# Electric displacement as the fundamental variable in electronic-structure calculations

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# Acknowledgements

Nicola Spaldin
UC Santa Barbara

David Vanderbilt
Rutgers University

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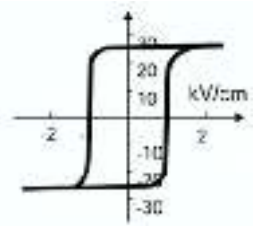
# Ferroelectrics: bulk

- Macroscopic description
  - Spontaneous $P$, switchable with $\mathcal{E}$

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  - Unstable polar phonon mode
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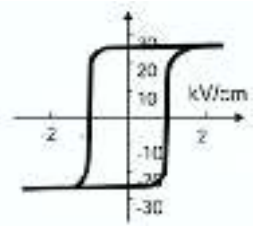


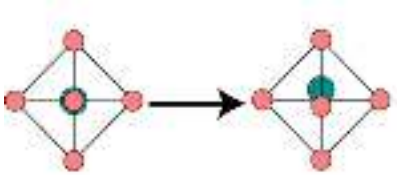

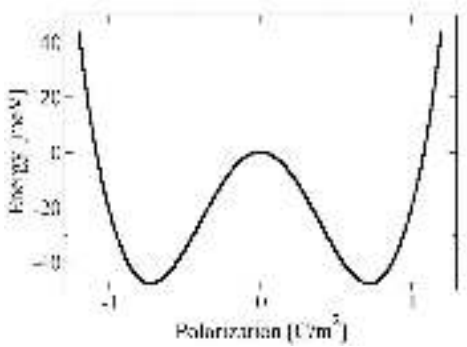

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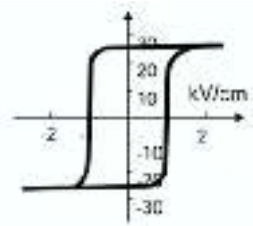


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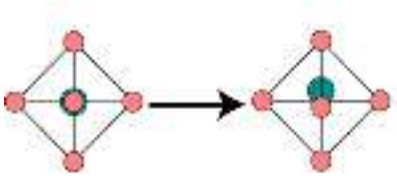
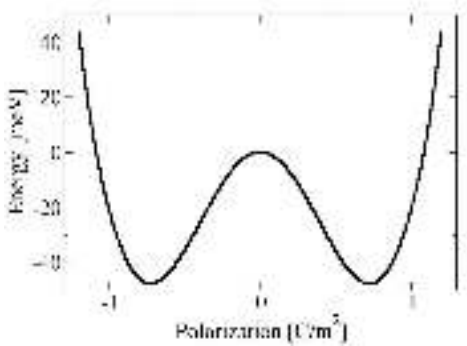


*Collective phenomenon: does it survive in thin films?*



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- Thin films desirable for applications
  - Ferroelectric memories
  - Gate dielectrics

However:

- Strong size effects
  - Polarization is reduced

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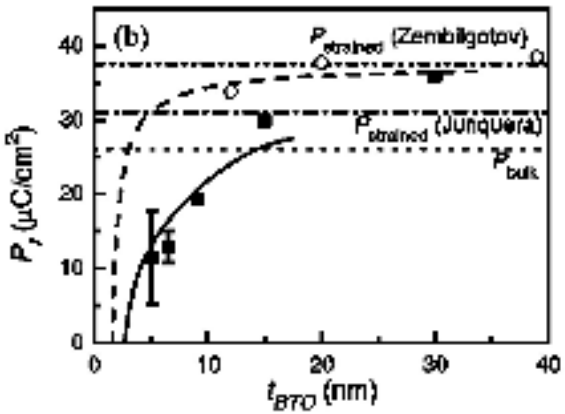


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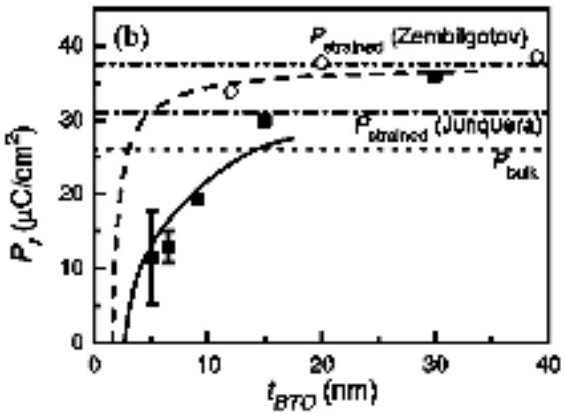


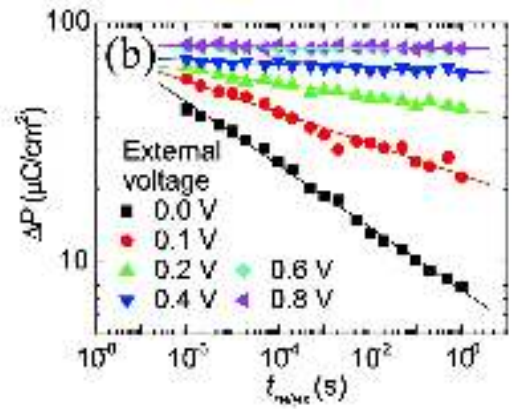

# What is the origin of the problem?

- Strong dependence on electrical boundary conditions
  - No screening: uniform $P$ is suppressed by *depolarizing field*
  - Imperfect screening: $P$ might be allowed *if thick enough*
  - Popular explanation: Intrinsic interface effect, Thomas-Fermi model

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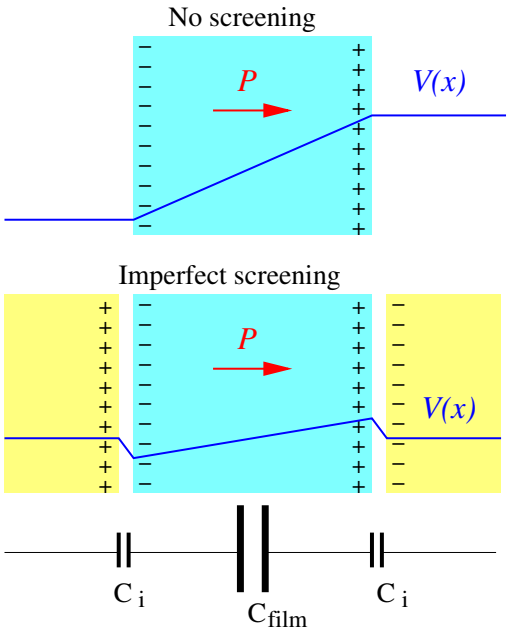


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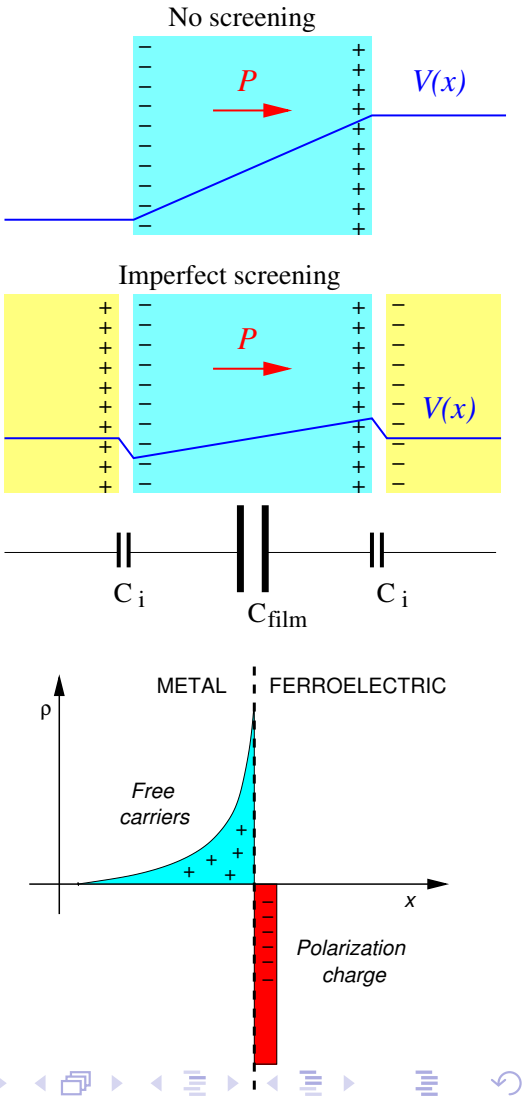

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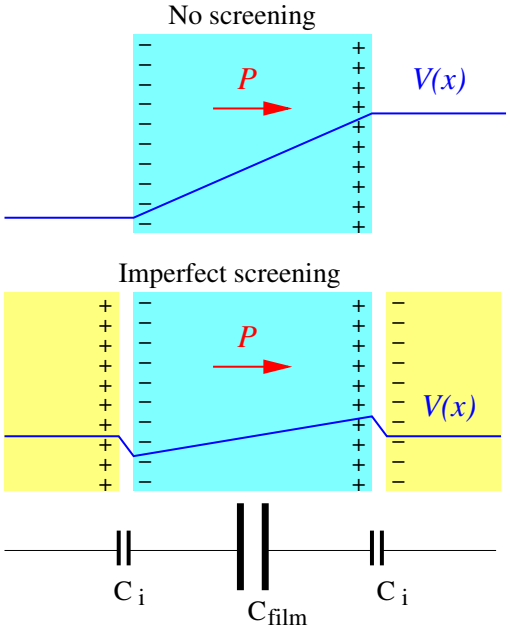
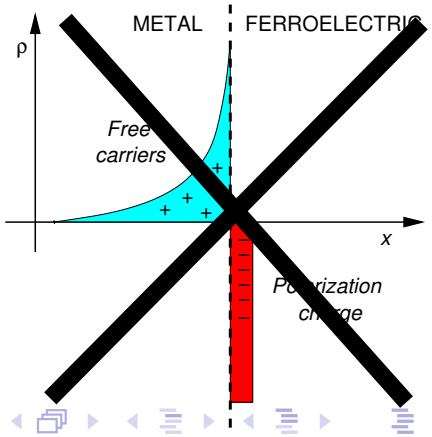


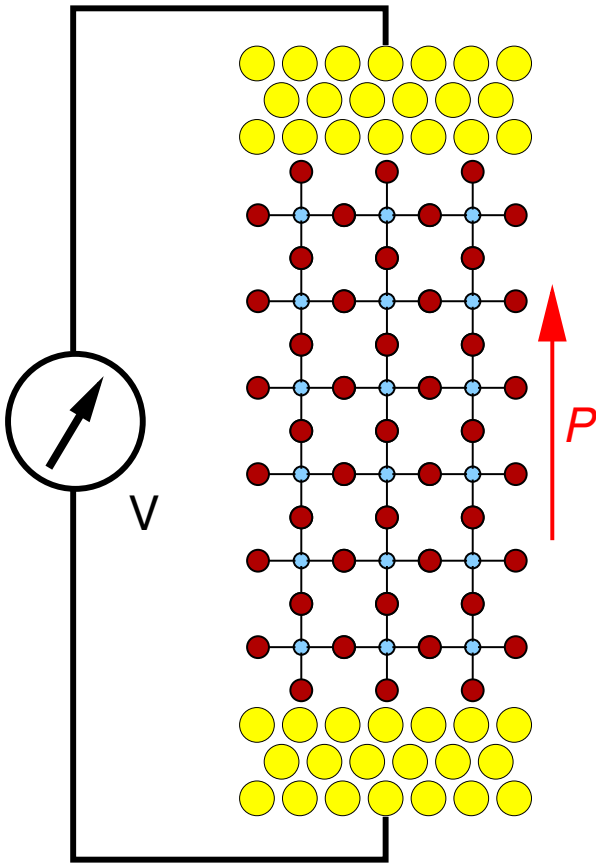



# What theory to use?

- Want a microscopic description of realistic metal-ferroelectric interfaces
  - Density-functional theory

$$E(\rho) = E_{Kinetic}(\rho) + E_{Hartree}(\rho) + E_{XC}(\rho)$$

- Want to calculate the electrical properties (e.g. polarization, capacitance, ...)
  - Finite electric fields, modern theory of polarization
  - Very recent developments...

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# Outline

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# Finite fields in periodic solids

- Want to apply a uniform external electric field $\mathcal{E}$
- Idea:

$$\mathcal{F}(\rho, \mathcal{E}) = E(\rho) + \int \rho(\mathbf{r}) V(\mathbf{r}) d^3 r, \qquad V(\mathbf{r}) = -\boldsymbol{\mathcal{E}} \cdot \mathbf{r}$$

- The scalar potential is not periodic
  - Finite potential drop $\Delta V$

Solution:

- Rewrite the coupling term $\int \rho(\mathbf{r}) V(\mathbf{r}) d^3 r \longrightarrow -\Omega \boldsymbol{\mathcal{E}} \cdot \mathbf{P}$

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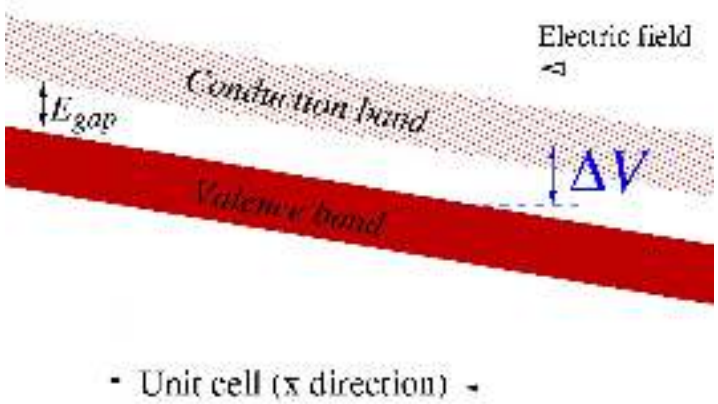


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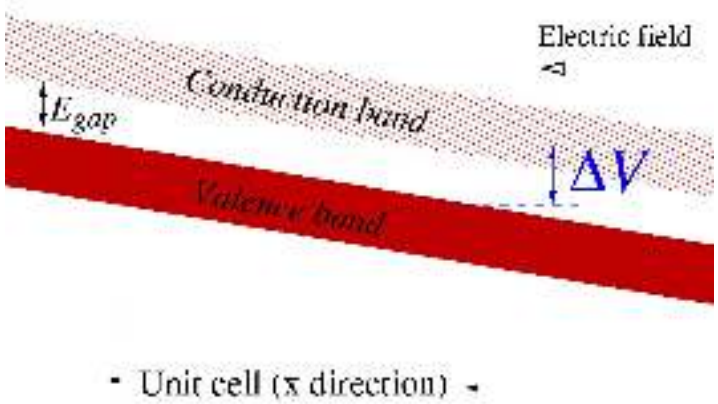


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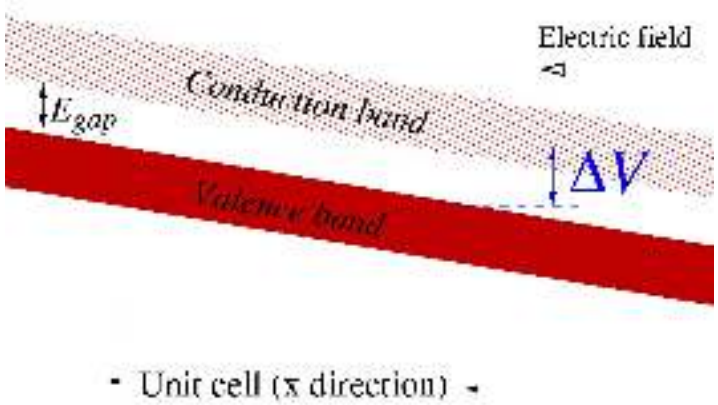
- $P$ defined as a Berry phase

King-Smith and Vanderbilt, PRB 47, 1651 (1993); Resta, Ferroelectrics 136, 51 (1992).

# Finite fields in periodic solids

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  - Electric enthalpy: $\mathcal{F}(\mathcal{E}) = E_{KS} - \Omega\mathcal{E} \cdot \mathbf{P}$
- There is no electronic ground state
  - Zener tunneling instability

  Solution:
  - Finite $k$-point sampling makes the electrons "nearsighted"

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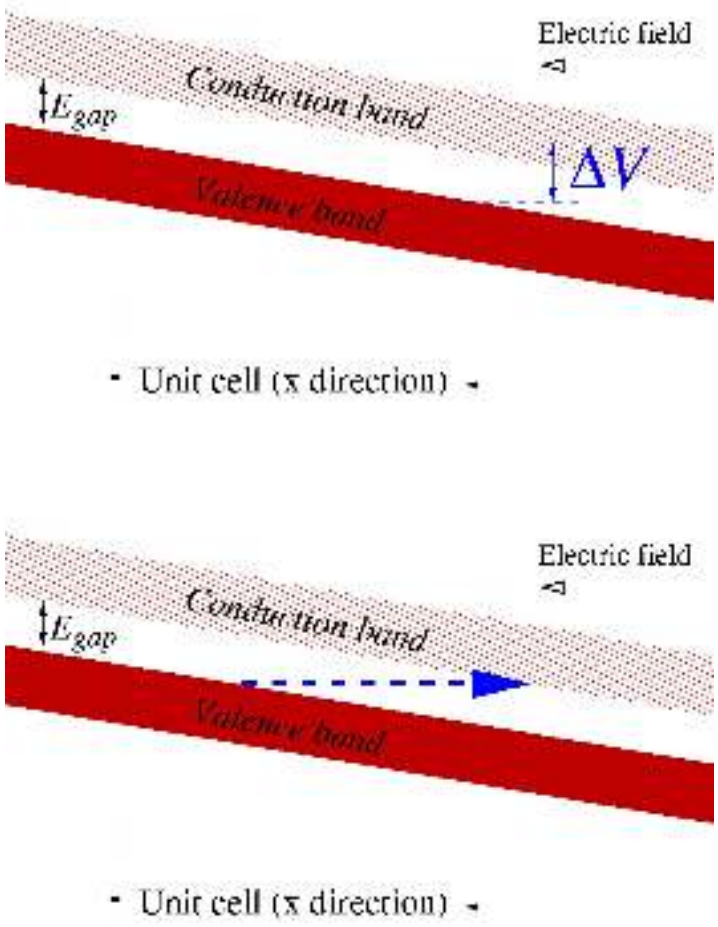


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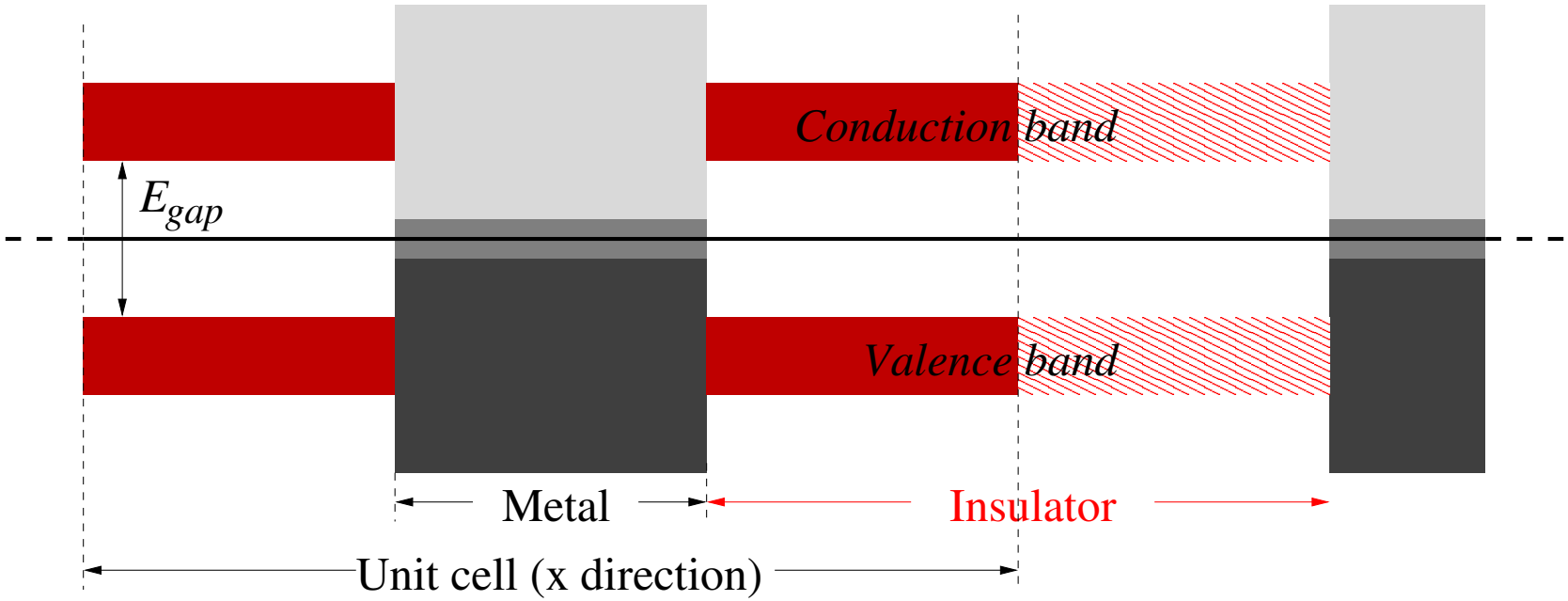
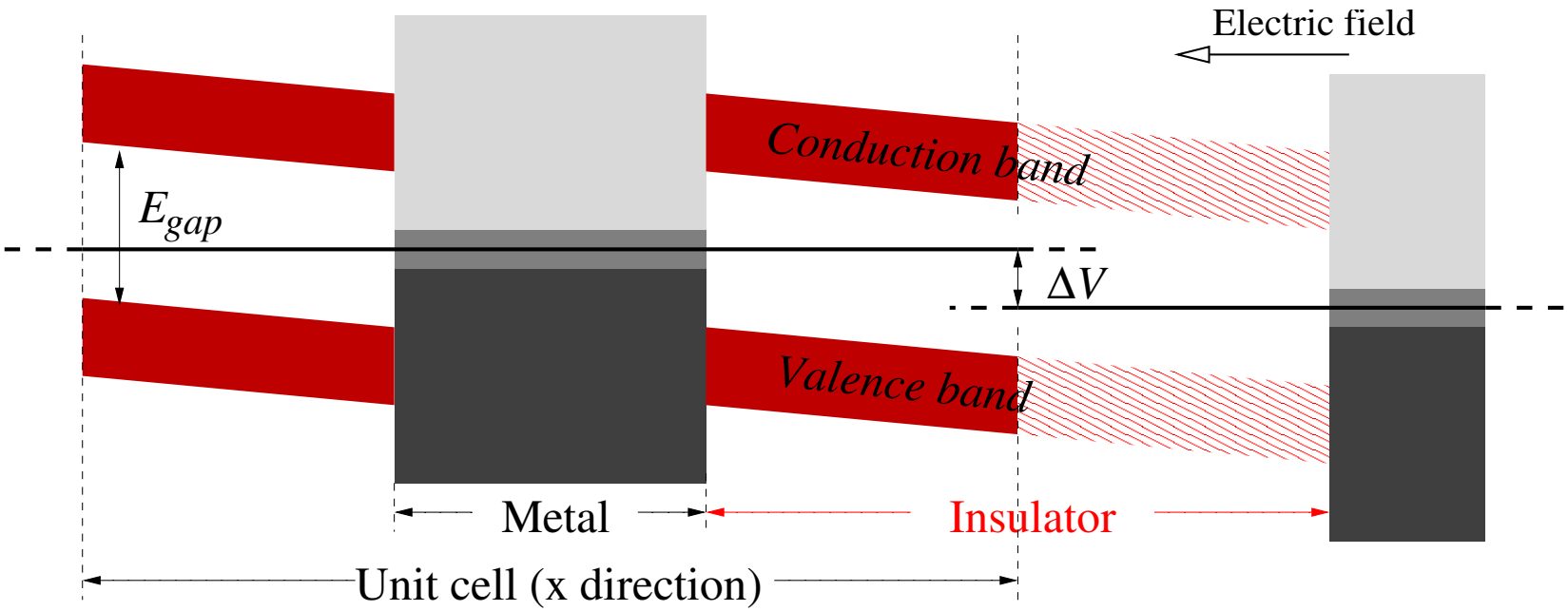
# Metal-insulator heterostructures




- *Conducting* in plane, *insulating* along *x*
- I should be able to apply a finite bias potential...

# Capacitors at finite $\mathcal{E}$




- $P$ and coupling to $\mathcal{E}$ defined with Wannier functions
- The metastable polarized state is well defined as long as $\Delta V < E_{gap}$ (no Schottky tunneling)

M. Stengel and N. A. Spaldin, PRB 75, 205121 (2007).

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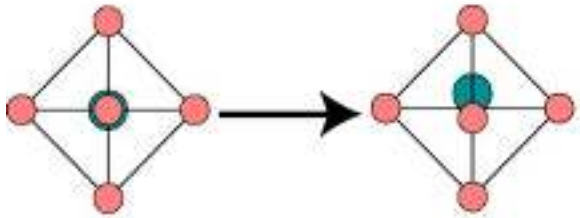
# Is $\mathcal{E}$ a good choice?

- Ferroelectrics (e.g. $PbTiO_3$) have a *polar instability* in the centrosymmetric configuration



- Double-well potential
  - Start from $P = 0$
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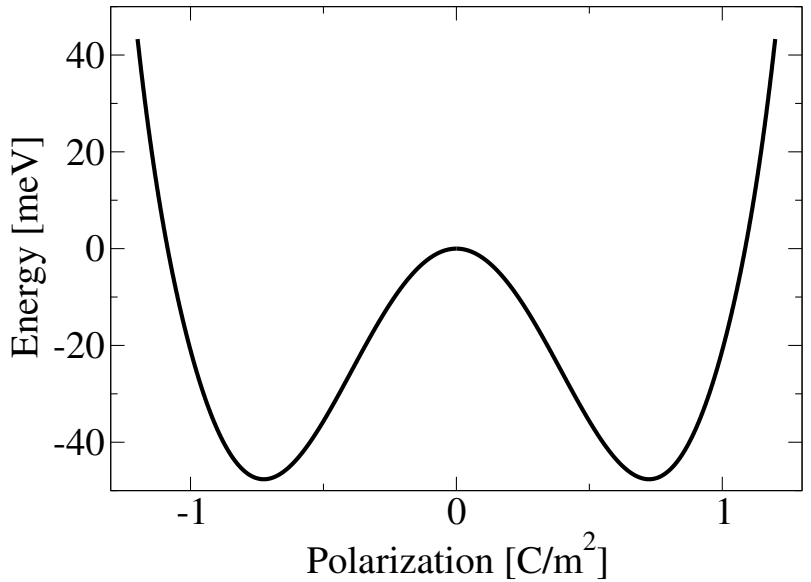
  - Large response
  - I cannot access the unstable region!

    This region is necessary for modeling, so the answer is NO



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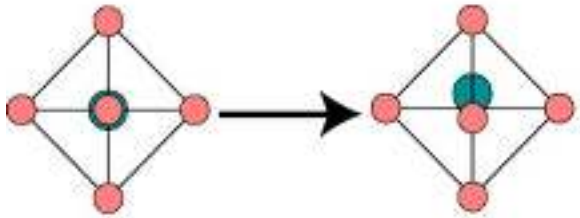

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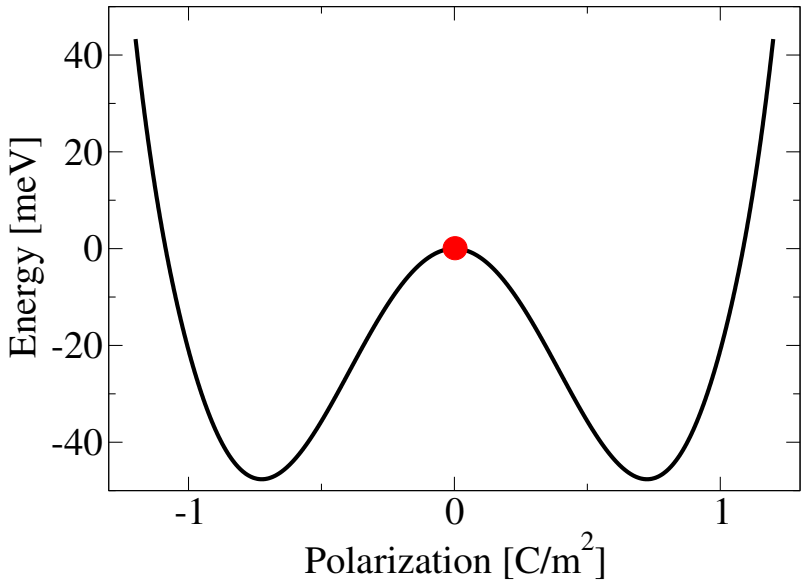

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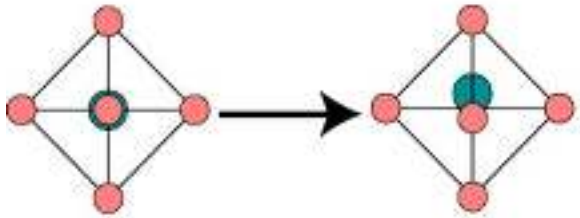

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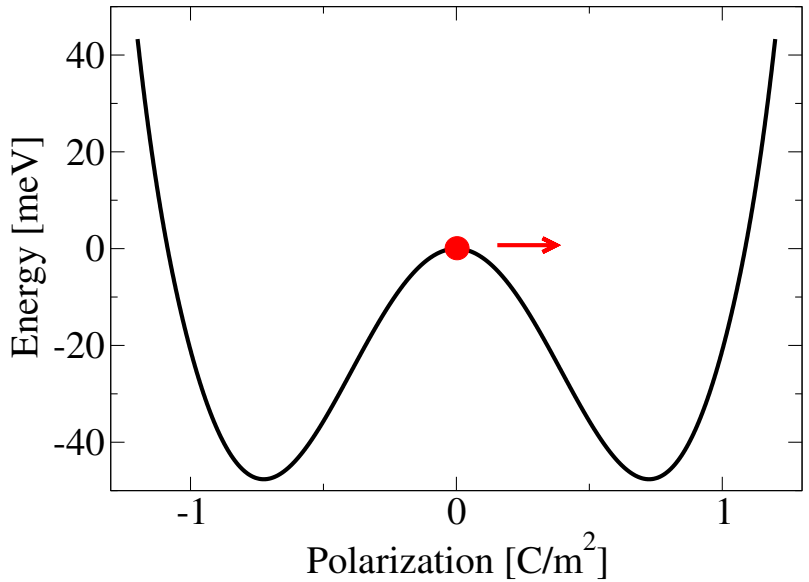

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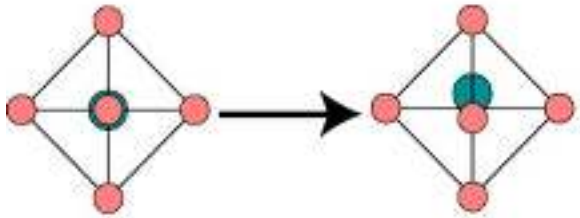

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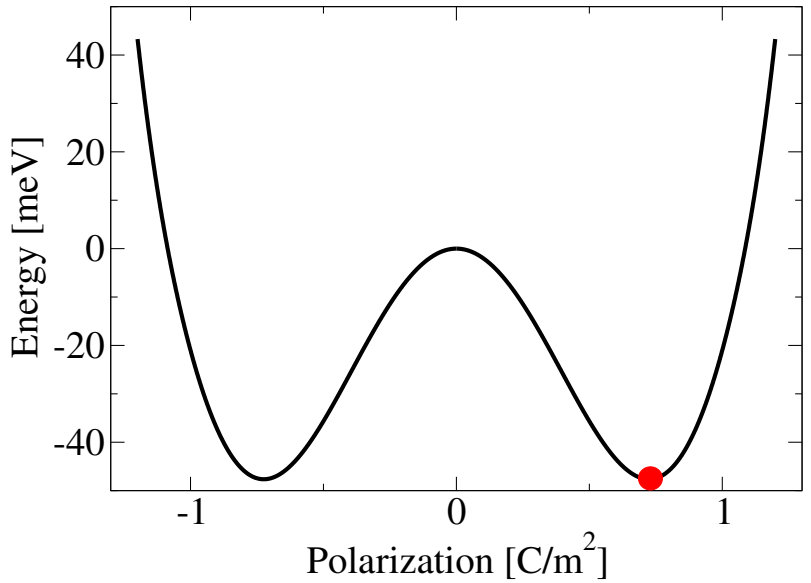

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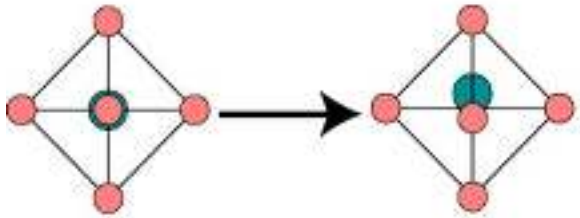

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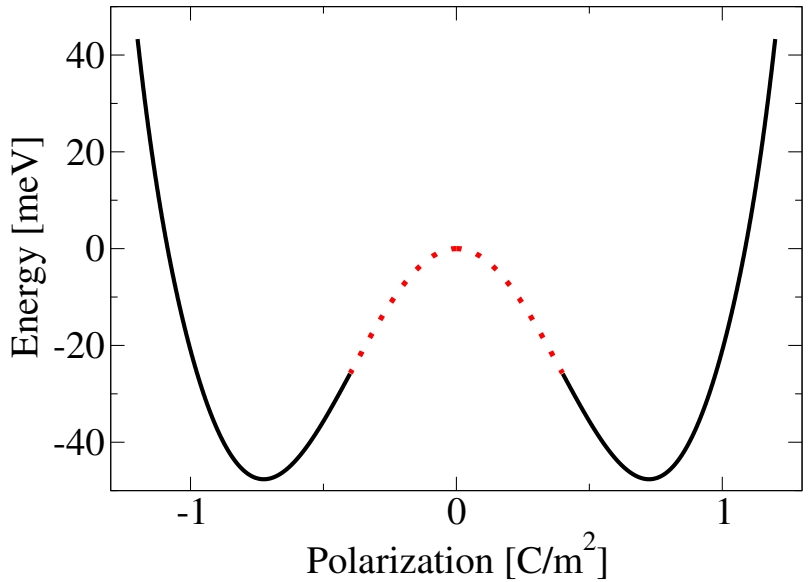


Idea: Try constraining $D = \mathcal{E} + 4\pi P$ instead...

# Solution: Fixed-$D$ method

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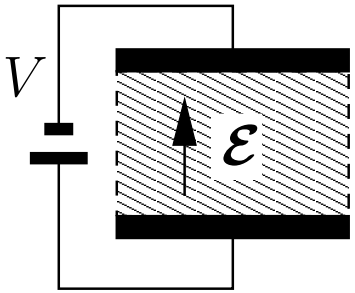


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- In open circuit the polar instability is removed

M. Stengel, N. Spaldin and D. Vanderbilt, Nature Physics 5, 304 (2009).

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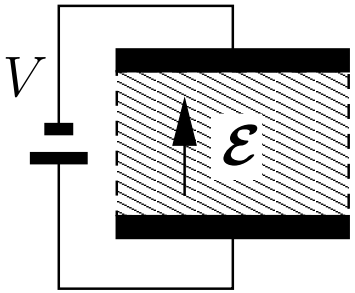


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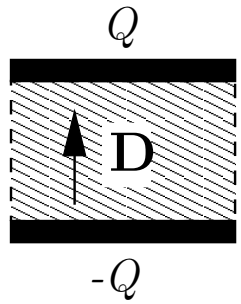


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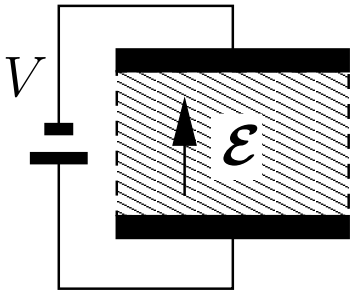


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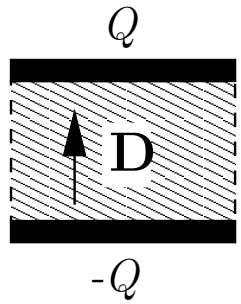
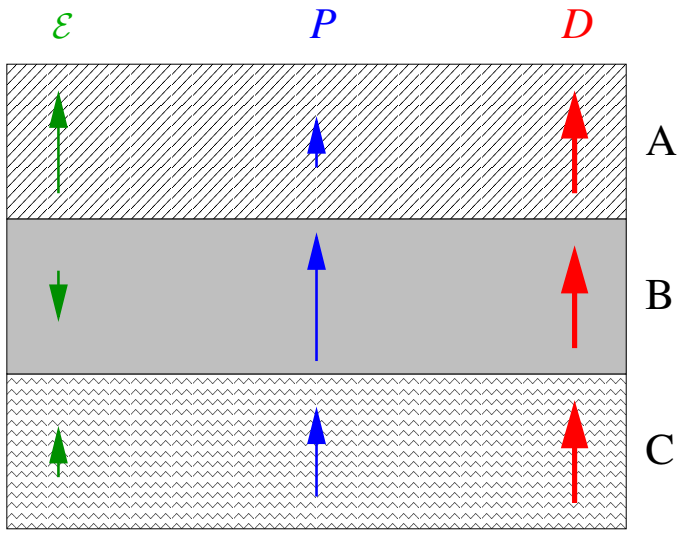



- Full control over the electrical boundary conditions
- In open circuit the polar instability is removed

M. Stengel, N. Spaldin and D. Vanderbilt, Nature Physics 5, 304 (2009).

# Further advantages of using $D$: "locality principle"

- $D$ is constant throughout a layered heterostructure...

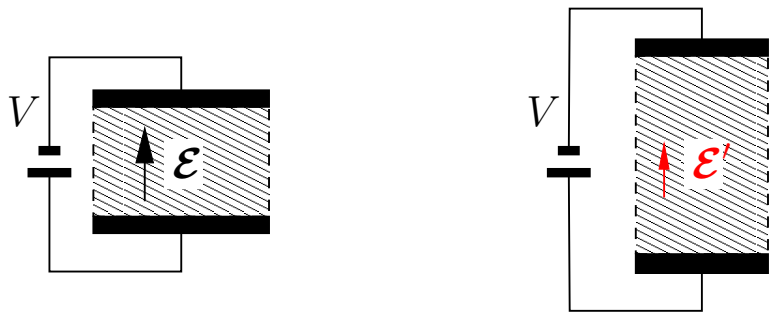



- ...if we know A, B and C we can predict ABC!

$$U_{ABC}(D) = U_A(D) + U_B(D) + U_C(D)$$

*Quantum theory + "old-school" electrostatics*

# Piezoelectricity: treatment of strains




- $V$ or $Q$ remain constant under an applied strain, not $\mathcal{E}$ or $\mathbf{D}$
  - "Proper" treatment of piezoelectric effects
- Relationship to the fields: $V = \mathcal{E} \cdot \mathbf{a}_3, \quad Q = \frac{\mathbf{D} \cdot (\mathbf{a}_1 \times \mathbf{a}_2)}{4\pi}$
- Legendre transform: $\mathcal{F}(V) = \min_Q [U(Q) - QV]$

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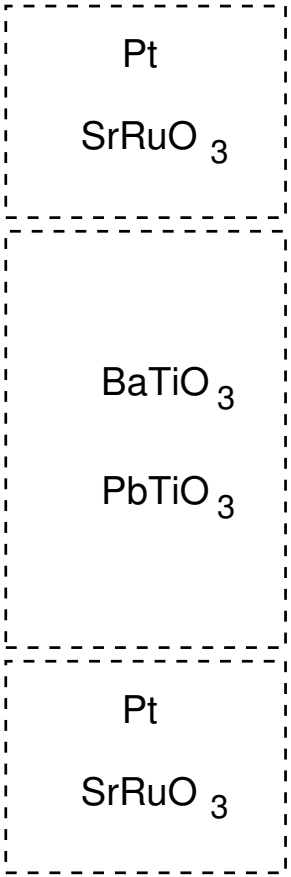
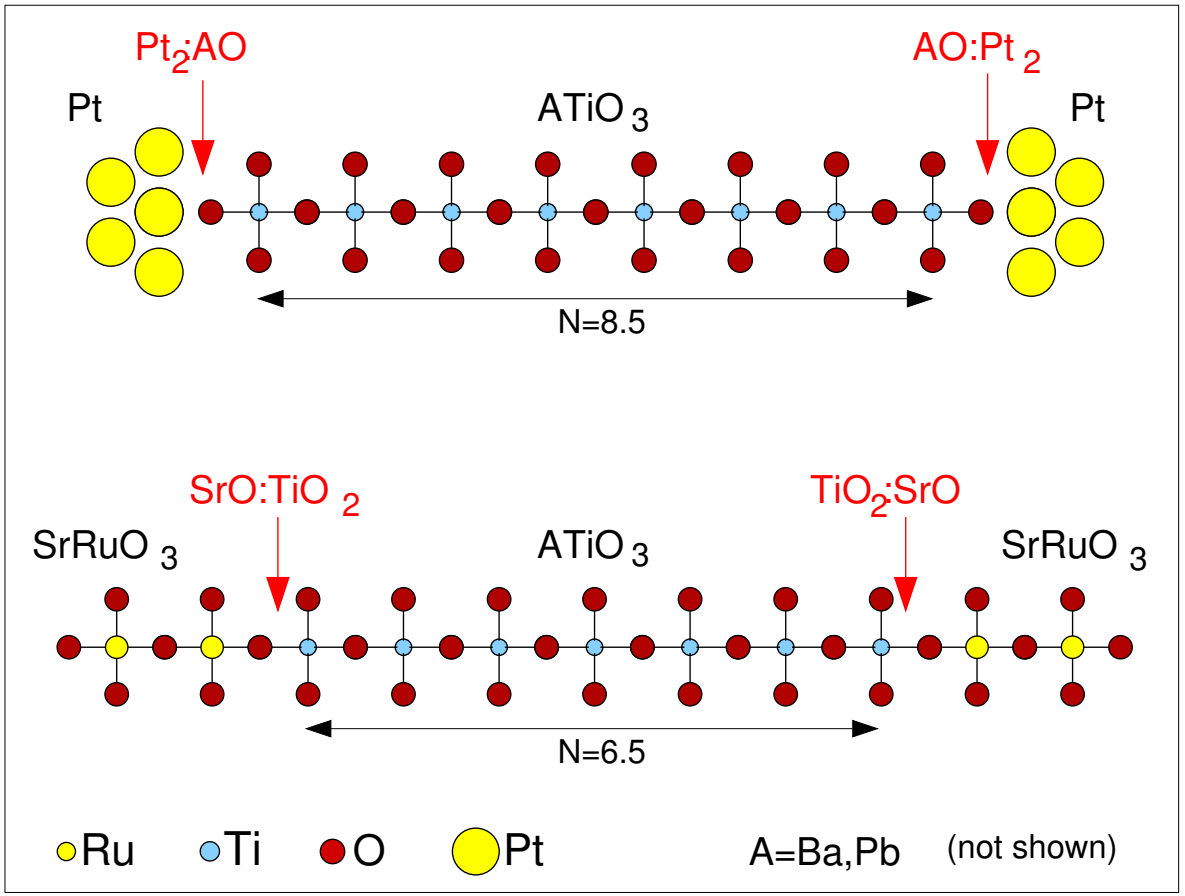
# Outline

# Computational models: four capacitors



# Stability of the paraelectric state

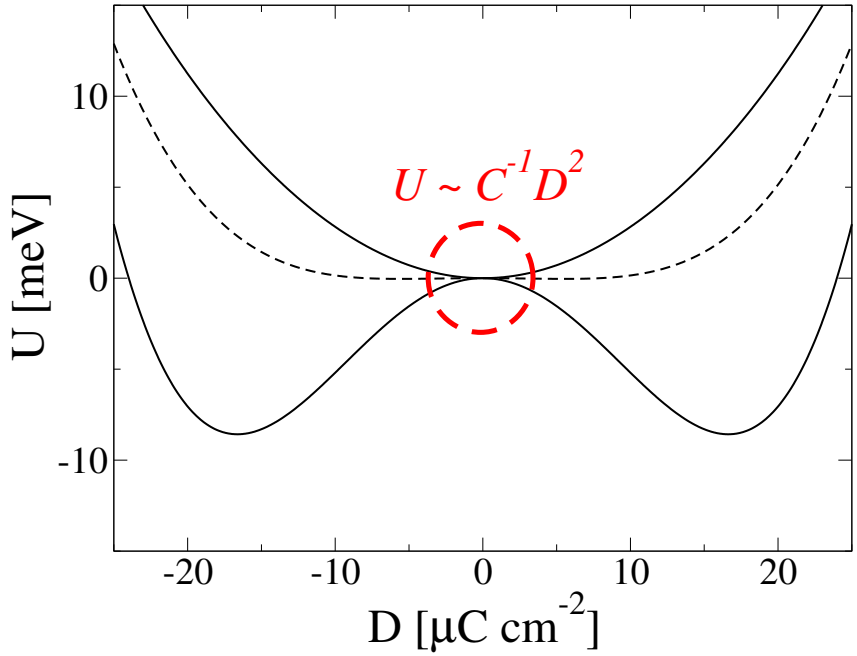
- Inverse capacitance

$$C^{-1} = \left(\frac{4\pi}{S}\right)^2 \frac{d^2U}{dD^2}\bigg|_{D=0}$$

- Stability against polar distortion
  - $C^{-1} > 0 \rightarrow$ stable
  - $C^{-1} < 0 \rightarrow$ unstable

- Results for $C^{-1}S$ [m$^2$/F]

*Impact of bulk vs. interface effects?*




| | $SrRuO_3$ | Pt |
|---|---|---|
| $PbTiO_3$ | 0.44 | -1.43 |
| $BaTiO_3$ | -1.55 | -7.92 |

# Local dielectric response: ferroelectric regime

Inverse permittivity profile: $\epsilon^{-1}(z) = \left.\frac{d\mathcal{E}(z)}{dD}\right|_{D=0}$

- Strong intrinsic effect, localized at the interface
- Series capacitor model $C^{-1} = 2C_I^{-1} + NC_{\text{bulk}}^{-1}$
- Interface term $C_I^{-1}$:

| | $SrRuO_3$ | Pt |
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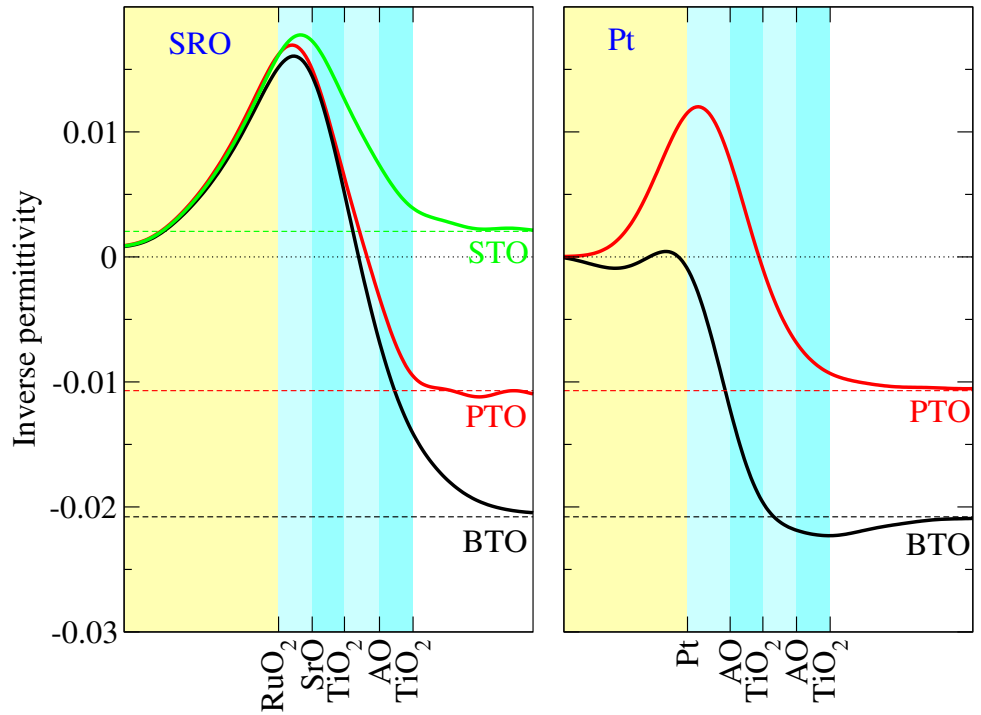
| $BaTiO_3$ | 2.28 | 0.04 |

Units of inv. capacitance density, $m^2/F$



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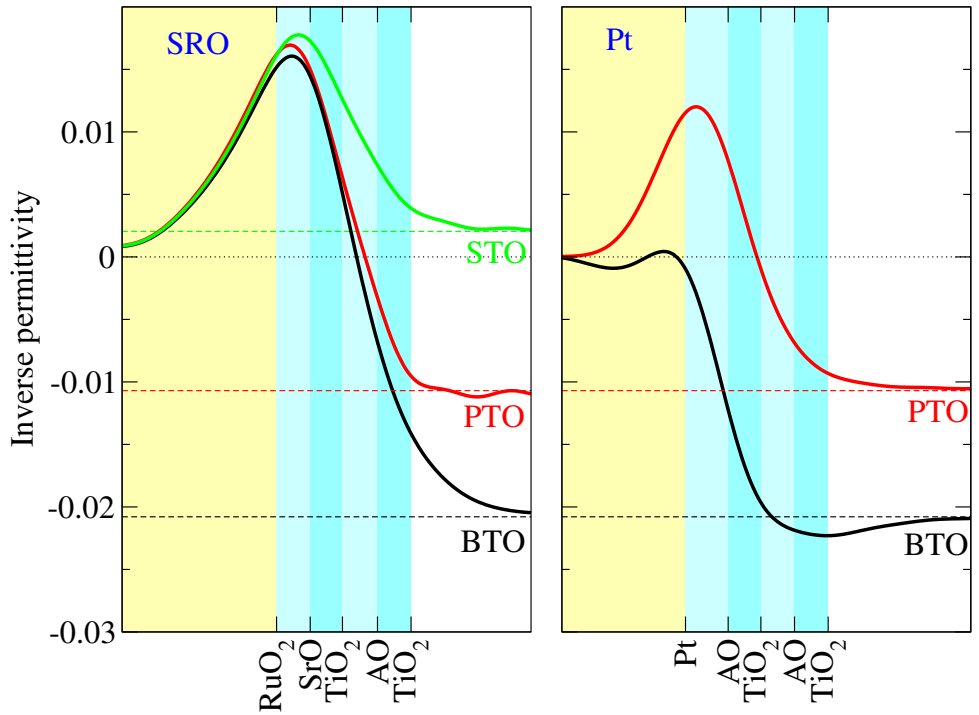

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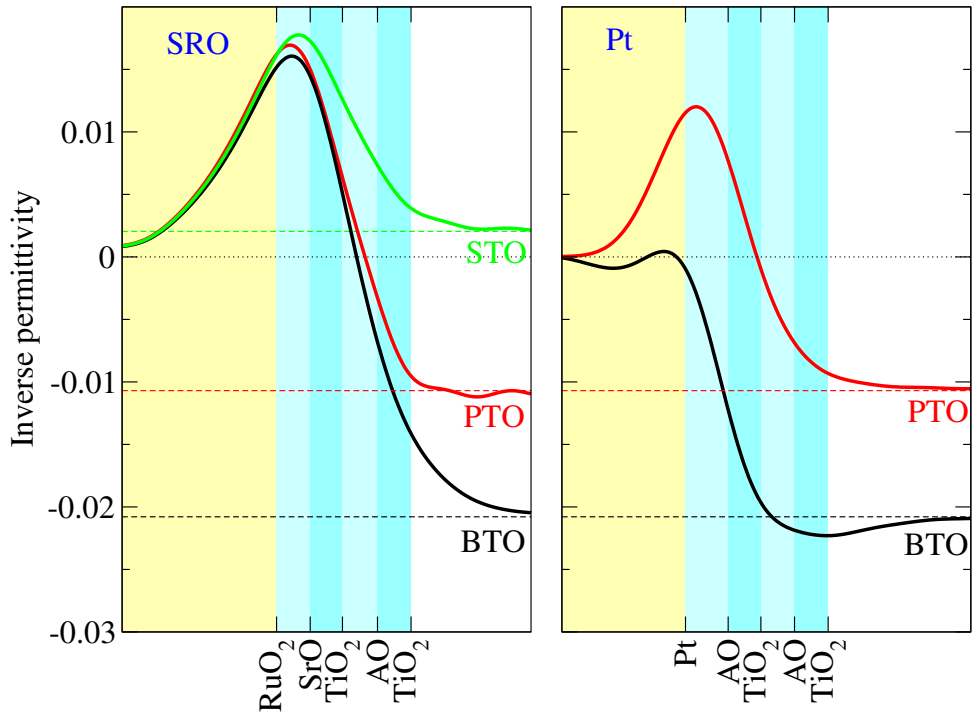

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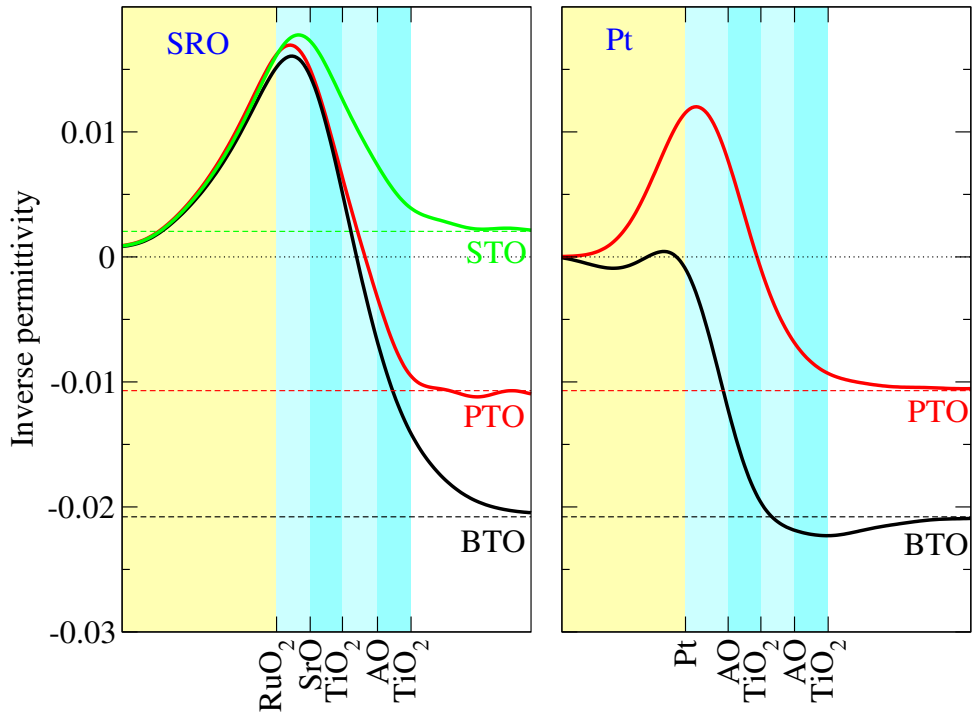


# Critical thickness for ferroelectricity

- Series capacitor model:

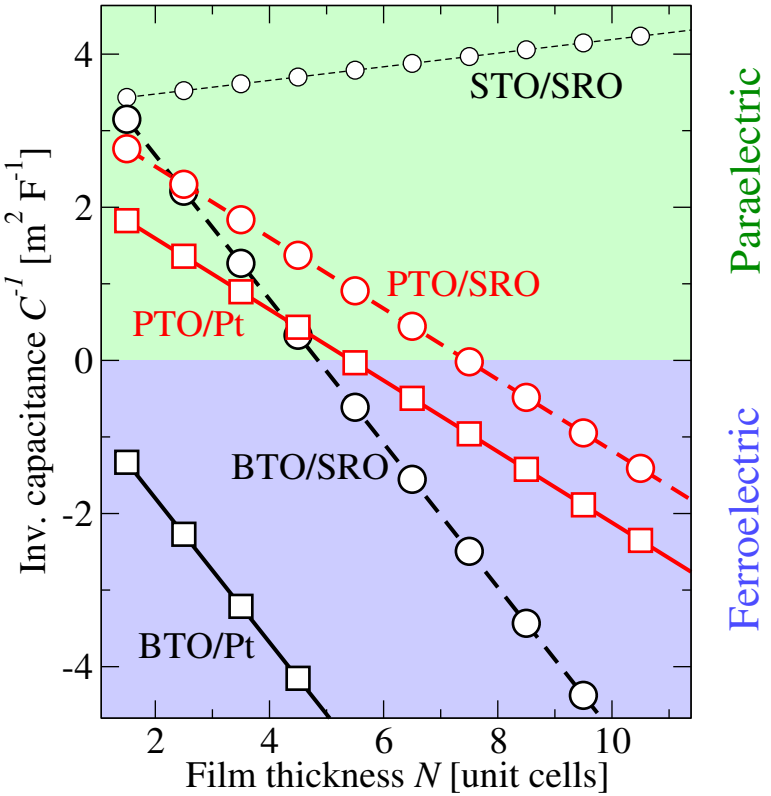
$$C^{-1}(N) = 2C_I^{-1} + NC_{\text{bulk}}^{-1}$$

- Critical thickness for FE:

$$C^{-1} = 0 \quad \Rightarrow \quad N_{\text{crit}} = -\frac{2C_I^{-1}}{C_{\text{bulk}}^{-1}}$$

| | SRO | Pt |
|---|---|---|
| $PbTiO_3$ | 8 | 6 |
| $BaTiO_3$ | 5 | 0 |

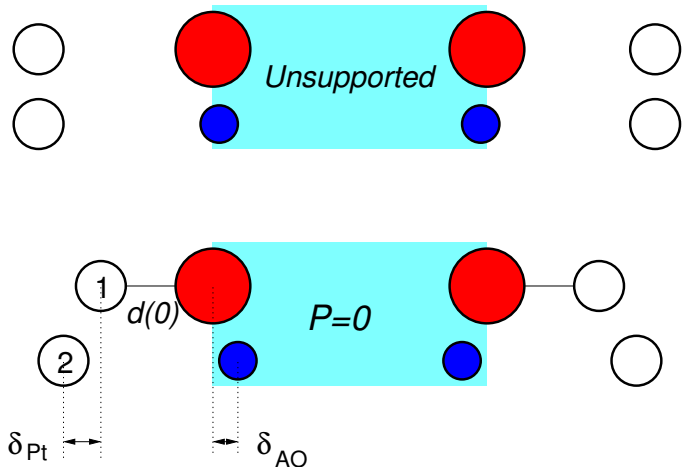
Thickness in number of unit cells




$N_{\text{crit}} = 0$ in $BaTiO_3$/Pt?!

# Chemical bonding at the AO-Pt interface

- AO-terminated interfaces
  - Both O and A in the *atop* site
- Frustrated bonding environment, two competing effects:
  - Pt-O attraction (bonding)
  - Pt-A repulsion (non-bonding)



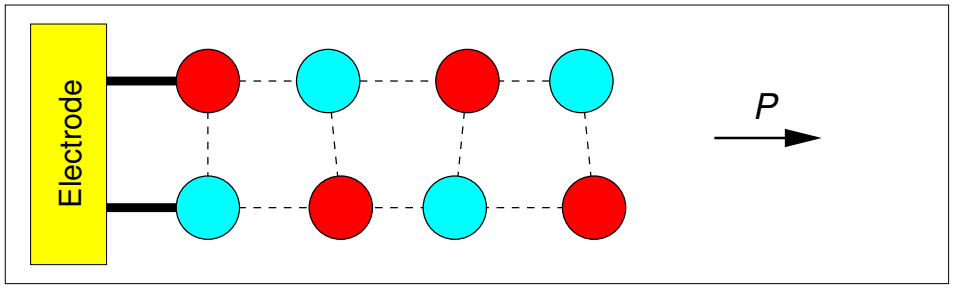

| | $d$ (Å) | $\delta_{Pt}$ (Å) | $\delta_{AO}$ (Å) |
|---|---|---|---|
| A=Ba | 2.26 | 0.46 | 0.12 |
| A=Pb | 2.11 | 0.34 | 0.19 |

Pt-O $\sim$ 2.0 Å in bulk oxide phases

# Interface bonding and ferroelectricity

## Idea:

- "Loose" interface bonds favor *P*




- Force constants at the interface:

| | $PbTiO_3$ | $BaTiO_3$ |
|---|---|---|
| $-K^L_{Pt-O}$ | 3.9 | -0.1 |

($K_{ij} = \frac{\partial^2 U}{\partial z_i \partial z_j}$, units of $10^{-3}$ a.u.)

- Computational experiment: Artificially "soften" Pt-O bond in $PbTiO_3$/Pt

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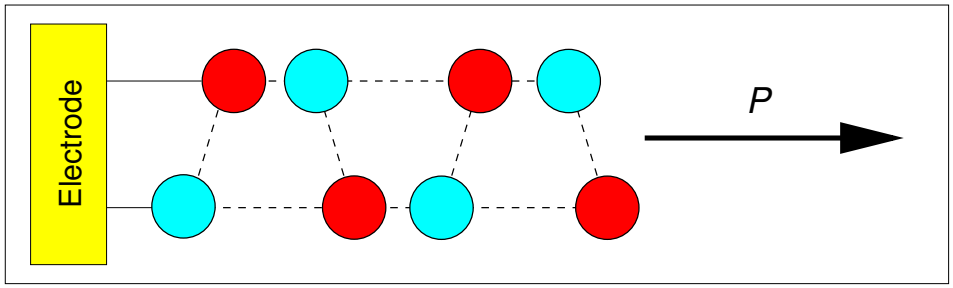


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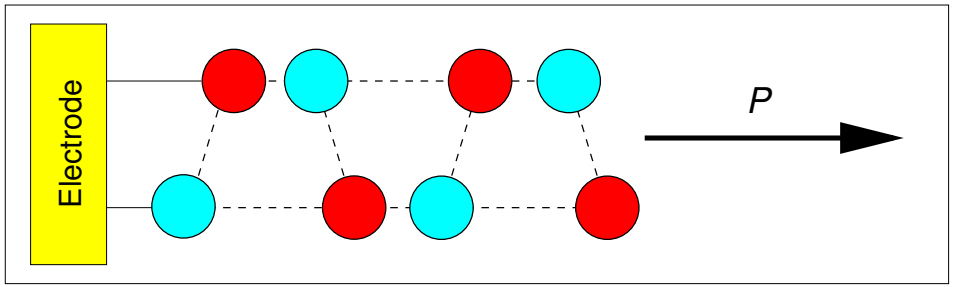


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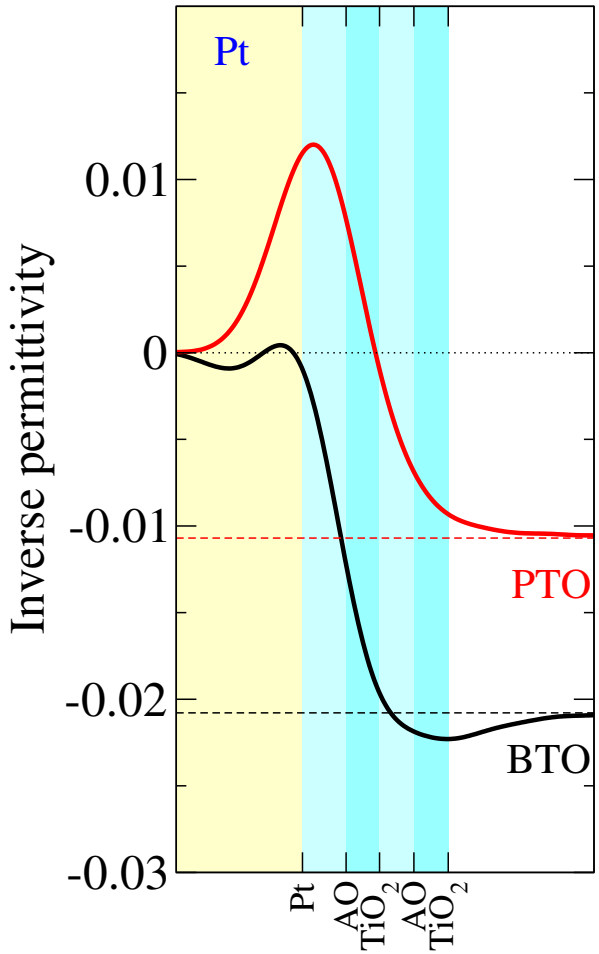

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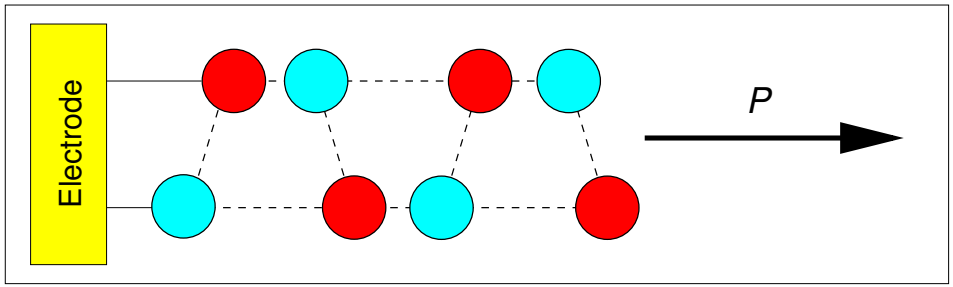


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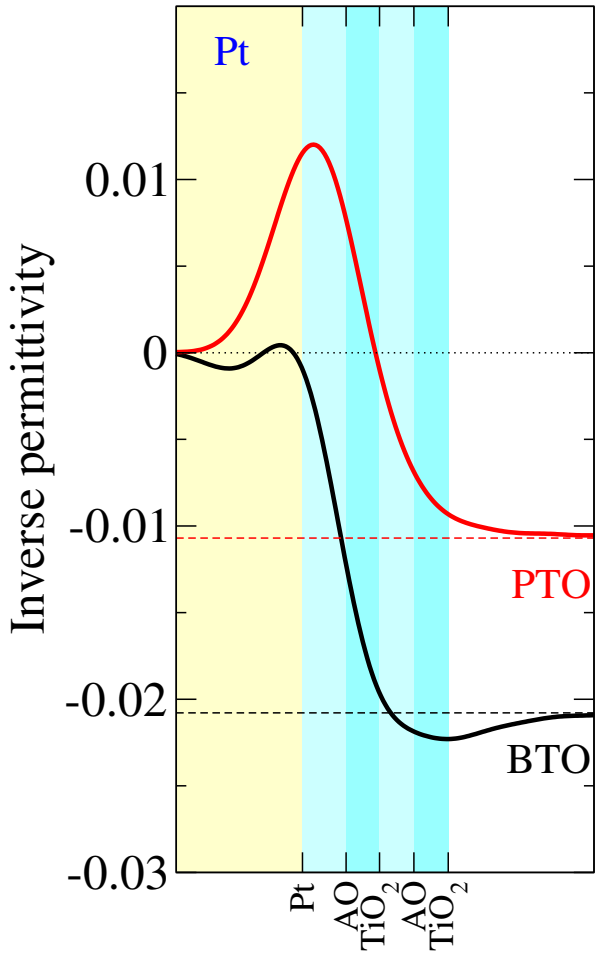

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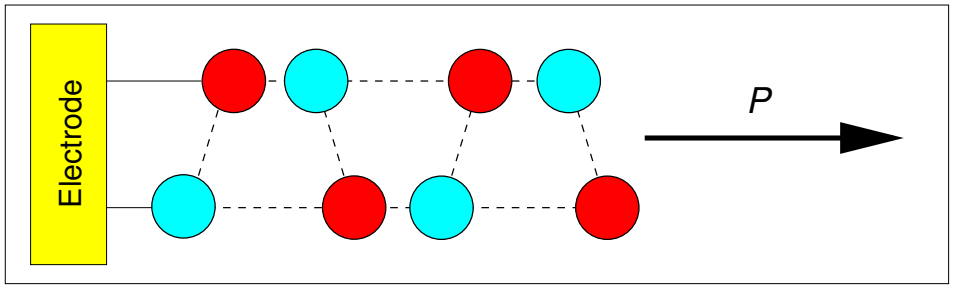


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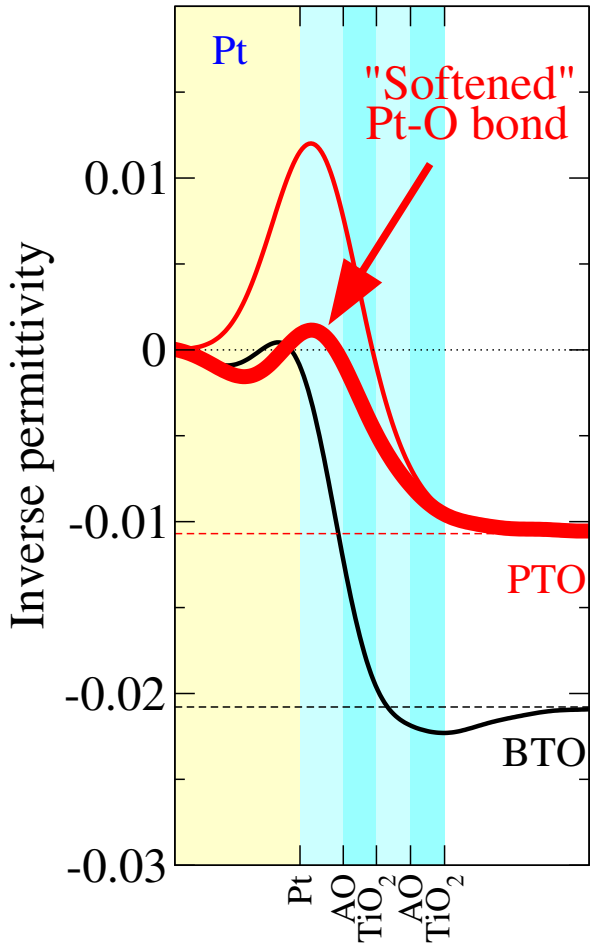
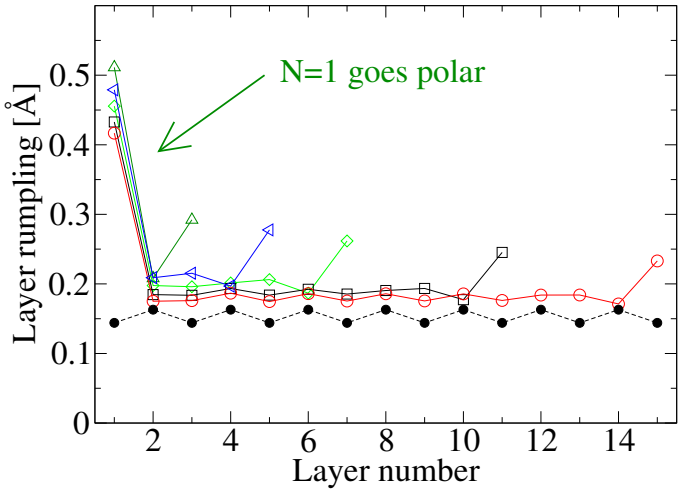
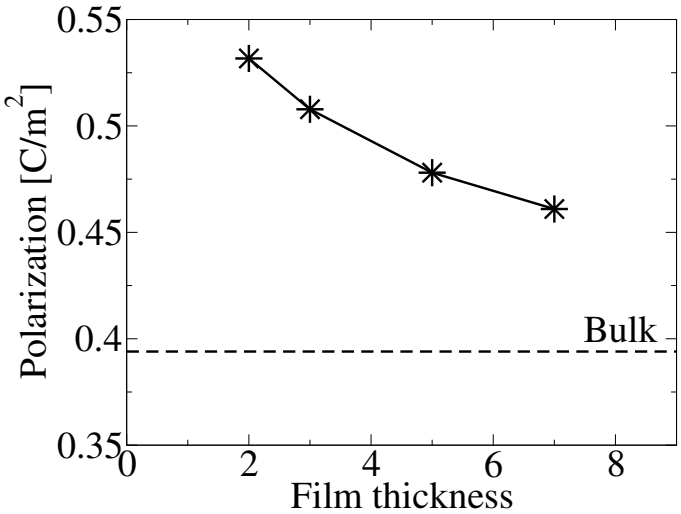



*Interface ferroelectricity driven by Pt-O bond!*

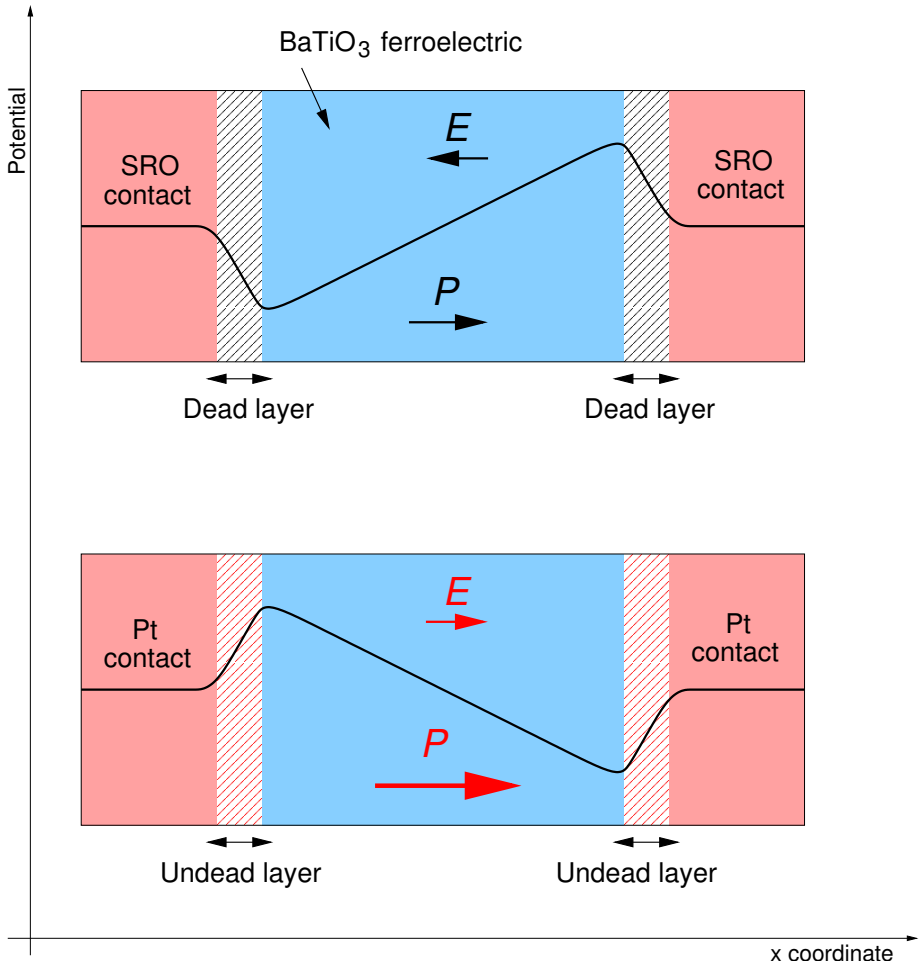
# What about the polar ground state?

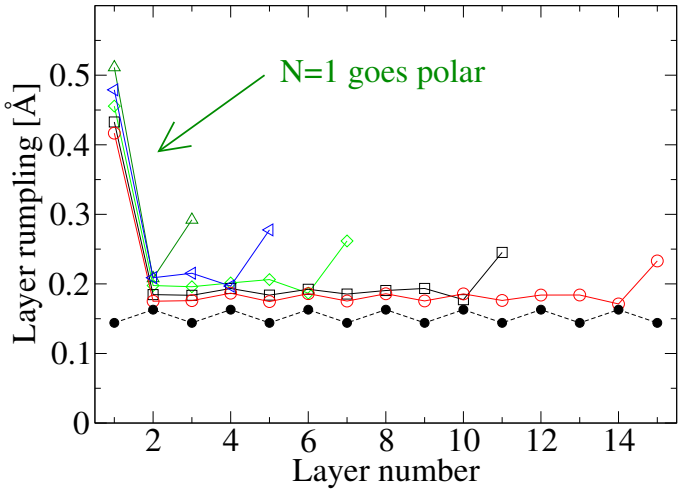
- So far: paraelectric reference structure
- Out of curiosity: look at $P$ in the ferroelectric state ($BaTiO_3$/Pt)
  - $N = 1, 2, 3, 5, 7$
  - Standard short-circuit
- Polarization and distortions increase the thinner the film
- Chemical bonding mechanism even stronger in the FE state!

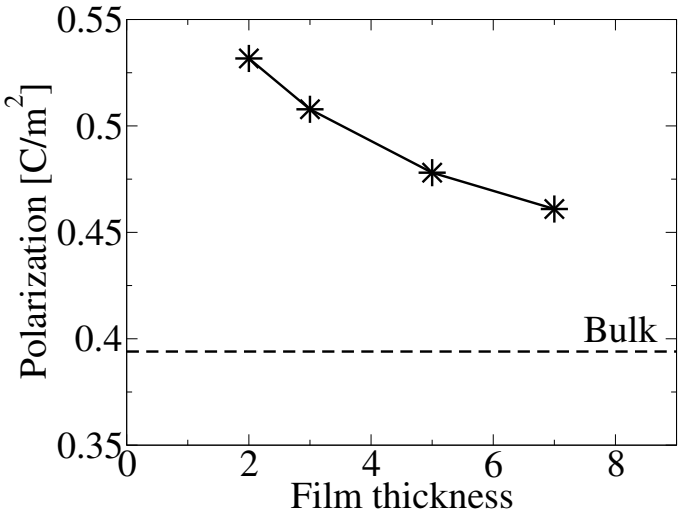


# “Negative dead layer” regime



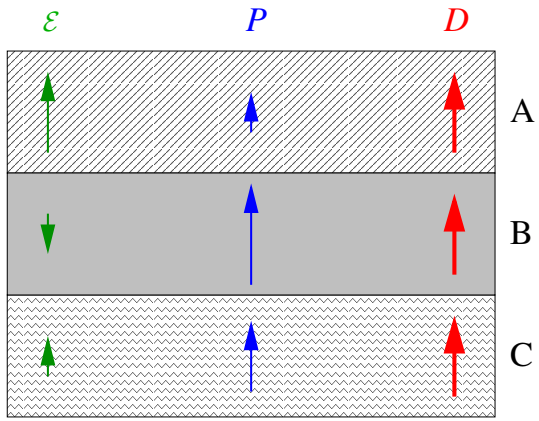



# Summary

- Layer-by-layer device design via constrained-$D$ density-functional theory

  M. Stengel, N. A. Spaldin and D. Vanderbilt,

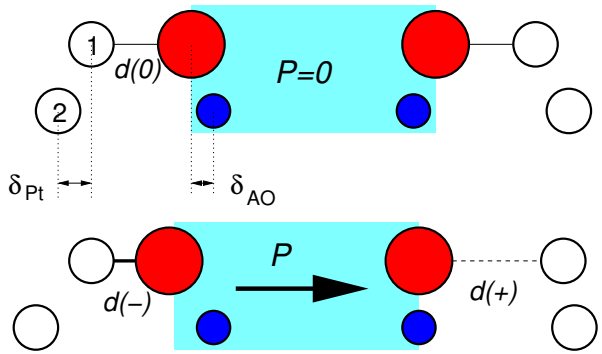
  *Nature Physics* 5, 304 (2009).




- Enhancement of ferroelectricity driven by electrode-film bonding

  M. Stengel, D. Vanderbilt and N. A. Spaldin,

  *Nature Materials* 8, 392 (2009).



# Microscopic analysis of $C^{-1}$

- Decomposition into LO polar modes

$$C^{-1} = (C^{\infty})^{-1} - \left(\frac{4\pi}{S}\right)^2 \sum_{ij} Z^L_{i,x} (K^L)^{-1}_{ij} Z^L_{j,x}$$

- Three basic ingredients:
  1. Electronic capacitance $C^{\infty}$ (frozen ionic positions)
  2. LO dynamical charges $Z^L$ (lattice-electric field coupling)
  3. Interatomic force constants $K^L_{ij}$ (bond "stiffness")

# Purely electronic effects ($C^{\infty}$ and $Z^{L}$)

- $C^{\infty}$ (frozen ions) depends on center of induced $\rho$

  *PTO/Pt better than BTO/Pt!*

- Dynamical charges are smaller near the interface

  *PTO/Pt similar to BTO/Pt!*