Continuum dielectric model for STO-LAO-STO-vacuum cells

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October 7, 2013

The figure below shows the overall geometry. From $\nabla \cdot D = 4\pi\rho_{free}$, which is only nonzero at the STO-LAO interfaces and is given by the sheet charges $+\sigma$ and $-\sigma$ (see Figure). In one dimension we have

$$D_L - D_S = 4\pi\sigma\,.$$

Also, $D_V = D_S$ so we'll just D_S for both. The net potential drop across the supercell is zero due to the periodic boundary conditions, and using $E_i = D_i/\epsilon_i$ in each region, we must have

$$0 = 2sE_S + lE_L + vE_V = \frac{2sD_S}{\epsilon_S} + \frac{lD_L}{\epsilon_L} + \frac{vD_V}{\epsilon_V}\,.$$

Using the two relations together, we can solve for D_L and D_S,

$$\begin{aligned} D_S &= -4\pi\sigma \cdot \frac{l/\epsilon_L}{2s/\epsilon_S + l/\epsilon_L + v/\epsilon_V} \\ D_L &= 4\pi\sigma \cdot \frac{2s/\epsilon_S + v/\epsilon_V}{2s/\epsilon_S + l/\epsilon_L + v/\epsilon_V}\,. \end{aligned}$$

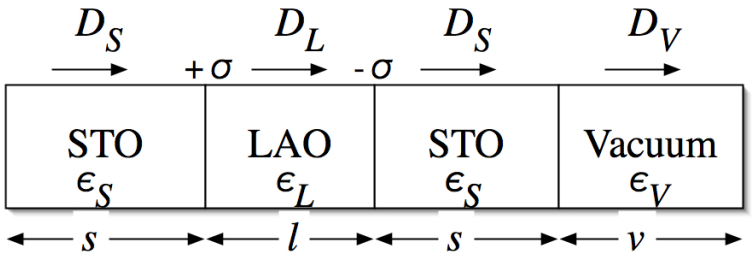

Figure 1: Geometry and key parameters for STO-LAO-STO-vacuum cell. The "free charges" are the interface charges at the STO-LAO interfaces, here the $+\sigma$ and $-\sigma$ sheet charge as indicated. Each region has the length indicated (s, l, or v) and corresponding dielectric constant ($\epsilon_{S/L/V}$) and dielectric displacement ($D_{S/L/V}$).

These are exact relations. To get a sense of what they mean, we have roughly

$$\epsilon_S \approx 300 \gg \epsilon_L \approx 25 \gg \epsilon_V = 1\,.$$

As for the lengths, in any of our calculations, most of them are a few bulk unit cells in length, so within a factor of two or so, we have that $l \sim s \sim v$. Hence the relations simplify to

$$D_V = D_S \approx -4\pi\sigma \cdot \frac{l}{v} \cdot \frac{\epsilon_V}{\epsilon_L} \qquad \text{and} \qquad D_L \approx 4\pi\sigma \cdot \left(1 - \frac{l}{v\epsilon_L}\right)\,.$$

So, although one might have intuitively guessed that D_L and D_S might be equal and opposite and equal to $2\pi\sigma$ by symmetry, this is not the typical case because of the very disparate screening constants. (Of course, for some unusual choices of s, l, and v we could make them equal.) As far as controlled convergence is concerned, $D_V = D_S$ go to zero as $1/v$.

Since D, P, and E are all proportional, the displacement/polarization/electric field in the STO is $\epsilon_L \approx 25$ times smaller than in the LAO. Thus the polarization of the STO region, while nonzero, is actually quite small on the scale of things.

The electric fields are approximately

$$\begin{aligned} E_L &\approx 4\pi\sigma \cdot \frac{1}{\epsilon_L} \\ E_S &\approx -4\pi\sigma \cdot \frac{l}{v} \cdot \frac{\epsilon_V}{\epsilon_L\epsilon_S} \approx -E_L \cdot \frac{l}{v} \cdot \frac{\epsilon_V}{\epsilon_S} \\ E_V &\approx -4\pi\sigma \cdot \frac{l}{v} \cdot \frac{1}{\epsilon_L} \approx -E_L \cdot \frac{l}{v} \end{aligned}$$

so as expected most of the LAO voltage drop lE_L is across the vacuum vE_V and the remaining fraction $\sim 1/\epsilon_S$ is across the STO regions.

At any rate, the point is that the fields in the STO are reduced quite a bit in this continuum model compared to assuming the displacement fields are equal in LAO and STO. As an added note on the microscopic side, in order to best simulate the STO being bulk-like as we move away from the interface (as per the experiments we are trying to model), we freeze the outer two layers of the STO at the vacuum interfaces to have their bulk-like geometries (inter-layer distances and pure planar arrangement of atoms in each layer with no anion/cation rumplings).

This does two things: first, we avoid any unusual electronic behavior at the STO surfaces from competing with the interface ones (and there are some), and second, this clamping choice forces the ionic polarization to become zero as we move away from the interface and into the bulk-like STO. While this will not be useful for very long STO cells (s very large), we found it to make a practical difference for the unit cell sizes we can afford in our calculations. Of course, if for some reason one is actually interested in modeling a system where the STO is a few layers thick and actually (physically) facing the vacuum with exposed surface, then

one should not clamp anything and just let the atoms move and relax freely, and one needs to worry more about the fields at the surface and in the vacuum.

In the experimental situation we are trying to model, the electric fields going away from the interface drop sharply to zero as we go through the charge densities associated with the interface states; so we expect that after a few layers going into the STO, the polarization and electric field need to go to zero. All our gymnastics with vacuum and surface clamping are trying to achieve this boundary condition in an affordable computational cell.