**Free Energy Functional**

Thermodynamics follows the minimization of energy. Every system in nature will tend towards the lowest possible energy. A rock falls, when dropped because a lower altitude has a lower gravitational potential energy. In our case, we formulate the free energy of our ferroelectric sample in terms of several fundamental energies. The total free energy functional is:

The integral is over the entire volume of our sample system. The terms inside the integral are energy densities, with units of J/m-3, giving the total free energy units of J.

is the Landau free energy. The Landau constants are measured under the stress free condition.

is the gradient energy, which accounts for the energy of domain walls and the inhomogeneous spatial distribution of polarization, which is given by:

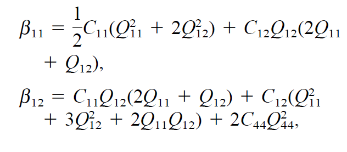
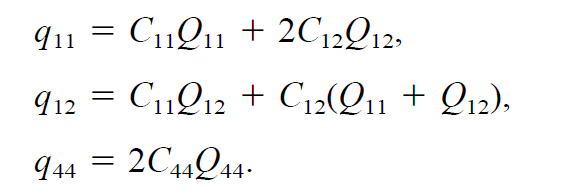
Isotropic gradient energy:

is the elastic energy, where is the stress free transformation strain or eigenstrain.

The stress free eigenstrains are:

Physically, the elastic strain energy comes from Eshelby’s theory of inclusions. The elastic strain is the total strain subtracted by the stress free heterogeneous strain . The elastic energy is then simply the multiplication of the elastic stress with the elastic strain . The elastic strain energy will be discussed in depth later.

Expansion of the Landau and elastic free energy leads to:



The strain solution satisfying boundary conditions and mechanical equilibrium () can be placed within the free energy functional. To solve the mechanical equilibrium equation, we separate the total strain into a sum of the homogenous and heterogeneous strains:

Substituting the strain back into the free energy functional, becomes:

The total free energy becomes:

is the electrical energy due to the depolarization field. The depolarization field is the electric field generated by the multiple polarization dipoles within the sample and by any uncompensated surface charges. This energy is given by:

The depolarization field is found by solving the electrical equilibrium equation, where :

An in-depth discussion of the electrical energy will be provided later.

The energy due to an externally applied electric field is: