The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific
and Cultural Organization

International Atomic
Energy Agency

SMR.1824 - 14

**13th International Workshop on
Computational Physics and Materials Science:
Total Energy and Force Methods**

11 - 13 January 2007

First-principles calculations of capacitors at finite bias

Massimiliano STENGEL
University of California at Santa Barbara
Department of Materials
CA 93117-5050 Santa Barbara
U.S.A.

First-principles calculations of capacitors at finite bias

Massimiliano Stengel and Nicola A. Spaldin

Materials Department, University of California, Santa Barbara
CA 93106-5050, USA

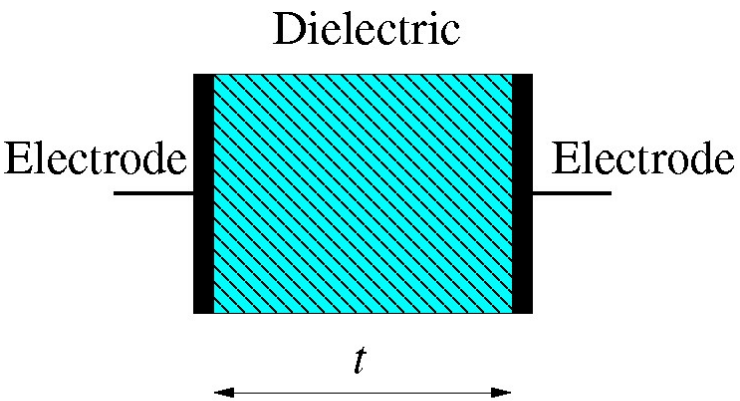
Why capacitors?

- Capacitors are omnipresent in electronic circuits and devices
- Often they are the largest components, and reducing their size is crucial
- Size and thickness have reached a regime where classical and phenomenological models are no longer reliable (<10 nm)

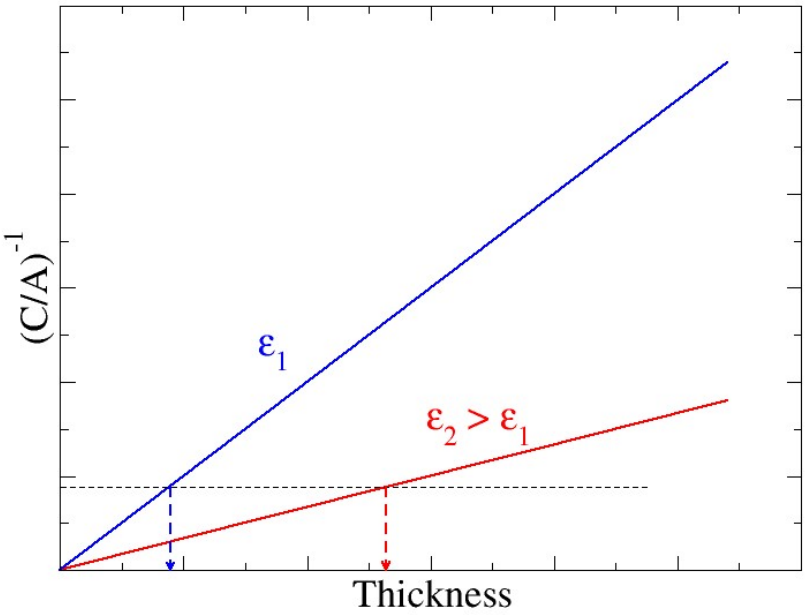
Outline

- **Motivation from the experiments**
- Theoretical methods
- Results
- Conclusions

Classical capacitor

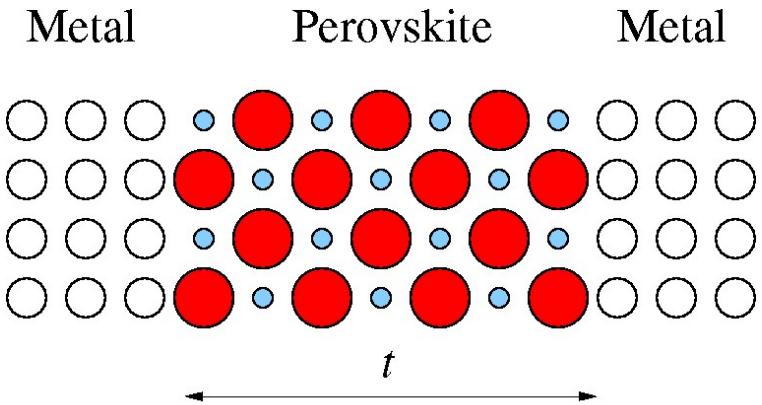


$$C/A = \varepsilon_0 \frac{\varepsilon}{t}$$

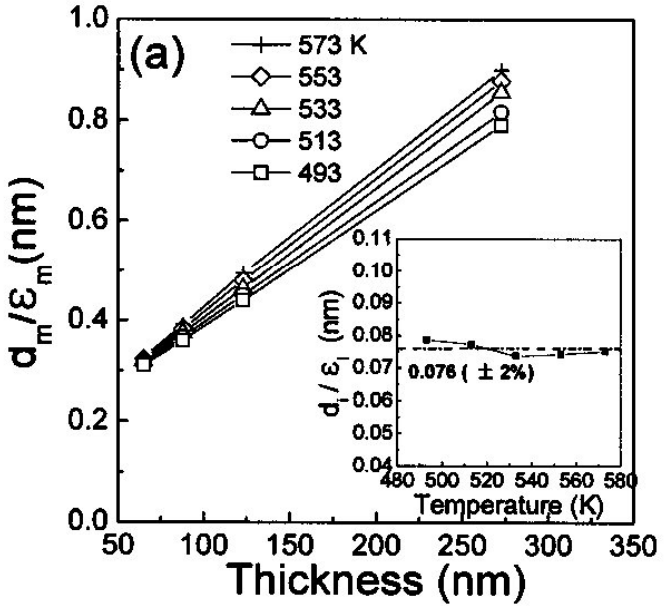


- Miniaturization → we have to increase C/A
  - Thinner films
  - Materials with higher permittivity ε

Thin-film high-ε devices



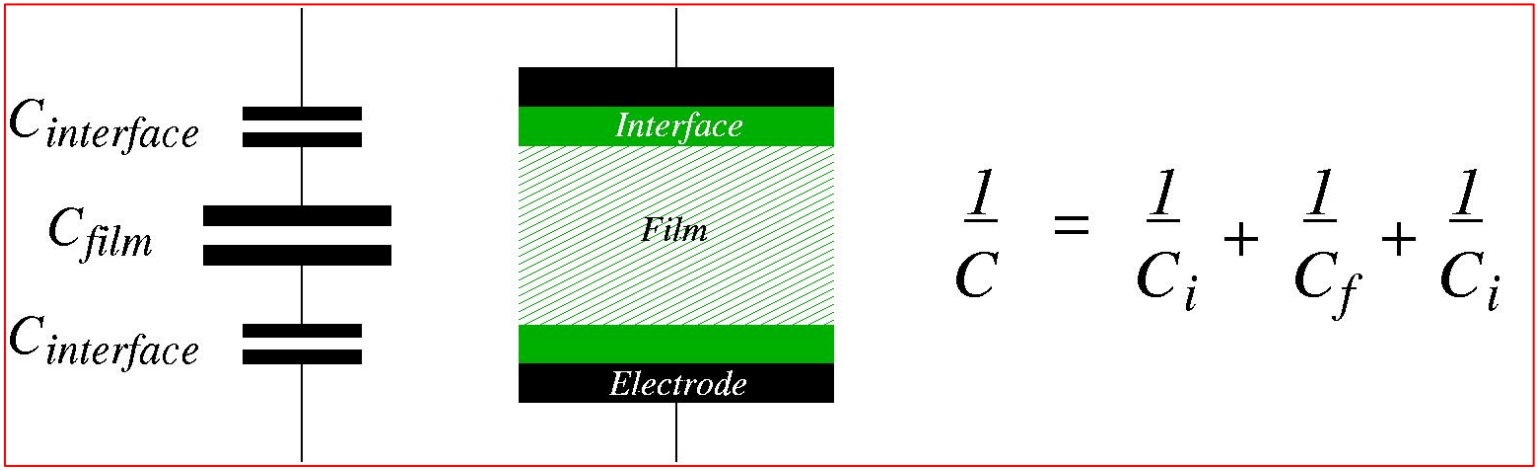
$$C/A << \varepsilon_0 \frac{\varepsilon}{t} \quad (exp.)$$



C. S. Hwang, JAP 92, 432 (2002).

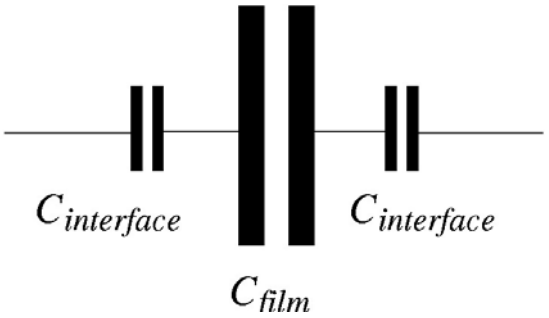
- Finite intercept for t→0: here *C/A* = 30 fF/μm^2
- Linear behavior: *1/C* = *at*+*b*

Dielectric “dead” layer

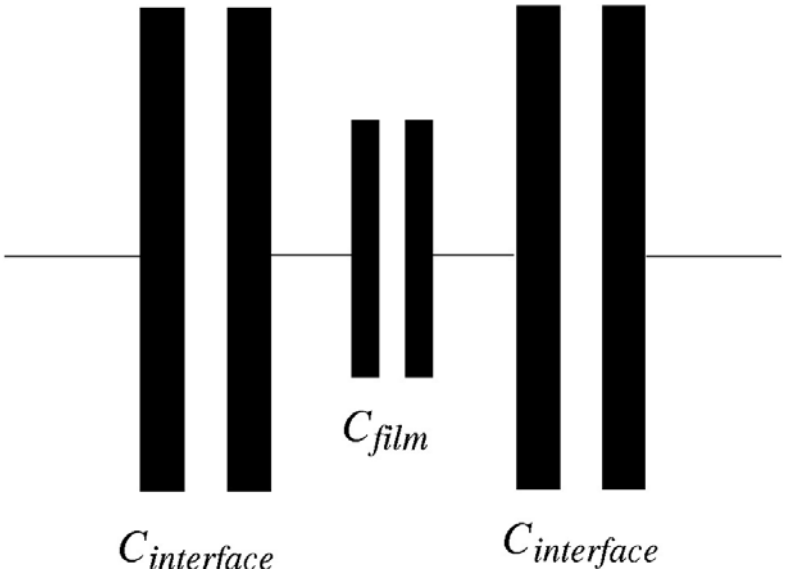


- Physical origin: Intrinsic or defect-induced?
- Role of the electrode: elemental metals (Pt, Au) vs. metallic oxides ($SrRuO_3$)?
- Practical question: how can we avoid it?

Interfacial capacitance



- **Dead layer**
  - $C_{interface} << C_{film}$
  - $C \sim C_{interface}/2$

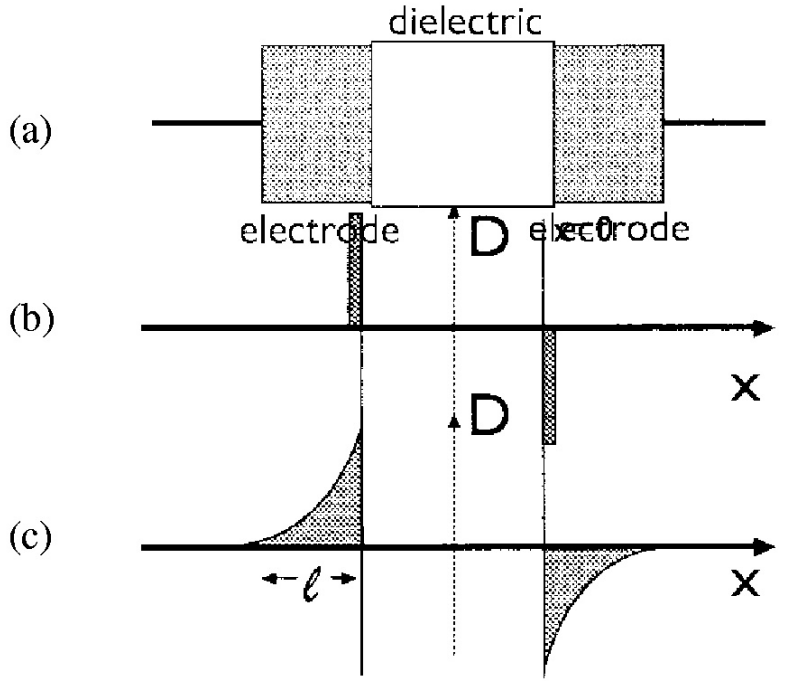


- **No dead layer**
  - $C_{interface} >> C_{film}$
  - $C \sim C_{film}$

We want an interfacial capacitance as high as possible!

What is the origin of C_i?

- Imperfect screening at the interface
- Phenomenological model: metallic oxide electrodes ($SrRuO_3$) are intrinsically better than Pt because of lattice contribution to the screening



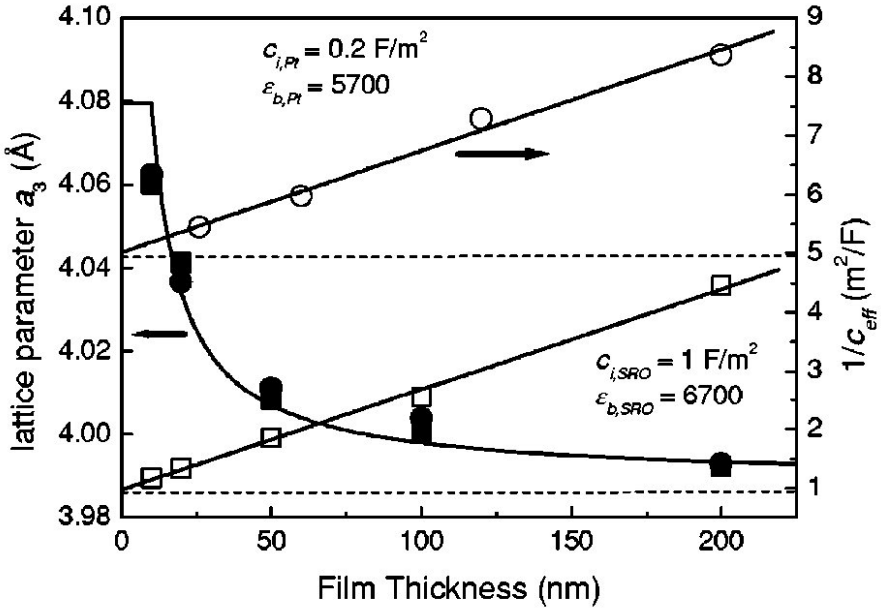
C_{SRO}~900 fF/um^2, C_{Pt}~200 fF/um^2

C. C. Black & J. J. Welser, IEEE Trans. 46, 776 (1999)

Many results support this model…

- Much higher C_i with $SrRuO_3$ electrodes compared to Pt, in agreement with the model
- These results seem to confirm the importance of ionic screening, which is absent in Pt

-Thin epitaxial $(Ba,Sr)TiO_3$ films
-Capacitance & strain measured as a function of thickness



R. Plonka et al., APL 86, 202908 (2005)

…but others don't!

- No T shifts in $BaTiO_3$ single-crystal lamellae (as thin as t=75 nm) with Au electrodes!

$$\frac{1}{\mathcal{C}(T)} = \frac{4\pi t}{\epsilon_{bulk}(T)} + 2/\mathcal{C}_i$$

Curie-Weiss law

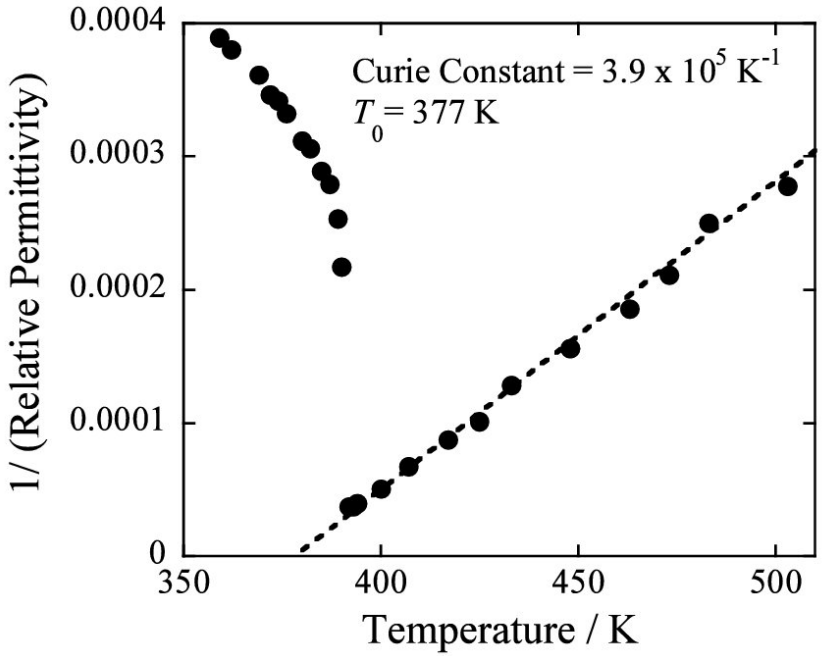
$$\frac{1}{\epsilon_{bulk}(T)} = (T - T_0)/\alpha$$

$$\frac{1}{\mathcal{C}(T)} = \frac{4\pi t}{\epsilon_{bulk}(T + \Delta T)}$$

Temperature shift

$$\Delta T = \frac{2\alpha}{4\pi t \mathcal{C}_i}$$

If C_i=200 fF/um2, ΔT~150 K!

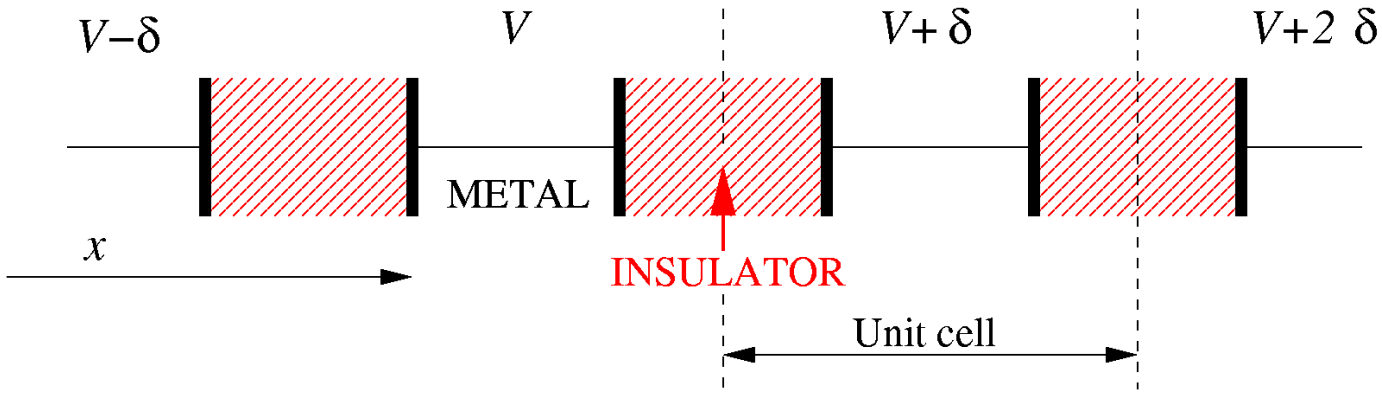


M. M. Saad *et al.*, J. Phys. Cond. Mat. 16, L451 (2004).

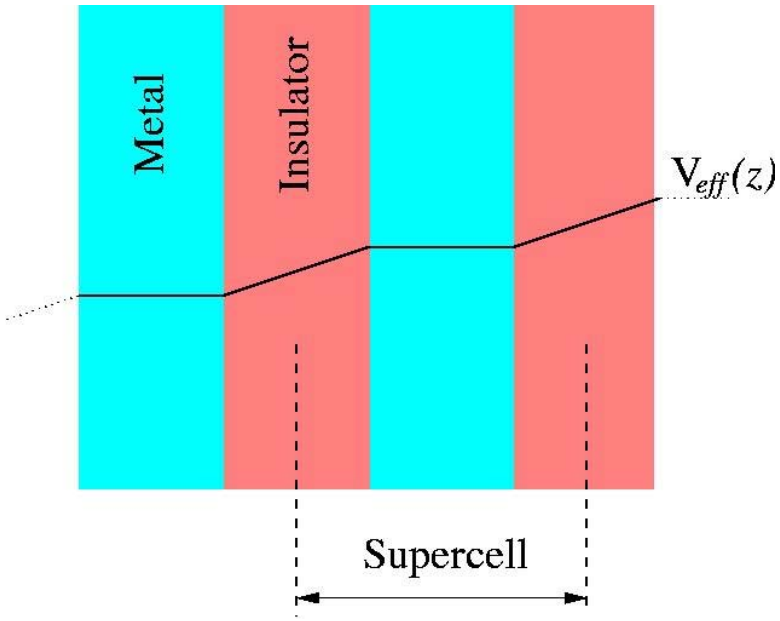
Outline

- Motivation from the experiments
- **Theoretical methods**
- Results
- Conclusions

Computational setup

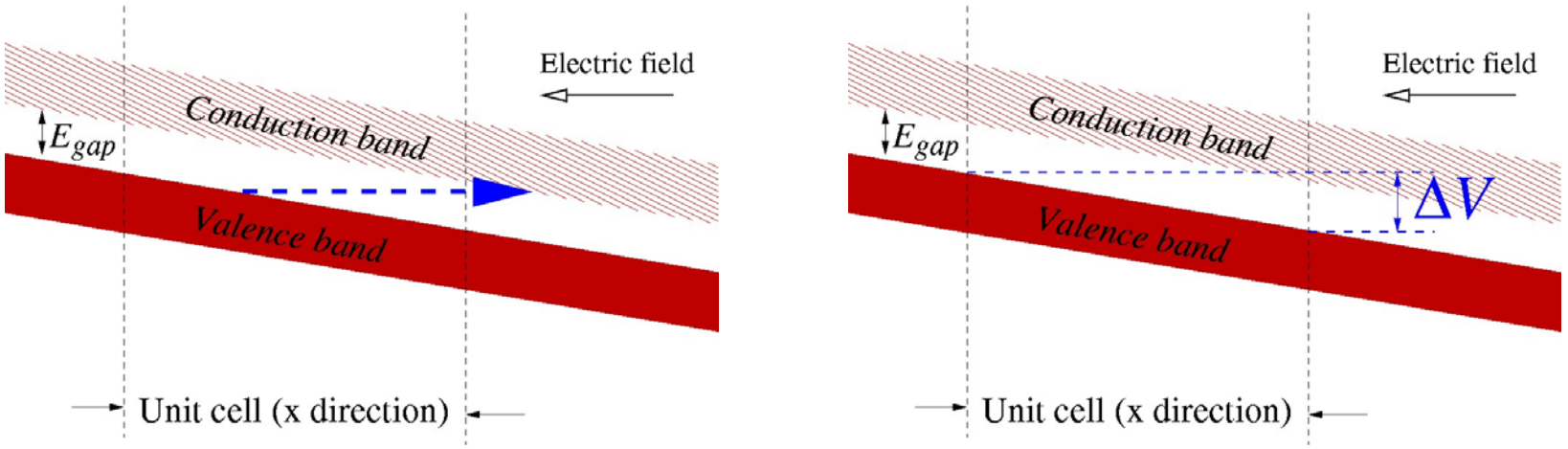


- Supercell technique + Periodic boundary conditions
- Finite electric fields



$$E^{\mathcal{E}} = E_{KS} - \Omega\mathcal{E}.\langle P\rangle = E_{KS} - e\mathcal{E}.\langle x\rangle$$

Electric fields + PBC?



- An infinite crystal in a uniform external field *does not have a ground state*
- Scalar potential is *non-periodic*
- Recently solved for pure insulators*

*I. Souza, J. Iñiguez and D. Vanderbilt, PRL 2002
P. Umari and A. Pasquarello, PRL 2002

Polarization in insulators

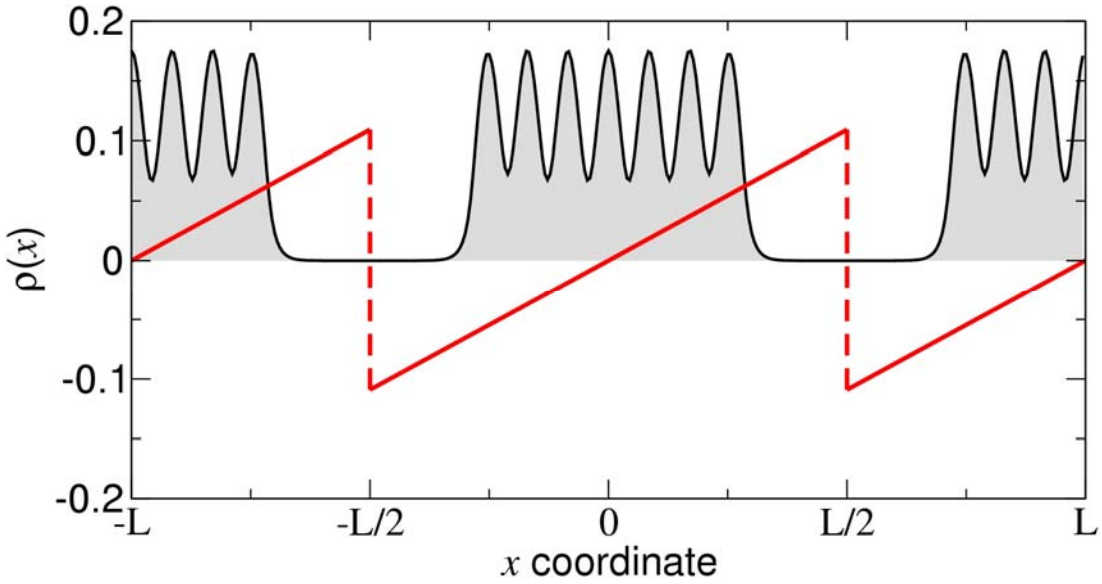
- The position operator in a **pure insulator** can be expressed in ***k*-space** as a Berry phase*

$$\langle x \rangle_{Berry} = \frac{L}{2\pi} \mathrm{Im} \ln \det M$$

$$M_{mn} = \langle \psi_m | e^{i \frac{2\pi}{L} x} | \psi_n \rangle$$

*R. D. King-Smith and D. Vanderbilt, PRB **47**, 1651 (1993)

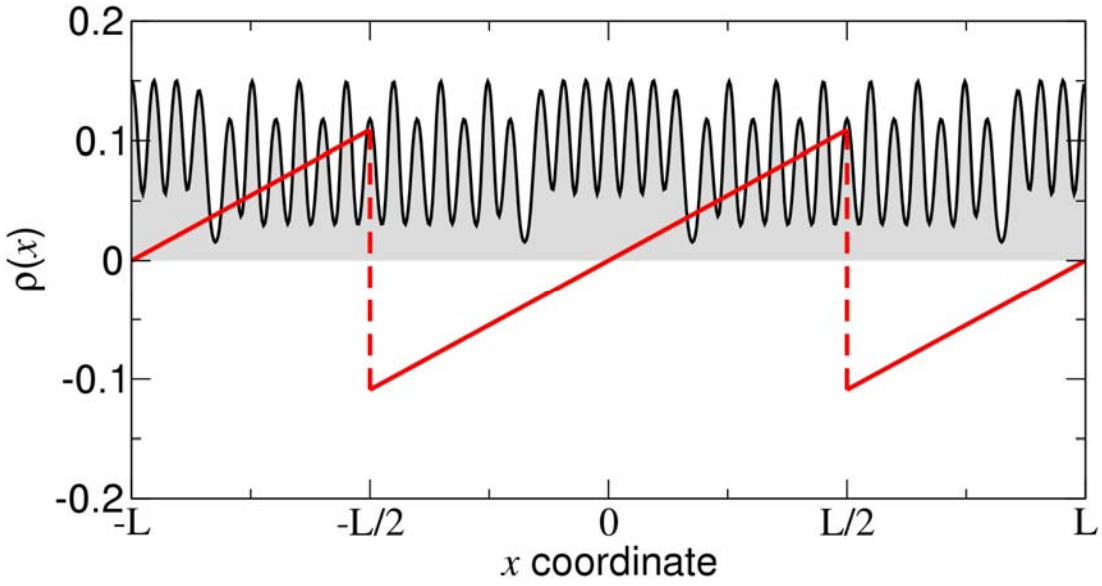
Metallic slab in vacuum



- Polarization (dipole moment) can be calculated in real space with a saw-tooth function

$$\langle x \rangle = \int_{-L/2}^{L/2} x\rho(x)dx$$

And a capacitor?



- Saw-tooth function has unphysical discontinuities where *ρ(x)* is large
- Partially filled bands at the Fermi level → the Berry phase expression does not work

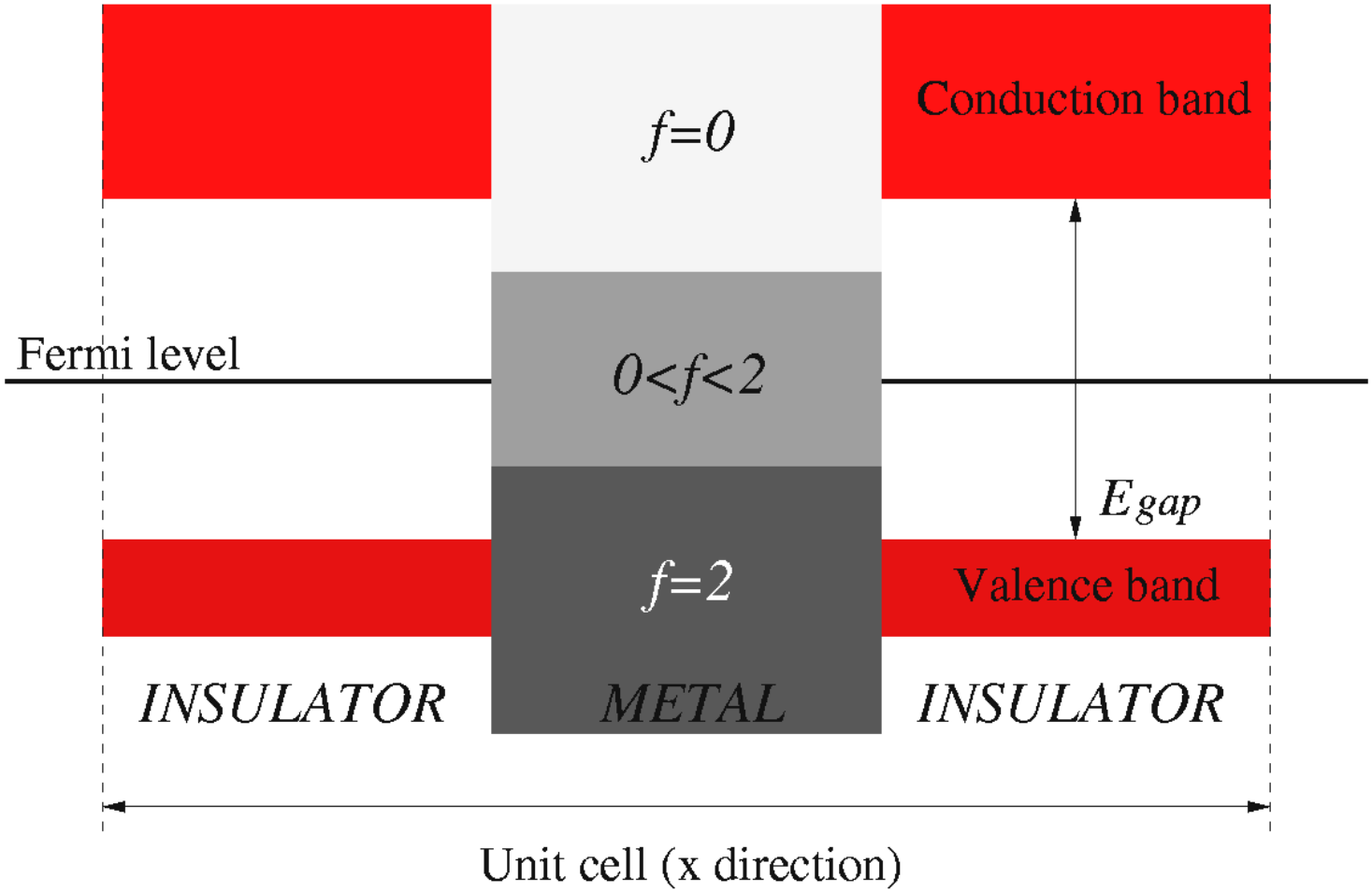
Polarization in insulators (again)

- In alternative to the Berry phase, the position operator can be written in **real space** using Wannier functions

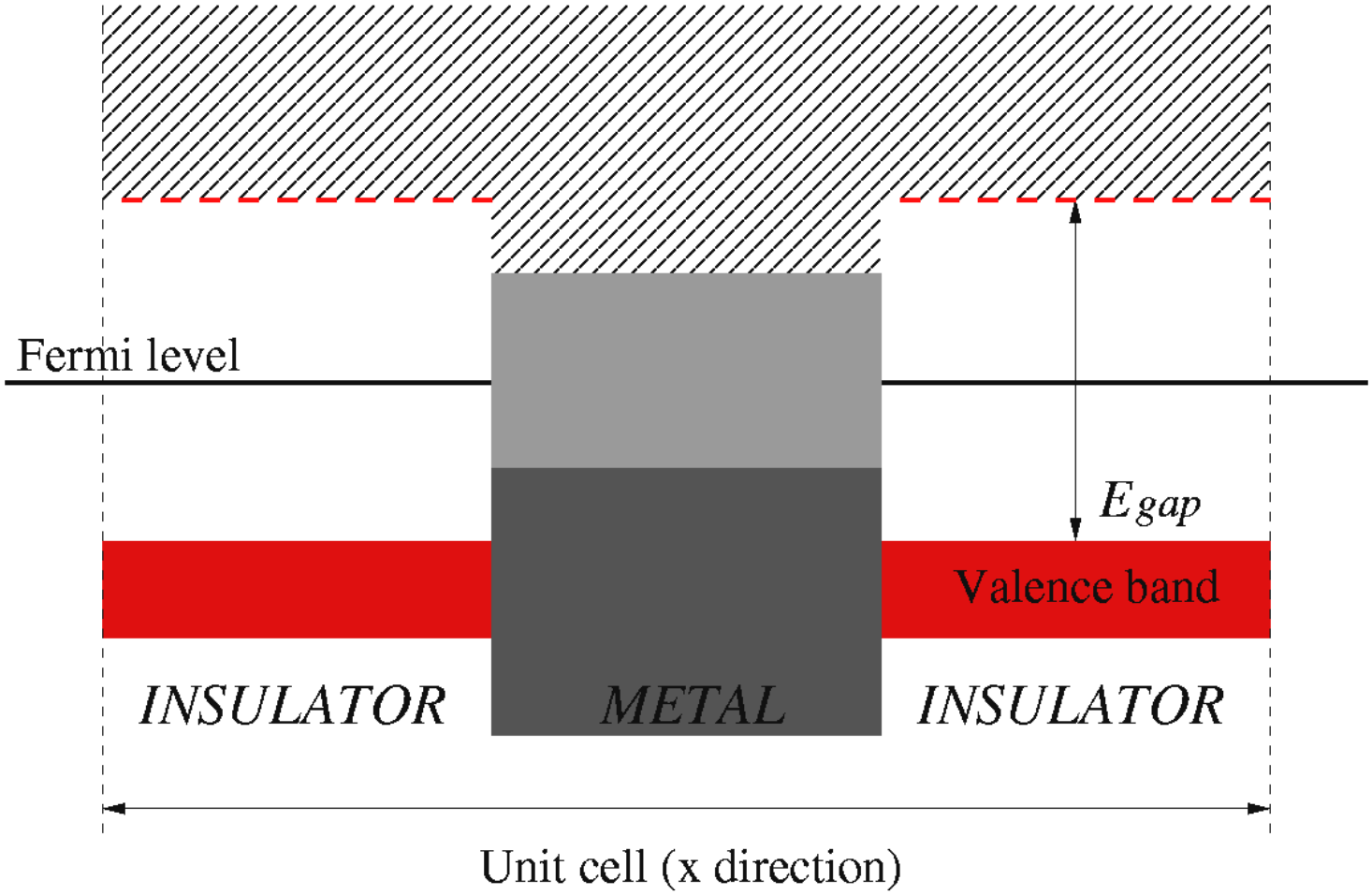
$$\langle x \rangle = 2 \sum_i \langle w_i | x | w_i \rangle$$

- The goal is to find a **localized representation** (always possible in insulators)

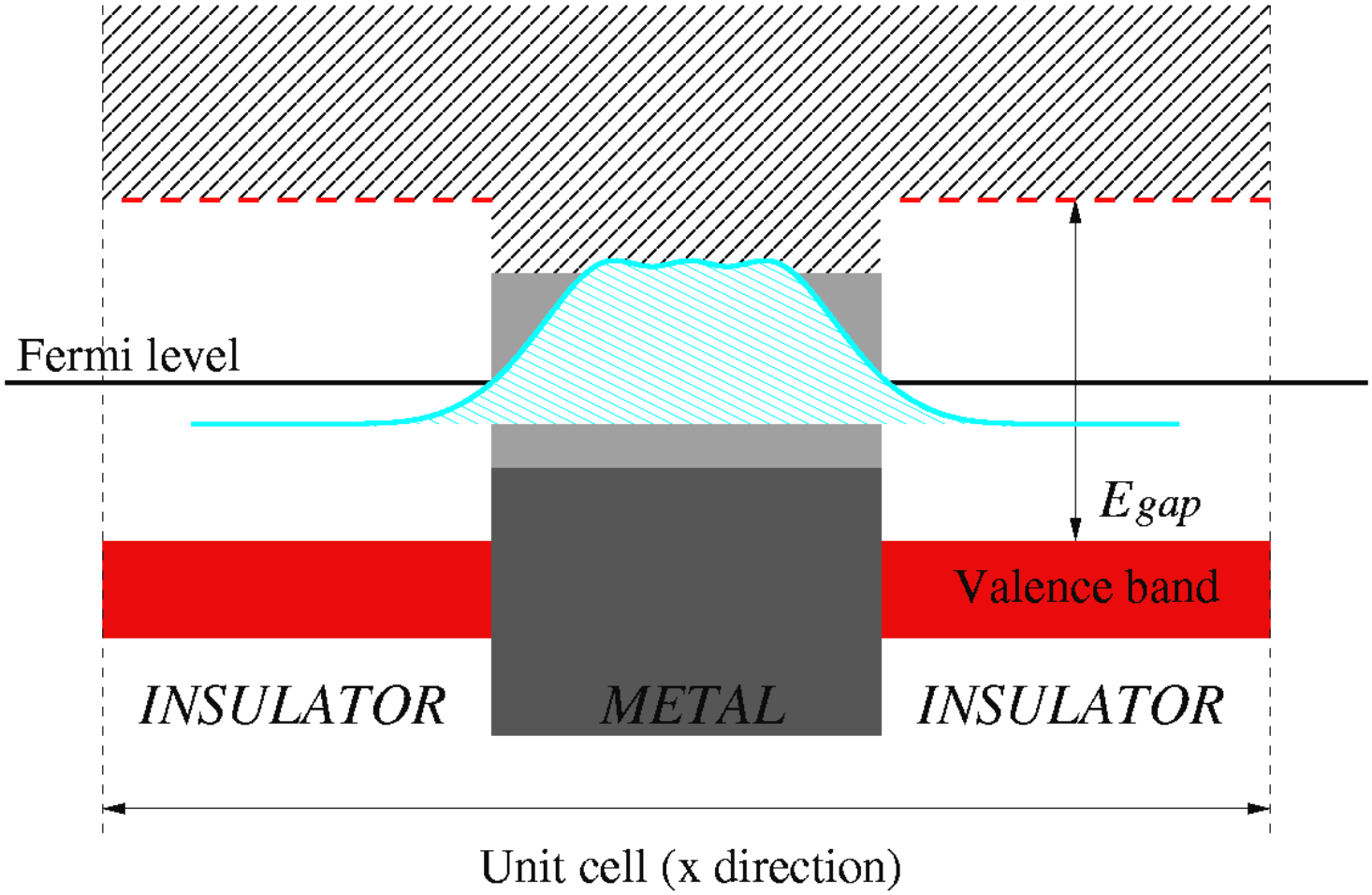
1D band structure: three energy windows



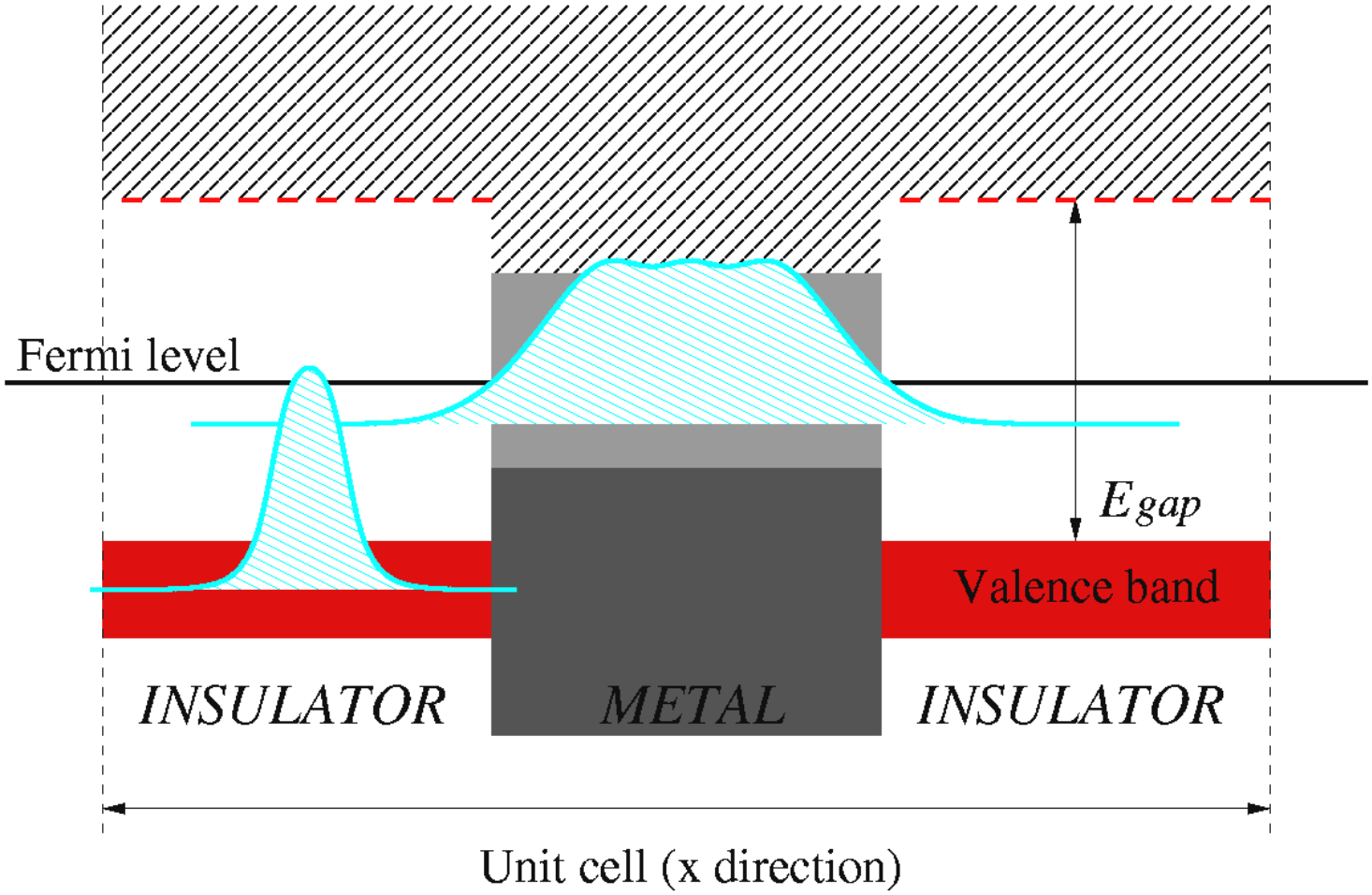
1. Conduction states are discarded



2. MIGS are already localized!



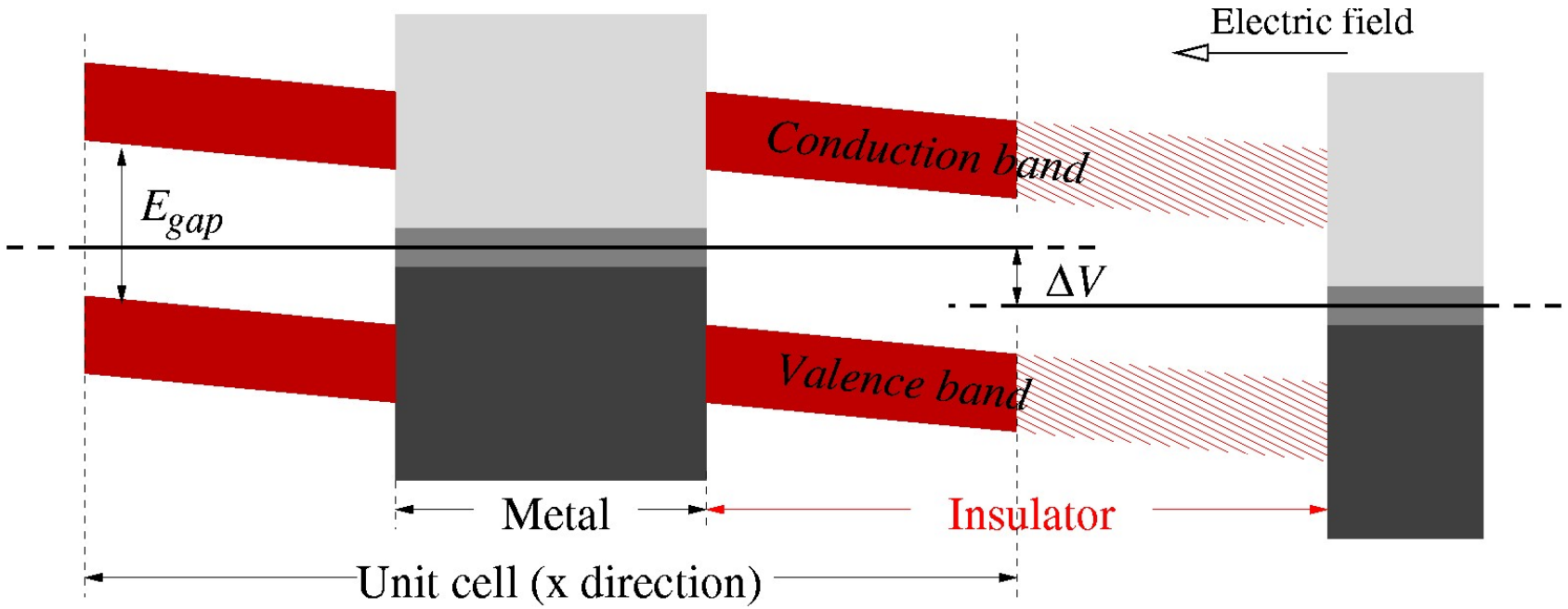
3. “Parallel transport” for fully occupied states



All states localized along x!

$$\rightarrow \quad \langle x \rangle = \sum_i f_i \langle w_i | x | w_i \rangle$$

Finite bias potential



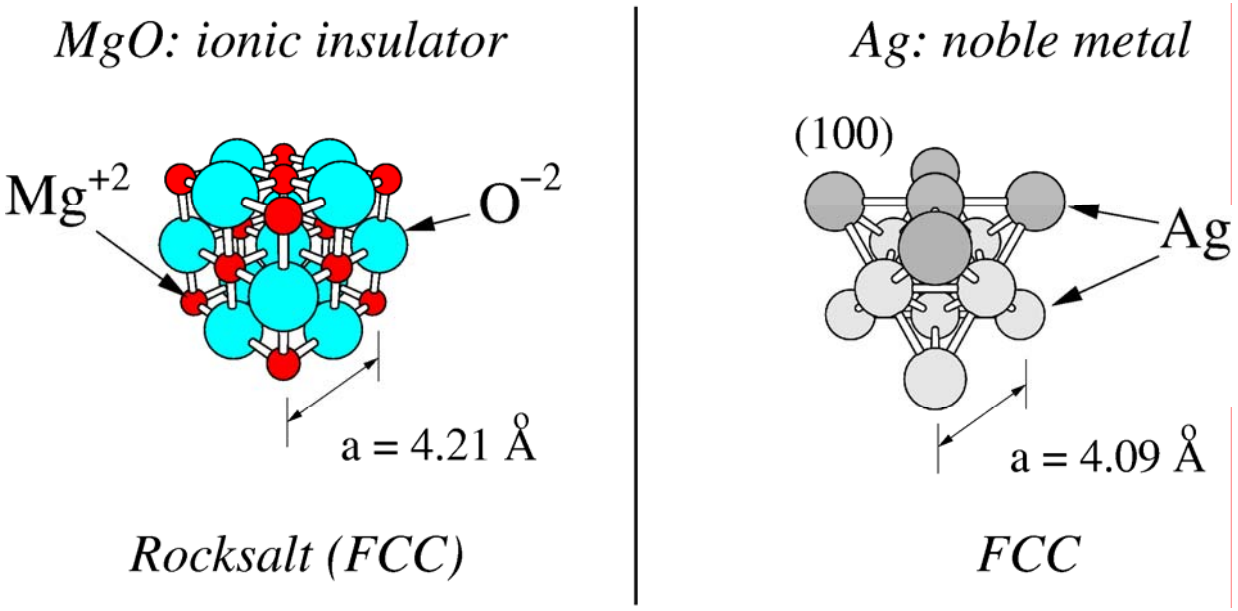
- Localized orbitals polarized individually by state-dependent saw-tooth potentials in real space

M. Stengel and N. Spaldin, *Ab-initio theory of metal-insulator interfaces in finite electric field,* cond-mat/0506389 (2005).

Outline

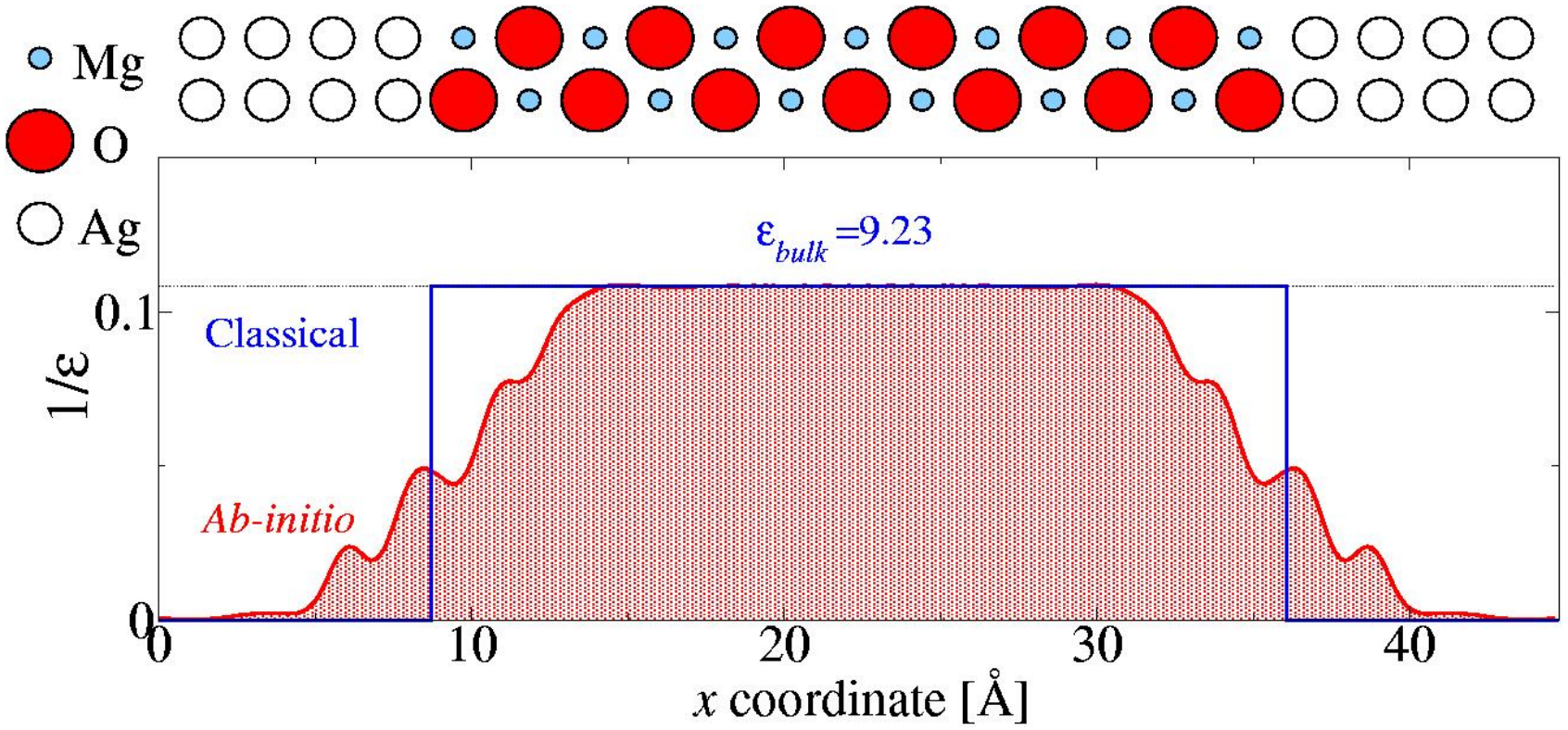
- Motivation from the experiments
- Theoretical methods
- **Results**
- Conclusions

Test: MgO/Ag(100)



- Favorable lattice matching
- Well-studied interface between a simple metal and a wide-gap insulator

Capacitance & permittivity profile



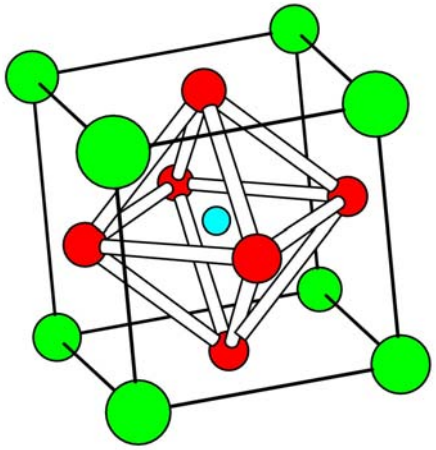
C_{CL}=30.3 fF/μm^2

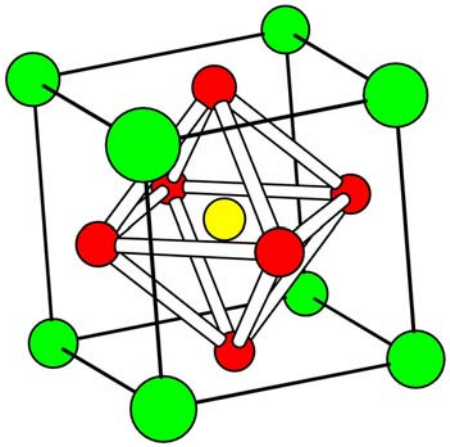
C_{AI}=31.2 fF/μm^2

Ideal classical behavior in the ultrathin limit!

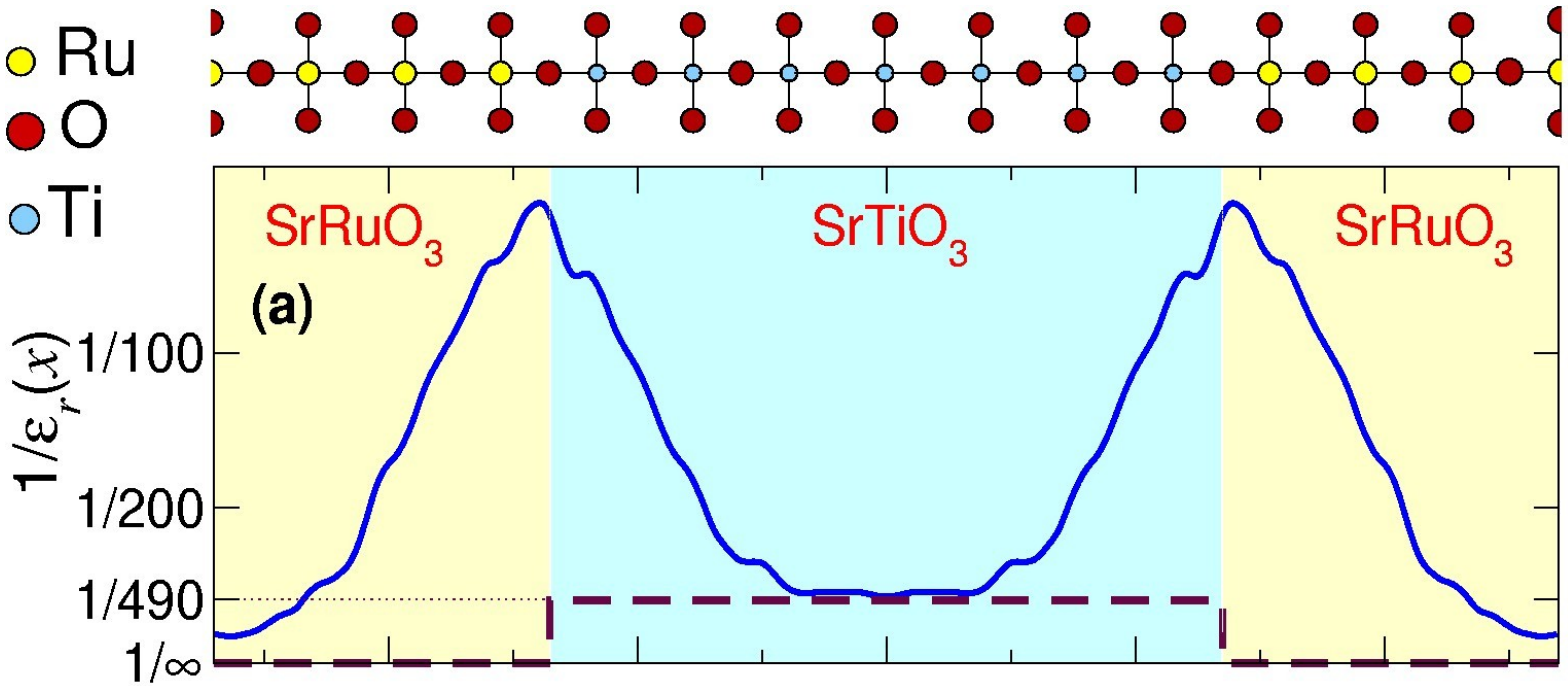
$SrTiO_3/SrRuO_3$

- STO: insulating perovskite with high permittivity
  - ε_{exp} ~ 20000 (0 K), 290 (RT)
  - ε_{th} = 490
- SRO: metallic perovskite, very popular electrode for capacitor applications





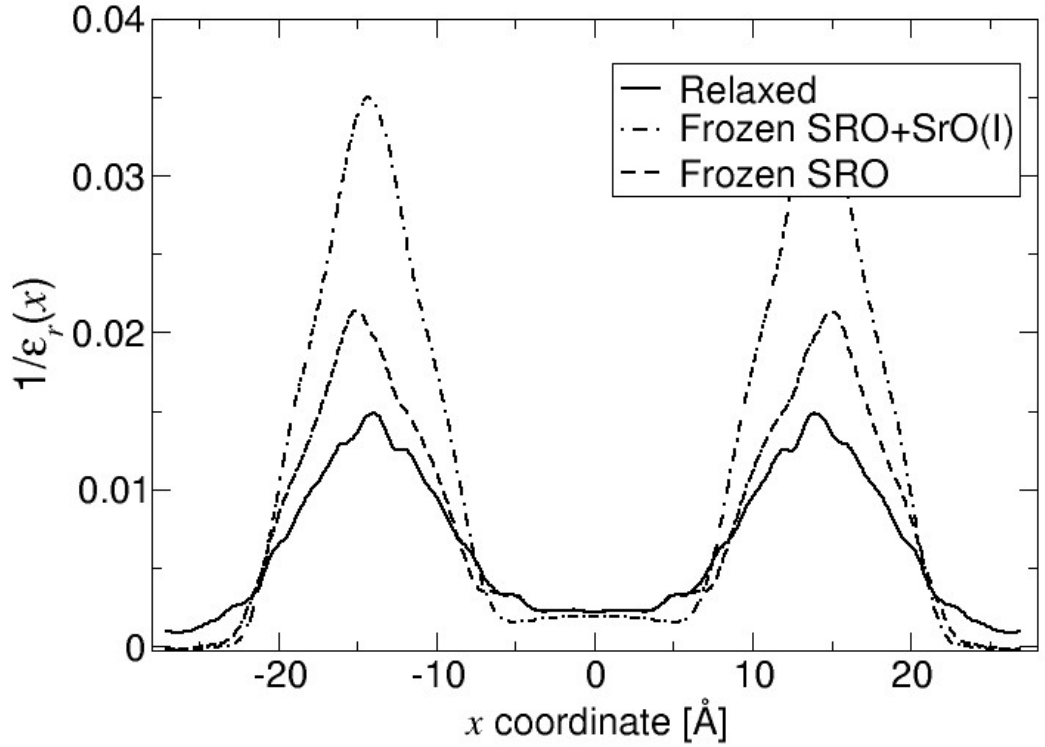
SRO/STO: inv. permittivity profile



- C_{cl} = 1610 fF/um^2, C_{fp} = 258 fF/um^2
- No defects, ideal interface → "intrinsic" dead layer!

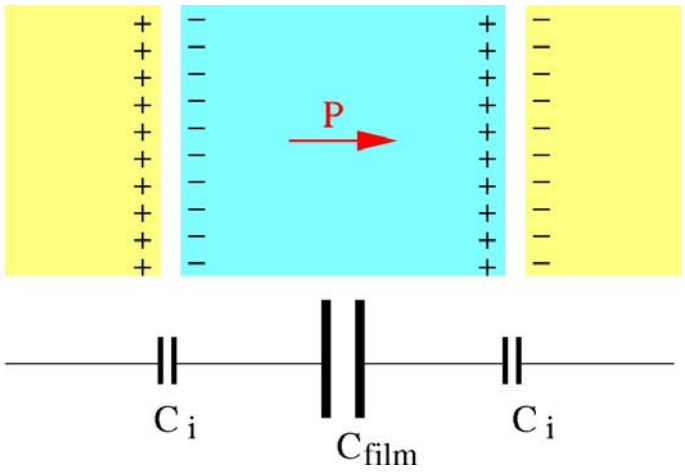
M. Stengel and N. Spaldin, Nature **443**, 679 (2006).

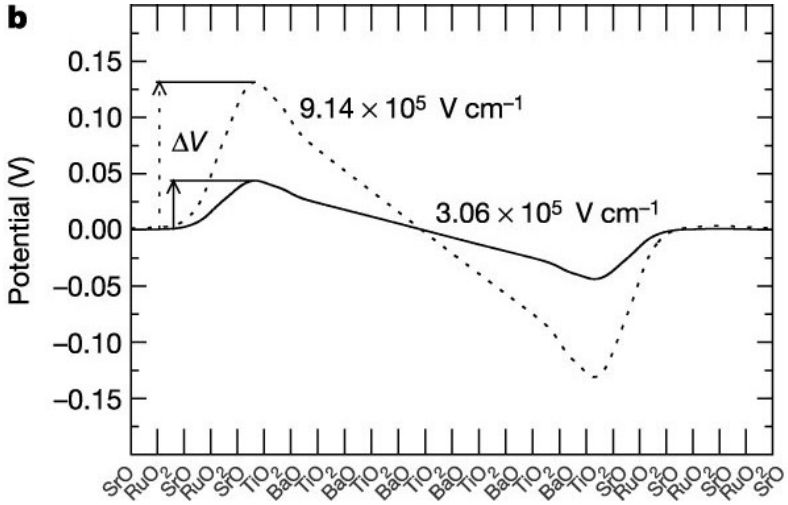
Influence of ionic relaxations in the $SrRuO_3$ electrodes



- Relaxation of electrode lattice reduces the dead layer by a factor of 2, but does not remove it!

Screening & depolarizing field

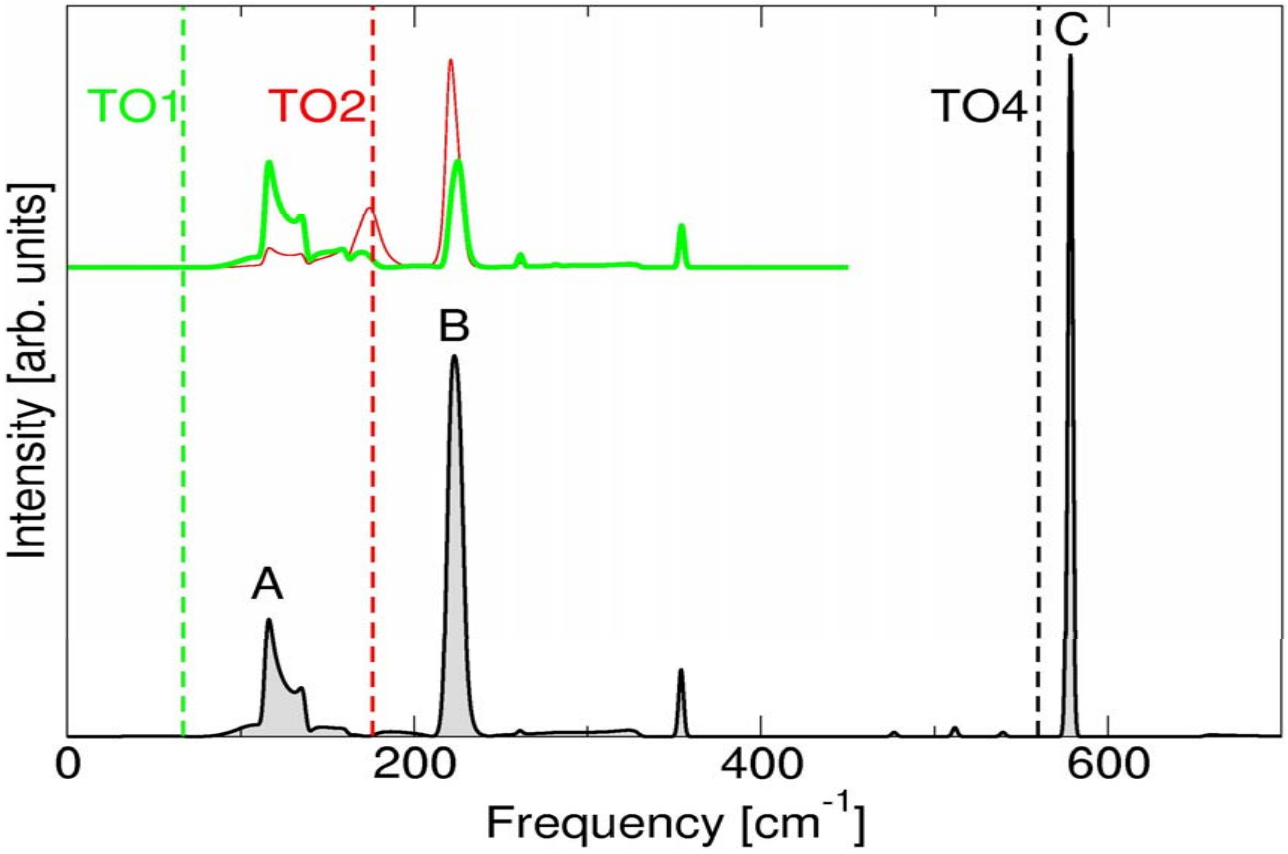




- Well-known concept for *ferroelectric* capacitors*
- At the electrode, the polarization charge of the dielectric is not completely screened
- The field contrasts *P*, thus suppressing the dielectric response

*J. Junquera & P. Ghosez, Nature 422, 506 (2003)

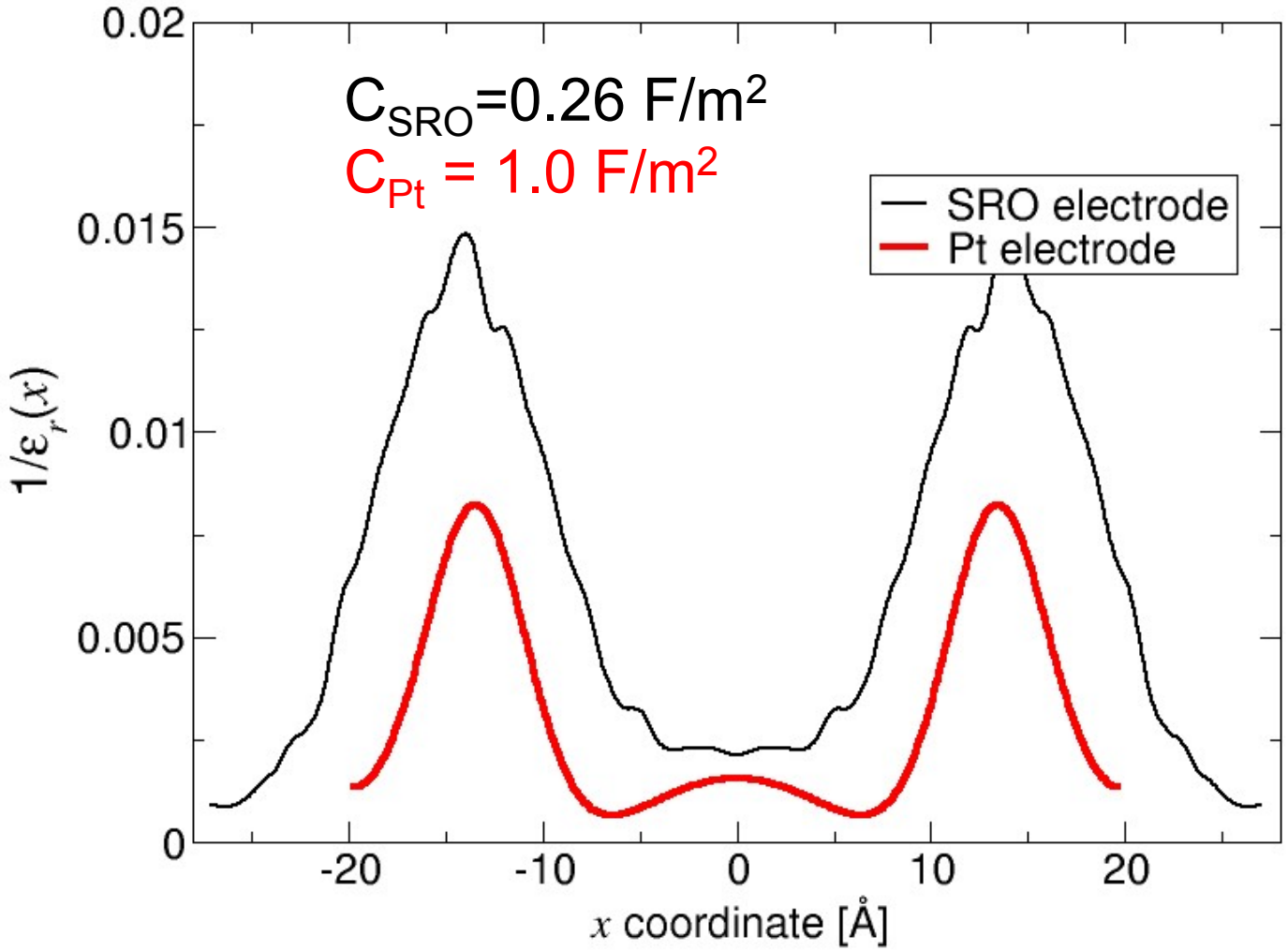
Soft-mode hardening effect



$\varepsilon \sim 1/\omega^2$

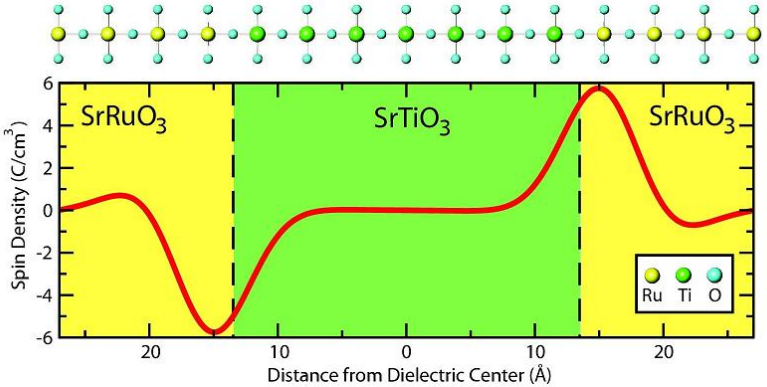
Dipolar-active optical modes shift to higher frequencies and mix

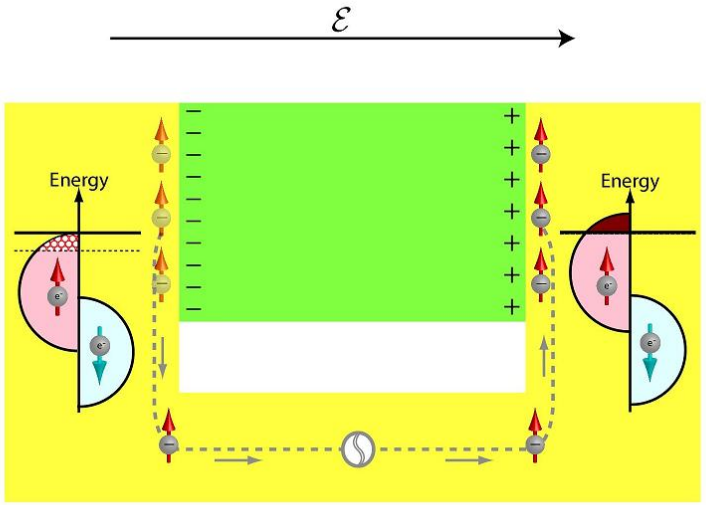
Pt or $SrRuO_3$?


C_{SRO}=0.26 F/m²
C_{Pt} = 1.0 F/m²
SRO electrode
Pt electrode
0.02
0.015
0.01
0.005
0
$1/\varepsilon_r(x)$
-20
-10
0
10
20
x coordinate [Å]

Spin capacitors

- Ferromagnetic electrodes
- Spin-polarized carriers → storage of spin density!





J. Rondinelli, M. Stengel and N. A. Spaldin, in preparation

Conclusions

- New, powerful finite-field method
- Pt electrodes are intrinsically better than $SrRuO_3$ ones
- Bad performance of Pt in the experiments has to be ascribed to processing issues
- Challenge for the future: production of high-quality interfaces with free-electron metals