

# ADVANCED MATERIALS

## Supporting Information

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Emergence of Negative Capacitance in Multidomain  
Ferroelectric–Paraelectric Nanocapacitors at Finite Bias

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## 1 Evaluation of the local permittivity

The local permittivity can be calculated using the orbital-separation approach (OSA) as follows. First, the change in the  $xy$ -plane-averaged electrostatic potential induced by the external bias is calculated:

$$\Delta V_{\text{H}}(z) = \frac{1}{L_x L_y} \int_0^{L_x} dx \int_0^{L_y} dy [V_{\text{H}}(x, y, z; V) - V_{\text{H}}(x, y, z; 0)], \quad (\text{S1})$$

where  $L_x$  and  $L_y$  are supercell lengths in the directions perpendicular to the interface, and  $V_{\text{H}}(x, y, z; V)$  is the electrostatic potential at position  $(x, y, z)$  under an applied bias voltage  $V$ .  $\Delta V_{\text{H}}(z)$  shows large atomic-scale oscillations when ionic relaxation is considered. Here, we are interested in variations over length scales that correspond to interatomic distances, so we apply the macroscopic averaging technique [1] to smoothen out such oscillations:

$$\overline{\Delta V_{\text{H}}}(z) = \frac{1}{l_1 l_2} \int_{z-(l_1/2)}^{z+(l_1/2)} dz' \int_{z'-(l_2/2)}^{z'+(l_2/2)} dz'' \Delta V_{\text{H}}(z''), \quad (\text{S2})$$

where  $l_1$  and  $l_2$  are the lattice periodicities in the metal and dielectric regions.

From the quantities calculated above, we can also define the local dielectric constant. We start from the definition discussed in Ref. [2]:

$$\frac{1}{\varepsilon_{\text{r}}(z)} = \frac{\varepsilon_0 \overline{\Delta E}(z)}{\varepsilon_0 \overline{\Delta E}(z) + \overline{\Delta P}(z)}, \quad (\text{S3})$$

where  $\overline{\Delta E}(z)$  and  $\overline{\Delta P}(z)$  are the macroscopically averaged electric field and polarization induced by an external field. Also note that the denominator on the right hand side equals the induced electric displacement  $\overline{\Delta D}(z)$ . The situation simulated in the OSA does not have an external field but an external battery [Fig. S1a], so this expression cannot be

directly used. However, by considering an analogous system under an external field  $E_{\text{ext}}$  that yields the same amount of surface charge  $\sigma$  [Fig. S1b], this expression can be applied trivially. In the following, local quantities in this auxiliary system are denoted by a prime (e.g., the local induced potential is written as  $\Delta\bar{V}'_{\text{H}}$ ) to distinguish from the system that is simulated by the OSA. From the Gauss relation in one dimension:

$$\frac{d}{dz}\Delta\bar{E}'(z) = \frac{\bar{\rho}'_{\text{ind}}(z)}{\epsilon_0}, \quad (\text{S4})$$

we have

$$\Delta\bar{E}'(z) = \int_0^z \frac{\bar{\rho}'_{\text{ind}}(z)}{\epsilon_0} dz + \Delta\bar{E}'(0), \quad (\text{S5})$$

where  $\bar{\rho}'_{\text{ind}}(z)$  is the local charge induced by the external field. Similarly, for the polarization, we have

$$\frac{d}{dz}\Delta\bar{P}'(z) = -\bar{\rho}'_{\text{ind}}(z) \quad (\text{S6})$$

so that

$$\Delta\bar{P}'(z) = -\int_0^z \bar{\rho}'_{\text{ind}}(z) dz + \Delta\bar{P}'(0). \quad (\text{S7})$$

We can set  $z = 0$  in the vacuum region on the left hand side so that  $\Delta\bar{E}'(0) = E_{\text{ext}}$  and  $\Delta\bar{P}'(0) = 0$ . Thus, by combining Eqs. (S5) and (S7), we find that  $\Delta\bar{D}'(z) = \epsilon_0\Delta\bar{E}'(z) + \Delta\bar{P}'(z) = \epsilon_0 E_{\text{ext}}$ , that is, the induced electric displacement is constant throughout the capacitor. Furthermore,  $\bar{E}'(z)$  is equal to the negative of the gradient of the induced potential profile  $\bar{V}'_{\text{H}}(z)$  [Eq. (S2)], so that we can rewrite Eq. (S3) as

$$\frac{1}{\varepsilon_r(z)} = -\frac{1}{E_{\text{ext}}} \frac{d}{dz} \Delta \bar{V}'_{\text{H}}(z). \quad (\text{S8})$$

In fact, this is the definition that was used in the half-capacitor approach [3]. Next, we have to replace the quantities in this auxiliary system by the quantities that can be directly calculated by the OSA. If the metal is thick enough to completely screen the external field,  $E_{\text{ext}} = \sigma / \varepsilon_0$ , where  $\sigma = Q/A$  is the induced surface free charge per unit area. This can be calculated from the differential capacitance [Eq. (3) in the main text] as  $\sigma = \int_0^V C(V) dV / A$ . Also,  $\Delta \bar{V}_{\text{H}}$  calculated by OSA [Eq. (S2)] and  $\Delta \bar{V}'_{\text{H}}$  are identical between the centers of the electrodes. Summing up the above, we can calculate the local dielectric constant in the region between the centers of the two electrodes as

$$\frac{1}{\varepsilon_r(z)} = -\frac{\varepsilon_0}{\sigma} \frac{d}{dz} \Delta \bar{V}_{\text{H}}(z). \quad (\text{S9})$$

For nonlinear dielectrics, it is sometimes more appropriate to examine the differential permittivity defined as

$$\frac{1}{\varepsilon_r(z, D(z))} = \varepsilon_0 \frac{d[\Delta \bar{E}(z)]}{d[\Delta D(z)]}. \quad (\text{S10})$$

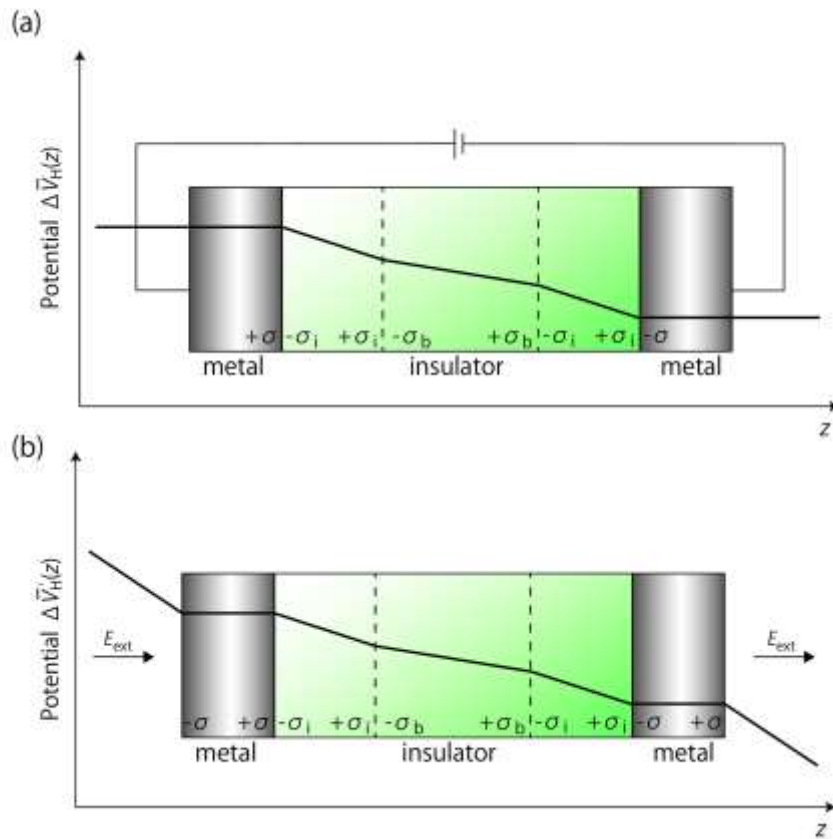
After similar discussion as above, we obtain

$$\begin{aligned} \frac{1}{\varepsilon_r(z, V)} &= -\varepsilon_0 \frac{\partial^2 [\Delta \bar{V}_{\text{H}}(z, V)]}{\partial \sigma(V) \partial z} \\ &= -\varepsilon_0 \frac{\partial^2 [\Delta \bar{V}_{\text{H}}(z, V)]}{\partial V \partial z} \frac{dV}{d\sigma} \\ &= -\frac{\varepsilon_0 A}{C(V)} \frac{\partial^2 [\Delta \bar{V}_{\text{H}}(z, V)]}{\partial V \partial z}, \end{aligned} \quad (\text{S11})$$

where we have used the applied bias  $V$  as the independent variable that is controlled in our simulation. This is naturally related to the differential capacitance as

$$\begin{aligned}
\int_{z_L}^{z_R} \frac{dz}{\varepsilon_r(z, V)} &= -\frac{\varepsilon_0 A}{C(V)} \frac{\partial}{\partial V} \int_{z_L}^{z_R} \frac{\partial[\Delta\bar{V}_H(z, V)]}{\partial z} dz \\
&= \frac{\varepsilon_0 A}{C(V)},
\end{aligned}
\tag{S12}$$

where  $z_L$  and  $z_R$  correspond to the centers of the two electrodes.



**Figure S1:** Schematic of the induced potential and charges in an OSA simulation (a) and the corresponding auxiliary system under an external electric field  $E_{\text{ext}}$  (b).  $\sigma$  represents induced free charges in the metal, while  $\sigma_i$  and  $\sigma_b$  represent induced polarization charges inside the dielectric in the interfacial and bulk regions, respectively. The potential and charge profiles of the two systems are identical in the region between the centers of the two electrodes. Although discrete charges are depicted here, the discussion in the text applies to continuous variations in the induced charge.



## 2 The depolarizing field and the dead layer effect

In the following, we try to clarify the relationship between the depolarizing field and the dead layer capacitance in terms of the total energy landscape based on Landau-Devonshire theory. The following discussion is restricted to a parallel-plate capacitor with two electrodes, whose structure is periodic in the in-plane directions.

We start from the phenomenological Landau-Devonshire theory description of the electric energy density (energy per unit volume)  $u$ :

$$u(D) = A_0 + A_2 D^2 + A_4 D^4 + O(D^6) \quad (\text{S13})$$

Here,  $D$  is the component of the electric displacement vector  $\mathbf{D}$  perpendicular to the electrode plates. A ferroelectric material is characterized by a double-well potential, so  $A_2$  is negative, the highest order coefficient is positive, and  $A_0$  is an arbitrary reference energy. On the other hand, for a perfectly linear dielectric,  $A_2$  is positive and higher coefficients are zero. If the dielectric is sandwiched by perfect conductors with the same work function and if interface/surface effects are negligible, the inverse capacitance per unit area at fixed  $D$  is simply given as the curvature of the electric energy per unit area vs  $D$ :

$$C^{-1} = \frac{d^2}{dD^2} l_{\text{DE}} u_{\text{DE}}(D) = l_{\text{DE}} \bar{C}_{\text{DE}}^{-1}(D), \quad (\text{S14})$$

where  $l_{\text{DE}}$  is the dielectric film thickness. Here, we have defined the bulk inverse capacitance per unit volume  $\bar{C}_{\text{DE}}^{-1}(D) = d^2 u / dD^2 = 2A_2 + 12A_4 D^2 + O(D^4)$ , which actually equals the inverse of the dielectric permittivity  $\varepsilon^{-1}(D)$ . This quantity is independent of  $D$  for a linear dielectric, while it depends on  $D$  for nonlinear dielectrics including ferroelectric materials. If the electrodes have different work functions, a term

linear in  $D$  also appears, but we will not consider that here. For a ferroelectric, this value  $\varepsilon_{\text{FE}}^{-1}$  is negative at  $D = 0$ , meaning that it is unstable towards ferroelectric distortion. Once the distortion occurs,  $\varepsilon_{\text{FE}}^{-1}$  becomes positive.

We now consider a capacitor where a dielectric material is sandwiched by non-ideal but identical electrodes giving rise to a depolarizing field  $E_{\text{dep}}$ . The effect of the depolarizing field is to generate a restoring force that is roughly proportional to the polarization  $P$ . In the harmonic limit, this causes a positive energy contribution that is proportional to  $E_{\text{dep}}P$  and thus  $D^2$ :

$$U_{\text{dep}}(D) = \alpha D^2. \quad (\text{S15})$$

The total energy per unit area can be written as

$$U(D) = u_{\text{DE}}(D)l_{\text{DE}} + \alpha D^2, \quad (\text{S16})$$

and the inverse capacitance is thus

$$C^{-1}(D) = \frac{d^2U(D)}{dD^2} = \bar{C}_{\text{DE}}^{-1}(D)l_{\text{DE}} + 2\alpha. \quad (\text{S17})$$

The stationary (short-circuit) value of  $D$  can be obtained from

$$\frac{dU(D)}{dD} = 0. \quad (\text{S18})$$

These equations show that the depolarizing field can be regarded as giving rise to an extra interfacial capacitance density  $C_i^{-1} = \alpha$  that is connected in series with the bulk capacitance. In terms of the local permittivity, this appears as an interfacial dead layer having a degraded dielectric constant. Although we've considered the depolarizing field as the source of the interface effect here, it should be pointed out that in the harmonic limit, all conceivable chemical and electronic effects at the interface can be represented

in this manner. We also note that there is a report of  $C_i$  being negative at certain interfaces [4].

Now, if we consider a ferroelectric, we find that the total inverse capacitance can become positive at  $D = 0$  if  $\bar{C}_{\text{FE}}^{-1}(0)l_{\text{FE}} + 2C_i^{-1} > 0$ . This leads to the following expression of the critical thickness for monodomain ferroelectricity [4]:

$$l_{\text{crit}} = -2 \frac{\bar{C}_{\text{FE}}^{-1}(0)}{C_i}. \quad (\text{S19})$$

When the ferroelectric film sandwiched by metal electrodes is thinner than  $l_{\text{crit}}$ , the monodomain ferroelectricity is suppressed. If we consider a ferroelectric/paraelectric capacitor, then we naturally end up with the following expression:

$$C^{-1} = l_{\text{FE}} \bar{C}_{\text{FE}}^{-1} + l_{\text{PE}} \bar{C}_{\text{PE}}^{-1} + \sum_i C_i^{-1}, \quad (\text{S20})$$

where the last term is the summation over all interfaces in the capacitor heterostructure. If  $C^{-1}$  is positive at  $D \sim 0$ , the ferroelectric is stabilized in the negative capacitance state and provides capacitance enhancement over the paraelectric capacitor. Of course, the situation is actually not so simple since ferroelectrics tend to form striped domains as discussed in the main text.

### **3 The effect of the local density approximation on the obtained dielectric properties**

As noted in the main text, our simulations are performed at zero temperature, but the results have implications for operating temperatures as discussed in the following. STO undergoes a phase transition from cubic to tetragonal antiferrodistortive phase as it is cooled below 105 K, and is extremely close to a ferroelectric transition near 0 K. This

transition is barely suppressed by quantum fluctuations of the ions, and thus STO is known as a ‘quantum paraelectric’ [5]. However, because the local density approximation (LDA) employed in this work (see methods section) underestimates the lattice constant and tends to slightly suppress ferroelectricity, the zero-temperature LDA system actually mimics the near-room temperature dielectric response of cubic STO [6]. To check whether the situation is similar for the  $c$ -axis dielectric response of BTO, we performed a density functional perturbation theory (DFPT) [7] calculation on tetragonal BTO with lattice parameters obtained using LDA ( $a = 3.943 \text{ \AA}$ ,  $c = 3.993 \text{ \AA}$ ). We obtained a  $c$ -axis dielectric constant of 39, which is not too far off from the value 56 obtained experimentally [8]. Therefore, although we are performing simulations at 0 K, we can infer from the results a picture of the dielectric behavior near room temperature.

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