Ferroelectric surface charge and polarization

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The discussion below starts with macroscopic electrostatics (Maxwell equations). Later there is some discussion of a microscopic picture.

Imagine we have a ferroelectric slab periodic in the xy plane and of thickness L extending from $z = 0$ to $z = L$. It has a continuous and differentiable but arbitrary polarization profile $P(z)$ and we will assume $P(z)$ goes to zero at the interfaces so $P(0) = P(L) = 0$. This ferroelectric is sandwiched on both sides by metal electrodes that are grounded (or connected to each other). Any screening charges in the metals will be modeled as being a uniform sheet charge λ away from the interfaces (at $z = -\lambda$ and $z = L + \lambda$.) Thus the charges in the system are the two screening sheets with sheet densities σ_{left} and σ_{right} as well as the bound charge density ρ_b

$$\rho_b(z) = -dP/dz\,.$$

We are going to ask about what the electrostatic potential looks like in this system. We will set $\phi(z < -\lambda) = 0$ and so by the grounding assumption $\phi(z > L + \lambda) = 0$ as well. Poisson's equation

$$d^2\phi/dz^2 = -4\pi\rho(z)$$

can be integrated to give

$$d\phi/dz = \begin{cases} 0 & \text{for } z < -\lambda \\ -4\pi\sigma_{left} & \text{for } -\lambda < z < 0 \\ -4\pi\sigma_{left} + 4\pi P(z) & \text{for } 0 < z < L \\ -4\pi\sigma_{left} & \text{for } L < z < L+\lambda \\ -4\pi(\sigma_{left} + \sigma_{right}) & \text{for } L < z \end{cases}\,.$$

The potential is flat for $z > L + \lambda$ so the field must be zero. So we can immediately conclude (as would have been obvious intuitively) that the screening charges must be equal and opposite $-\sigma_{left} = \sigma_{right} \equiv \sigma$ to enforce neutrality of net charge since the ferroelectric only has bound charge from polarization gradients which never give actual net charge (just motion of charge which is dipole formation). Also, the field inside the ferroelectric does not have to be uniform but instead follows $P(z)$.

Integrating again to get the potential, we have

$$\phi(z) = \begin{cases} 0 & \text{for } z < -\lambda \\ 4\pi\sigma(z+\lambda) & \text{for } -\lambda < z < 0 \\ 4\pi\sigma(z+\lambda) + 4\pi\int_0^z dz' P(z') & \text{for } 0 < z < L \\ 4\pi\sigma(z+\lambda) + 4\pi\int_0^L dz' P(z') & \text{for } L < z < L+\lambda \\ 4\pi\sigma(L+2\lambda) + 4\pi\int_0^L dz' P(z') & \text{for } L < z \end{cases}.$$

Again, insisting that $\phi(z > L+\lambda) = 0$ means

$$\sigma = -\frac{\int_0^L dz' P(z')}{L+2\lambda}.$$

This is easier to digest if we define the average polarization of the film

$$\bar{P} = \frac{1}{L}\int_0^L dz' P(z')$$

so we have

$$\sigma = -\frac{\bar{P}}{1+2\lambda/L}.$$

The screening charge is what one can measure in an experiment: when the polarization changes, the screening charge accommodates accordingly and changes in it require currents to flow in the metal (or between the metals if under closed circuit with connection) and we can measure currents. **This is thus a good operational definition of surface polarization charge.** The above relation shows that for a film with uniform polarization so $P(z) = \bar{P}$ that is very thick $L \gg \lambda$, the surface polarization charge is indeed $\bar{P}$ as we learn in class. So the definition is also giving the right answer in the appropriate case (a good check).

What about thin films and non-uniform polarizations? Even with uniform polarization in a thin film, the denominator that has λ/L which suppresses σ compared to $\bar{P}$. However, for a thin film, there is no reason for $P(z) = \bar{P}$ for z close to 0 or L due to interface effects. The above relation shows that the average polarization matters, so if the interface regions have depressed $P(z)$ for some reason, this lowers the average. Of course, for a very thick film, the interior region — making up the majority of the film — will have the bulk polarization at zero field and thus the interface contribution to the average will be a correction of order d/L where d is the thickness of the interface region. Thus, thin film effects should change the surface polarization charge as defined via the screening charge, but as the film thickens the value of σ should approach the bulk polarization with corrections scaling like constant$/L$.

One thing that might seem worrisome is that we've assumed the entire system has no structure in the xy direction and is thus one-dimensional. Perhaps the fact that actual materials have atoms and thus modulations in charge density in xy makes this more complex and different? The answer is that of course inside the materials, these microscopic fluctuations matter for the actual value of the potential and fields, but once one is "far away" they do not. Showing this relies on what the potential is from a periodic 2D array of charges. The key result is that for a 2D sheet density $\sigma(x,y)$ with periodicity in the xy plane and which is located at $z=0$, the potential is

$$\phi(x,y,z) = -2\pi\bar{\sigma}|z| + \sum_{g_{xy}\neq 0} \frac{2\pi\hat{\sigma}(g_{xy})}{|g_{xy}|} e^{ig_{xy}\cdot r_{xy}} e^{-|z||g_{xy}|}$$

where $\bar{\sigma}$ is the average sheet charge in a 2D unit cell, $\hat{\sigma}(g_{xy})$ are the Fourier components of $\sigma(x,y)$, and g_{xy} are the 2D reciprocal lattice vectors. (Thus $\bar{\sigma} = \hat{\sigma}(0)$.)

For an arbitrary charge distribution $\rho(x,y,z)$ that is in the form of a slab extending from z_1 to z_2 and periodic in xy, we can slice it up into thin sheets and use the above result. The potential is then

$$\phi(x,y,z) = \int_{z_1}^{z_2} dz' \left[-2\pi\bar{\rho}(z)|z-z'| + \sum_{g_{xy}\neq 0} \frac{2\pi\hat{\rho}(g_{xy},z)}{|g_{xy}|} e^{ig_{xy}\cdot r_{xy}} e^{-|z-z'||g_{xy}|} \right]$$

where

$$\bar{\rho}(z) = \hat{\rho}(0,z) \qquad \text{and} \qquad \hat{\rho}(g_{xy},z) = \frac{1}{A}\int_{u.c.} dx\,dy\,\rho(x,y,z)e^{-ig_{xy}\cdot r_{xy}}\,.$$

What this shows is that as z gets far from the slab boundaries, the fluctuating parts of the potential die off exponentially with a typical length scale of the lattice constant(s) in the xy plane (i.e. $\sim 1/|g_{xy}|$). Thus, once one is a few unit cell distances away from the slab, the potential is just what one would have gotten from averaging the charges in the xy planes to give the simple model above. So, if one asks that the potential be zero and flat inside the metallic regions, then this means that the charges entering consideration are just the average sheet charges and bound charges we looked at in the simple model. Namely, given the actual charge distribution $\rho(x,y,z)$ of the system that is periodic in xy, the long-range electrostatics is governed only by the averaged $\bar{\rho}(z)$ charge distribution: we're back to one dimension.