Multi-domain ferroelectricity treated in an elementary analytical manner

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We are interested in making simple models of multi-domain ferroelectric behavior mainly for STO/Si but perhaps with other systems too. The models are continuum ones. We have a film of a ferroelectric that is d thick along the z direction and of infinite extent in the x-y plane. The polarization will only point along the z direction, and furthermore the polarization is uniform for fixed (x, y) when going along z: the multi-domain structures have polarizations taking only only two values $\pm P$ and the domain walls are sharp. We consider structures only made of up/down domains laid out in some periodic lattice, each domain being of extent a or equivalently the lattice constant in the xy plane is a. We may or may not have electrodes around the film.

1 Hartree (electrostatic) energy

The first order of business is to figure out the electrostatic energy of the multi-domain structure. We will go about this in a step-by-step fashion. The basic point is that our assumptions say that the only charges present are the surface polarization charges which are either P or $-P$ and are laid out periodically on a flat plane at constant z.

1.1 A single periodic neutral sheet

Consider one such plane at $z = 0$. Its volume charge density is given by

$$\rho(x, y, z) = \delta(z)\sigma(x, y) \quad , \quad \sigma(x, y) = P \sum_g \hat{u}(g) e^{ig\cdot r}$$

where $g = (g_x, g_y)$ are the reciprocal lattice vectors in the xy plane, $r = (x, y)$, and we have written the fourier series for the surface charge density σ by explicitly pulling out the overall scale factor P and leaving the detailed lattice structure to the dimensionless function $\hat{u}(g)$. Since we have a multi-domain periodic lattice, there are many up as down domains and thus the sheet density σ is overall neutral:

$$\int dx\, dy\, \sigma(x,y) = 0 \quad \rightarrow \quad \hat{u}(0) = 0\,.$$

The solution to the Poisson equation $\nabla^2\phi = -4\pi\rho$ going to zero for $z \rightarrow \pm\infty$ for this ρ is

$$\phi(x,y,z) = P\sum_{g\neq 0} \frac{2\pi\hat{u}(g)e^{ig\cdot r-|g||z|}}{|g|}\,.$$

This can proved in many ways but the most elementary is: you can plug it in, it works and by uniqueness it is the answer. Basically, the potential (and thus the electric field) dies of exponentially away from the sheet. The length scale of the decay is the lattice constant or domain size a since $|g| \sim 1/a$.

The Hartree energy for this assembly per unit area is

$$E_H^{(1)} = \frac{1}{A}\int_{-\infty}^{\infty} dz \int_{u.c.} dx\, dy\, \frac{\vec{E}^2}{8\pi} = \frac{1}{2A}\int_{-\infty}^{\infty} dz \int_{u.c.} dx\, dy\, \rho\phi = \pi P^2 \sum_{g\neq 0}\frac{|\hat{u}(g)|^2}{|g|}$$

where u.c. is a unit cell and A is the area of the unit cell in the xy plane. This is simply the energy to assemble this arrangement of charges. Since $|g| \sim 1/a$ and $\hat{u}(g)$ is unitless, the result must scale as

$$E_H^{(1)} \sim \pi P^2 a\,.$$

This is easy to understand: the electric field right above the surface of the sheet is of strength $2\pi P$ and decays away over a length scale a going away from the sheet. So $|\vec{E}|^2/8\pi \sim P^2$ and we are integrating it over an extent of size a along z.

1.2 Ferroelectric with no electrodes

The next case is the more physical one of the surface polarization charges of the ferroelectric itself. The sheet at $z = 0$ has surface density $\sigma(x,y)$ while the other sheet at d must have surface density $-\sigma(x,y)$ since the polarization pattern is opposite on that surface. Obviously, no electrodes are present.

For reference, the generalization of our above key results for potential and energy to a system of N periodic sheets at positions z_j with sheet densities $\sigma_j(x,y)$ (all neutral) are

$$\phi(x,y,z) = 2\pi Pa\sum_{g\neq 0}\frac{e^{ig\cdot r}}{a|g|}\sum_{j=1}^{N}\hat{u}_j(g)e^{-|g||z-z_j|}$$

and

$$E_H^{(N)} = \pi P^2 a \sum_{g\neq 0} \frac{1}{a|g|} \sum_{j,k=1}^{N} \hat{u}_j(g)^* \hat{u}_k(g) \exp(-|g||z_j - z_k|) \, .$$

For $N = 2$ with $z_1 = 0$, $z_2 = d$, $\hat{u}_1 = -\hat{u}_2 \equiv \hat{u}$ the energy is

$$E_H^{(2)} = 2\pi P^2 a \sum_{g\neq 0} \frac{|\hat{u}(g)|^2}{a|g|} \left(1 - e^{-|g|d}\right) \, .$$

Without knowing the actual lattice structure and thus $\hat{u}(g)$, one can't do the sum. But one can get pretty far without the details! Let us define the following dimensionless function $f(x)$ to be the sum in question

$$f(d/a) \equiv \sum_{g\neq 0} \frac{|\hat{u}(g)|^2}{a|g|} e^{-|g|d} \, .$$

We have written the argument as d/a since the only place that d appears is in the exponent $|g|d$ and $|g| = 2\pi/a \times \sqrt{\text{integer}}$. The function $\hat{u}(g)$ tells us the details of how charges are arranged in a primitive cell and can't depend on a itself — i.e., it is some dimensionless function of the two dimensionless integers indexing g.

The energy can be therefore written as

$$E_H^{(2)} = 2\pi P^2 a \left[f(0) - f(d/a)\right] \, .$$

We can say a few general things about $f(x)$: since $g \neq 0$ in the sum defining f and there is a minimal length to the $|g|$ which we can call h/a (for some dimensionless constant h of order unity), we conclude that for large argument d/a we must have

$$f(d/a \gg 1) \sim \exp(-hd/a)$$

which just says it gets exponentially small. Therefore, for large sheet separations $d \gg a$, we just have to separate sheets with their own energies because the fields from the sheets die off quickly between the sheets: the sheets don't interact. Comparing to the single sheet result, it is indeed true that

$$E_H^{(2)}(d/a \gg 1) = 2E_H^{(1)}$$

where, again,

$$E_H^{(1)} = \pi P^2 a f(0) \sim \pi P^2 a \, .$$

The opposite limit of $d \ll a$ is even more instructive: here the sheets are very close, so close that over most of a domain it looks like parallel plates separated by d with uniform surface charge densities $\pm P$. Therefore, the energy must become the standard one

$$E_H^{(2)}(d/a \ll 1) \to 2\pi P^2 d \, .$$

So we conclude immediately that

$$f'(0) = -1 \, .$$

The structure of $f(x)$ is rather simple due to the exponential damping $e^{-|g|d}$ in its definition: as d/a increases, $f(d/a)$ drops. Its slope is finite an negative at the origin (-1), and it falls off exponentially in d/a for increasing d/a. The very simplest example of what $f(x)$ could be is just $\exp(-x)$. However, $f(0)$ has no reason to exactly equal to unity so maybe a more reasonable from is $\exp(-hx)/h$.

At any rate, the final summary is that $E_H^{(2)}$ is a monotonically increasing function of a for fixed d. It starts at 0 at $a = 0$ with finite slope $2\pi P^2 f(0)$ and increases to asymptote to $2\pi P^2 d$ for $a \gg d$. An possible approximate form would be $2\pi P^2 a[1 - \exp(-hd/a)]/h$ for some $f(0) = 1/h \sim 1$. $h = f(0)$ is a definite choice and for stripe domains actually gives a reasonable approximation to $f(x)$.

1.3 Ferroelectric with electrodes on both sides

We will model this as four sheets of charge: two from the ferroelectric surface polarization charges (just as above) and two from the screening charges in the metallic electrodes below and above the film. In general, one should solve some type of screening equation to find the charge distribution in the electrode. We will make the simplest possible assumption: the screening charge can be represented as a sheet of charge λ away from the ferroelectric surface. Physically, $\lambda \ll a$ is probably the regime of main interest since the electrode screening distance is likely a microscopic quantity that is smaller than the domain size, or put another way, the domain size must be larger than the microscopic lengths to make the entire continuum approach valid!

If one puts all the screening charge at a fixed distance on a plane, the condition to determine the screening charge is that the electrostatic potential is flat beyond that surface going into the electrode. To see what this does, let's warm up with one given sheet at $z = 0$ with surface charge $\sigma(x, y)$ and a screening charge at $z = \lambda$ with charge $\sigma_s(x, y)$. Looking back at the potential ϕ coming from $N = 2$ sheets above, we want

$$\phi(x, y, z) = 2\pi P a \sum_{g\neq 0} \frac{e^{ig\cdot r}}{a|g|} \left(\hat{u}(g) e^{-|g||z|} + \hat{u}_s(g) e^{-|g||z-\lambda|}\right) = 0 \quad \forall x, y \text{ and } z > \lambda\,.$$

This enforces

$$\hat{u}_s(g) = -\hat{u}(g) e^{-|g|\lambda}\,.$$

So the corrugations in the screening charge get attenuated in strength as the distance from the surface is larger, as expected. Also $|g|\lambda \sim \lambda/a$ so for $\lambda/a \ll 1$, the screening charge is basically the opposite of the surface charge. The more advanced version is to put the two ferroelectric surface charges $\hat{u}(g)$ at $z = 0$ and $-\hat{u}(g)$ at $z = d$ and to solve for the screening charges $\hat{u}_s(g)$ at $z = -\lambda$ and $-\hat{u}_s(g)$ at $z = d + \lambda$ that enforce $\phi = 0$ for $z > d + \lambda$ an $z < -\lambda$. By reflection symmetry the two screening charges are equal ans opposite. This is a straightforward exercise in writing out the sum of the four sheet charges and enforcing the condition we want. We find the more complex looking

$$u_s(g) = -\hat{u}(g)\frac{e^{|g|d}-1}{e^{|g|d+|g|\lambda}-e^{-|g|\lambda}} \equiv -\hat{u}(g)k_s(g)\,.$$

As a check, for large d or for large $|g|$ we get the previous result of a single sheet plus screening charge. This is a very messy expression but for $\lambda \ll a$ so $|g|\lambda \ll 1$ we series expand in $|g|\lambda$ to get

$$\hat{u}_s(g) = -\hat{u}(g)\cdot\left(1-\frac{e^{|g|d}+1}{e^{|g|d}-1}|g|\lambda+(|g|\lambda)^2\right)\,.$$

Again, for $\lambda \ll a$, the screening charges are basically exactly the opposite of the ferroelectric surface charges facing them.

With these preliminaries and assumptions, we can now model the screened ferroelectric. We put these four sheets into our multi-sheet energy formula for $N = 4$ and get a complex expression

$$E_H^{(4)} = \pi P^2 a\left[2f(0)+2s_2(0)-4s_1(\lambda/a)-2f(d/a)+4s_1(d/a+\lambda/a)-2s_2(d/a+2\lambda/a)\right]$$

where we have defined the new sum functions

$$s_n(x) = \sum_{g\neq 0}\frac{|\hat{u}(g)|^2}{a|g|}k_s(g)^n e^{-a|g|x}\,.$$

One can't make too much progress with all of this. But if we are interested in the limit $\lambda/a \ll 1$ so we can series expand the $s_n(x)$ since we know the series expansion of k_s:

$$s_n(x) = f(x) + n(\lambda/a)t(x) + O(\lambda/a)^2$$

where

$$t(x) = -\sum_{g\neq 0}\frac{|\hat{u}(g)|^2}{a|g|}\frac{e^{|g|d}+1}{e^{|g|d}-1}e^{-a|g|x}\,.$$

We will only use the fact that $t(0)$ is finite and that $t(x)$ has a series expansion in x.

If you plug this expansion for $s_n(x)$ into our energy and series expand, it becomes

$$E_H^{(4)} = \pi P^2 a\Big[4f(0)-4f(\lambda/a)-2f(d/a)+4f(d/a+\lambda/a)-2f(d/a+2\lambda/a)+C\cdot(\lambda/a)^2\Big]$$

where we note that the linear coefficient in λ/a is zero. The quadratic coefficient C is a dimensionless function of d/a that has a limited range of variation between two numbers of order unity. Thus we can safely ignore that term. The rest of this is just what one would expect from interacting sheets placed at their various separations. For example, for $d/a \gg 1$ we get two separate pairs of sheets and the energy becomes $4\pi P^2 a(f(0)-f(\lambda/a))$ as expected. We can actually further series expand this in λ/a to get

$$E_H^{(4)} = 4\pi P^2\lambda\cdot\Big[1-[2f''(0)+2f''(d/a)-C](\lambda/a)+O(\lambda/a)^2\Big]\,.$$

Basically, in this $\lambda/a \ll 1$ limit, the Hartree energy hardly depends on a as the screening gets rid of all the straying fields: we just have the fields between each ferroelectric surface and its screening companion. This is true for all values of d/a that are not too small.

It is much harder to look at the $\lambda \sim a$ cases and/or simultaneously have $d/a \ll 1$. What we can do is set some bounds. To do this, we start with the screening factor $k_s(g)$

$$k_s(g) = \frac{e^{|g|d} - 1}{e^{|g|d+|g|\lambda} - e^{-|g|\lambda}} .$$

Since $e^{|g|d} \geq 1$ and $e^{|g|\lambda} \geq 1$, it is straightforward to put the bound

$$e^{-|g|\lambda}(1 - e^{-|g|d}) \leq k_s(g) \leq e^{-|g|\lambda} .$$

This then leads to the two bounds

$$f(x + \lambda/a) - f(x + \lambda/a + d/a) \leq s_1(x) \leq f(x + \lambda/a)$$

and

$$f(x + 2\lambda/a) - 2f(x + d/a + 2\lambda/a) + f(x + 2d/a + 2\lambda/a) \leq s_2(x) \leq f(x + 2\lambda/a) .$$

Due to the exponentials in $e^{-|g|d}$, the bounds are actually very tight as long as d/a is not too small. One could use these bounds to approximate $E_H^{(4)}$, but we'll just proceed to do an example numerically.

Consider a stripe domain pattern where we get domains of size a along x and they are infinitely long along y. The Fourier series is easy: we get non-zero coefficient only when $g_y = 0$. Since $g_x = n_x\pi/a$ for integer n_x, we get

$$\hat{u}(n_x) = \frac{(-1)^{n_x} - 1}{\pi n_x}$$

so that

$$f(x) = \frac{8}{\pi^3} \sum_{m=0}^{\infty} \frac{\exp(-(2m+1)\pi x)}{(2m+1)^3}$$

and

$$s_n(x) = \frac{8}{\pi^3} \sum_{m=0}^{\infty} \frac{\exp(-(2m+1)\pi x)}{(2m+1)^3} \left(\frac{e^{(2m+1)d\pi/a} - 1}{e^{(2m+1)\pi(d/a+\lambda/a)} - e^{-(2m+1)\pi\lambda/a}} \right)^n .$$

We will write the energy as

$$E_H^{(4)} = 2\pi P^2 d \cdot S(a/d, \lambda/d)$$

which is measuring the energy in units of the parallel plates result and we measure distances in units of the thickness (i.e. $d = 1$). For reference, $f(0) \cong 0.271$. The dimensionless S is computed and tabulated for various values of a/d and λ/d below for the stripe domain system: Some observations and confirmations: for λ larger than both d and a (last column two columns excluding the bottom regions), the screening is irrelevant and we are just back

	λ/d									
a/d	0.01	0.1	0.2	0.5	1	2	5	10	100	1000
0.01	0.0027	0.0027	0.0027	0.0027	0.0027	0.0027	0.0027	0.0027	0.0027	0.0027
0.1	0.0132	0.0271	0.0271	0.0271	0.0271	0.0271	0.0271	0.0271	0.0271	0.0271
0.2	0.0157	0.0520	0.0542	0.0543	0.0543	0.0543	0.0543	0.0543	0.0543	0.0543
0.5	0.0178	0.0987	0.1250	0.1352	0.1354	0.1354	0.1354	0.1354	0.1354	0.1354
1	0.0187	0.1297	0.1919	0.2500	0.2598	0.2602	0.2602	0.2602	0.2602	0.2602
2	0.0192	0.1481	0.2380	0.3648	0.4212	0.4347	0.4353	0.4353	0.4353	0.4353
5	0.0194	0.1592	0.2666	0.4457	0.5659	0.6371	0.6604	0.6609	0.6609	0.6609
10	0.0195	0.1629	0.2762	0.4729	0.6163	0.7183	0.7782	0.7862	0.7866	0.7866
100	0.0196	0.1663	0.2848	0.4973	0.6616	0.7918	0.8960	0.9351	0.9640	0.9640
1000	0.0196	0.1666	0.2856	0.4997	0.6662	0.7992	0.9078	0.9507	0.9919	0.9949

to two sheets which show classic parallel plate behavior for $a \gg d$. On the contrary, when λ is smaller than a or d so we have an excellent electrode with a microscopic screening length (first column ignoring top portions), the energy is basically constant and independent of a since the fields are just classic parallel plate energies between the screening charges and their closest ferroelectric surface; the energy is also very close to $4\pi P^2\lambda$ or $S = 2\lambda$.

2 Domain wall energy

This is easy! We assume there is a constant C that is the energy cost per unit area of having a domain wall. Then this contribution to the energy is always positive and gets large as the domain size a shrinks. It is of order

$$E_{dw} \sim \frac{Cd}{a}$$

by elementary considerations. For stripe domains, the factor of proportionality is 2 since there are two domain walls per unit cell. For a checkerboard pattern, it is 4.

3 Total energy

The total energy is the sum of the above two contributions

$$E_{tot} = E_{dw} + E_H \, .$$

The question is if there is a minimum versus a for finite a so we get multi-domain structures. This will obviously depend on the numerical value of the domain-wall cost C compared to the electrostatic terms.

To be specific, let's consider something like $\mathrm{PbTiO_3}$ with a polarization around 80 μC/cm^2 and stripe domains of width a. The total energy is then

$$E_{tot} = \frac{2Cd}{a} + 2\pi P^2 d \cdot S(a/d, \lambda/d)\,.$$

The most favorable condition to get multi-domain is to not have any screening. So we set $\lambda = \infty$ which simplifies to

$$E_{tot} = \frac{2Cd}{a} + 2\pi P^2 a\,[f(0) - f(d/a)]\ .$$

The electrostatic part has the largest slope at $a = 0$ which is $2\pi P^2 f(0)$ which for our example system is 0.70 eV/Å^3 and this slope gets much smaller once $a \sim d$. The domain wall part has slope $-2Cd/a^2$. One gets a finite a solution only for $2Cd$ less than about 5 eV/Å. More reasonably, however, one wants to get $a \lesssim d$ which translates to $Cd \lesssim 0.35$ eV/Å. For a perovskite cell of 3.9 Å on the side and for d one unit cell, this means $C \lesssim 1.4$ eV/uc^2 which is rather large but not ridiculous. So we expect multi-domain with no screening.

With screening, it depends on how good the screening is. For very small λ, E_H is basically flat with a very small slope so we won't get multi-domain. When we do get multi-domain depends on the value of Cd as well as λ/d. For example, the previous table for S shows that the typical slopes versus a for $\lambda/d = 0.01$ are about 100 times smaller than for $\lambda = \infty$ while for $\lambda/d = 0.1$ they are only about 5-10 times smaller.