pq}^{r}\Delta\varepsilon_{pq}^{r}}}{\sqrt{6}\sigma_{0}}\left[2\mu(de_{ij} - d\varepsilon_{ij}^{r}) - H_{ijkl}d\varepsilon_{kl}^{r}\right] = 0$$

$$\left[\delta_{ik}\delta_{jl} - \frac{3\left(s_{ij}^{I+1} - s_{ij}^{B}\right)\Delta\varepsilon_{kl}^{r}}{\sqrt{6}\sigma_{0}\sqrt{\Delta\varepsilon_{pq}^{r}\Delta\varepsilon_{pq}^{r}}} + \frac{3\sqrt{\Delta\varepsilon_{pq}^{r}\Delta\varepsilon_{pq}^{r}}}{\sqrt{6}\sigma_{0}}\left(2\mu\delta_{ik}\delta_{jl} + H_{ijkl}\right)\right]d\varepsilon_{kl}^{r} = \frac{6\mu\sqrt{\Delta\varepsilon_{pq}^{r}\Delta\varepsilon_{pq}^{r}}}{\sqrt{6}\sigma_{0}}de_{ij}$$

This can be simplified by noting that for the converged solution we have $\Delta\varepsilon_{ij}^{r} = 3\lambda(s_{ij}^{I+1} - s_{ij}^{B})$. Then,

$$\underbrace{\left[\delta_{ik}\delta_{jl} - \frac{9\left(s_{ij}^{I+1} - s_{ij}^{B}\right)\left(s_{kl}^{I+1} - s_{kl}^{B}\right)}{6\sigma_{0}^{2}} + 6\lambda\mu\delta_{ik}\delta_{jl} + 3\lambda H_{ijkl}\right]}_{A_{ijkl}^{-1}}d\varepsilon_{kl}^{r} = 6\mu\lambda de_{ij}$$

So, $d\varepsilon_{ij}^{r} = 6\mu\lambda A_{ijkl}de_{kl}$

and $d\sigma_{ij} = (\lambda_{e} + \frac{2}{3}\mu)\delta_{ij}d\varepsilon_{kk} + 2\mu(\delta_{ik}\delta_{jl} - 6\mu\lambda A_{ijkl})de_{kl}$

This, finally, gives the tangent moduli for the finite element method. Note that this entire derivation has assumed that the material point is in the process of changing its remanent strain. So, prior to going through all of this work at a given integration point you first assume that $\Delta\varepsilon_{ij}^{r} = 0$, compute the new stress state based on this assumption and the new strain state, and then check to see if this stress state violates the switching criterion. If the switching criterion is satisfied then the point has simply deformed elastically and this solution is accepted and the tangent moduli are just the linear elastic moduli, but if the criterion is violated then the point is changing its remanent strain and we proceed through this constitutive integration step.

Application of this Theoretical Structure to Ferroelectricity

In and of itself, ferroelasticity is not a particularly "smart" behavior. However, we have gone through this exercise because you are all most familiar with mechanical fields and so the terms are easier for you to understand. But if you are able to understand all of this then the application to ferroelectric behavior is not really all that much more complicated. Let's return to the second law to take a look at what we have to do for ferroelectricity.

$$\sigma_{ij}\dot{\varepsilon}_{ij} + E_i\dot{D}_i - \dot{\psi} \geq 0$$

In other words the dissipation rate must be non-negative. Now let's assume a free energy of the form,

$$\psi = \psi(\varepsilon_{ij}, D_i, \varepsilon^r_{ij}, P^r_{ij})$$

So we have our standard strain and electric displacement configurational variables, and additionally the remanent strain and remanent polarization as internal variables. Then the dissipation inequality becomes,

$$\left(\sigma_{ij} - \frac{\partial\psi}{\partial\varepsilon_{ij}}\right)\dot{\varepsilon}_{ij} + \left(E_i - \frac{\partial\psi}{\partial D_i}\right)\dot{D}_i - \frac{\partial\psi}{\partial\varepsilon^r_{ij}}\dot{\varepsilon}^r_{ij} - \frac{\partial\psi}{\partial P^r_i}\dot{P}^r_i \geq 0$$

By standard arguments we will take $\sigma_{ij} = \dfrac{\partial\psi}{\partial\varepsilon_{ij}}$ and $E_i = \dfrac{\partial\psi}{\partial D_i}$ to aid in the construction of the free energy functional. We will assume,

$$\psi = \tfrac{1}{2}c^D_{ijkl}(\varepsilon_{ij} - \varepsilon^r_{ij})(\varepsilon_{kl} - \varepsilon^r_{kl}) - h_{kij}(D_k - P^r_k)(\varepsilon_{ij} - \varepsilon^r_{ij}) + \tfrac{1}{2}\beta^\varepsilon_{ij}(D_i - P^r_i)(D_j - P^r_j) + \psi^r(\varepsilon^r_{ij}, P^r_i)$$

This yields the linear piezoelectric relationships for the stress and electric field as,

$$\sigma_{ij} = c^D_{ijkl}(\varepsilon_{kl} - \varepsilon^r_{kl}) - h_{kij}(D_k - P^r_k)$$

$$E_i = -h_{ikl}(\varepsilon_{kl} - \varepsilon^r_{kl}) + \beta^\varepsilon_{ij}(D_j - P^r_j)$$

With this form of the free energy the second law inequality now becomes,

$$\left[\sigma_{ij} - \frac{\partial\psi^r}{\partial\varepsilon^r_{ij}} - \frac{1}{2}\frac{\partial c^D_{mnpq}}{\partial\varepsilon^r_{ij}}(\varepsilon_{mn} - \varepsilon^r_{mn})(\varepsilon_{pq} - \varepsilon^r_{pq}) + \frac{\partial h_{mpq}}{\partial\varepsilon^r_{ij}}(D_m - P^r_m)(\varepsilon_{pq} - \varepsilon^r_{pq}) - \frac{1}{2}\frac{\partial\beta^\varepsilon_{mn}}{\partial\varepsilon^r_{ij}}(D_m - P^r_m)(D_n - P^r_n)\right]\dot{\varepsilon}^r_{ij} +$$
$$\left[E_i - \frac{\partial\psi^r}{\partial P^r_i} - \frac{1}{2}\frac{\partial c^D_{mnpq}}{\partial P^r_i}(\varepsilon_{mn} - \varepsilon^r_{mn})(\varepsilon_{pq} - \varepsilon^r_{pq}) + \frac{\partial h_{mpq}}{\partial P^r_i}(D_m - P^r_m)(\varepsilon_{pq} - \varepsilon^r_{pq}) - \frac{1}{2}\frac{\partial\beta^\varepsilon_{mn}}{\partial P^r_i}(D_m - P^r_m)(D_n - P^r_n)\right]\dot{P}^r_i \geq 0$$

This equation identifies the driving forces, which are "dissipation conjugate" to the internal variables. Unfortunately there is a mixture of stresses, strains, electric fields, and electric displacements in these driving forces. We would prefer to have these driving forces simply in terms of the stresses and electric fields. One approach for doing this would be to invert the linear piezoelectricity relationships and solve for $(\varepsilon_{ij} - \varepsilon^r_{ij})$ and $(D_i - P^r_i)$ in terms of σ_{ij} and E_i, but there is another method. Consider the stored part of the Helmholtz free energy and a Legendre transformation to obtain the stored part of the Gibbs free energy.

$$\psi^s = \tfrac{1}{2} c^D_{ijkl}(\varepsilon_{ij} - \varepsilon^r_{ij})(\varepsilon_{kl} - \varepsilon^r_{kl}) - h_{kij}(D_k - P^r_k)(\varepsilon_{ij} - \varepsilon^r_{ij}) + \tfrac{1}{2}\beta^\varepsilon_{ij}(D_i - P^r_i)(D_j - P^r_j)$$

$$g^s = \psi^s - \sigma_{ij}(\varepsilon_{ij} - \varepsilon^r_{ij}) - E_i(D_i - P^r_i)$$

The Legnedre transformation gives us $\dfrac{\partial g^s}{\partial \sigma_{ij}} = -\left(\varepsilon_{ij} - \varepsilon^r_{ij}\right)$ and $\dfrac{\partial g^s}{\partial E_i} = -\left(D_i - P^r_i\right)$.

Therfore we have,

$$g^s = -\tfrac{1}{2} s^E_{ijkl}\sigma_{ij}\sigma_{kl} - d_{kij}E_k\sigma_{ij} - \tfrac{1}{2}\kappa^\sigma_{ij}E_iE_j$$

Next, consider

$$\frac{\partial \psi^s}{\partial \varepsilon^r_{ij}} = -\sigma_{ij} + \frac{1}{2}\frac{\partial c^D_{mnpq}}{\partial \varepsilon^r_{ij}}(\varepsilon_{mn} - \varepsilon^r_{mn})(\varepsilon_{pq} - \varepsilon^r_{pq}) - \frac{\partial h_{mpq}}{\partial \varepsilon^r_{ij}}(D_m - P^r_m)(\varepsilon_{pq} - \varepsilon^r_{pq}) + \frac{1}{2}\frac{\partial \beta^\varepsilon_{mn}}{\partial \varepsilon^r_{ij}}(D_m - P^r_m)(D_n - P^r_n)$$

$$\frac{\partial \psi^s}{\partial P^r_i} = -E_i + \frac{1}{2}\frac{\partial c^D_{mnpq}}{\partial P^r_i}(\varepsilon_{mn} - \varepsilon^r_{mn})(\varepsilon_{pq} - \varepsilon^r_{pq}) - \frac{\partial h_{mpq}}{\partial P^r_i}(D_m - P^r_m)(\varepsilon_{pq} - \varepsilon^r_{pq}) + \frac{1}{2}\frac{\partial \beta^\varepsilon_{mn}}{\partial P^r_i}(D_m - P^r_m)(D_n - P^r_n)$$

and

$$\begin{aligned}\frac{\partial g^s}{\partial \varepsilon^r_{ij}} &= -\frac{1}{2}\frac{\partial s^E_{mnpq}}{\partial \varepsilon^r_{ij}}\sigma_{mn}\sigma_{pq} - \frac{\partial d_{mpq}}{\partial \varepsilon^r_{ij}}E_m\sigma_{pq} - \tfrac{1}{2}\frac{\partial \kappa^\sigma_{mn}}{\partial \varepsilon^r_{ij}}E_mE_n \\ &= \frac{\partial \psi^s}{\partial \varepsilon^r_{ij}} + \sigma_{ij}\end{aligned}$$

$$\frac{\partial g^s}{\partial P^r_i} = -\frac{1}{2}\frac{\partial s^E_{mnpq}}{\partial P^r_i}\sigma_{mn}\sigma_{pq} - \frac{\partial d_{mpq}}{\partial P^r_i}E_m\sigma_{pq} - \frac{1}{2}\frac{\partial \kappa^\sigma_{mn}}{\partial P^r_i}E_m E_n$$
$$= \frac{\partial \psi^s}{\partial P^r_i} + E_i$$

These sets of equations imply that,

$$\frac{1}{2}\frac{\partial c^D_{mnpq}}{\partial \varepsilon^r_{ij}}(\varepsilon_{mn}-\varepsilon^r_{mn})(\varepsilon_{pq}-\varepsilon^r_{pq}) - \frac{\partial h_{mpq}}{\partial \varepsilon^r_{ij}}(D_m - P^r_m)(\varepsilon_{pq}-\varepsilon^r_{pq}) + \frac{1}{2}\frac{\partial \beta^\varepsilon_{mn}}{\partial \varepsilon^r_{ij}}(D_m-P^r_m)(D_n-P^r_n)$$
$$= -\frac{1}{2}\frac{\partial s^E_{mnpq}}{\partial \varepsilon^r_{ij}}\sigma_{mn}\sigma_{pq} - \frac{\partial d_{mpq}}{\partial \varepsilon^r_{ij}}E_m\sigma_{pq} - \frac{1}{2}\frac{\partial \kappa^\sigma_{mn}}{\partial \varepsilon^r_{ij}}E_m E_n \equiv -\overline{\sigma}_{ij}$$

and

$$\frac{1}{2}\frac{\partial c^D_{mnpq}}{\partial P^r_i}(\varepsilon_{mn}-\varepsilon^r_{mn})(\varepsilon_{pq}-\varepsilon^r_{pq}) - \frac{\partial h_{mpq}}{\partial P^r_i}(D_m - P^r_m)(\varepsilon_{pq}-\varepsilon^r_{pq}) + \frac{1}{2}\frac{\partial \beta^\varepsilon_{mn}}{\partial P^r_i}(D_m-P^r_m)(D_n-P^r_n)$$
$$= -\frac{1}{2}\frac{\partial s^E_{mnpq}}{\partial P^r_i}\sigma_{mn}\sigma_{pq} - \frac{\partial d_{mpq}}{\partial P^r_i}E_m\sigma_{pq} - \frac{1}{2}\frac{\partial \kappa^\sigma_{mn}}{\partial P^r_i}E_m E_n \equiv -\overline{E}_i$$

These new definitions of stress-like and electric field-like variables allow for a compact form of the dissipation inequality as,

$$\underbrace{(\sigma_{ij} - \sigma^B_{ij} + \overline{\sigma}_{ij})}_{\hat{\sigma}_{ij}}\dot{\varepsilon}^r_{ij} + \underbrace{(E_i - E^B_i + \overline{E}_i)}_{\hat{E}_i}\dot{P}^r_i \geq 0$$

Where the back stress and back electric field are $\sigma^B_{ij} = \dfrac{\partial \psi^r}{\partial \varepsilon^r_{ij}}$ and $E^B_i = \dfrac{\partial \psi^r}{\partial P^r_i}$. Finally, if we assume that the postulate of maximum dissipation holds then we will have a convex switching surface in driving force space,

$$\Phi(\hat{\sigma}_{ij}, \hat{E}_i, \varepsilon^r_{ij}, P^r_i) \leq 0$$

and an associated flow rule for the remanent increments,

$$\dot{\varepsilon}^r_{ij} = \lambda\frac{\partial \Phi}{\partial \hat{\sigma}_{ij}} \quad \text{and} \quad \dot{P}^r_i = \lambda\frac{\partial \Phi}{\partial \hat{E}_i}.$$

Macro Single Crystal Constitutive Laws

Our previous descriptions of material behavior were based on a "material point" that consisted of several grains. If we go down in scale, or if we consider very large single crystals (with lengths in the centimeter range), then we might consider or "material point" to be within a given crystal but comprised of several domains. In such a case we need to decide on what to use as internal variables. Again, a fully detailed continuum description would require us to know the locations of each of the domain walls. We will get to a theoretical framework that does study these materials at this level, but here we want something a bit more macroscopic. One natural set of internal variables to describe our many-domain material point includes the volume concentrations of each domain variant. In this case, our Helmholtz free energy looks like,

$$\psi = \psi(\varepsilon_{ij}, D_i, c^I)\,,$$

where the c^I are the volume concentrations of each of the domain variants. For a tetragonal material there will be 6 variants and so I will range from 1 to 6. Let's take a look at how this fits into the second law.

$$\sigma_{ij}\dot{\varepsilon}_{ij} + E_i\dot{D}_i - \dot{\psi} \geq 0$$

$$\sigma_{ji}\dot{\varepsilon}_{ij} + E_i\dot{D}_i - \frac{\partial\psi}{\partial\varepsilon_{ij}}\dot{\varepsilon}_{ij} - \frac{\partial\psi}{\partial D_i}\dot{D}_i - \sum_I \frac{\partial\psi}{\partial c^I}\dot{c}^I \geq 0$$

Again, there are several different arguments used for the analysis of this inequality, for our purposes we will take the easy way out and simply claim that this inequality is satisfied if,

$$\sigma_{ji} = \frac{\partial\psi}{\partial\varepsilon_{ij}}, \quad E_i = \frac{\partial\psi}{\partial D_i}, \quad \text{and} \quad -\sum_I \frac{\partial\psi}{\partial c^I}\dot{c}^I \geq 0$$

Next, let's determine how we will be describing the reversible behavior of the material. In other words, for a fixed set of c^I how does the material respond? We will assume standard linear piezoelectric response about a fixed remanent state. Before we do this, it will eventually become useful to look at the Gibbs free energy instead of the Helmholtz free energy. The Gibbs free energy is defined through the Legendre transformation, $g = \psi - \sigma_{ij}\varepsilon_{ij} - E_iD_i$. This transformation allows us to see that the Gibbs free energy is a functional of the stress, electric field, and variant concentrations, $g = g(\sigma_{ij}, E_i, c^I)$. In terms of the Gibbs free energy, the second law and the constitutive relations look like,

$$-\dot{\sigma}_{ij}\varepsilon_{ij} - \dot{E}_i D_i - \frac{\partial g}{\partial \sigma_{ij}}\dot{\sigma}_{ji} - \frac{\partial g}{\partial E_i}\dot{E}_i - \sum_I \frac{\partial g}{\partial c^I}\dot{c}^I \geq 0$$

$$\varepsilon_{ij} = -\frac{\partial g}{\partial \sigma_{ij}}, \quad D_i = -\frac{\partial g}{\partial E_i}, \text{ and } \quad -\sum_I \frac{\partial g}{\partial c^I}\dot{c}^I \geq 0$$

We now return to our description of the linear response about a fixed remanent state. The strain and electric displacement are assumed to have the form,

$$\varepsilon_{ij} = s^E_{ijkl}\sigma_{kl} + d_{kij}E_k + \varepsilon^r_{ij}$$

$$D_i = d_{ikl}\sigma_{kl} + \kappa^\sigma_{ij}E_j + P^r_i$$

These equations suggest the following form for the Gibbs free energy.

$$g = -\tfrac{1}{2}s^E_{ijkl}\sigma_{ij}\sigma_{kl} - d_{kij}E_k\sigma_{ij} - \tfrac{1}{2}\kappa^\sigma_{ij}E_iE_j - \sigma_{ij}\varepsilon^r_{ij} - E_iP^r_i + g^r(c^I)$$

Note that the "remanent" part of the Gibbs free energy will be equal to the "remanent" part of the Helmholtz free energy. The next question that we need to address is, how do the quantities s^E_{ijkl}, d_{kij}, κ^σ_{ij}, ε^r_{ij}, and P^r_i each depend on the c^I? In order to answer this question in a rigorous way, we would need to know the actual configuration of the domains and the domain walls. Since we have resigned ourselves to not do this, we will have to resort to some approximation. The simplest approximation to use is to assume that the stress and electric field states in the "material point" are homogeneous. This assumption satisfies mechanical equilibrium and the continuity requirements on the electric field, but in general it will violate kinematic compatibility and Gauss' law across domain walls. Other assumptions or more rigorous analyses can be performed assuming specific domain structures, but for our purposes we will use the uniform stress and electric field assumption. Under this assumption each of the s^E_{ijkl}, d_{kij}, κ^σ_{ij}, ε^r_{ij}, and P^r_i are simply the volume averages at the point in questions, i.e.

$$s^E_{ijkl} = \sum_I c^I s^I_{ijkl}, \quad d_{kij} = \sum_I c^I d^I_{kij}, \quad \kappa^\sigma_{ij} = \sum_I c^I \kappa^I_{ij}, \quad \varepsilon^r_{ij} = \sum_I c^I \varepsilon^I_{ij}, \text{ and } \quad P^r_i = \sum_I c^I P^I_i$$

Each of the quantities with a superscript I represents the constant value of the property within a mono-domain of that variant type. For a tetragonal crystal, if we know the properties of one mono-domain type, then the properties of each of the other variants are simply 90° or 180° tensor rotations of the originals.

Now, with these relationships we can write our Gibbs free energy in terms of only the stress, electric field, and variant concentrations. Prior to attempting to analyze the dissipation inequality associated with the second law, it is useful to attempt to

incorporate the mechanisms for domain switching into the model. To do this we recognize that switching occurs by transforming one variant type into another. If we account for forward and backward transformations separately, then there will be $I(I-1)$ different transformation types possible. We will say that each one of these transformations occurs along a specific "transformation system", and we will label these transformation systems as $\alpha = 1 \ldots I(I-1)$. Assuming that a given transformation system is active, then we will call the rate of transformation along that system $\dot{f}^{\alpha}$. In order to relate these transformation rates to the rates of change of the variant concentrations we need to introduce the connectivity matrix $A^{I\alpha}$ such that,

$$\dot{c}^{I} = \sum_{\alpha} A^{I\alpha} \dot{f}^{\alpha}$$

$$\text{where } A^{I\alpha} = \begin{cases} 1 & \text{if system } \alpha \text{ feeds into variant } I \\ -1 & \text{if system } \alpha \text{ depletes variant } I \\ 0 & \text{if system } \alpha \text{ does not affect variant } I \end{cases}$$

Now we can look at the dissipation inequality.

$$-\sum_{I} \frac{\partial g}{\partial c^{I}} \dot{c}^{I} = \sum_{\alpha} \underbrace{\left(-\sum_{I} \frac{\partial g}{\partial c^{I}} A^{I\alpha} \right)}_{G^{\alpha}} \dot{f}^{\alpha} = \sum_{\alpha} G^{\alpha} \dot{f}^{\alpha} \geq 0$$

This equation has helped us to define the driving forces G^{α} that are work/dissipation conjugate to the transformation rates. We can now specifically analyze each of the G^{α} as,

$$G^{\alpha} = \sigma_{ij} \Delta \varepsilon^{\alpha}_{ij} + E_i \Delta P^{\alpha}_{i} + \tfrac{1}{2} \Delta s^{\alpha}_{ijkl} \sigma_{ij} \sigma_{kl} + \Delta d^{\alpha}_{kij} E_k \sigma_{ij} + \tfrac{1}{2} \Delta \kappa^{\alpha}_{ij} E_i E_j + \sum_{I} \frac{\partial g^{r}}{\partial c^{I}} A^{I\alpha} \,,$$

where the $\Delta property^{\alpha}$ is the value of the property for the variant that system α transforms to, minus the value of the property for the variant that system α transforms from.

In class we discussed what these driving forces looked like for both the 90° and 180° transformation types. I will not go through those descriptions again here. In order to complete the constitutive description we still need some kinetic law relating the transformation rates. First, we can note that since we are already accounting for forward and reverse transformations separately we can, and in fact should, constrain $\dot{f}^{\alpha} \geq 0$. The dissipation inequality then implies that a given transformation system can only be active if $G^{\alpha} \geq 0$. From here there are two commonly used forms for a kinetic law, a simple power law,

$$\dot{f}^\alpha = \dot{f}_0^\alpha \left(\frac{G^\alpha}{G_0^\alpha} \right)^m$$

or an "overstress" power law,

$$\dot{f}^\alpha = \begin{cases} 0 & \text{if } G^\alpha < G_0^\alpha \\ \dot{f}_0^\alpha \left(\dfrac{G^\alpha - G_0^\alpha}{G_0^\alpha} \right)^m & \text{if } G^\alpha \geq G_0^\alpha \end{cases}$$

The overstress power law gives a distinct rate-independent linear piezoelectric response. Note that we did not discuss the remanent part of the potential in great detail. Again, this term will be responsible for kinematic hardening within the model, and it is intended to, in some qualitative way, account for the residual stresses and electric fields that we have "swept under the rug" by assuming uniform stresses and electric fields within our material point.

A Model for Domain Structure Evolution

In our previous macroscopic models we described our "material point" as a collection of grains, or a collection of domains, always keeping in the back of our minds that in order to truly compute all of the fields we are interested in we need to know the locations of every domain wall. One reason why we devised the prior models is because tracking the positions of every domain wall in a volume of significant size can quickly become an intractable problem. But let's say that we are now interested in interactions and domain structure evolution at a much smaller scale. Let's devise a *continuum* theory to model such situations.

In our prior theories we always resorted to a linear piezoelectric response about some remanent state of the material. If we are interested in describing the structure of the domain walls themselves then our theory must allow for significant departures from the states that can be described using linear piezoelectricity. Specifically, we need a description of the free energy that includes the energy minima associated with the different variant types, along with the energy barriers separating these minima. For ferroelectric materials and "internal variable" or "order parameter" that can be used to describe this "energy landscape" is the polarization vector. For a tetragonal material at least part of the free energy can be represented as,

$$\begin{aligned}\psi = &\ldots + \frac{a_1}{2}(P_x^2 + P_y^2 + P_z^2) + \frac{a_2}{4}(P_x^4 + P_y^4 + P_z^4) + \frac{a_3}{2}(P_x^2P_y^2 + P_x^2P_z^2 + P_y^2P_z^2) + \ldots \\ &-\frac{b_1}{2}(\varepsilon_{xx}P_x^2 + \varepsilon_{yy}P_y^2 + \varepsilon_{zz}P_z^2) - \frac{b_2}{2}[\varepsilon_{xx}(P_y^2 + P_z^2) + \varepsilon_{yy}(P_x^2 + P_z^2) + \varepsilon_{zz}(P_y^2 + P_x^2)] \\ &-b_3[(\varepsilon_{xy} + \varepsilon_{yx})P_xP_y + (\varepsilon_{xz} + \varepsilon_{zx})P_xP_z + (\varepsilon_{yz} + \varepsilon_{zy})P_zP_y] + \ldots \\ &+\frac{c_1}{2}(\varepsilon_{xx}^2 + \varepsilon_{yy}^2 + \varepsilon_{zz}^2) + c_2(\varepsilon_{xx}\varepsilon_{yy} + \varepsilon_{zz}\varepsilon_{yy} + \varepsilon_{xx}\varepsilon_{zz}) + \frac{c_3}{2}(\varepsilon_{xy}^2 + \varepsilon_{yx}^2 + \varepsilon_{xz}^2 + \varepsilon_{zx}^2 + \varepsilon_{yz}^2 + \varepsilon_{zy}^2) + \ldots \\ &+\frac{1}{2\kappa_0}(D_i - P_i)(D_i - P_i)\end{aligned}$$

The … are meant to represent terms that we have not included yet, or terms that can be included to yield a more refined description of the energy landscape. Briefly, the first line can be used to represent the distinct energy minima associated with the different polarization variants. The second and third lines include "electrostriction-like" terms in that they couple the strain and the "square" of the polarization. Note, however, that if these terms are linearized about one of the energy minima, then they account for linear piezoelectricity. The fourth line includes elastic terms that, as shown, can only describe cubic elastic properties, so additional terms are needed to obtain tetragonal properties. Finally, the last line will ultimately yield the relationship between the electric field, electric displacement, and material polarization, $D_i = \kappa_0 E_i + P_i$.

Within this theory we will still be solving the standard small deformation equations for mechanics and electrostatics. Let's list these equations here.

$$\sigma_{ji,j} + b_i = \rho \ddot{u}_i \text{ in } V, \quad \sigma_{ji} = \sigma_{ij} \text{ in } V, \quad \sigma_{ji} n_j = t_i \text{ on } S$$

$$\varepsilon_{ij} = \tfrac{1}{2}(u_{i,j} + u_{j,i})$$

$$D_{i,i} = q \text{ in } V, \; D_i n_i = -\omega \text{ on } S$$

$$E_i = -\phi_{,i}$$

$$D_i = \kappa_0 E_i + P_i$$

Now, if we attempt to solve these equations with the non-convex free energy given above (assuming constitutive relationships can be derived in a consistent manner), then what results are states of the material "near" the minimum separated by zero-thickness, zero-energy boundaries. These are the domain walls, and across such a wall the gradients of the polarization will be singular. In order to give the domain walls thickness, and more importantly energy, we can penalize such sharp gradients of polarization by including a term in the free energy of the form,

$$\begin{aligned}\psi_{exchange} = {} & \tfrac{1}{2} a_0 (P_{x,x}^2 + P_{y,y}^2 + P_{z,z}^2) + \tfrac{1}{2} \overline{a}_0 (P_{x,y}^2 + P_{x,z}^2 + P_{y,x}^2 + P_{y,z}^2 + P_{z,x}^2 + P_{z,y}^2) \\ & + \tilde{a}_0 (P_{x,x} P_{y,y} + P_{x,x} P_{z,z} + P_{z,z} P_{y,y}) + \hat{a}_0 (P_{x,y} P_{y,x} + P_{x,z} P_{z,x} + P_{z,y} P_{y,z})\end{aligned} .$$

In general we will simplify this considerably, using $\overline{a}_0 = a_0$ and $\tilde{a}_0 = \hat{a}_0 = 0$. With this term in the free energy, singular polarization gradients imply an infinite energy density. To reduce the "exchange" energy of the system the transition between polarization states will "smooth out" at the expense of additional strain and electrical energy within the wall.

We have not yet addressed the fact that we have added an independent variable in the free energy, but we have not included a work conjugate force that is able to drive changes in this variable. To address this, we introduce a micro-force tensor ξ_{ji} such that $g_i \dot{P}_i$ represents a power density expended across surfaces by neighboring configurations, an *internal* micro-force vector π_i such that $\pi_i \dot{P}_i$ is the power density expended by the material internally, e.g. in the ordering of atoms within unit cells of the lattice (this force will account for dissipation in the material), and an external micro-force vector γ_i such that $\gamma_i \dot{P}_i$ is a power density expended on the material by external sources. Then, the integral balance of this set of configurational forces leads to the differential balance law

$$\int_S g_i\, dS + \int_V \pi_i\, dV + \int_V \gamma_i\, dV = 0 \,\text{in}\quad V$$

We will assume that there is a micro-force balance at the surface of the form, $g_i = \xi_{ji} n_j$, where the tensor ξ_{ji} is representative of the material reaction to the surface micro-forces. Then, the integral micro-force balance can be shown to reduce to the point-wise form,

$$\xi_{ji,j} + \pi_i + \gamma_i = 0$$

Now that we have defined our micro-forces and how they do work, we can go on to analyze the second law.

$$\int_V \dot{\psi}\, dV + \tfrac{d}{dt}\int_V \tfrac{1}{2}\rho \dot{u}_i \dot{u}_i\, dV \le \int_V \Big(b_i \dot{u}_i + \phi\dot{q} + \gamma_i \dot{P}_i\Big) dV + \int_S \Big(t_i \dot{u}_i + \phi\dot{\omega} + \xi_{ji} n_j \dot{P}_i\Big) dS$$

As always, the left hand side represents the rate of stored plus kinetic energy in the material and the right hand side represents the power expended by *external* sources on the body. Note that the internal force π_i does not contribute to this external power term. We now analyze this equation using the divergence theorem where applicable and the balance laws to cancel terms to get for an arbitrary volume,

$$\left(\sigma_{ji} - \frac{\partial\psi}{\partial\varepsilon_{ij}}\right)\dot{\varepsilon}_{ij} + \left(E_i - \frac{\partial\psi}{\partial D_i}\right)\dot{D}_i - \left(\pi_i + \frac{\partial\psi}{\partial P_i}\right)\dot{P}_i + \left(\xi_{ji} - \frac{\partial\psi}{\partial P_{i,j}}\right)\dot{P}_{i,j} + \frac{\partial\psi}{\partial\dot{P}_i}\ddot{P}_i \ge 0$$

Note that we have assumed that the stress, electric field, micro-force tensor, and internal micro-force each are allowed to depend on ε_{ij}, D_i, P_i, $P_{i,j}$ and $\dot{P}_i$. The question can be raised as to why the free energy must be allowed to depend on $\dot{P}_i$. The answer being that since the internal micro-force π_i is allowed to depend on $\dot{P}_i$, then all of the thermodynamic forces must also potentially have such dependence. This is the principle of *equi-presence*. It will be shown that the second law inequality ultimately allows only π_i to depend on $\dot{P}_i$. Following Coleman and Noll (1963), it is assumed that for a given thermodynamic state, arbitrary levels of ε_{ij}, D_i, P_i, $P_{i,j}$ and $\dot{P}_i$ are permissible through the appropriate control of the external sources b_i, q, and γ_i. Then, given that our inequality must hold for all permissible processes, and the last term is the only one linear in $\ddot{P}_i$, we must have,

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

otherwise there will always be some value of $\ddot{P}_i$ that can be selected to violate the inequality. Next, the first second and fourth terms are linear in $\dot{\varepsilon}_{ij}$, $\dot{D}_i$, and $\dot{P}_{i,j}$, and hence we must have,

$$\sigma_{ji} = \frac{\partial \psi}{\partial \varepsilon_{ij}},\ E_i = \frac{\partial \psi}{\partial D_i}, \text{ and } \xi_{ji} = \frac{\partial \psi}{\partial P_{i,j}}$$

otherwise we could always find some set of $\dot{\varepsilon}_{ij}$, $\dot{D}_i$, and $\dot{P}_{i,j}$ to violate the inequality. Finally, after defining $\eta_i \equiv \dfrac{\partial \psi}{\partial P_i}$, the internal micro-force π_i must satisfy

$$\left(\pi_i + \eta_i\right)\dot{P}_i \leq 0 \ \Rightarrow\ \pi_i = -\eta_i - \beta_{ij}\dot{P}_j \ \text{ with } \ \beta_{ij}=\beta_{ij}\left(\varepsilon_{kl}, D_k, P_k, P_{k,l}, \dot{P}_k\right) \text{ positive definite}$$

If we place the constitutive relationships back into our balance laws, we obtain the following governing equations for our independent variables.

$$\left(\frac{\partial \psi}{\partial \varepsilon_{ij}}\right)_{,j} + b_i = \rho \ddot{u}_i \ \text{ in } V, \quad \frac{\partial \psi}{\partial \varepsilon_{ij}} n_j = t_i \ \text{ on } S$$

$$\frac{\partial \psi}{\partial D_i} = -\phi_i \ \text{ everywhere}$$

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

We can also obtain the rate independent form of these equations using the minimization of the potential energy. We define the potential energy as a functional of the displacement field, the charges, and the polarization field. The strain field is then derived from the displacements from the linear kinematics equations, and the electric displacements are related to (but cannot be derived from) the charges through Gauss' law. The potential energy is written as,

$$PE = \int_V \psi \, dV - \int_V b_i u_i + \phi q + \gamma_i P_i \, dV - \int_S t_i u_i + \phi \omega + g_i P_i \, dS$$

Note that we have explicitly included the potential energy of the micro-forces here. If it is argued that such forces do not exist, then these quantities can simply be set to zero. The minimization of the potential energy then proceeds as follows.

$$
\begin{aligned}
\delta PE &= \int_V \delta\psi \, dV - \int_V b_i \, \delta u_i + \phi \, \delta q + \gamma_i \delta P_i \, dV - \int_S t_i \, \delta u_i + \phi \delta\omega + g_i \delta P_i \, dS \\
&= \int_V \frac{\partial \psi}{\partial \varepsilon_{ij}} \delta \varepsilon_{ij} + \frac{\partial \psi}{\partial D_i} \delta D_i + \frac{\partial \psi}{\partial P_i} \delta P_i + \frac{\partial \psi}{\partial P_{i,j}} \delta P_{i,j} + \frac{\partial \psi}{\partial \dot{P}_i} \delta \dot{P}_i \, dV \\
&\quad - \int_V b_i \, \delta u_i + \phi \, \delta D_{i,i} + \gamma_i \delta P_i \, dV - \int_S t_i \, \delta u_i - \phi \delta D_i n_i + g_i \delta P_i \, dS \\
&= \int_V \left(\frac{\partial \psi}{\partial \varepsilon_{ij}} \delta u_i \right)_{,j} - \left(\frac{\partial \psi}{\partial \varepsilon_{ij}} \right)_{,j} \delta u_i + \frac{\partial \psi}{\partial D_i} \delta D_i + \frac{\partial \psi}{\partial P_i} \delta P_i + \left(\frac{\partial \psi}{\partial P_{i,j}} \delta P_i \right)_{,j} - \left(\frac{\partial \psi}{\partial P_{i,j}} \right)_{,j} \delta P_i + \frac{\partial \psi}{\partial \dot{P}_i} \delta \dot{P}_i \, dV \\
&\quad - \int_V b_i \, \delta u_i + \left(\phi \delta D_i \right)_{,i} - \phi_{,i} \delta D_i + \gamma_i \delta P_i \, dV - \int_S t_i \, \delta u_i - \phi \delta D_i n_i + g_i \delta P_i \, dS \\
&= \int_S \frac{\partial \psi}{\partial \varepsilon_{ij}} n_j \, \delta u_i + \frac{\partial \psi}{\partial P_{i,j}} n_j \delta P_i \, dS + \int_V - \left(\frac{\partial \psi}{\partial \varepsilon_{ij}} \right)_{,j} \delta u_i + \frac{\partial \psi}{\partial D_i} \delta D_i + \frac{\partial \psi}{\partial P_i} \delta P_i - \left(\frac{\partial \psi}{\partial P_{i,j}} \right)_{,j} \delta P_i + \frac{\partial \psi}{\partial \dot{P}_i} \delta \dot{P}_i \, dV \\
&\quad - \int_V b_i \, \delta u_i - \phi_{,i} \delta D_i + \gamma_i \delta P_i \, dV - \int_S t_i \, \delta u_i + \phi n_i \delta D_i - \phi \delta D_i n_i + g_i \delta P_i \, dS \\
&= 0
\end{aligned}
$$

This equation must hold for arbitrary variation in the volume and on the surface, and this then implies that the following equations must hold,

$$
\delta u_i \rightarrow \quad \left(\frac{\partial \psi}{\partial \varepsilon_{ij}} \right)_{,j} + b_i = 0 \ \text{ in } V, \quad \text{and} \quad \frac{\partial \psi}{\partial \varepsilon_{ij}} n_j = t_i \ \text{ on } S
$$

$$
\delta D_i \rightarrow \quad \frac{\partial \psi}{\partial D_i} = -\phi_{,i}
$$

$$
\delta P_i \rightarrow \quad \left(\frac{\partial \psi}{\partial P_{i,j}} \right)_{,j} - \frac{\partial \psi}{\partial P_i} + \gamma_i = 0 \ \text{ in } V, \quad \frac{\partial \psi}{\partial P_{i,j}} n_j = g_i \ \text{ on } S
$$

$$
\delta \dot{P}_i \rightarrow \quad \frac{\partial \psi}{\partial \dot{P}_i} = 0
$$

Note that these equations are a result of the minimization of the potential energy and thus are equations that must hold in equilibrium. In order to account for dissipation arguments can be made that the internal variables are allowed to evolve towards equilibrium. We will not get into these arguments here, but we will note that the minimization of the potential energy approach yields the same generalized equilibrium equations as the balance law approach, but without the need to ever introduce the concepts of the material stress, electric field or material micro-forces.

In any case, we now have the governing equations of our theory in hand, so let's now investigate perhaps the most fundamental type of solution for this theory; the domain wall. Let's consider solutions for initially straight domain walls in the y-z plane moving at constant velocity v in the x-direction. The polarization and any applied electric fields

will exist in the x-y plane, i.e. $P_z = 0$ and $E_z = 0$, and generalized plane strain is assumed, i.e. $\varepsilon_{xz} = \varepsilon_{yz} = 0$ and ε_{zz} is uniform. Transforming to a coordinate system that is moving along with the domain wall at constant velocity v, symmetry considerations dictate that the solutions for stresses, strains, electric fields, electric displacements, polarizations and micro-forces are functions of x only. Given these constraints, let's look at the conditions imposed by strain compatibility.

$$\frac{\partial \varepsilon_{xx}}{\partial y} = \frac{\partial^2 u}{\partial x \partial y} = 0 \rightarrow u = f_1(x) + g_1(y)$$

$$\frac{\partial \varepsilon_{yy}}{\partial y} = \frac{\partial^2 v}{\partial y^2} = 0 \rightarrow v = f_2(x) y + g_2(x)$$

$$\begin{aligned}\frac{\partial \varepsilon_{xy}}{\partial y} = \frac{1}{2}\left(\frac{\partial^2 v}{\partial x \partial y} + \frac{\partial^2 u}{\partial y^2}\right) = 0 &\rightarrow f_2'(x) + g_1''(y) = 0 \\ &\rightarrow -g_1''(y) = f_2'(x) = c_0 \\ &\rightarrow g_1(y) = -\tfrac{1}{2} c_0 y^2 + c_1 y + c_2 \\ &\quad f_2(x) = c_0 x + c_3\end{aligned}$$

So, let's see what all of this implies for the strains.

$$\varepsilon_{xx} = \frac{\partial u}{\partial x} = f_1'(x)$$

This says that ε_{xx} is still and arbitrary function of x.

$$2\varepsilon_{xy} = \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} = -c_0 y + c_1 + c_0 y + g_2'(x) = c_1 + g_2'(x)$$

This says that ε_{xy} is still and arbitrary function of x. However, if we look at the rotation,

$$2\omega_{xy} = \frac{\partial u}{\partial y} - \frac{\partial v}{\partial x} = -c_0 y + c_1 - c_0 y - g_2'(x) = -2c_0 y + c_1 - g_2'(x)$$

If we also claim that the rotation must also only be a function of x, then the coefficient $c_0 = 0$. This condition implies that we are not bending the specimen such that the domain wall becomes curved. Finally, the ε_{yy} component of the strain is,

$$\varepsilon_{yy} = \frac{\partial v}{\partial y} = f_2(x) = c_0 x + c_3$$

Again, imposing the no wall bending constraint, this equation simplifies to the claim that the ε_{yy} component of the strain is constant. In this case we will rewrite this condition as,

$$\varepsilon_{yy} = \varepsilon^0_{yy}$$

Next, let's look at the electrostatic equations. With no free charge q, Maxwell's laws governing the quasi-static electric displacement and the electric field distributions imply that,

$$\frac{dD_x}{dx} + \cancel{\frac{dD_x}{dx}} = 0 \quad \Rightarrow \quad D_x = D^0_x$$

$$\frac{dE_y}{dx} - \cancel{\frac{dE_x}{dy}} = 0 \quad \Rightarrow \quad E_y = E^0_y$$

The parameters ε^0_{yy}, D^0_x and E^0_y are the constant axial strain, electric displacement and electric field in the associated directions.

Next, let's look at the mechanical momentum balances. With the fact that $\varepsilon_{xx} = \varepsilon_{xx}(x)$ and hence $u_{x,yx} = \varepsilon_{xx,y} = 0$, the momentum balances imply,

$$\frac{d}{dx}\left(\sigma_{xx} - \rho v^2 \varepsilon_{xx}\right) = 0 \quad \Rightarrow \quad \sigma_{xx} = \rho v^2 \varepsilon_{xx} + \sigma^0_{xx}$$

$$\frac{d}{dx}\left(\sigma_{xy} - 2\rho v^2 \varepsilon_{xy}\right) = 0 \quad \Rightarrow \quad \sigma_{xy} = 2\rho v^2 \varepsilon_{xy} + \sigma^0_{xy}$$

where σ^0_{xx} and σ^0_{xy} are constants. Finally, the micro-force balances from Equations (2.16) become

$$\frac{d\xi_{xx}}{dx} - \eta_x = -v\beta_{xx}\frac{dP_x}{dx} - v\beta_{xy}\frac{dP_y}{dx}$$

$$\frac{d\xi_{xy}}{dx} - \eta_y = -v\beta_{yx}\frac{dP_x}{dx} - v\beta_{yy}\frac{dP_y}{dx}$$

The solutions to these equations are subject to the boundary conditions $\sigma_{xx}\left(\infty\right) = \sigma^+_{xx}$, $\sigma_{xx}\left(-\infty\right) = \sigma^-_{xx}$, $\sigma_{xy}\left(\infty\right) = \sigma^+_{xy}$, $\sigma_{xy}\left(-\infty\right) = \sigma^-_{xy}$, $D_x\left(\infty\right) = D^0_x$, $D_x\left(-\infty\right) = D^0_x$, $\eta_x\left(\infty\right) = 0$, $\eta_x\left(-\infty\right) = 0$, $\eta_y\left(\infty\right) = 0$, and $\eta_y\left(-\infty\right) = 0$. Along with these boundary conditions the governing equations can be solved for the electromechanical structure of a planar domain wall moving at constant velocity. Prior to trying to solve these equations for a

specific material free energy, let's first derive an expression for the Eshelby driving force on a domain wall.

Sharp interface theories of domain wall dynamics require a kinetic law that describes the normal velocity of points along the interface. Such kinetic laws usually relate the normal velocity to the jump in the Eshelby tensor across the wall. The following derivation provides this relationship based on this diffuse interface theory. First, multiply the associated balance equations by $-E_x$, ε_{xx}, $2\varepsilon_{xy}$, $P_{x,x}$ and $P_{y,x}$ respectively. Then, defining the electrical enthalpy h as $h = \psi - E_i D_i$, the sum of these equations can be rearranged as follows,

$$\frac{d}{dx}\left(\xi_{xx}P_{x,x} + \xi_{xy}P_{y,x} + \sigma_{xx}\varepsilon_{xx} - \frac{1}{2}\rho v^2\varepsilon_{xx}^2 + 2\sigma_{xy}\varepsilon_{xy} - 2\rho v^2\varepsilon_{xy}^2 - E_x D_x - h\right)$$
$$= -v\left[\beta_{xx}P_{x,x}^2 + \left(\beta_{xy} + \beta_{yx}\right)P_{y,x}P_{x,x} + \beta_{yy}P_{y,x}^2\right]$$

After defining $\left[\!\left[a\right]\!\right] = a\left(\infty\right) - a\left(-\infty\right)$ and $\left\langle a\right\rangle = \left[a\left(\infty\right) + a\left(-\infty\right)\right]\big/2$, and applying the identity $\left[\!\left[ab\right]\!\right] = \left\langle a\right\rangle\left[\!\left[b\right]\!\right] + \left\langle b\right\rangle\left[\!\left[a\right]\!\right]$, the integral of Equation (3.8) from $x = -\infty$ to $x = \infty$ can be shown to yield

$$f \equiv \left[\!\left[h\right]\!\right] - \left\langle\sigma_{xx}\right\rangle\left[\!\left[\varepsilon_{xx}\right]\!\right] - 2\left\langle\sigma_{xy}\right\rangle\left[\!\left[\varepsilon_{xy}\right]\!\right] + \left\langle D_x\right\rangle\left[\!\left[E_x\right]\!\right] = \frac{1}{\mu}v$$

where the Eshelby driving traction f is defined within this equation and the domain wall mobility μ is defined as

$$\frac{1}{\mu} = \int_{-\infty}^{\infty}\left[\beta_{xx}P_{x,x}^2 + \left(\beta_{xy} + \beta_{yx}\right)P_{x,x}P_{y,x} + \beta_{yy}P_{y,x}^2\right]dx$$

The left-hand side of the equation is the jump in Eshelby's energy-momentum tensor across a flat planar domain wall moving in the x-direction.

Let's now return to the explicit solution of the governing equations for a 180° domain wall. The 180° domain wall simplifies the picture considerably because symmetry considerations for the case where there is zero far field loading indicates that $P_x = \varepsilon_{xy} = 0$. This also implies that $\sigma_{xy} = \sigma_{xy}^0 = 0$. Expanding the free energy into the terms that are needed we have,

$$\psi = \tfrac{1}{2}a_0 P_{y,x}^2 + \frac{a_1}{2}P_y^2 + \frac{a_2}{4}P_y^4 - \frac{b_1}{2}\varepsilon_{yy}P_y^2 - \frac{b_2}{2}(\varepsilon_{xx} + \varepsilon_{zz})P_y^2 + \frac{1}{2\kappa_0}(D_i - P_i)(D_i - P_i)$$
$$+ \frac{c_1}{2}(\varepsilon_{xx}^2 + \varepsilon_{yy}^2 + \varepsilon_{zz}^2) + c_2(\varepsilon_{xx}\varepsilon_{yy} + \varepsilon_{zz}\varepsilon_{yy} + \varepsilon_{xx}\varepsilon_{zz})$$

Furthermore, let's look at the case where the domain wall is stationary, giving us $v = 0$. Our governing equations become,

$$E_x = \frac{\partial \psi}{\partial D_x} = \frac{1}{\kappa_0} D_x^0$$

$$E_y = E_y^0 = \frac{\partial \psi}{\partial D_y} = \frac{1}{\kappa_0}(D_y - P_y)$$

$$\sigma_{xx} = \sigma_{xx}^0 = \frac{\partial \psi}{\partial \varepsilon_{xx}} = c_1 \varepsilon_{xx} + c_2(\varepsilon_{yy}^0 + \varepsilon_{zz}^0) - \frac{b_2}{2} P_y^2$$

$$\sigma_{yy} = \frac{\partial \psi}{\partial \varepsilon_{yy}} = c_1 \varepsilon_{yy}^0 + c_2(\varepsilon_{xx} + \varepsilon_{zz}^0) - \frac{b_1}{2} P_y^2$$

$$\sigma_{zz} = \frac{\partial \psi}{\partial \varepsilon_{zz}} = c_1 \varepsilon_{zz}^0 + c_2(\varepsilon_{xx} + \varepsilon_{yy}^0) - \frac{b_2}{2} P_y^2$$

$$\frac{d\xi_{xy}}{dx} - \eta_y = \frac{d}{dx}\left(\frac{\partial \psi}{\partial P_{y,x}}\right) - \frac{\partial \psi}{\partial P_y} = a_0 \frac{d^2 P_y}{dx^2} - a_1 P_y - a_2 P_y^3 + b_1 \varepsilon_{yy}^0 P_y + b_2(\varepsilon_{xx} + \varepsilon_{zz}^0) P_y + \frac{1}{\kappa_0}(D_y - P_y) = 0$$

First, let's consider the far field boundary conditions that we are interested in. Let's not consider any cases with electric field applied in the x-direction, therefore, $E_x = D_x = 0$. Next, we are looking for solutions where there is no far-field loading and gradients of the polarization vanish. The zero far-field loading condition allows us to solve for the ε_{xx} strain component in terms of the y-polarization.

$$\varepsilon_{xx} = -\frac{c_2}{c_1}(\varepsilon_{yy}^0 + \varepsilon_{zz}^0) + \frac{b_2}{2c_1} P_y^2$$

Then, the other two fixed strain components follow from conditions far from the domain wall,

$$c_1 \varepsilon_{yy}^0 + c_2(\varepsilon_{xx} + \varepsilon_{zz}^0) - \frac{b_1}{2} P_y^2 = 0 \quad \text{and} \quad c_1 \varepsilon_{zz}^0 + c_2(\varepsilon_{xx} + \varepsilon_{yy}^0) - \frac{b_2}{2} P_y^2 = 0$$

$$\rightarrow \quad \varepsilon_{yy}^0 = \frac{1}{2} \frac{\overline{c}_1 \overline{b}_1 - \overline{c}_2 \overline{b}_2}{\overline{c}_1^2 - \overline{c}_2^2} P_y^2 \quad \text{and} \quad \varepsilon_{zz}^0 = \frac{1}{2} \frac{\overline{c}_1 \overline{b}_2 - \overline{c}_2 \overline{b}_1}{\overline{c}_1^2 - \overline{c}_2^2} P_y^2$$

where $\overline{c}_1 = \dfrac{c_1^2 - c_2^2}{c_1}$, $\overline{c}_2 = \dfrac{c_2 c_1 - c_2^2}{c_1}$, $\overline{b}_1 = \dfrac{b_1 c_1 - b_2 c_2}{c_1}$, $\overline{b}_2 = \dfrac{b_2 c_1 - b_2 c_2}{c_1}$.

Finally, with $E_y = \frac{1}{\kappa_0}(D_y - P_y) = 0$, the micro-force balance far from the domain wall can be written as,

$$-a_1 P_y - \overline{a}_2 P_y^3 = 0$$

where $\overline{a}_2 = a_2 - \frac{1}{2}\left(2b_2 \frac{\overline{c}_1\overline{b}_2 - \overline{c}_2\overline{b}_1}{\overline{c}_1^2 - \overline{c}_2^2} + b_1 \frac{\overline{c}_1\overline{b}_1 - \overline{c}_2\overline{b}_2}{\overline{c}_1^2 - \overline{c}_2^2}\right)$.

The solutions for P_y to this equation are,

$$P_y = 0, \quad P_y = \pm\sqrt{-\frac{a_1}{\overline{a}_2}} \equiv \pm P_0 .$$

In order for the free energy to increase as the magnitude of the polarization gets very large under stress and electric field-free conditions we must have $\overline{a}_2 \geq 0$. Then, if $a_1 > 0$ the second set of roots is imaginary and the only real root is at $P_y = 0$, which will be a stable state if $a_1 > 0$. However, this is not a material that has a non-convex energy with multiple stable equilibria, and so there is no domain wall solution. The more interesting case is when $a_1 < 0$. In this case, the $P_y = 0$ state is unstable and there are two stable states at $P_y = \pm\sqrt{-(a_1 / \overline{a}_2)}$. For the solution to the governing equations we will force our functions to approach these values as $x \to \pm\infty$. Our micro-force balance equation is written as,

$$a_0 \frac{d^2 P_y}{dx^2} - \overline{a}_1 P_y - \overline{\overline{a}}_2 P_y^3 = 0$$

where $\overline{a}_1 = a_1 - \overline{b}_1 \varepsilon^0_{yy} - \overline{b}_2 \varepsilon^0_{zz}$ and $\overline{\overline{a}}_2 = a_2 - \frac{b_2^2}{2c_1}$

Using, $\frac{1}{2}\frac{d}{dP_y}\left(\frac{dP_y}{dx}\right)^2 = \frac{1}{2}2\frac{dP_y}{dx}\frac{d}{dP_y}\left(\frac{dP_y}{dx}\right) = \frac{dP_y}{dx}\frac{dx}{dP_y}\frac{d}{dx}\left(\frac{dP_y}{dx}\right) = \frac{d^2 P_y}{dx^2}$, we can re-write this equation as,

$$\frac{d}{dP_y}\left[\frac{a_0}{2}\left(\frac{dP_y}{dx}\right)^2 - \frac{\overline{a}_1}{2}P_y^2 - \frac{\overline{\overline{a}}_2}{4}P_y^4\right] = 0$$

Integrate this equation from $P_y = P_0$ to some arbitrary P_y value to get,

$$\int_{P_0}^{P_y} \frac{d}{dP'_y}\left[\frac{a_0}{2}\left(\frac{dP'_y}{dx}\right)^2 - \frac{\overline{a}_1}{2}P'^2_y - \frac{\overline{\overline{a}}_2}{4}P'^4_y\right] dP'_y = 0$$

$$\rightarrow \frac{a_0}{2}\left(\frac{dP_y}{dx}\right)^2 - \frac{\overline{a}_1}{2}P_y^2 - \frac{\overline{\overline{a}}_2}{4}P_y^4 - \frac{\overline{a}_1^2}{4\overline{\overline{a}}_2} = -\frac{\overline{a}_1}{2}P_0^2 - \frac{\overline{\overline{a}}_2}{4}P_0^4 - \frac{\overline{a}_1^2}{4\overline{\overline{a}}_2} = 0$$

Note that it can be shown algebraically that $\frac{a_1^2}{4\overline{a}_2} = \frac{\overline{a}_1^2}{4\overline{\overline{a}}_2}$. This equation can now be integrated as,

$$\int_0^{P_y} \frac{\sqrt{2a_0}dP'_y}{\sqrt{\overline{\overline{a}}_2}\sqrt{\left(P'^2_y - P_0^2\right)^2}} = \int_0^{P_y} \frac{\sqrt{2a_0}dP'_y}{\sqrt{\overline{\overline{a}}_2}\left(P'^2_y - P_0^2\right)} = \int_0^x dx'$$

$$\rightarrow x = -\frac{\sqrt{2a_0}}{P_0\sqrt{\overline{\overline{a}}_2}}\operatorname{arctanh}\left(\frac{P_y}{P_0}\right)$$

$$\rightarrow P_y = P_0 \tanh\left(-\sqrt{\frac{\overline{\overline{a}}_2 P_0^2}{2a_0}}x\right) = P_0 \tanh\left(-x/l_0\right)$$

This solution is called a "kink" solution. Notice that the domain wall length scale is defined as

$$l_0 = \sqrt{\frac{2a_0}{\overline{\overline{a}}_2 P_0^2}}$$

Also, the energy per unit area of the wall can be computed from,

$$\gamma_{wall} = \int_{-\infty}^{\infty} [\psi(P_y) - \psi(P_0)]\, dx$$
$$= \frac{2}{3}\overline{\overline{a}}_2 P_0^4 l_0$$

For this solution, half of the energy is due to the gradient term and the remaining half is due to the strain and polarization energy within the wall.

There are a couple of points to note about this solution. First, we *arbitrarily* placed the position where the polarization is zero at $x = 0$. We could have chosen this position to be anywhere we like and the kink solution simply shifts by that amount. The calculated energy of the domain wall will not be changed by such a shift. This implies that the domain wall solution is on a "flat energy landscape" and any energetic force on the wall, not matter how small, will cause it to move. The reason why domain walls do not

always move so easily is due to effects like lattice friction (a very small material resistance to defect motion) and interactions with defects like charges and dislocation (the defects act to "pin" the domain walls). The second feature is the material length scale associated with the domain wall and the energetic competition that makes this length scale finite. The elastic and polarization components of the wall surface energy will decrease if the wall thins because the volume of the wall will decrease (linearly) and the magnitude of this contribution does not depend on the wall thickness, hence the overall contribution is inversely proportional to the wall thickness. However, the polarization gradient contribution to the surface energy will increase as the wall thins because this term is inversely proportional to the square of the wall thickness and so as the wall thins the overall contribution is proportional to the wall thickness.

A similar, but slightly more complicated solution can be constructed for a 90° domain wall, however complete analytical solutions are not attainable. For the 90° wall the charge compatibility conditions require an x-component of the electric field to arise, which requires us to solve a second non-linear ODE for the electric potential. When there are two unknown fields the steps that we took to construct the kink solution are no longer valid and numerical methods (or perturbation solutions) are required.

Maxwell Stresses

In this last brief section we will take a look at the derivation of Maxwell stresses in free space and then at the modeling of dielectric elastomers where the identification of Maxwell stresses is ambiguous and entirely unnecessary. First, let's look at free space where there is no ambiguity. Consider the following energy balance in free space.

$$\frac{d}{dt}\int_V \tfrac{1}{2}\kappa_0 E_i E_i \, dV = \int_V b_i v_i \, dV + \int_S t_i v_i \, dS + \int_V \phi \frac{d}{dt}(q \, dV) + \int_S \phi \frac{d}{dt}(\omega \, dS)$$

At this point a few comments are of use. First, there are two non-standard representations that need to be clearly defined, $\frac{d}{dt}(qdV)$ and $\frac{d}{dt}(\omega dS)$. We also note some notation on time derivatives, the material time derivative is $\frac{d}{dt} \equiv \left.\frac{\partial}{\partial t}\right|_{X_I}$, i.e. the time rate of change at a fixed material point located at coordinates X_I in the reference configuration. We will also use an overdot $(\dot{})$ to represent the material time derivative. Then, when we write $\frac{\partial}{\partial t}$, it will be assumed to represent $\frac{\partial}{\partial t} \equiv \left.\frac{\partial}{\partial t}\right|_{x_i}$, which is the time rate of change at a fixed spatial point located at coordinates x_i in the current configuration. We note that the material time derivative can be written in terms of the spatial time derivative as, $\frac{d}{dt} = \left.\frac{\partial}{\partial t}\right|_{x_i} + \frac{\partial}{\partial x_i}\frac{\partial x_i}{\partial t} = \frac{\partial}{\partial t} + v_i \frac{\partial}{\partial x_i}$. Next, two continuum mechanics results for rates of change of volume and surface elements can be applied.

$$\frac{d}{dt}(dV) = v_{i,i} dV \quad \text{and} \quad \frac{d}{dt}(n_i dS) = (v_{k,k} n_i - v_{k,i} n_k) dS$$

These two results then allow us to consistently define what we mean by $\frac{d}{dt}(qdV)$ and $\frac{d}{dt}(\omega dS)$. Now we can analyze or energy balance.

$$\begin{aligned}&\int_V \kappa_0 E_i \dot{E}_i + \tfrac{1}{2}\kappa_0 E_i E_i v_{k,k} \, dV \\ &= \int_V b_i v_i \, dV + \int_S \sigma_{ji} n_j v_i \, dS + \int_V \phi(\dot{q} + q v_{k,k}) dV + \int_S \phi(-\dot{D}_i n_i - D_i n_i v_{k,k} + D_i n_k v_{k,i}) dS\end{aligned}$$

$$
\begin{aligned}
&\int_V \kappa_0 E_i \dot{E}_i + \tfrac{1}{2}\kappa_0 E_i E_i v_{k,k}\, dV \\
&= \int_V (b_i + \sigma_{ji,j}) v_i + \sigma_{ji} v_{i,j}\, dV \\
&\quad + \int_V \phi[\dot{q} + (\cancel{q - D_{i,i}}) v_{k,k} - \cancel{D_i v_{k,ki}} + D_{i,k} v_{k,i} + \cancel{D_i v_{k,ik}})\, dV \\
&\quad + \int_V \phi_{,i}(-D_i v_{k,k} + D_k v_{i,k})\, dV \\
&\quad - \int_S \phi(\frac{\partial D_i}{\partial t} + v_k D_{i,k}) n_i\, dS
\end{aligned}
$$

Using the constitutive law for free space, $D_i = \kappa_0 E_i$ and assuming that the stress and body force satisfy equilibrium we have:

$$
\begin{aligned}
&\int_V \cancel{\kappa_0 E_i \dot{E}_i} + \tfrac{1}{2}\kappa_0 E_i E_i v_{k,k}\, dV \\
&= \int_V (\cancel{b_i + \sigma_{ji,j}}) v_i + \sigma_{ji} v_{i,j}\, dV \\
&\quad + \int_V \phi[\cancel{\dot{q}} + \cancel{D_{i,k} v_{k,i}})\, dV \\
&\quad + \int_V \phi_{,i}(-D_i v_{k,k} + D_k v_{i,k})\, dV \\
&\quad - \int_V \cancel{\phi_{,i}(\underbrace{\frac{\partial D_i}{\partial t} + v_k D_{i,k}}_{\dot{D}_i})} + \cancel{\phi(\underbrace{\frac{\partial D_{i,i}}{\partial t} + v_k D_{i,ki}}_{\dot{D}_{i,i}} + \cancel{v_{k,i} D_{i,k}})}\, dV
\end{aligned}
$$

$$
\int_V (\sigma_{ji} - \kappa_0 E_i E_j + \tfrac{1}{2}\kappa_0 E_k E_k \delta_{ij}) v_{i,j}\, dV = 0
$$

Hence, the stress, or what is usually called the Maxwell stress in free space is,

$$
\sigma_{ji} = \kappa_0 E_i E_j - \tfrac{1}{2}\kappa_0 E_k E_k \delta_{ij}
$$

Now, let's consider the force required to maintain equilibrium of a region of space. To derive this relationship we will use several facts. First, in free space $\kappa_0 E_{i,i} = D_{i,i} = q$ and $\kappa_0 \left[\!\left[E_i \right]\!\right] n_i = \left[\!\left[D_i \right]\!\right] n_i = -\omega$. We also know that the tangential components of the electric field are continuous across and surface, which then implies that the jump of the electric field can be written as $\left[\!\left[E_i \right]\!\right] = \left[\!\left[E^n \right]\!\right] n_i$ where $E^n = E_i n_i$ is the normal component of the electric field.

$$
\begin{aligned}
F_i &= \int_V b_i \, dV + \int_S t_i \, dS \\
&= \int_V -\sigma_{ji,j} \, dV + \int_S \left[\!\left[\sigma_{ji} \right]\!\right] n_j \, dS \\
&= \int_V -(\kappa_0 E_i E_j - \tfrac{1}{2}\kappa_0 E_k E_k \delta_{ij})_{,j} \, dV + \int_S \left[\!\left[\kappa_0 E_i E_j - \tfrac{1}{2}\kappa_0 E_k E_k \delta_{ij} \right]\!\right] n_j \, dS \\
&= \int_V \cancel{-\kappa_0 E_{i,j} E_j} - \kappa_0 E_i E_{j,j} \cancel{+\kappa_0 E_k E_{k,i}} \, dV \\
&\quad + \int_S \kappa_0 \left\{ \left\langle E_i \right\rangle \left[\!\left[E_j \right]\!\right] + \left\langle E_j \right\rangle \left[\!\left[E_i \right]\!\right] - \tfrac{1}{2}\delta_{ij} \left(2 \left\langle E_k \right\rangle \left[\!\left[E_k \right]\!\right] \right) \right\} n_j \, dS \\
&= \int_V -\kappa_0 E_i E_{j,j} \, dV + \int_S \kappa_0 \left\{ \left\langle E_i \right\rangle \left[\!\left[E_j \right]\!\right] n_j + \cancel{\left\langle E_j \right\rangle n_j \left[\!\left[E^n \right]\!\right] n_i} - \cancel{n_i \left\langle E_k \right\rangle \left[\!\left[E^n \right]\!\right] n_k} \right\} dS \\
&= \int_V -E_i q \, dV - \int_S \left\langle E_i \right\rangle \omega \, dS
\end{aligned}
$$

This result should be pleasing as it states that the net force on a region is the sum of the electric field times the body charge throughout the volume and the surface charges times the average electric field across the surface along all surfaces with free charge.

