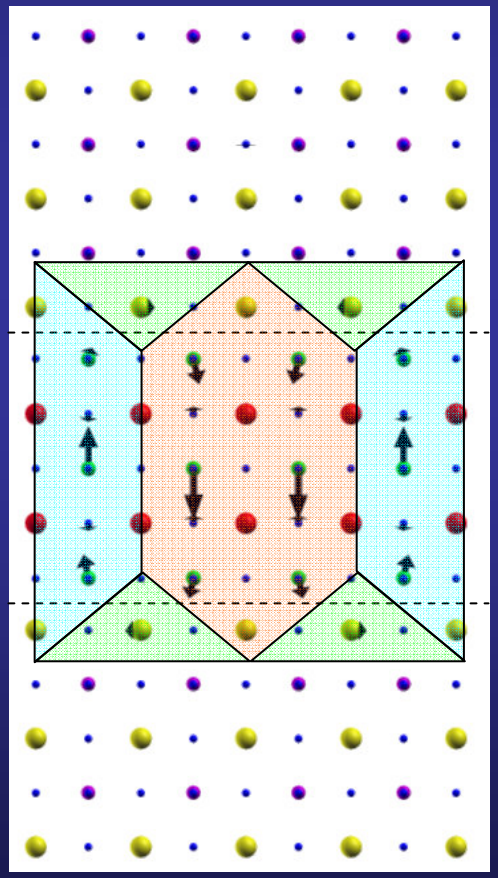
From 180º stripe domains to more exotic patterns of polarization in ferroelectric nanostructures. A first principles view



Pablo Aguado-Puente

Javier Junquera

UNIVERSIDAD DE CANTABRIA

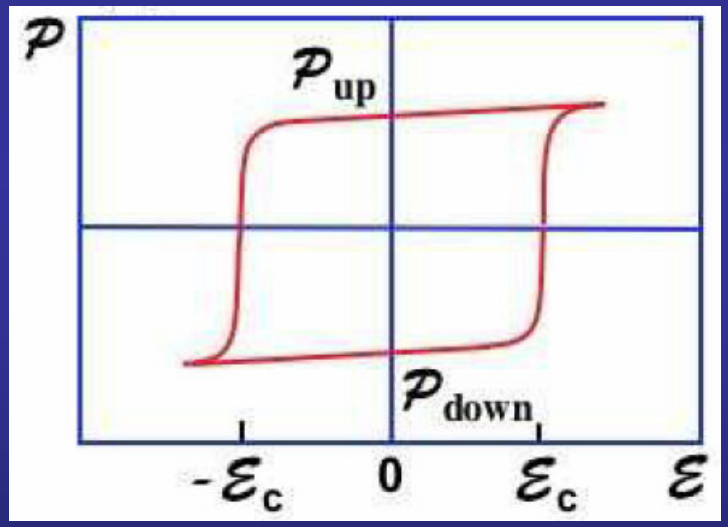
CITIMAC

Ferroelectricity: Basic definitions

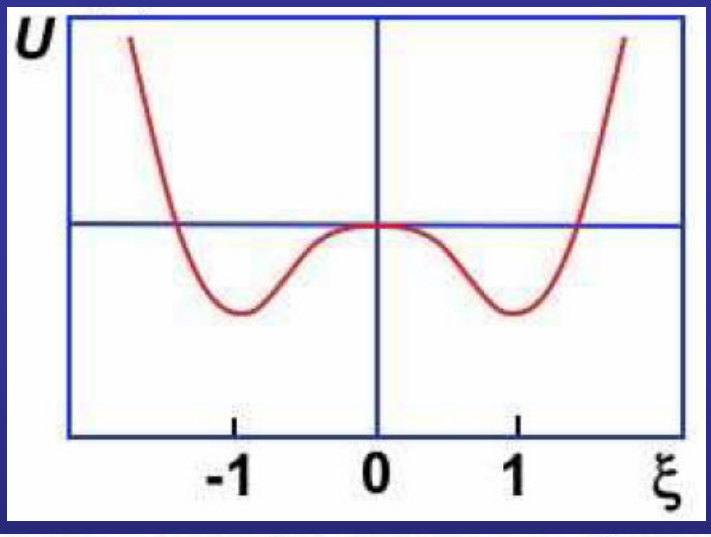
Existence of **two or more states** with a **non-zero polarization** in the **absence** of an electric **field**

Can be **shifted** from one to another of these states by the application of an electric field

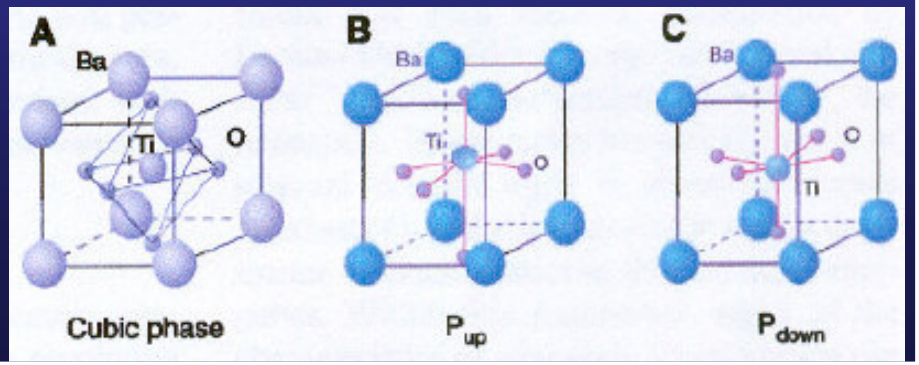
Hysteresis loop



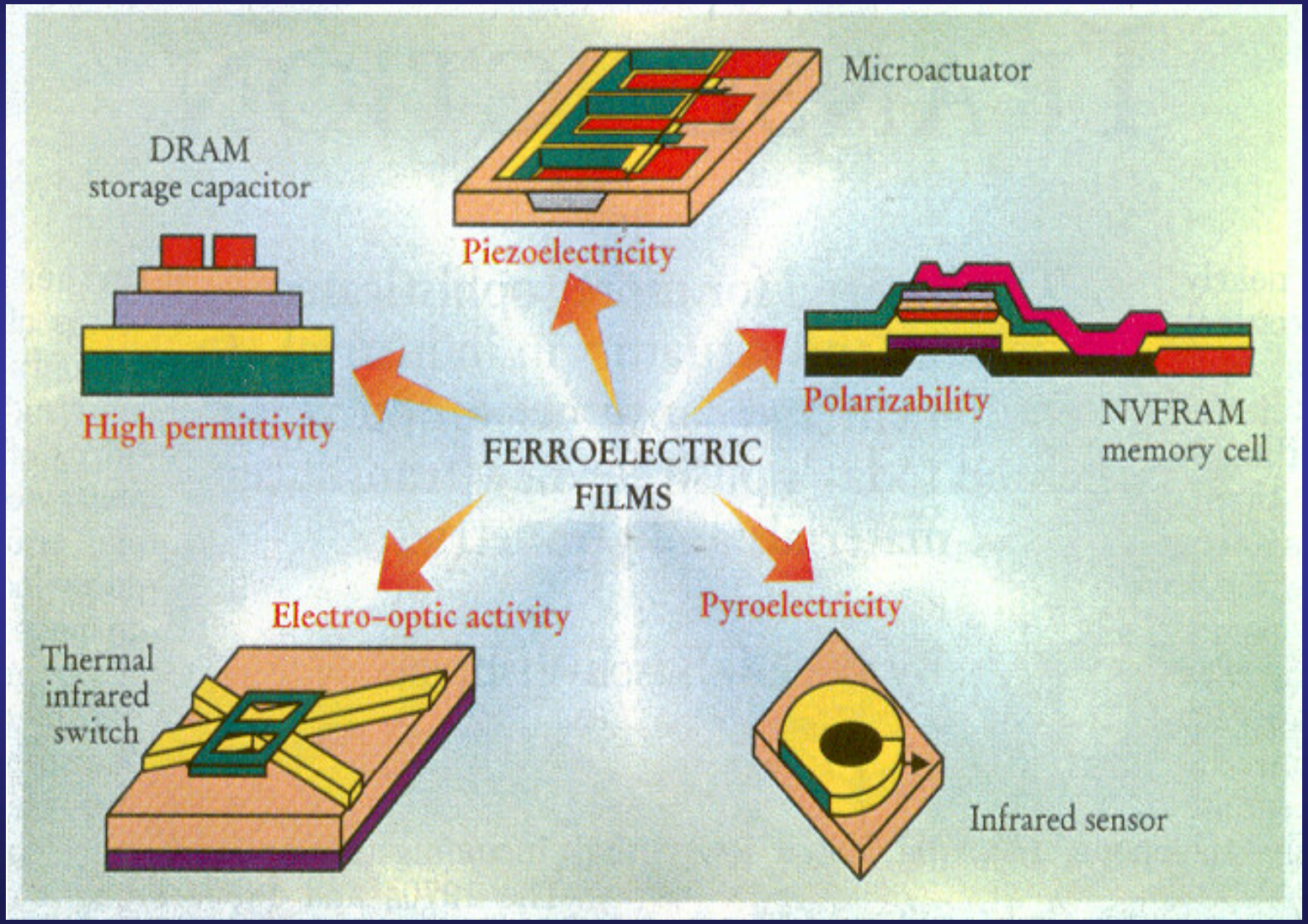
Double well energy



Soft-mode



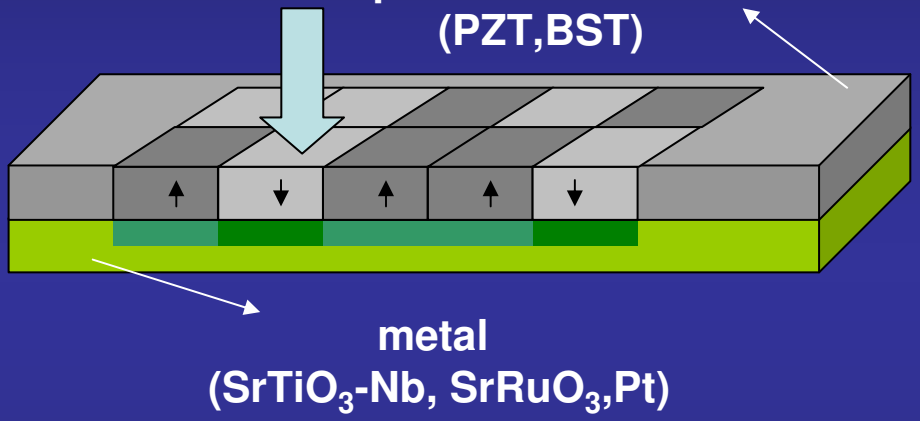
Technological applications:
ABO_3 perovskites oxides as multifunctional materials



O. Auciello *et al.*, Physics Today July 1998, 22-27

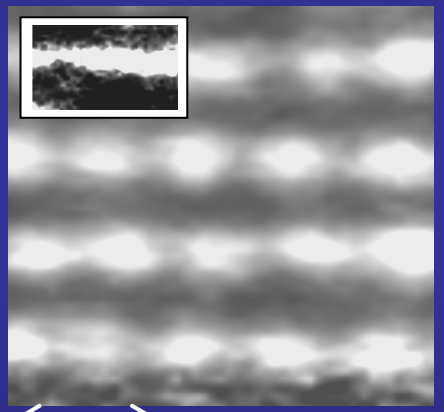
Many applications depend on the stability of films with a switchable polarization along the film normal

NV-FRAM



28 Gbit/cm²

Line width < 20nm



100 nm

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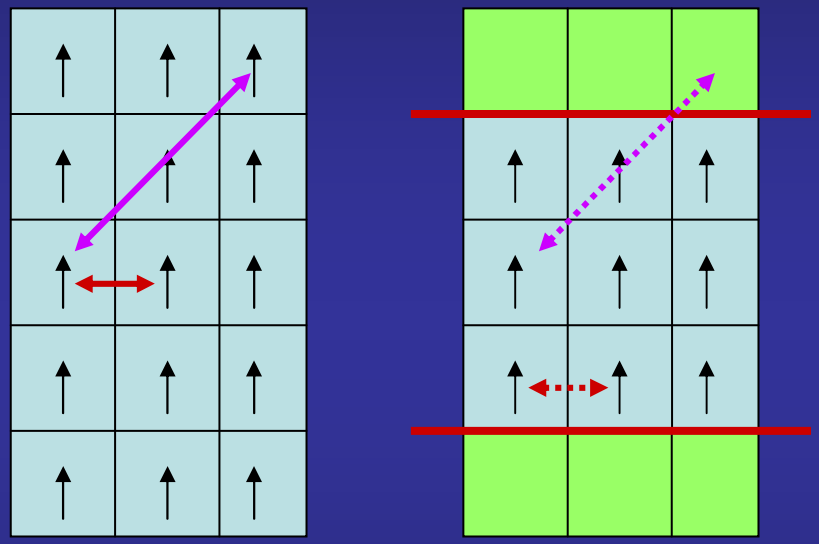
… is there a fundamental limit?

Ferroelectricity is a collective effect with delicate balance between short and long range interactions

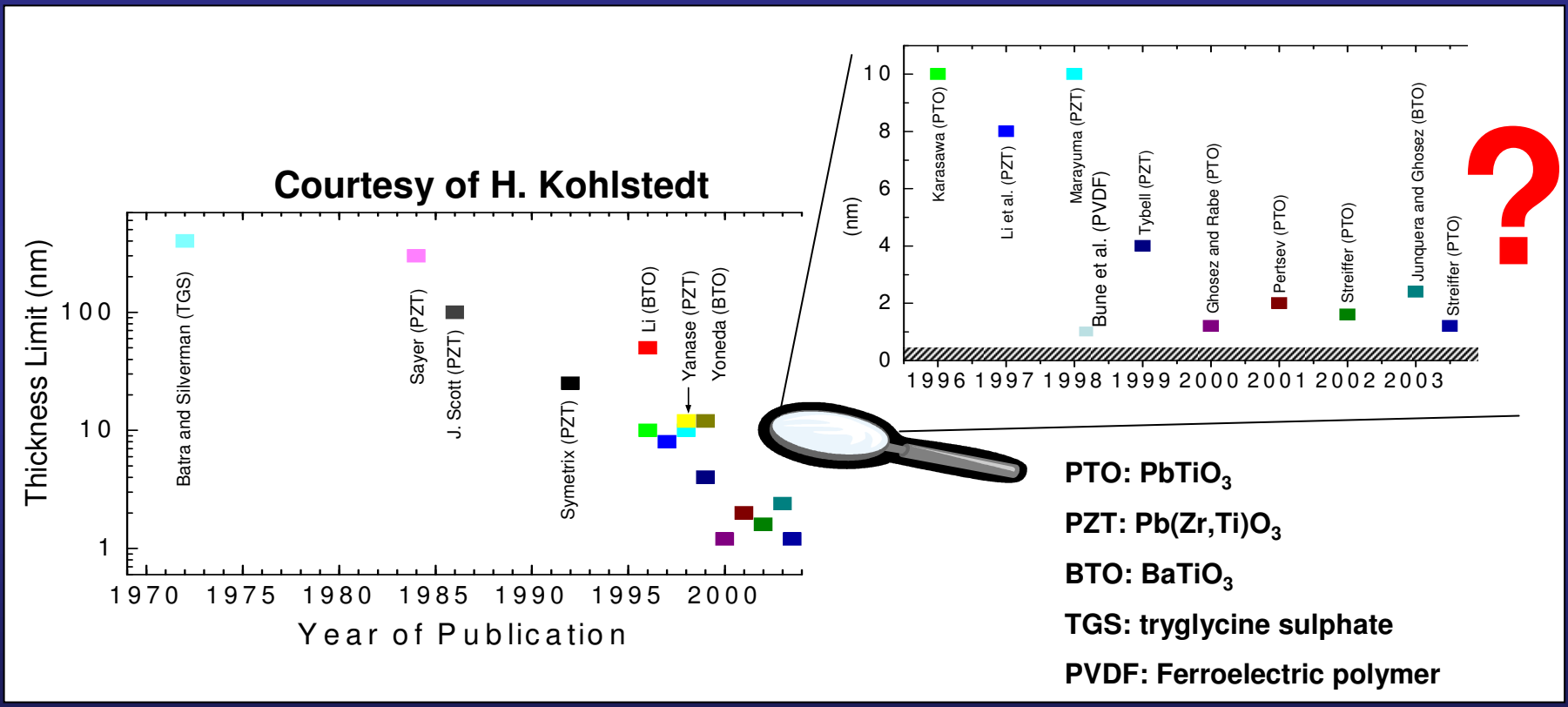


Both interactions strongly affected in small particles and thin films

Finite size effect: a subtle problem

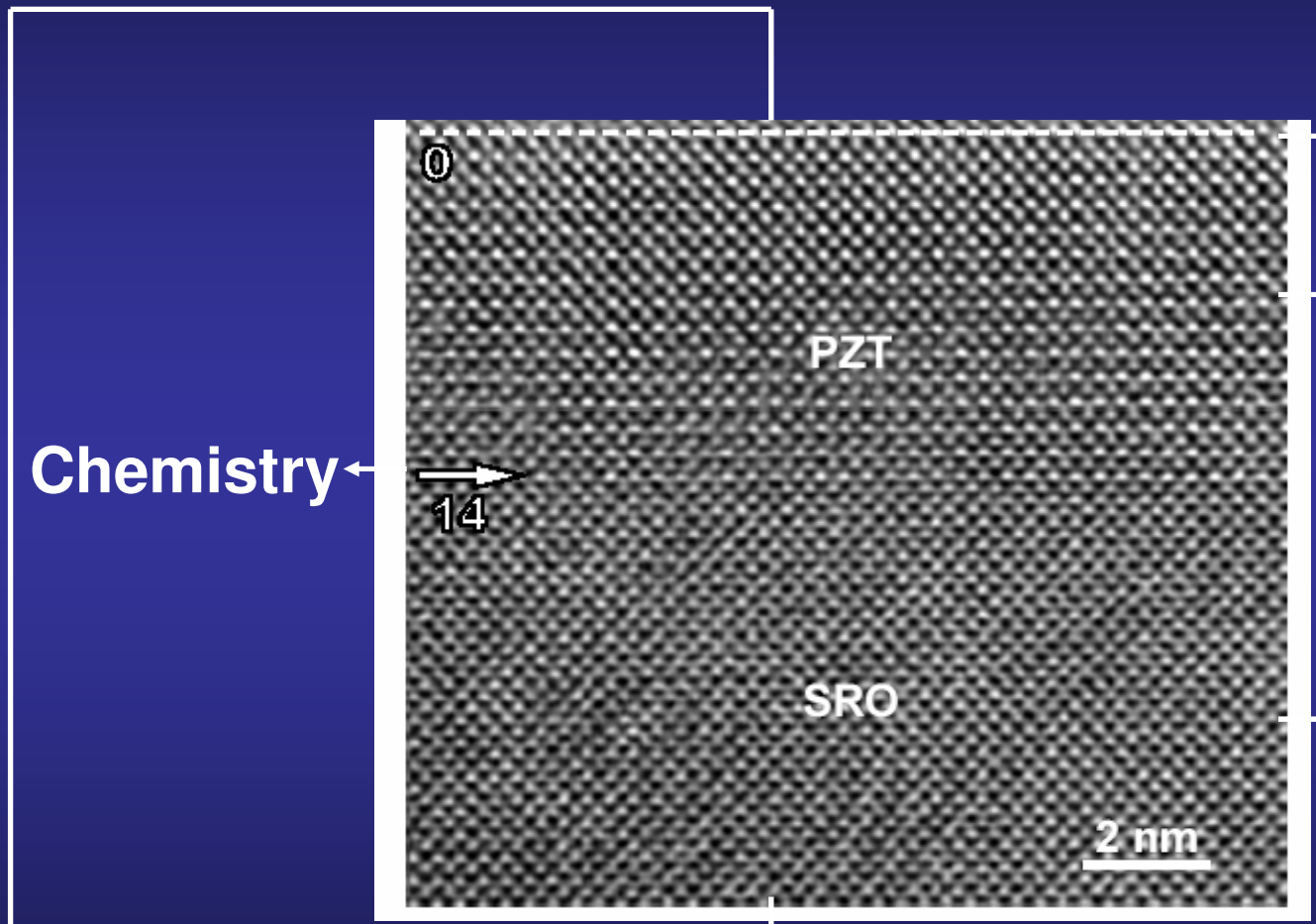
Fundamental motivation: what's the most stable phase for epitaxial ferroelectric ultrathin films?

- Long time question.
- Hot field.



Ph. Ghosez and J. Junquera, *First-Principles Modeling of Ferroelectric Oxide Nanostructures*, *Handbook of Theoretical and Computational Nanotechnology*, Vol. 9, Chap. 13, 623-728 (2006)
(http://xxx.lanl.gov/pdf/cond-mat/0605299)
and references therein.

Many effects might alter the delicate balance between long and short range forces



Surface

Defects

(vacancies, misfit dislocations…)

Finite conductivity

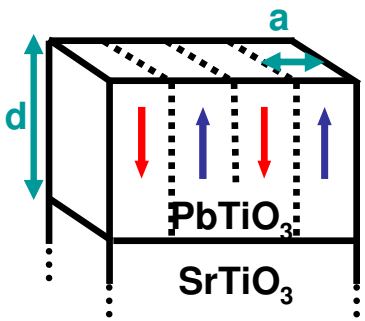
Mechanical

Chemistry

Electrostatic

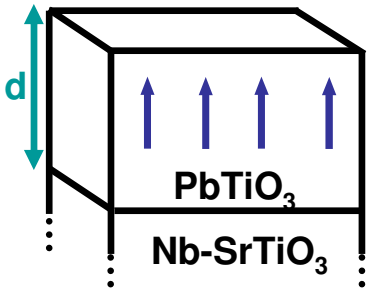
Experimental measurements, global result

Experimentally: small changes in boundary conditions, great changes in ground state



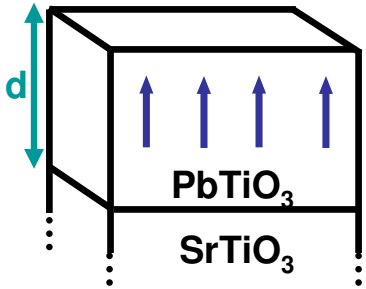
(insulator)

D. D. Fong et al. (2004)
S. K. Streiffer et al. (2002)



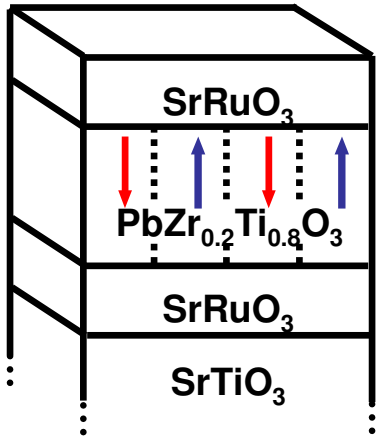
(metal)

C. Lichtensteiger et al. (2005)
A. T. J. van Helvoort et al. (2005)



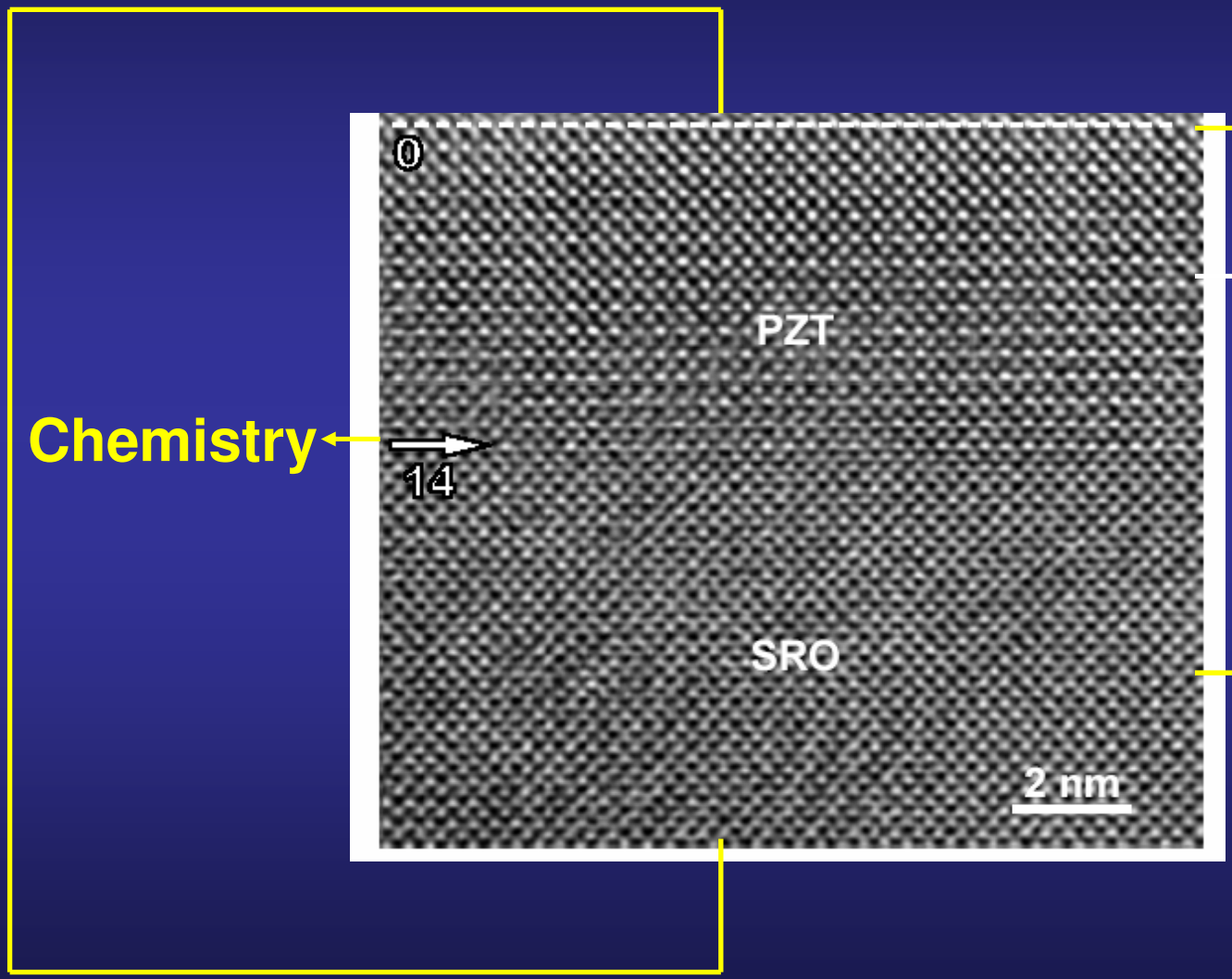
(insulator)

D. D. Fong et al. (2005)



V. Nagarajan et al. (2006)

First-principles calculations allow to isolate their respective influence



Surface

Defects

(vacancies, misfit dislocations…)

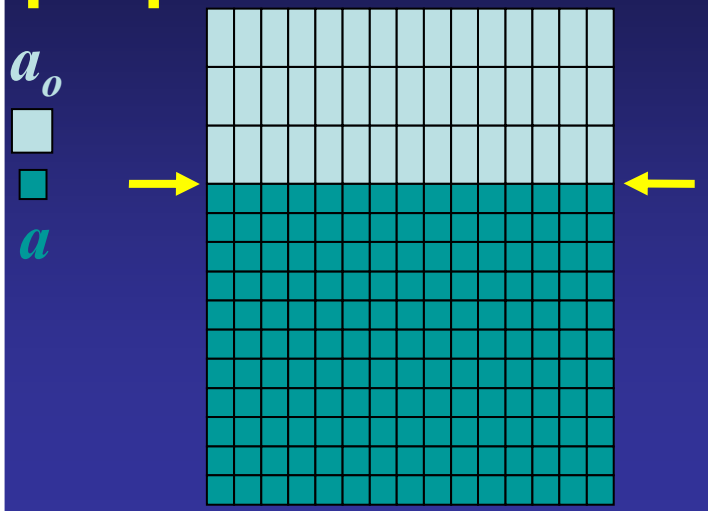
Finite conductivity

Mechanical

Chemistry

Electrostatic

Strain imposed by the substrate affects the properties of ferroelectric materials



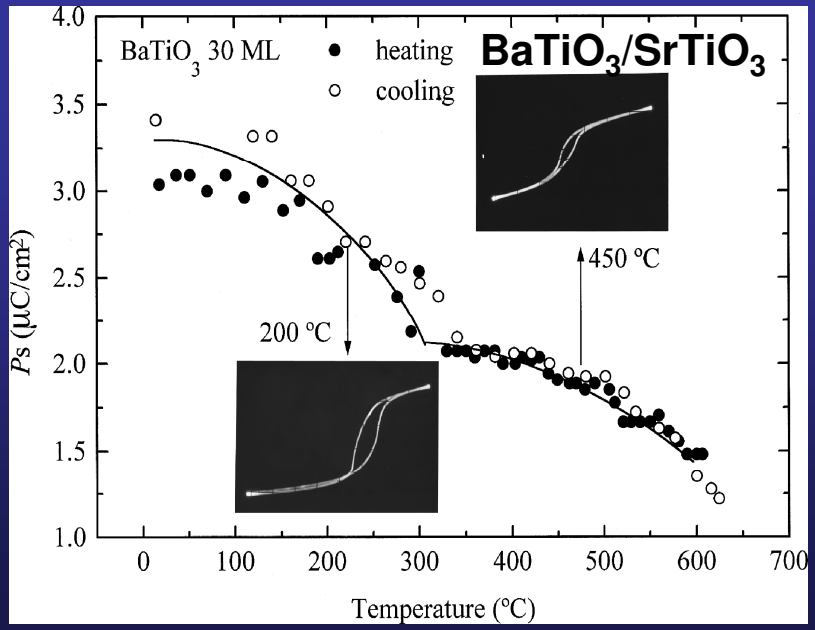
misfit strain

$u_m = (a-a_o)/a_o$

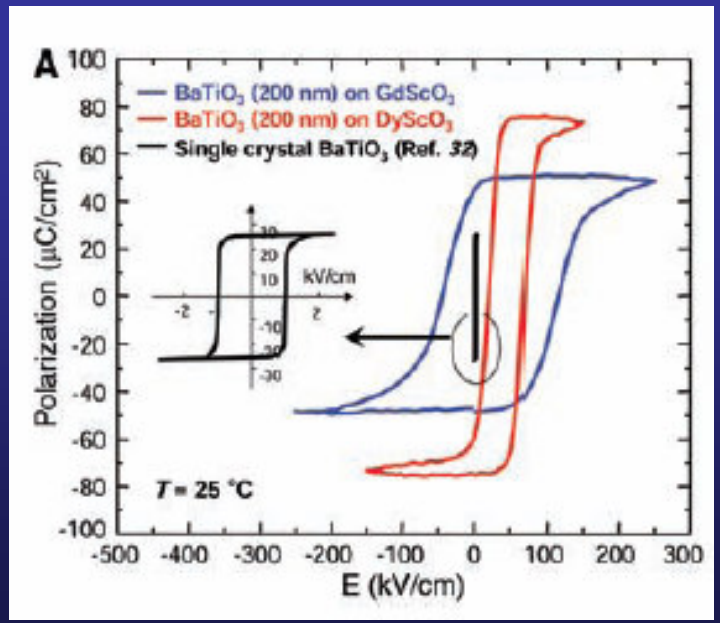
Typical picture:

Compressive strain ⇒ tetragonal *c*

Tensile strain ⇒ orthorrombic *aa*



Yoneda *et al.*, J. Appl. Phys. 83, 2458 (1998)

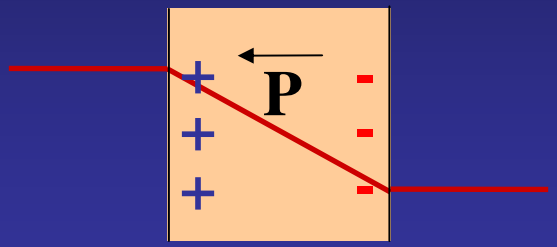


K. J. Choi *et al.*, Science 306, 1005 (2004)

Mechanisms for screening of the polarization charge

Vacuum

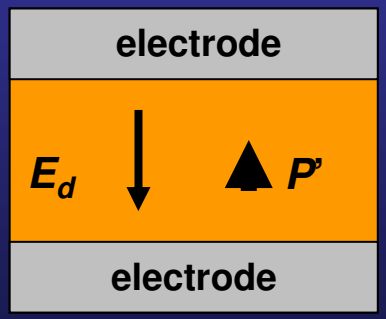
no screening



$\mathcal{E}_d = -4\pi P$

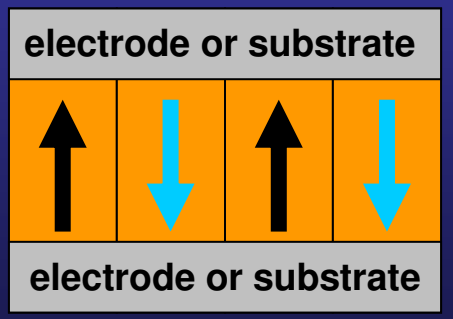
Screening by free charges

(electrodes or adsorbates)



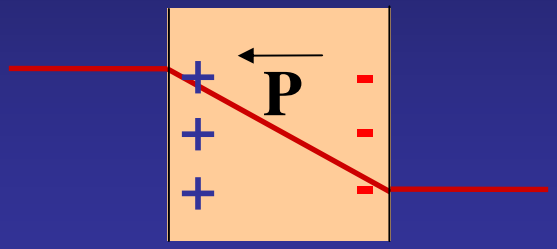
Formation of domains

(no net charge at surface)



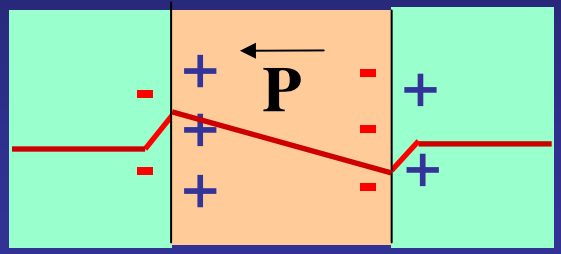
Imperfect screening by real metallic electrodes produces a depolarizing field

Vacuum
no screening



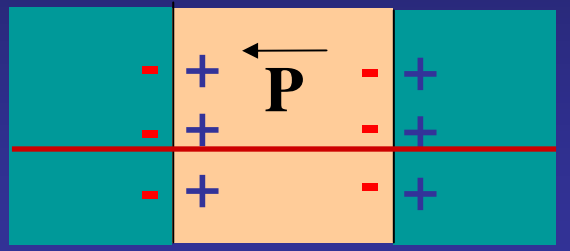
$\mathcal{E}_d = -4\pi P$

Real electrodes
imperfect screening



$\mathcal{E}_d = -4\pi\alpha P$

Ideal electrodes
perfect screening



$\mathcal{E}_d = 0$

Depolarizing field $\mathcal{E}_d$:

$\mathcal{E}_d = -2\,\Delta V / d$

$\Delta V = 4\pi\,\sigma_{pol}\,\lambda_{eff}$

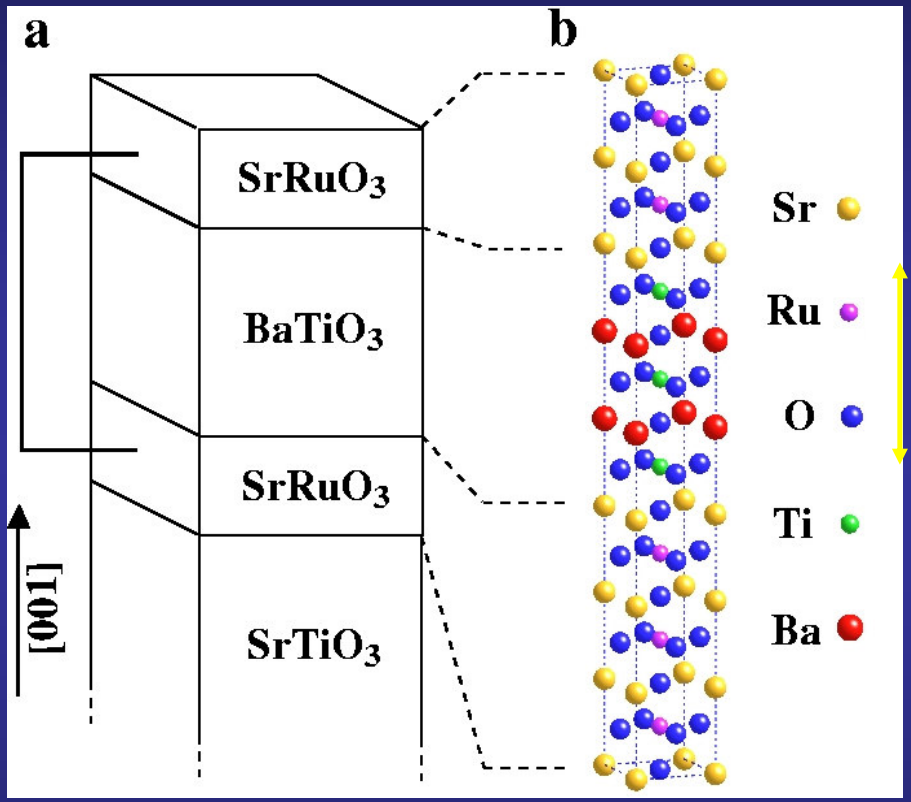
$\sigma_{pol} = \mathbf{P}\cdot\mathbf{n}$

$$\mathcal{E}_d = -4\pi \underbrace{[\,2\,.\,\lambda_{eff}\,/\,d\,]}_{\alpha}\cdot \mathbf{P}$$

depends on:

- the metal and interface chemistry: screening length λ_{eff}
- the ferroelectric: the spontaneous polarization $\mathbf{P}$
- the film thickness . d

Simulations of ferroelectric nanocapacitors from first-principles



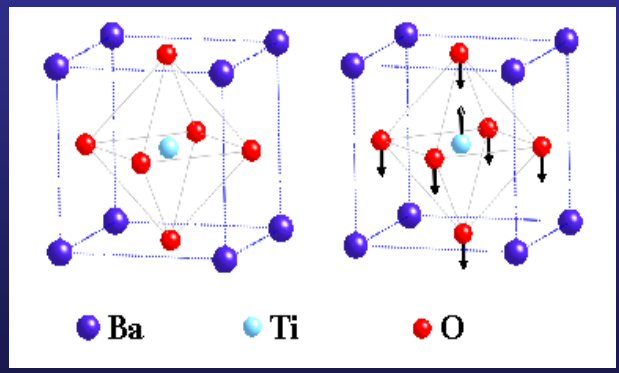
J. Junquera and Ph. Ghosez, Nature 422, 506 (2003)

Thickness:

m number of BTO cells

Polarization control:

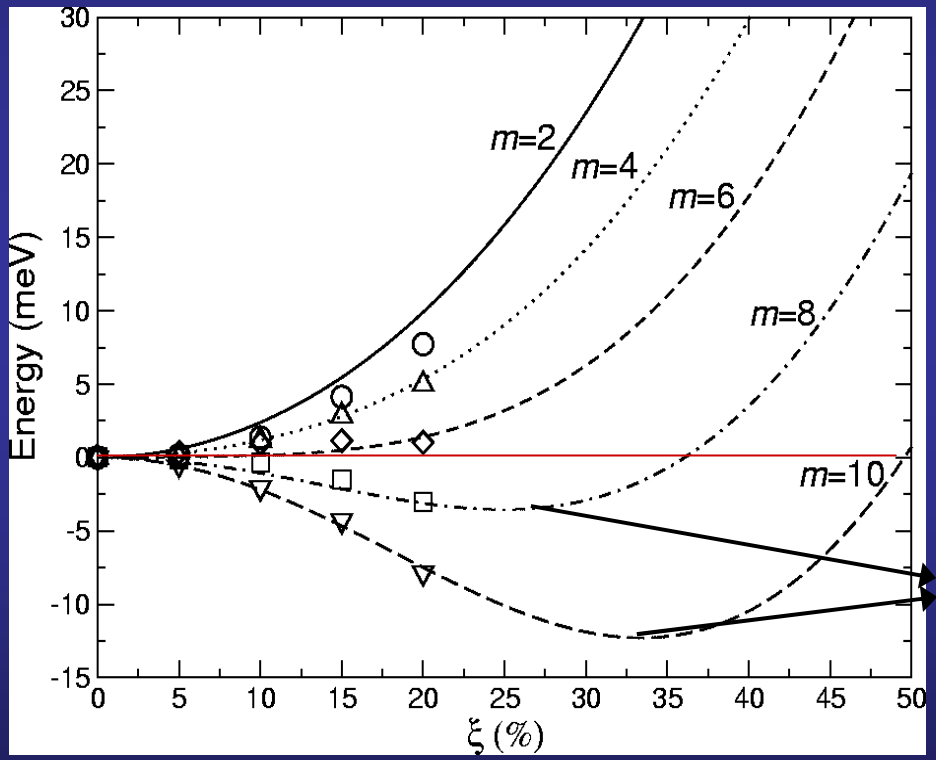
ξ percentage bulk soft mode



ξ=0 ξ=1

Existence of a critical thickness in monodomain films DFT versus model results

$$E = U - \mathcal{E}_d \cdot P$$



Minima below bulk ($\xi = 1$)

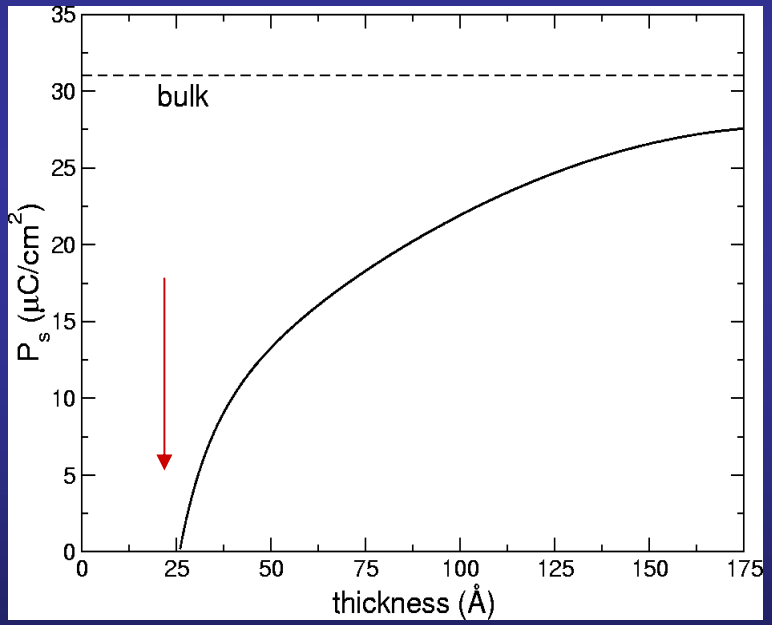
P_s deduced from ξ_{min}

Behavior can be explained by ***electrostatic*** effects.
The ***chemistry*** of the interface buried in λ_{eff}

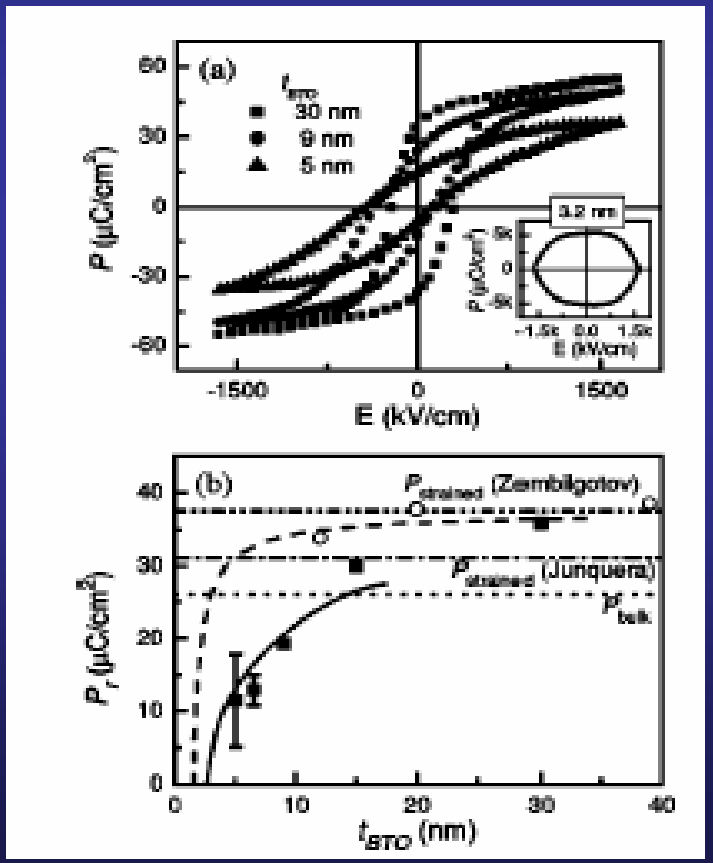
Twofold effect of the depolarizing field in monodomain films

$$\mathcal{E}_d = -4\pi\alpha P \qquad E = U - \mathcal{E}_d \cdot P$$

- Below the critical thickness: suppression of the ferroelectricity
- Above the critical thickness: reduction of spontaneous polarization



J. Junquera and Ph. Ghosez, Nature 422, 506 (2003)



Y. S. Kim et al., Appl. Phys. Lett. 86, 102907 (2005)

Many DFT first-principles computations on size effects in ferroelectric ultrathin films

PHYSICAL REVIEW B 72, 020101(R) (2005)

Ferroelectricity in ultrathin perovskite films

Na Sai, Alexie M. Kolpak, and Andrew M. Rappe

PRL 96, 107603 (2006) PHYSICAL REVIEW LETTERS week ending 17 MARCH 2006

Ionic Polarizability of Conductive Metal Oxides and Critical Thickness for Ferroelectricity in $BaTiO_3$

G. Gerra,[1,*] A. K. Tagantsev,[1] N. Setter,[1] and K. Parlinski[2]

PHYSICAL REVIEW B 74, 060101(R) (2006)

***Ab initio* study of the critical thickness for ferroelectricity in ultrathin $Pt/PbTiO_3/Pt$ films**

Yoshitaka Umeno,[1,2] Bernd Meyer,[3] Christian Elsässer,[4,1] and Peter Gumbsch[1,4]

Interface Effect on Ferroelectricity at the Nanoscale

Chun-Gang Duan,[†,‡,§] Renat F. Sabirianov,[‡,§] Wai-Ning Mei,[‡,§] Sitaram S. Jaswal,[†,§] and Evgeny Y. Tsymbal[*,†,§]

NANO LETTERS
2006
Vol. 6, No. 3
483−487

PRL 96, 127601 (2006) PHYSICAL REVIEW LETTERS week ending 31 MARCH 2006

Stabilization of Monodomain Polarization in Ultrathin $PbTiO_3$ Films

D. D. Fong,[1] A. M. Kolpak,[2] J. A. Eastman,[1] S. K. Streiffer,[1] P. H. Fuoss,[1] G. B. Stephenson,[1] Carol Thompson,[3] D. M. Kim,[4] K. J. Choi,[4] C. B. Eom,[4] I. Grinberg,[2] and A. M. Rappe[2]

Many DFT first-principles computations on size effects in ferroelectric ultrathin films

Reference	Heterostructure	Method	Functional	Interface	$a_{\parallel}$	t_c
Junquera *et al.* [56]	$SrRuO_3/BaTiO_3/SrRuO_3$	NAO	LDA (CA)	SrO-TiO_2	3.874 Å ($a^{th}_{SrTiO_3}$)	6
Junquera *et al.*	$SrRuO_3/PbTiO_3/SrRuO_3$	NAO	LDA (CA)	SrO-TiO_2	3.874 Å ($a^{th}_{SrTiO_3}$)	6
Gerra *et al.* [63]	$SrRuO_3/BaTiO_3/SrRuO_3$	PW	GGA (PW91)	SrO-TiO_2	3.94 Å ($a^{th}_{SrTiO_3}$)	3
Umeno *et al.* [89]	$Pt/PbTiO_3/Pt$	MBPP	LDA (CA)	Pt-PbO	3.845 Å ($a^{th}_{SrTiO_3}$)	4
				Pt-TiO_2		6
			GGA (PW91)	Pt-PbO	3.905 Å ($a^{exp}_{PbTiO_3}$)	No
				Pt-TiO_2		No
Duan *et al.* [86]	$SrRuO_3/KNbO_3/SrRuO_3$	PW	LDA (CA)	SrO-NbO_2	3.905 Å ($a^{exp}_{SrTiO_3}$)	4
	$Pt/KNbO_3/Pt$			Pt-NbO_2		2
Na Sai *et al.* [64,90]	$SrRuO_3/BaTiO_3/SrRuO_3$	PW	GGA	SrO-TiO_2	3.991 Å ($a^{exp}_{BaTiO_3}$)	> 4
				RuO_2-BaO		> 4
	$Pt/BaTiO_3/Pt$			Pt-TiO_2		> 4
				Pt-BaO		> 4
	$SrRuO_3/PbTiO_3/SrRuO_3$			SrO-TiO_2	3.905 Å ($a^{exp}_{PbTiO_3}$)	No
				RuO_2-PbO		No
	$Pt/PbTiO_3/Pt$			Pt-TiO_2		No
				Pt-PbO		No
D. D. Fong *et al.* [47]	$SrRuO_3/PbTiO_3$/vacuum	PW	GGA	SrO-TiO_2	$a^{th}_{PbTiO_3}$	> 3
	$SrRuO_3/PbTiO_3$/OH, O or H					< 3
	$SrRuO_3/PbTiO_3/CO_2$					~ 3
	$SrRuO_3/PbTiO_3/H_2O$					> 3

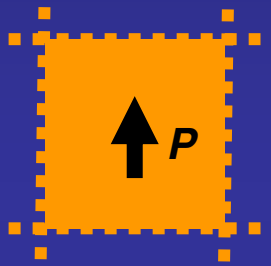
Be careful with the functional used…
GGA overestimates tetragonality and double-well depth in bulk $PbTiO_3$

	Cubic phase		Tetragonal phase						
	a	E_{gap}	a	c/a	$u_z(Ti)$	$u_z(O_1)$	$u_z(O_3)$	E_{gap}	ΔE
LDA, MBPP	3.880	1.55	3.853	1.050	0.5312	0.0923	0.6012	1.62	−0.053
LDA, PAW	3.894	1.48	3.867	1.043	0.5334	0.0883	0.6018		−0.056
LDA[a]	3.894		3.858	1.051					
PW91, MBPP	3.957	1.69	3.827	1.247	0.5571	0.1938	0.6670	2.04	−0.196
PW91, PAW	3.969	1.61	3.841	1.233	0.5559	0.1859	0.6660		−0.192
PBE, MBPP	3.962	1.69	3.836	1.244	0.5579	0.1949	0.6675	2.05	−0.208
PBE[a]	3.971		3.857	1.230					
Expt. (298 K)[b]	3.969		3.905	1.064	0.539	0.114	0.617	3.5	

…responsible for the absence of critical thickness in $PbTiO_3$ nanocapacitors?

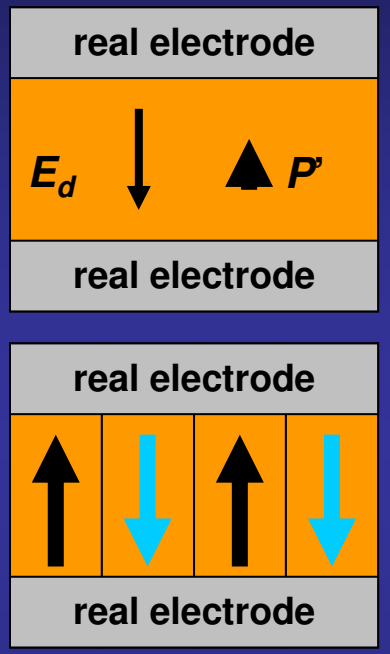
Y. Umeno et al., Phys. Rev. B 74 060101 (2006)

Until today, monodomain studies, goal of this work: *ab initio* multidomain simulations



- Uniform reduction of the polarization
- **Break down into domains**

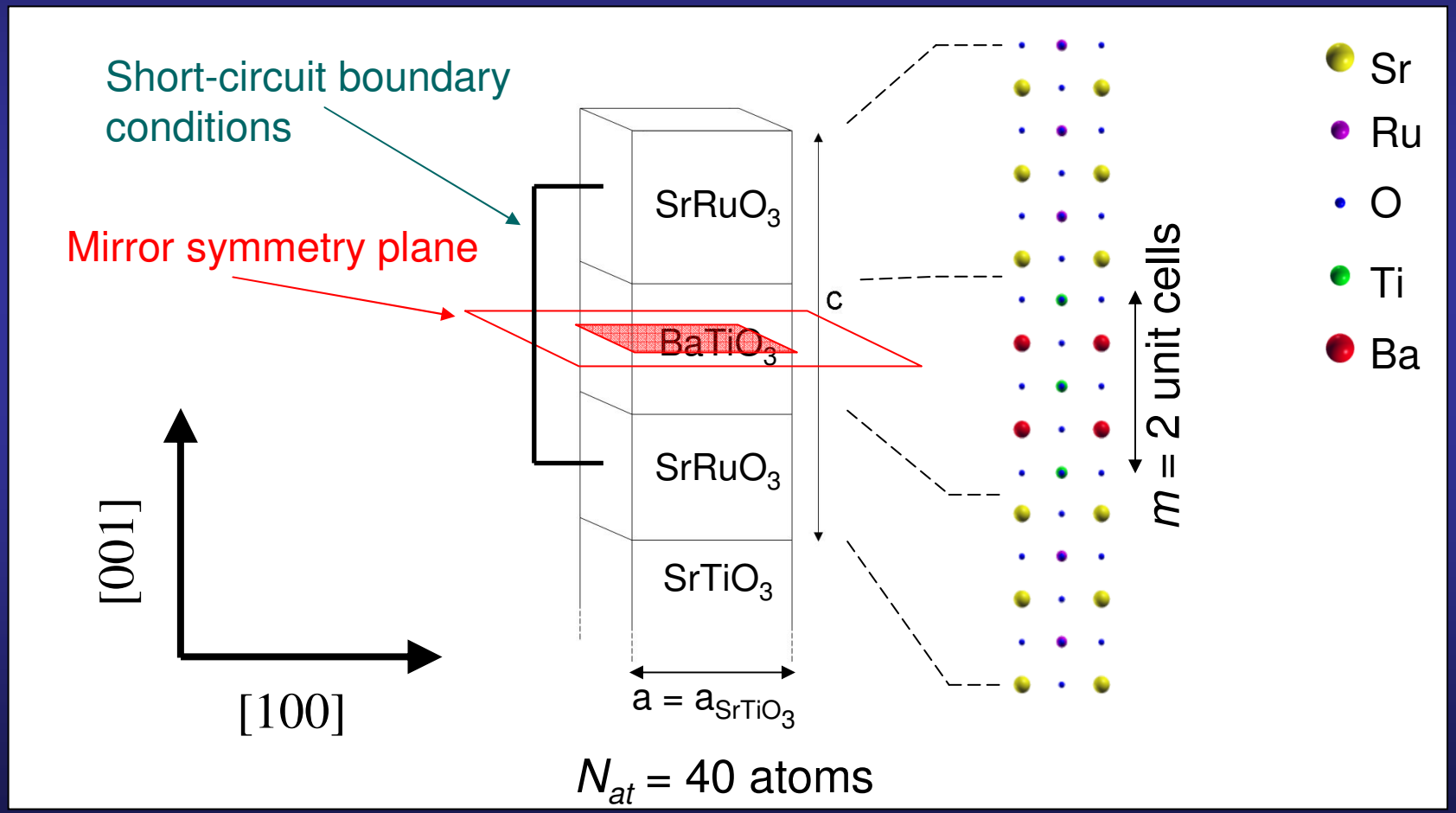
Present work



- Full first-principles simulation using siesta
- Explicitly included electrodes.

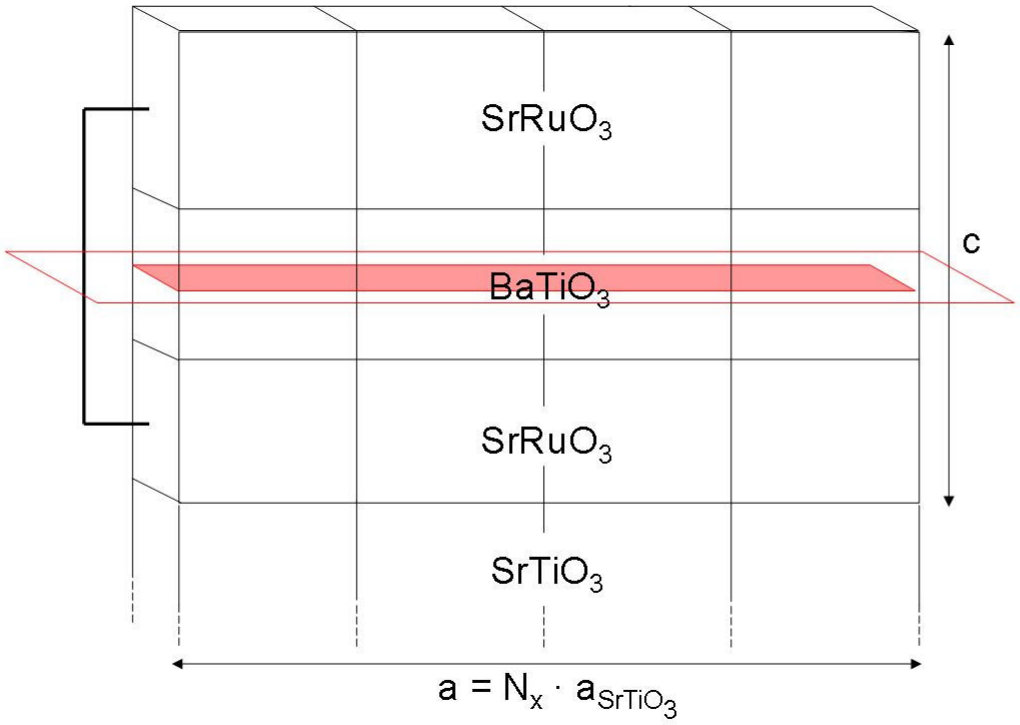
Building the cell: the paraelectric unit cell

- **Building the reference cell following the scheme of Junquera and Ghosez (2003).**



Building the cell: replicating the paraelectric structure

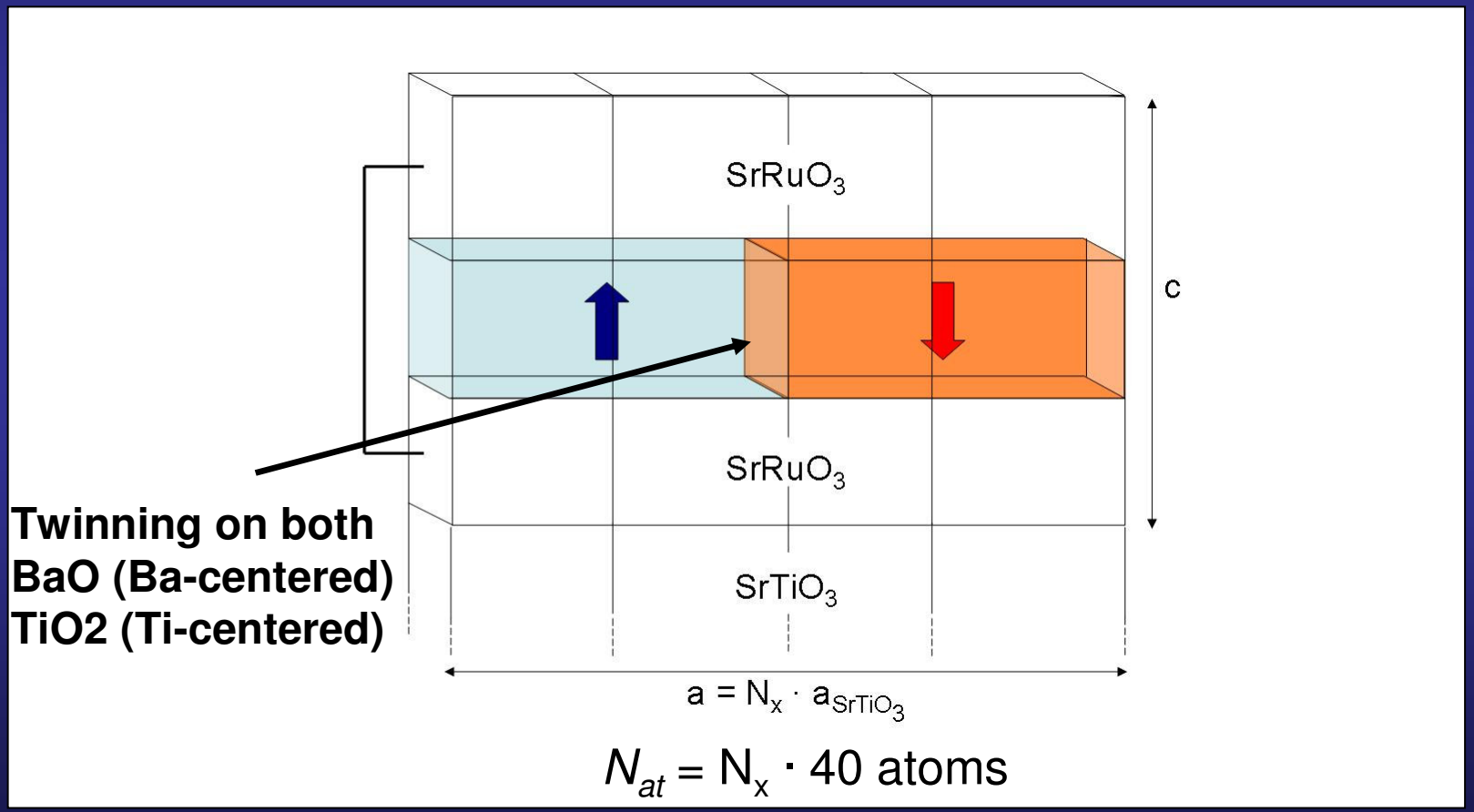
- N_x repetitions in [100] direction.
- The energies of these cells as references.



$N_{at} = N_x \cdot 40$ atoms

Building the cell: inducing a polarization by hand

- Chosing a domain wall.
- Inducing a polarization by hand in the FE layer displacing the atoms a percentage of the bulk soft mode.

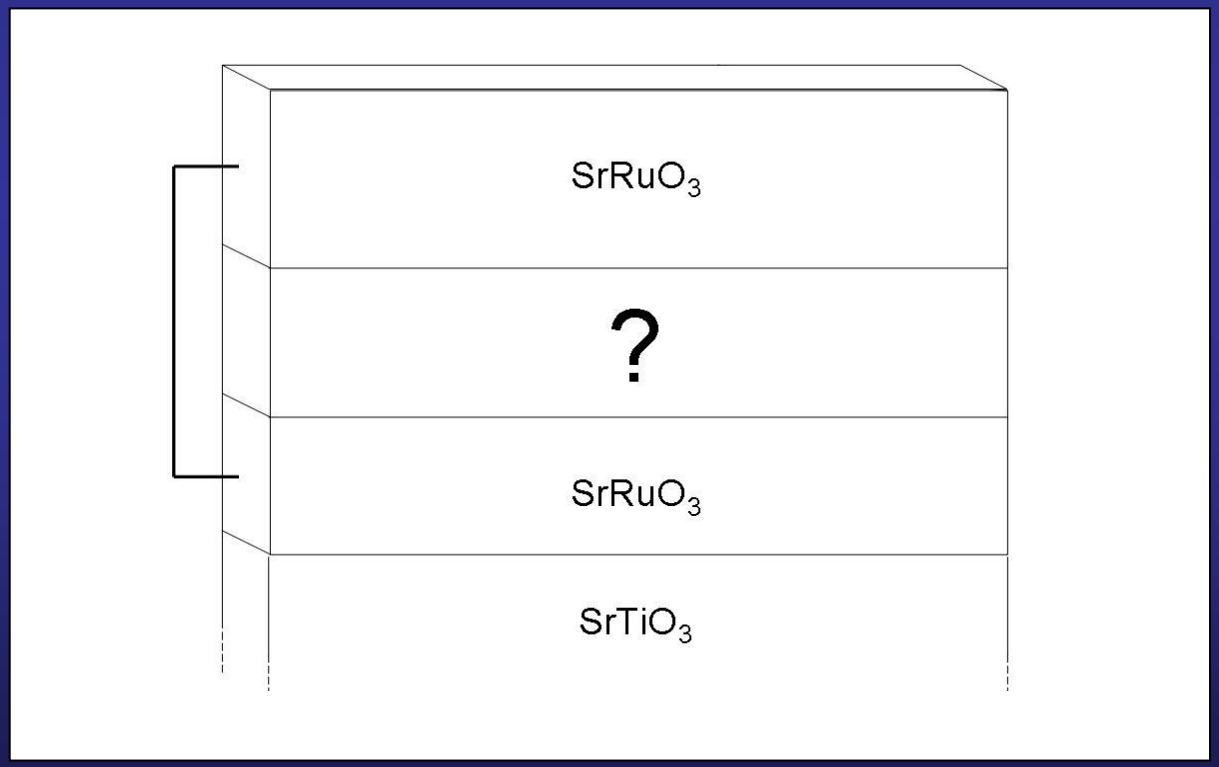


$N_{at} = N_x \cdot 40$ atoms

Relaxing all the atomic coordinates, both in the ferroelectric layer and the electrodes

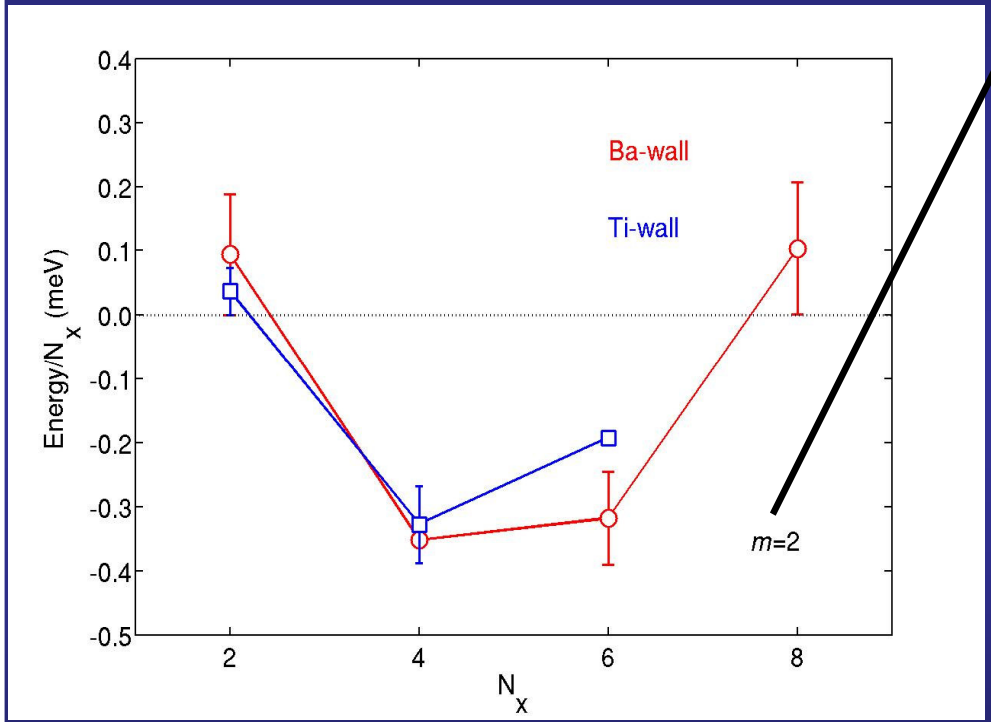
Forces smaller than 0.01 eV/Å

No constraints impossed on the atomic positions



Polydomain phases more stable than paraelectric structure for $2 < N_x < 8$

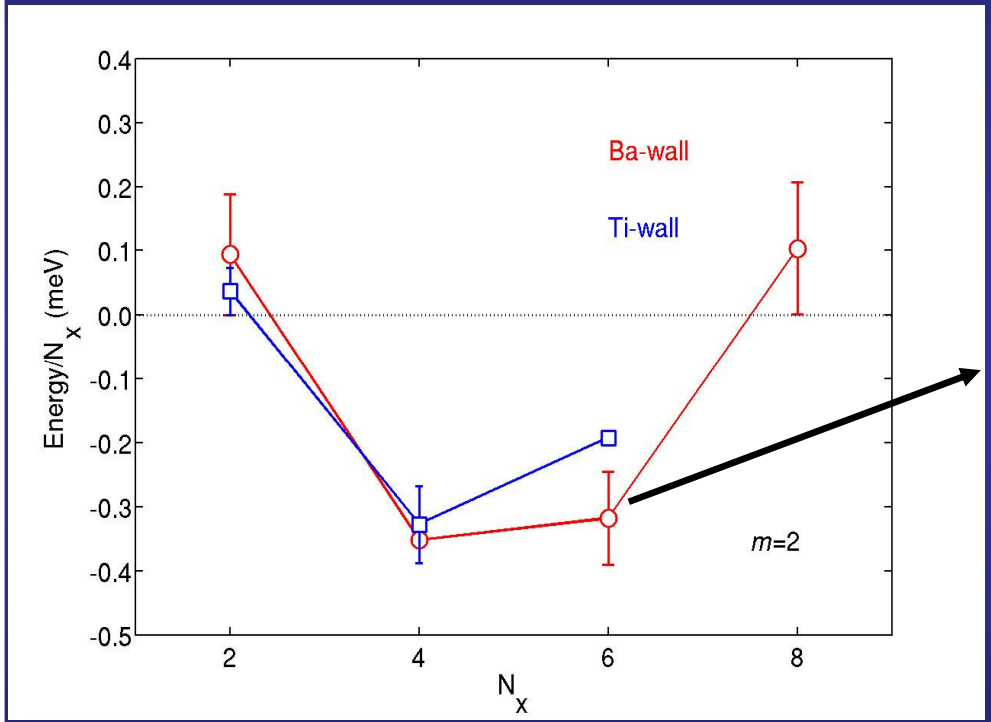
2-unit-cells thick $BaTiO_3$ layer



Polar **domains stabilized below critical thickness** for the **monodomain** configuration

Polydomain phases more stable than paraelectric structure for $2 < N_x < 8$

2-unit-cells thick $BaTiO_3$ layer



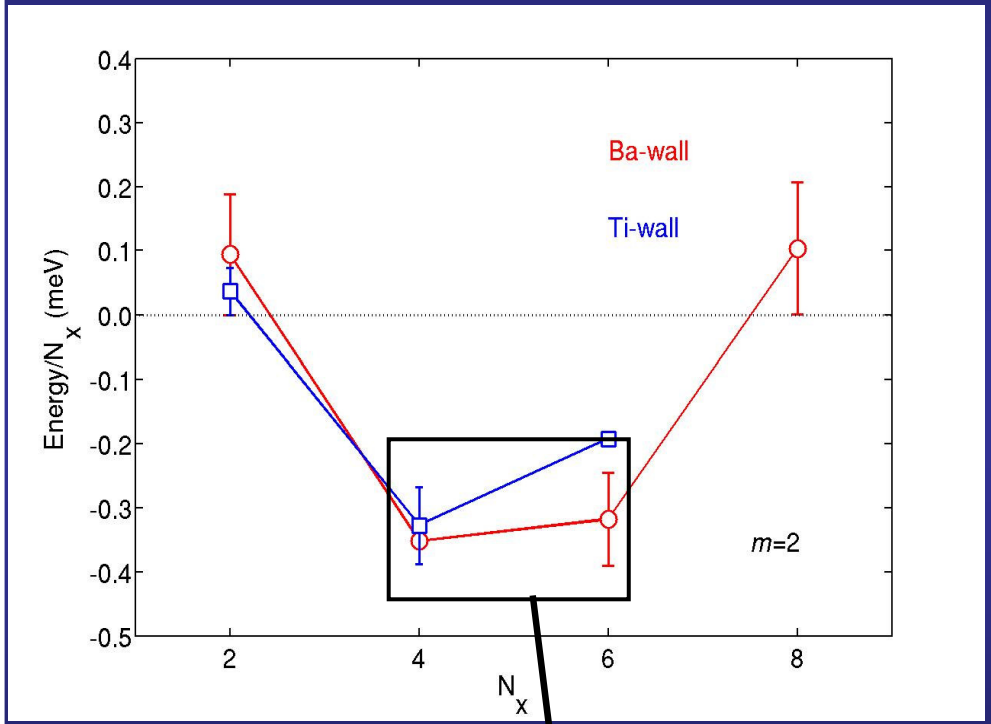
Polar **domains stabilized below critical thickness** for the **monodomain** configuration

As 180º domains in bulk,

Ba centered domain wall preferred

Polydomain phases more stable than paraelectric structure for $2 < N_x < 8$

2-unit-cells thick $BaTiO_3$ layer



Polar **domains stabilized below critical thickness** for the **monodomain** configuration

As 180º domains in bulk,

Ba centered domain wall preferred

No energy difference between $N_x = 4$ and $N_x = 6$

Both of them might be equally present in an sample

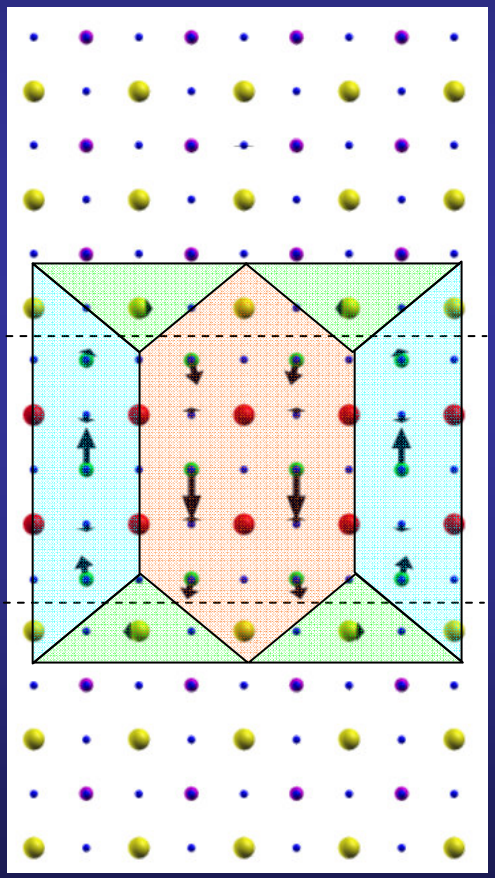
(α and β phases in $PbTiO_3/SrTiO_3$ interfaces?)

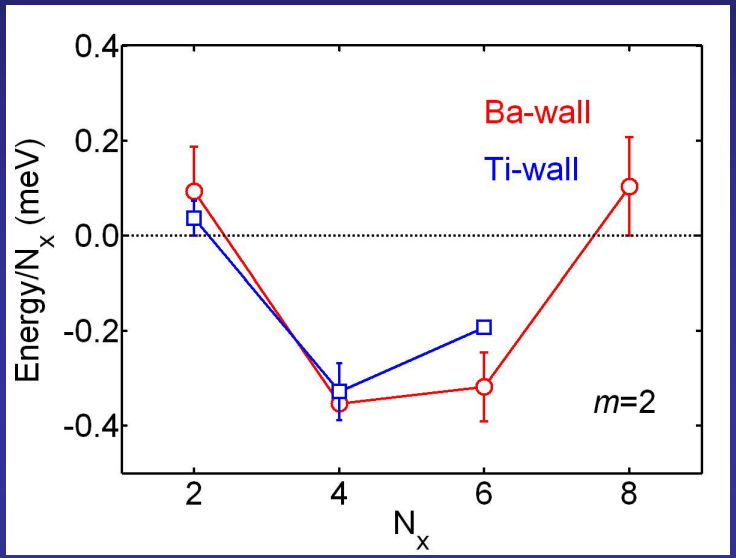
D. D. Fong *et al.*, Science 304, 1650 (2004)

Polydomain phases adopt the form of a "domain of closure", common in ferromagnets

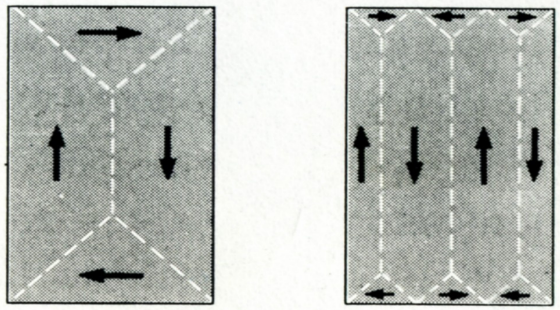
$N_x = 4$

BaO domain walls





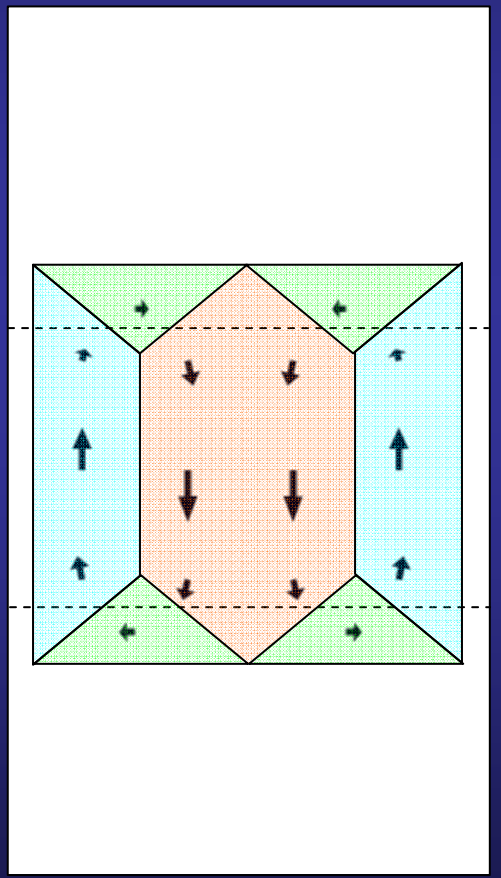
Ferromagnetic domains



C. Kittel (1971)

$N_x = 4$

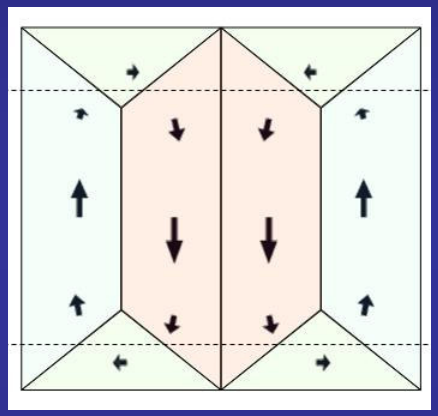
BaO domain walls



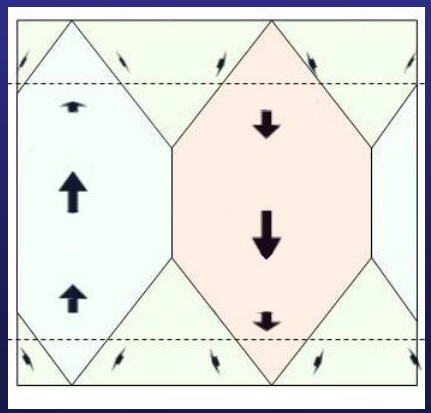
Polydomain phases adopt the form of a "domain of closure", common in ferromagnets

N_x=4

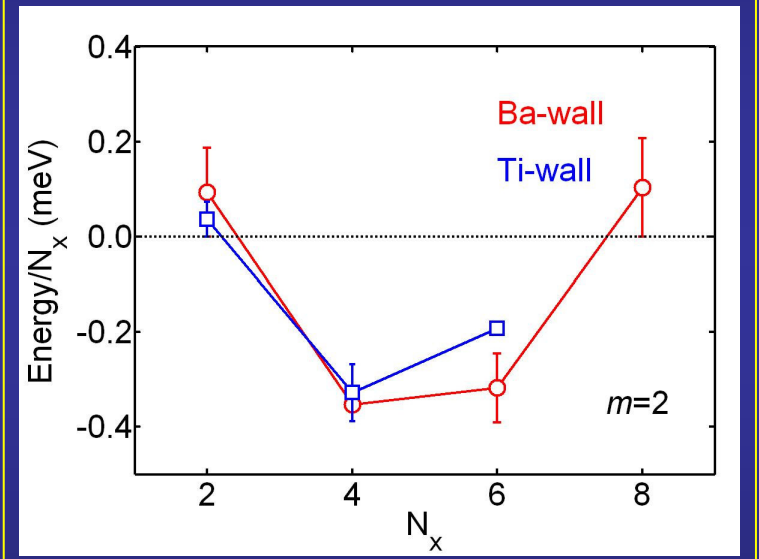
BaO wall



TiO_2 wall

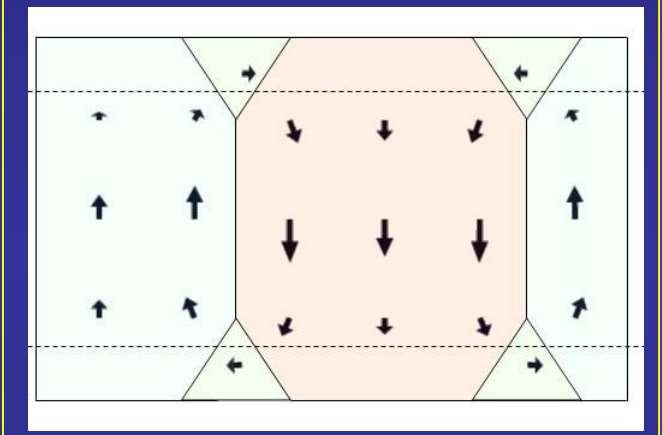


2-unit-cells thick $BaTiO_3$ layer

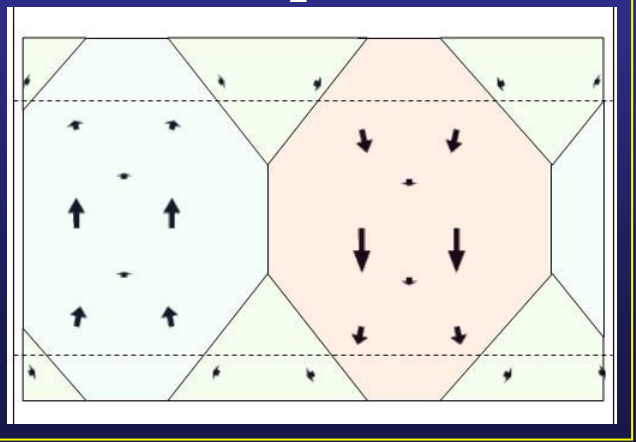


N_x=6

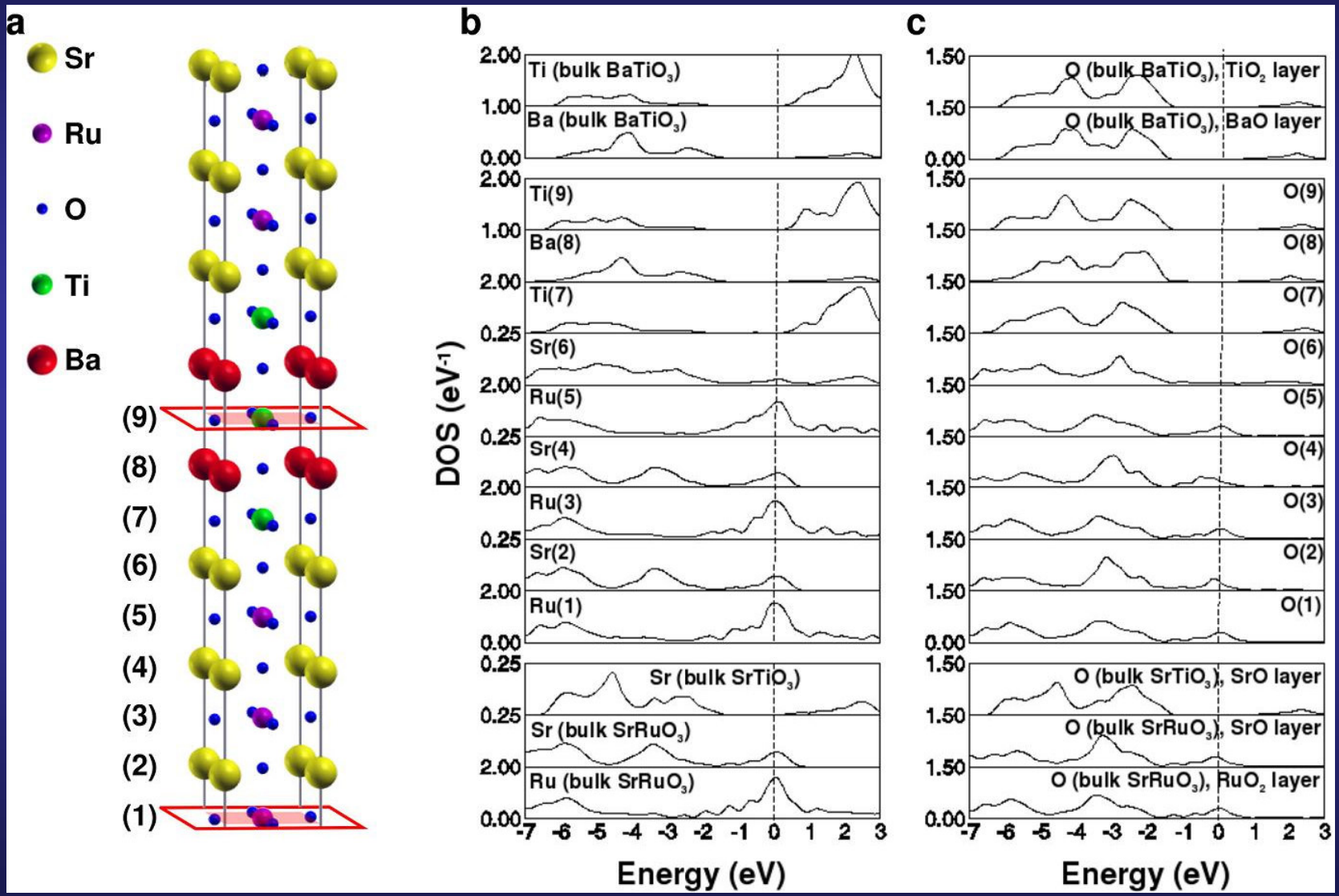
BaO wall



TiO_2 wall



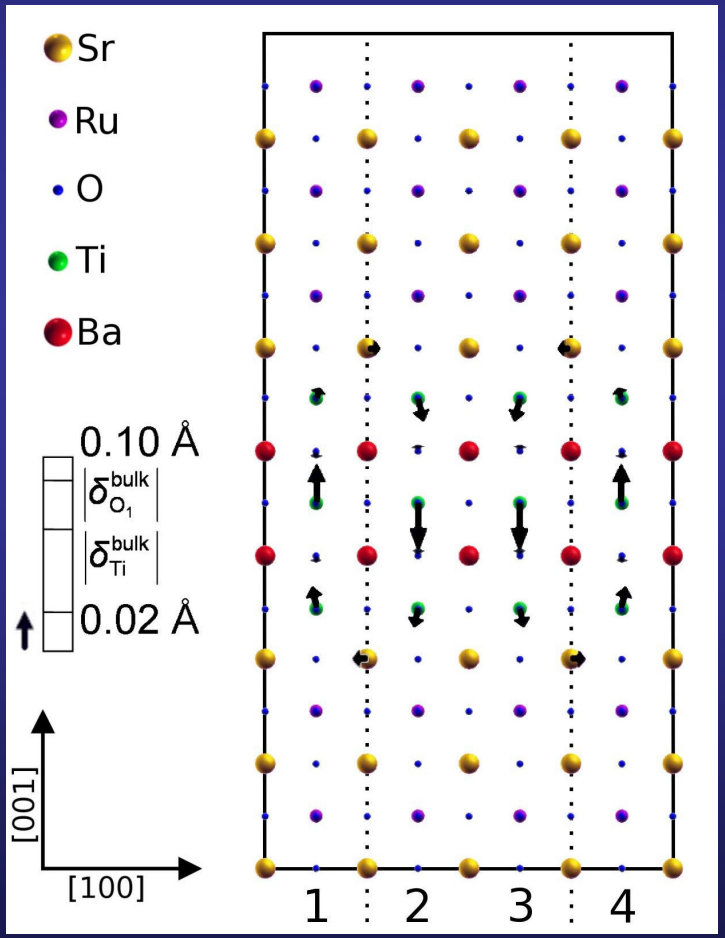
SrO layer at the interface behaves more like $SrTiO_3$ than $SrRuO_3$ ⇒ highly polarizable



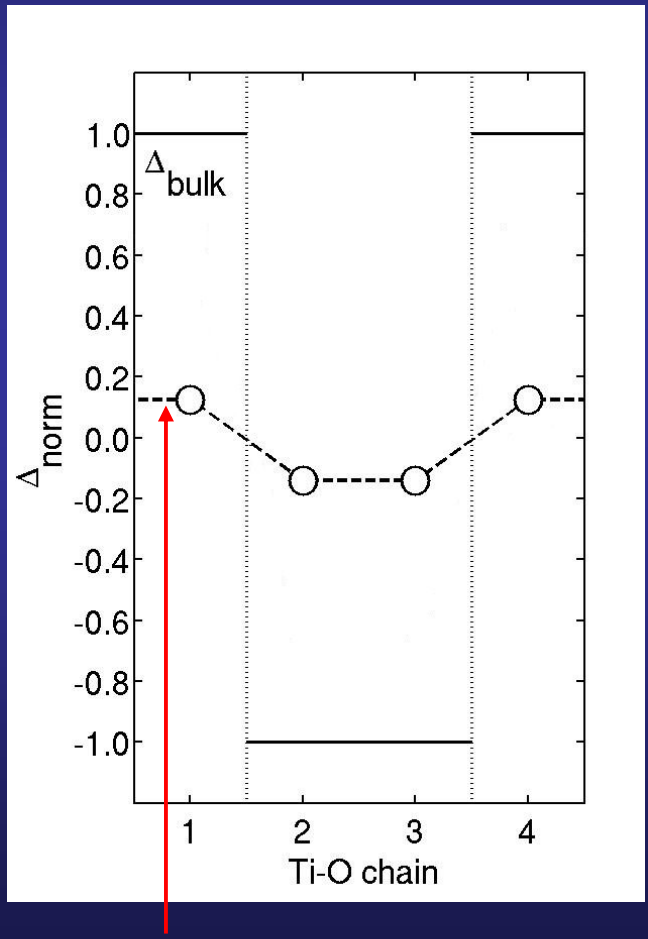
Projected Density of States in the reference paraelectric structure

Resulting phases show in-plane displacements and small polarization

$N_x = 4$ BaO domain walls



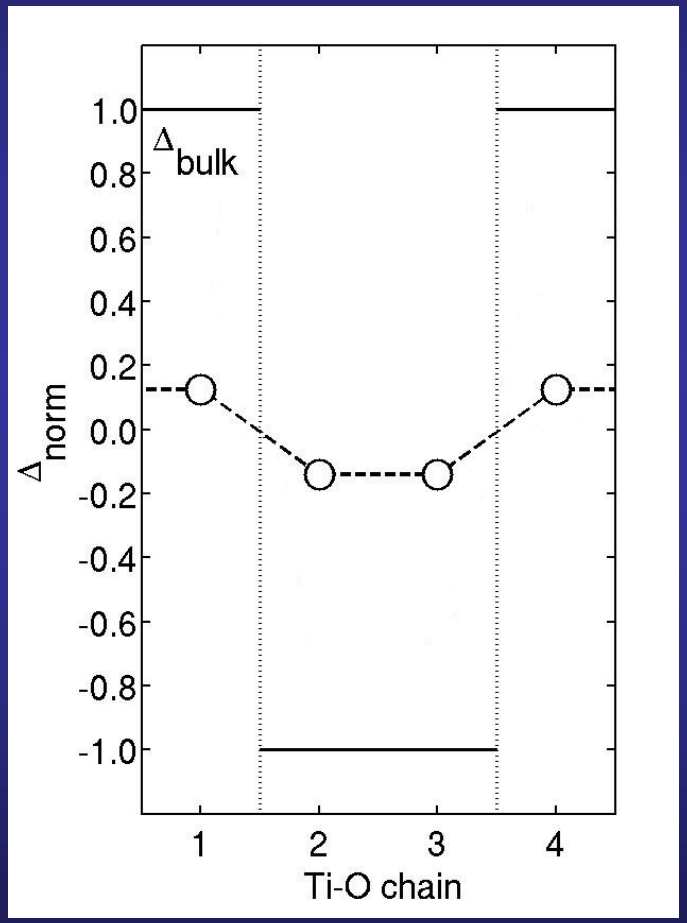
Small polarization inside the domains



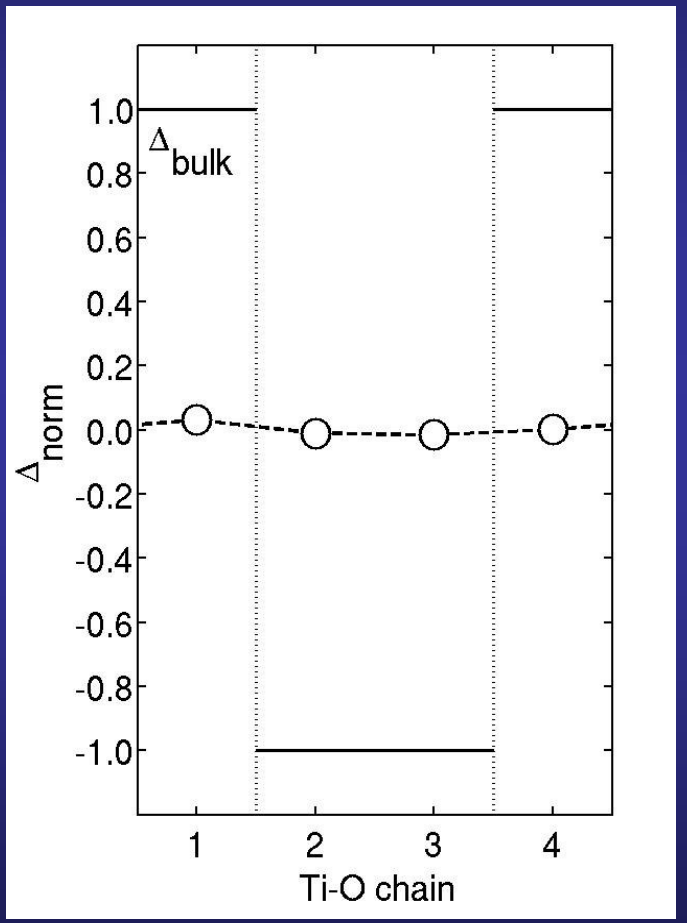
About 1/10 of bulk soft-mode polarization

In-plane displacements are essential to stabilize the domains

In-plane displacements: ON

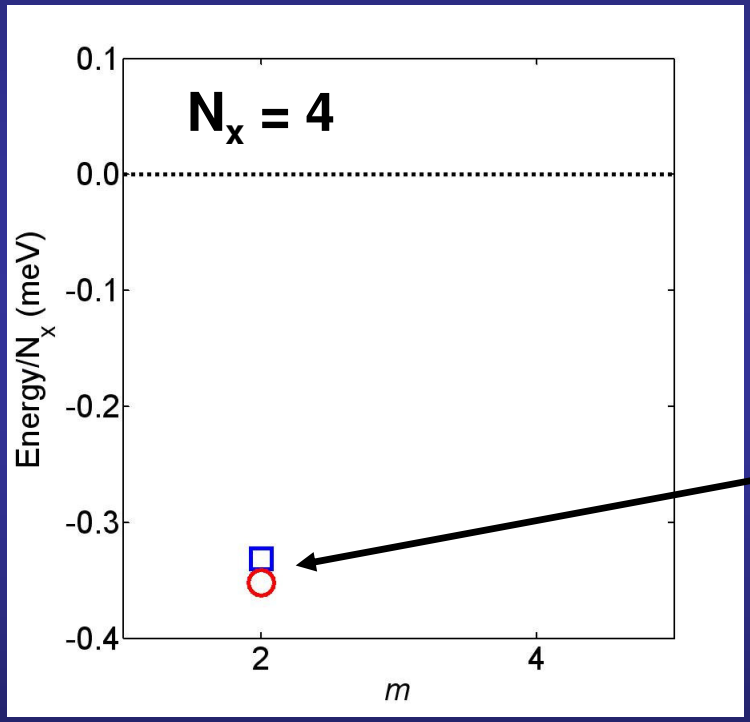


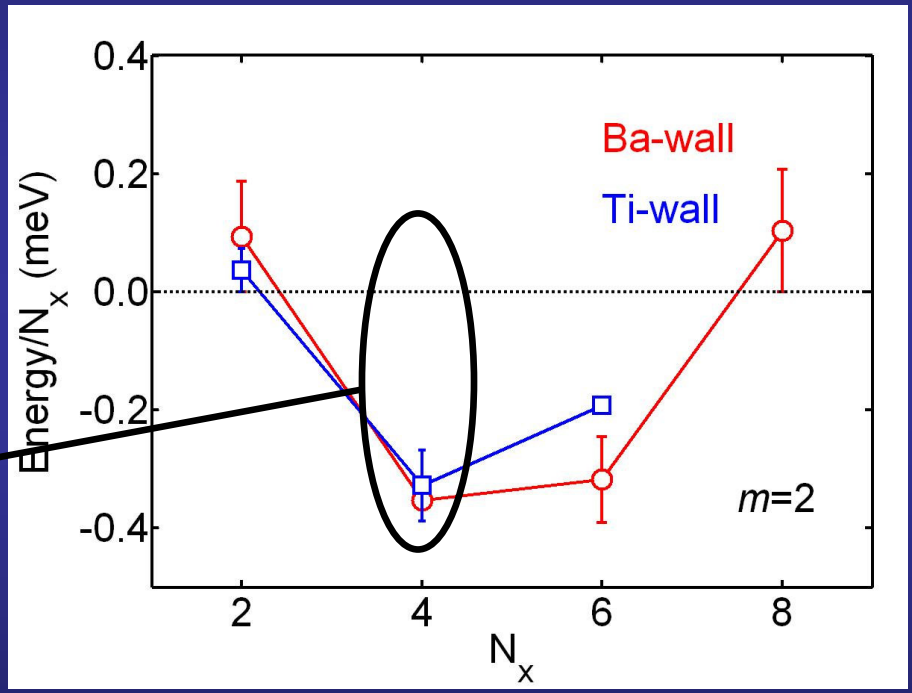
In-plane displacements: OFF



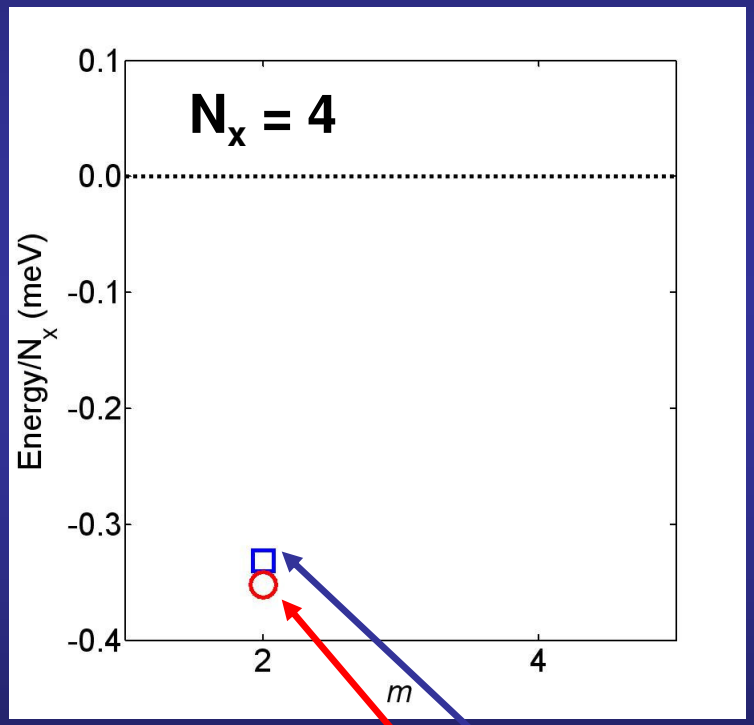
When in-plane coordinates are fixed, structure goes back to the paraelectric phase

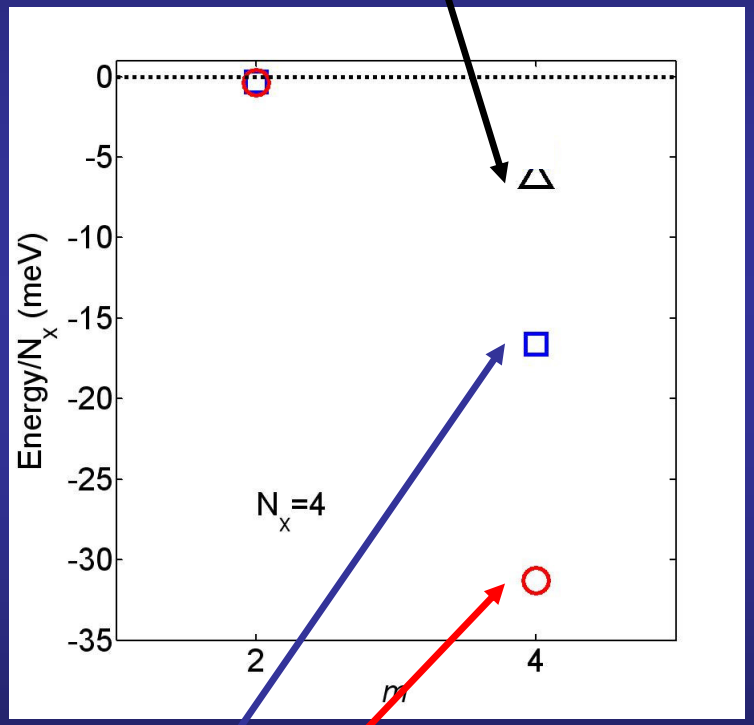
Relevant energy differences very small in the ultrathin m = 2 capacitors





Relevant energy differences increase with thickness



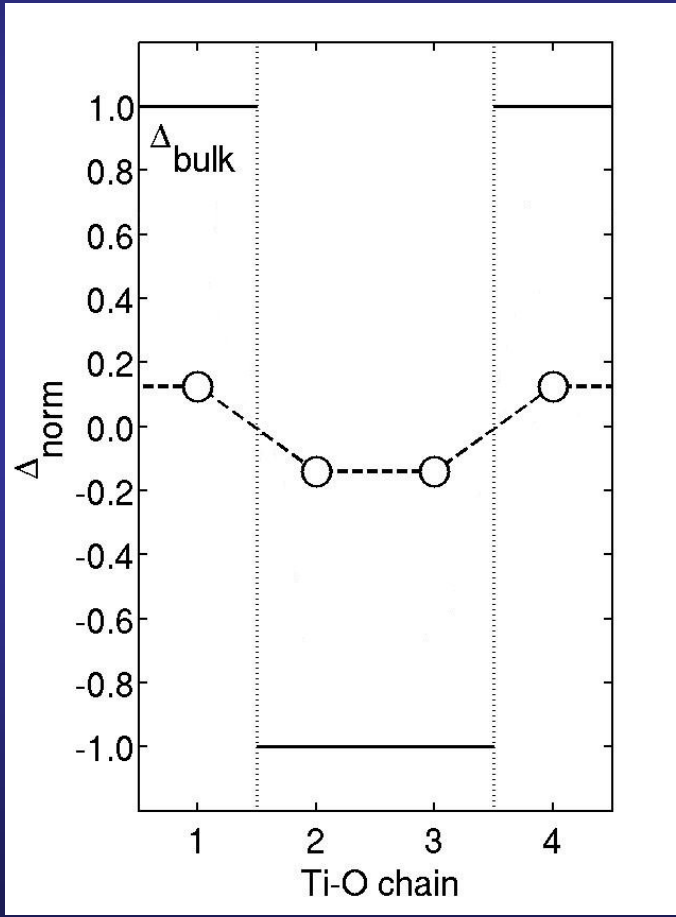


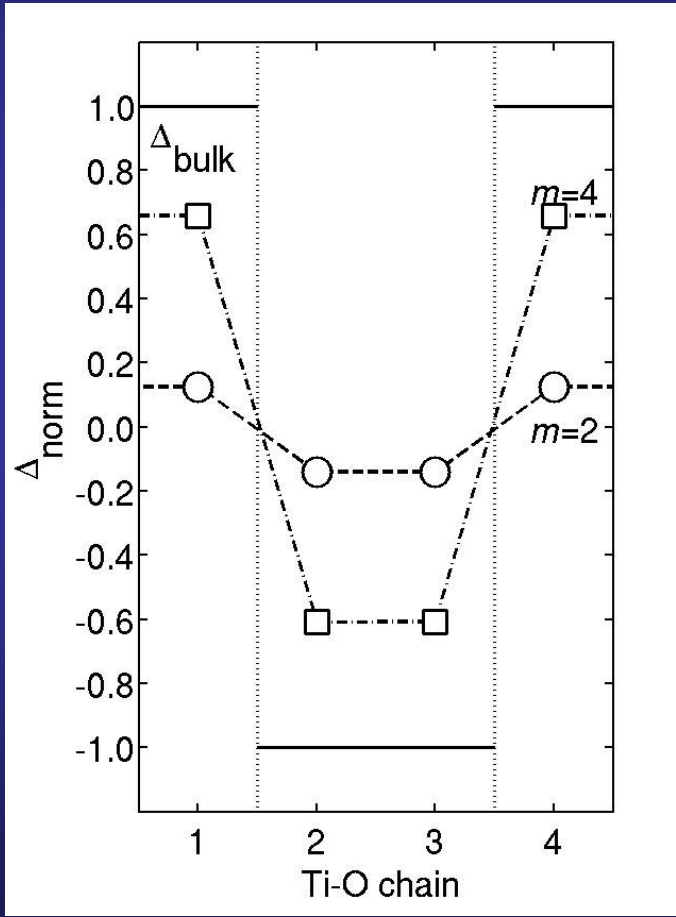
Monodomain

Ti-centered domains

Ba-centered domains

Transition from vortices to standard 180º domains. 4-unit-cell thick layer, great increase in polarization

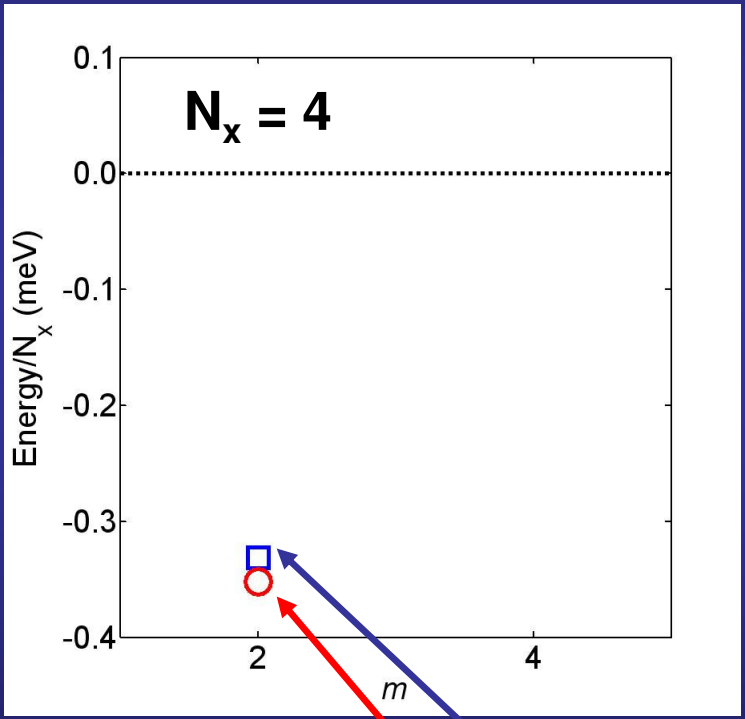


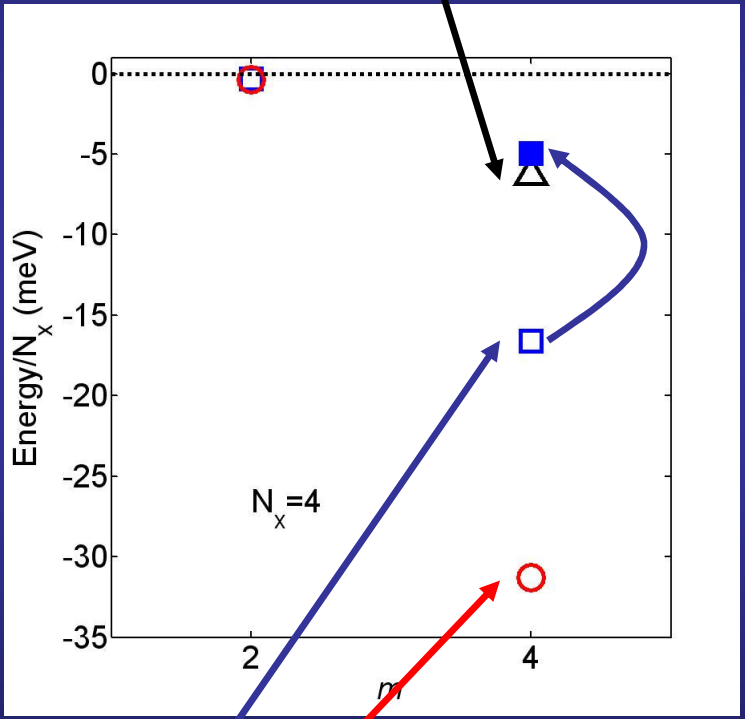


In-plane displacements, essential to stabilize domains

Monodomain

In-plane constraint





Ti-centered domains

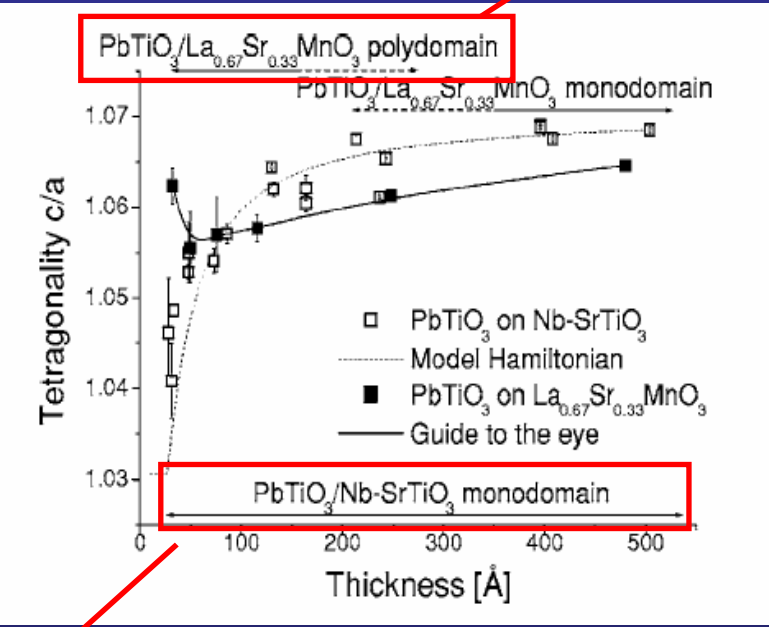
Ba-centered domains

Changing the electrode, the ground state of $PbTiO_3$ changes from monodomain to polydomain

APPLIED PHYSICS LETTERS 90, 052907 (2007)

Monodomain to polydomain transition in ferroelectric $PbTiO_3$ thin films with $La_{0.67}Sr_{0.33}MnO_3$ electrodes

Lichtensteiger, *et al.*

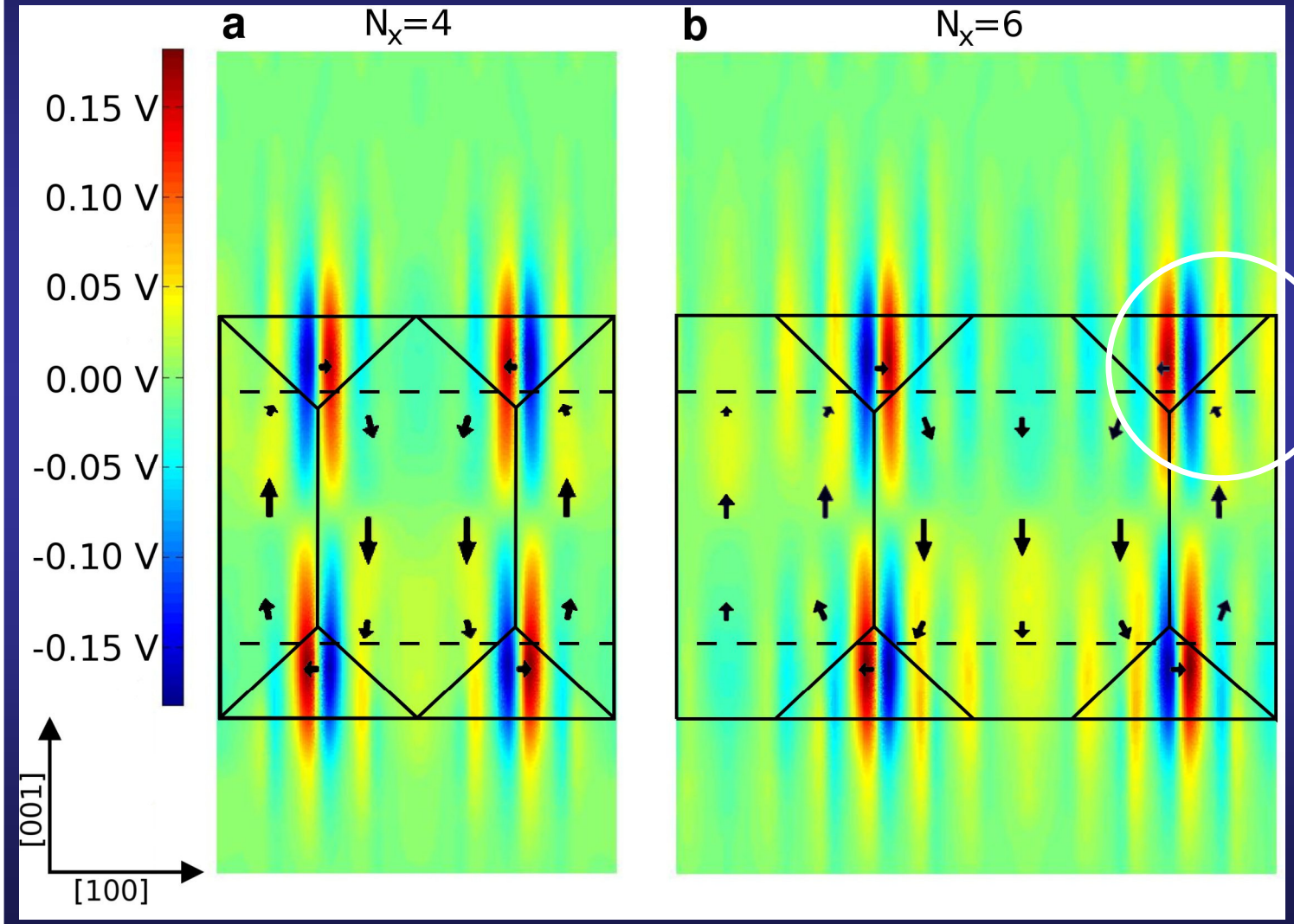


PRL **94,** 047603 (2005) PHYSICAL REVIEW LETTERS week ending 4 FEBRUARY 2005

Ferroelectricity and Tetragonality in Ultrathin $PbTiO_3$ Films

Lichtensteiger, Triscone, Junquera, Ghosez.

Analysis of the electrostatic potential:
large field in *x* at the interface, residual depolarizing field in *z*



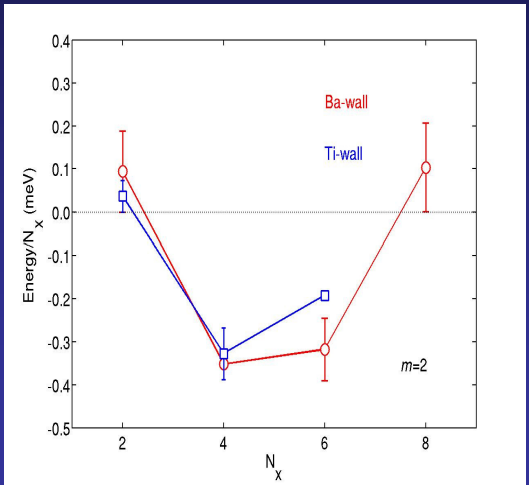
Pinning of charged defects at interface?

⇓

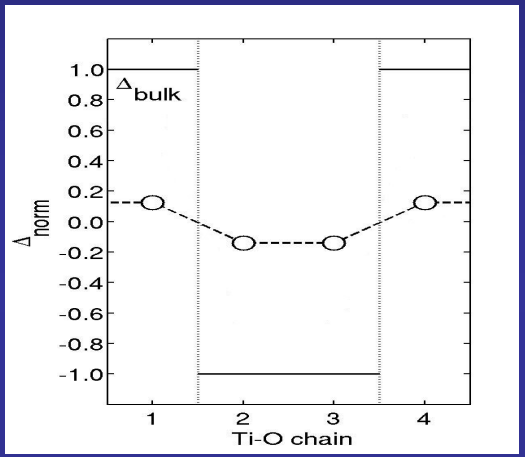
role on fatigue?

Two unit cells thick of $BaTiO_3$

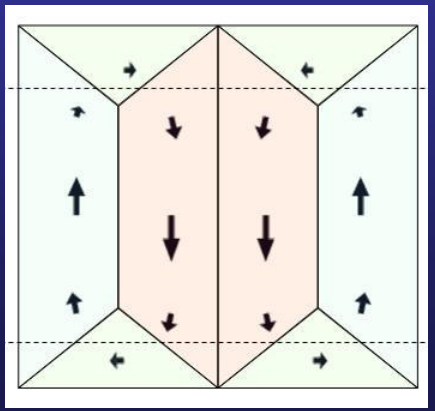
Conclusions



• **Polydomain phases** in ultrathin FE films are stabilized below critical thickness in monodomain configurations.



• The chemical interaction through the interface is an essential factor since it affects the **in-plane mobility** of the atoms.



• **Closure domains** in FE capacitors are predicted (recently detected expt. in FE ultrathin films by Scott).

Slides available at: **http://personales.unican.es/junqueraj**

Contact: **pablo.aguado@unican.es**

javier.junquera@unican.es

More information ...

Method: Computational details

First-principles calculations within
Kohn-Sham Density Functional Theory (DFT)

: Numerical Atomic Orbital DFT code.

http://www.uam.es/siesta

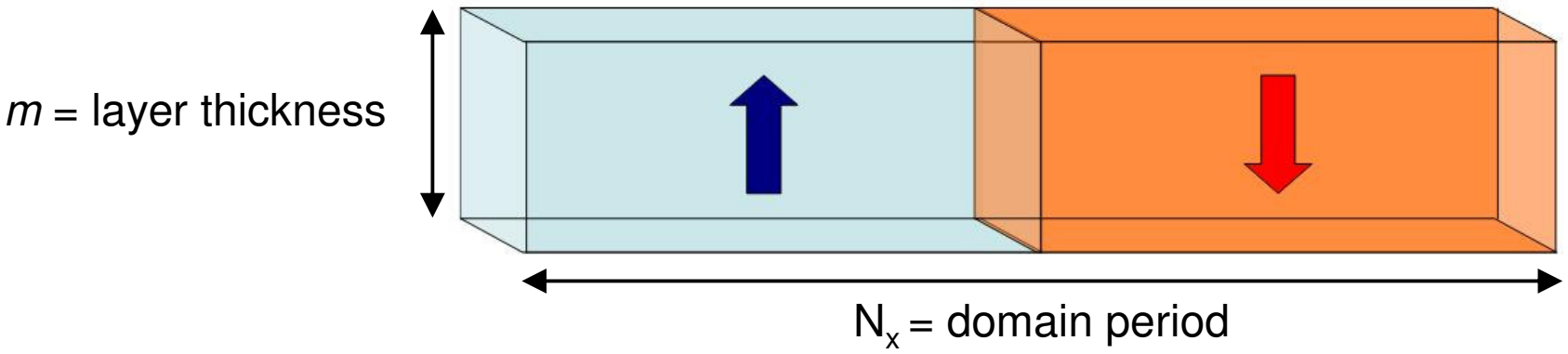
J. M. Soler et al., J. Phys. Condens. Matter **14**, 2745 (2002)

Exchange-correlation functional **:** LDA, fit to Ceperley-Alder data
Norm conserving pseudopotentials: Ti, Sr, Ba, Ru: semicore in valence

Basis set:
NAO: valence: Double-ζ + Polarization ; semicore: Single-ζ
Real-space grid cutoff **:** 400 Ry
k-point grid **:** equivalent to 12x12x12 for simple cubic perovskite
Supercell geometry

Ferroelectric layer: fundamental parameters of the simulations

FE layer: N_x repetitions in [100] direction and *m* cells in [001] direction

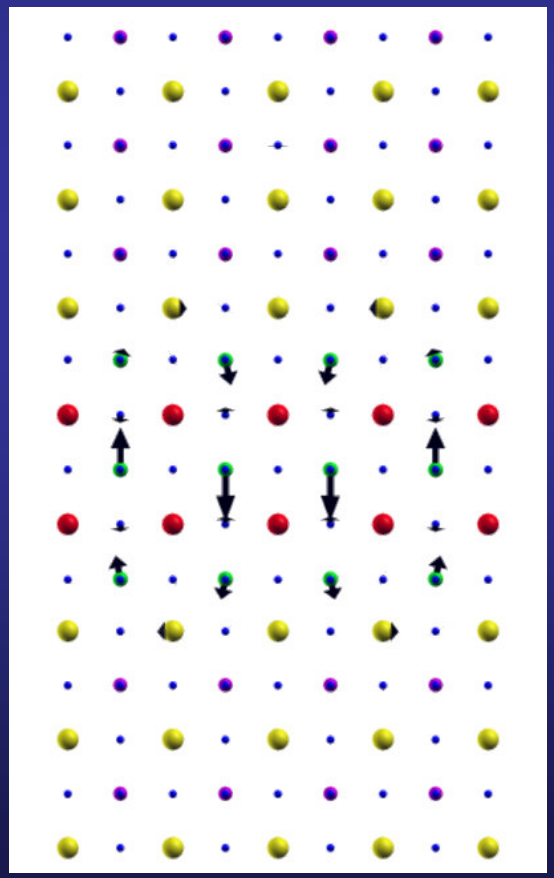


- N_x from 2 to 8 cells
- *m* from 2 to 4 cells
- FE layer made of $BaTiO_3$.
- Domain wall in BaO and TiO_2

Very small energy differences, very accurate simulations needed

m=2, $N_x = 4$

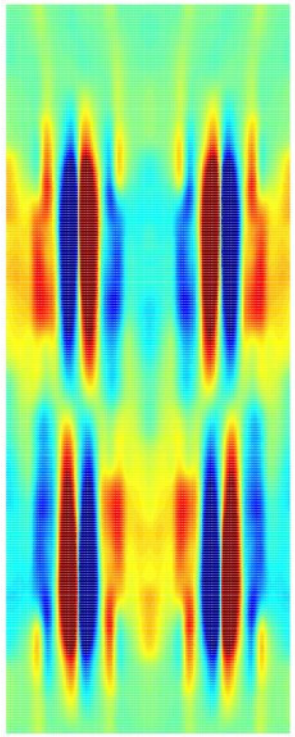
BaO domain walls



Structure	Total Energy (eV)
Paraelectric	-138326.083054
Multidomain	-138326.084463

(*E*-*E*para)/Nx = -0.00035 eV

Analysis of the electrostatic potential:
huge field in *x* at the interface, residual depolarizing field in *z*



Four unit cells thick of $BaTiO_3$