Lattice ($E^{(0)}$): Theory and models

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Outline

- Second-principles methods in SCALE-UP,

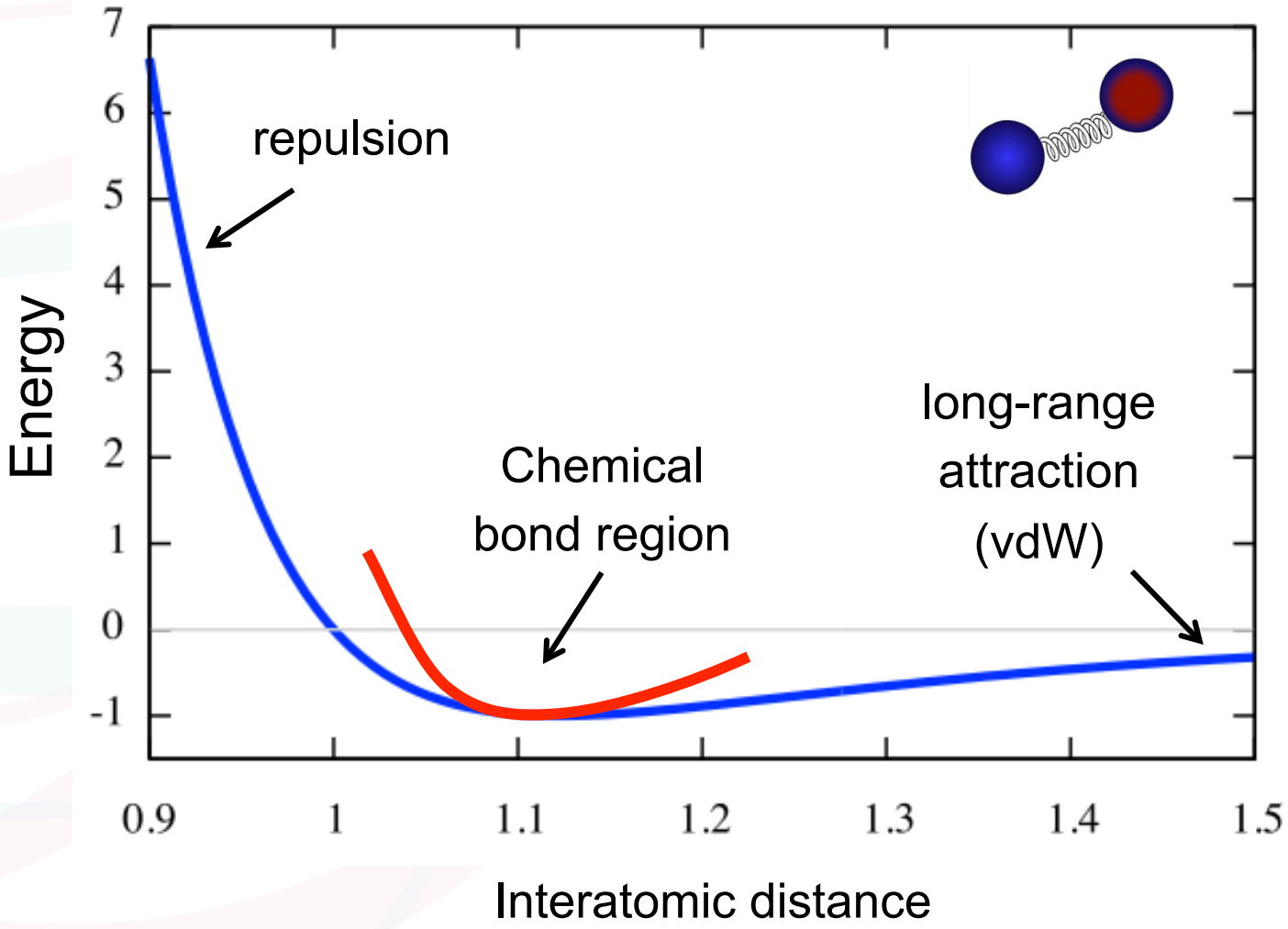
  basic notions & scope

- Lattice models, a particular choice that makes sense

- SCALE-UP, overview of current lattice capabilities

- Hands-on session: about the tutorials & tests

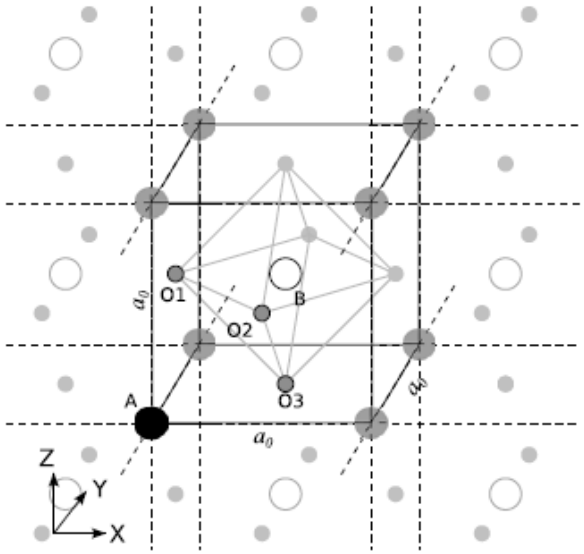
SCALE-UP is a perturbative approach

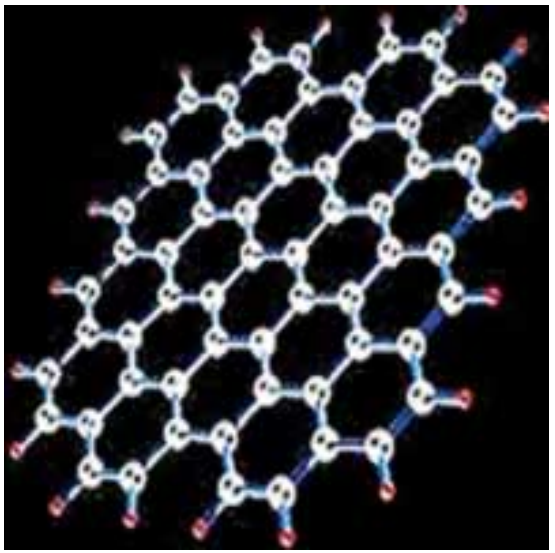


SCALE-UP is a perturbative approach

- We assume an underlying reference structure

RAG = Reference Atomic Geometry





The RAG can be **anything**, from a 3D periodic lattice... to a molecule.

Configuration = Reference + Distortion

$$r_{l\kappa\alpha} = \sum_{\beta} (\delta_{\alpha\beta} + \eta_{\alpha\beta})(R_{l\beta} + \tau_{\kappa\beta}) + u_{l\kappa\alpha}$$

$R_{l\beta}$ = RAG lattice vectors

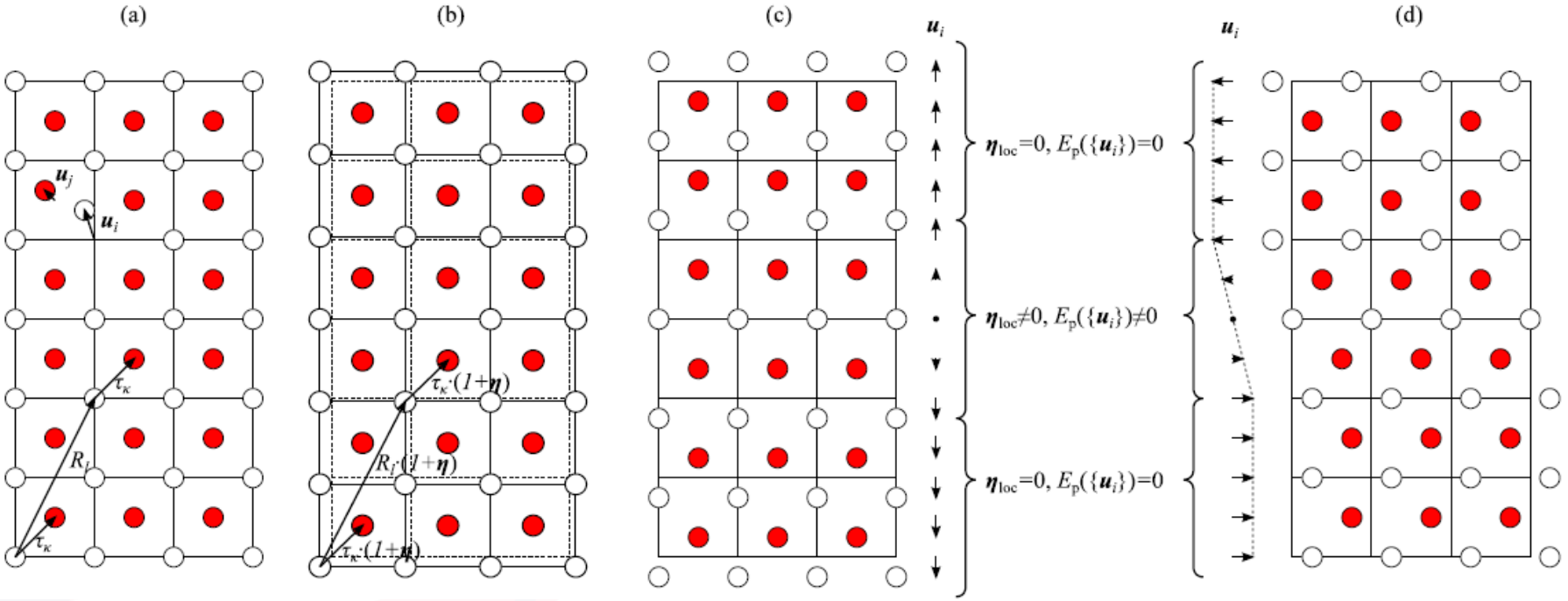
$\tau_{\kappa\beta}$ = RAG atomic positions in repeated unit

$\eta_{\alpha\beta}$ = homogeneous strain, applied to sim. supercell

$u_{l\kappa\alpha}$ = atomic displacement wrt strained RAG

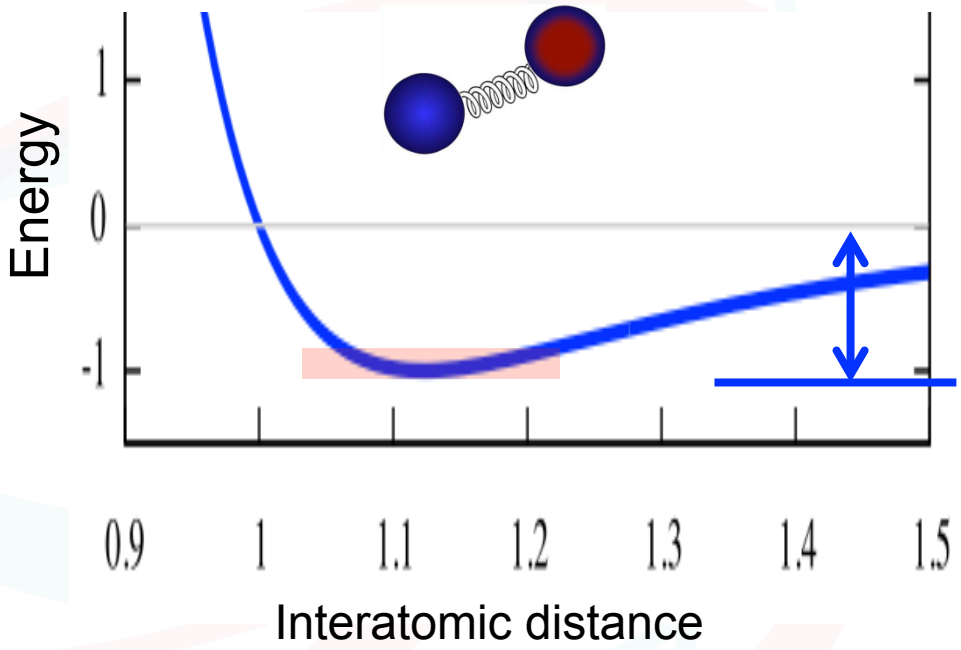
Configuration = Reference + Distortion

$$r_{l\kappa\alpha} = \sum_{\beta} (\delta_{\alpha\beta} + \eta_{\alpha\beta})(R_{l\beta} + \tau_{\kappa\beta}) + u_{l\kappa\alpha}$$



Energy for “arbitrary” atomic configurations

$$E = E_{RAG} + E(\{\eta_{\alpha\beta}\}, \{u_{l\kappa\alpha}\})$$



Cohesive energy: 1-10 eV/atom

Interactions controlling transitions, responses to perturbations:

1-100 meV/atom

SCALE-UP: Focus on the finer energy scale

→ quasi-perturbative conditions

→ cannot do chemistry

More on the energy...

- When we write this energy...

$$E = E_{RAG} + E(\{\eta_{\alpha\beta}\}, \{u_{l\kappa\alpha}\})$$

... what is the electronic configuration of the system?

We (typically) assume that the electrons are on the Born-Oppenheimer surface, following the atoms instantaneously.

This configuration-dependent state defines what we call

RED = Reference Electronic Density

Can we go beyond?

We write a general electronic state of the system as:

$$\rho(\{\eta_{\alpha\beta}\}, \{u_{I\kappa\alpha}\}) = \rho_{RED}(\{\eta_{\alpha\beta}\}, \{u_{I\kappa\alpha}\}) + \delta\rho$$

And we write the energy of this "excited" state as:

$$E = \underbrace{E_{RAG} + E(\{\eta_{\alpha\beta}\}, \{u_{I\kappa\alpha}\})}_{E^{(0)}} + \underbrace{\delta E(\{\eta_{\alpha\beta}\},\{u_{I\kappa\alpha}\},\delta\rho)}_{E^{(1)} + E^{(2)}}$$

(this lecture)

(tomorrow)

Motivating our choice of lattice models

- **The genesis of FP effective models for ferroelectrics**

  - Effective Hamiltonians for statistical simulations

Key references:

Phase transitions in $BaTiO_3$ from first-princples

W. Zhong, D. Vanderbilt, and K.M. Rabe

Physical Review Letters 73, 1861 (1994)

First-principles theory of ferroelectric phase transitions for perovskites: The case of $BaTiO_3$

W. Zhong, D. Vanderbilt, and K.M. Rabe

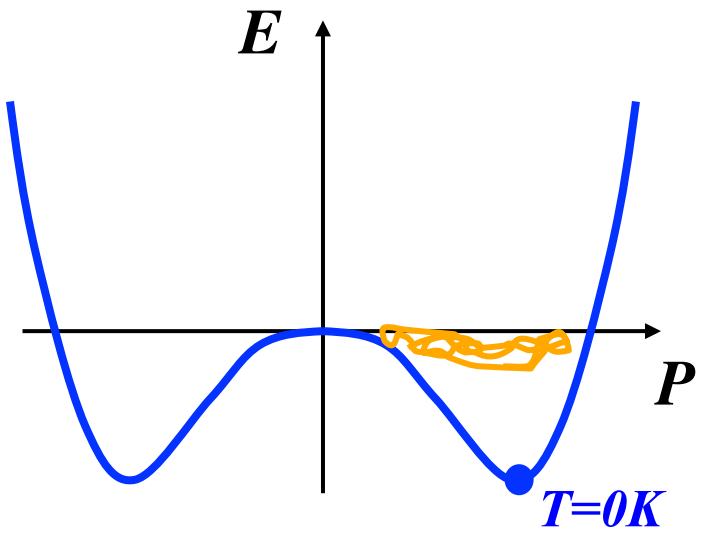
Physical Review B 52, 6301 (1995)

Can we study phase transitions from FP?

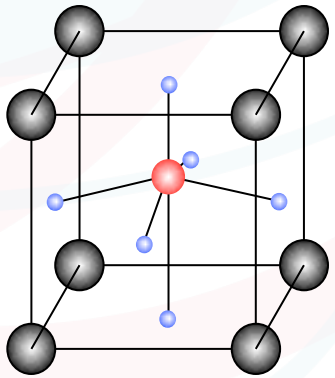
- We want to compute:

$$\langle P \rangle = \frac{1}{Z} \sum_x P[x] e^{-E[x]/k_B T}$$

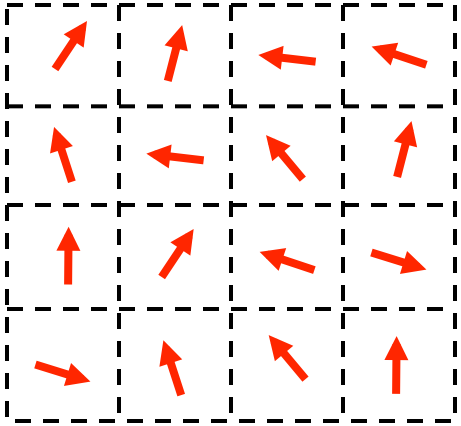
- The equilibrium value of P is a *thermal average* over all accessible states i



At *T=0K* only 1 state is accessible:



At ***finite temperatures*** **many** states are accessible:



First-principles effective models for ferroelectrics

- We want to compute:

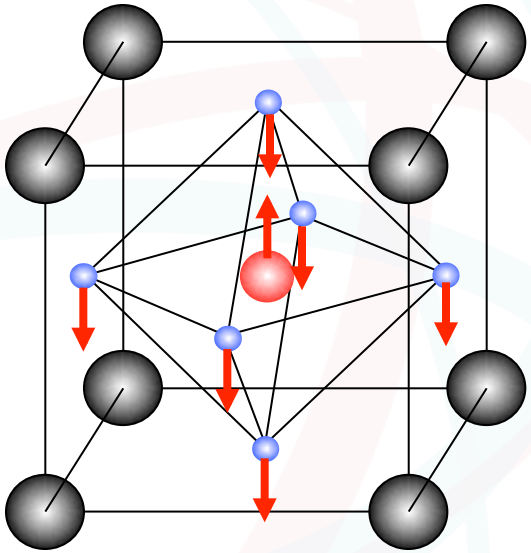
$$\langle P \rangle = \frac{1}{Z} \sum_{x} P[x] e^{-E[x]/k_B T}$$

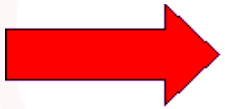
- Step 1: Identify *relevant* degrees of freedom

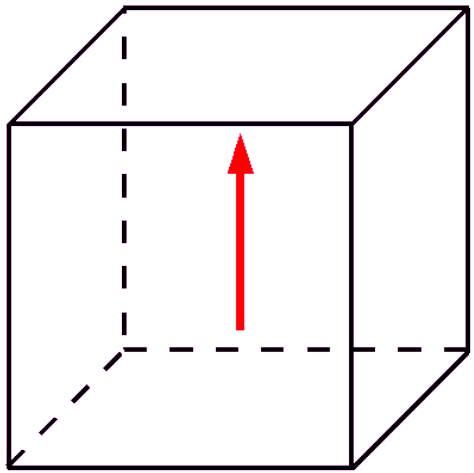
$$\{x\} \rightarrow \{u\} \subset \{x\}$$

$$\langle P \rangle = \frac{1}{Z} \sum_{u} P[u] e^{-E[u]/k_B T}$$

Relevant degrees of freedom







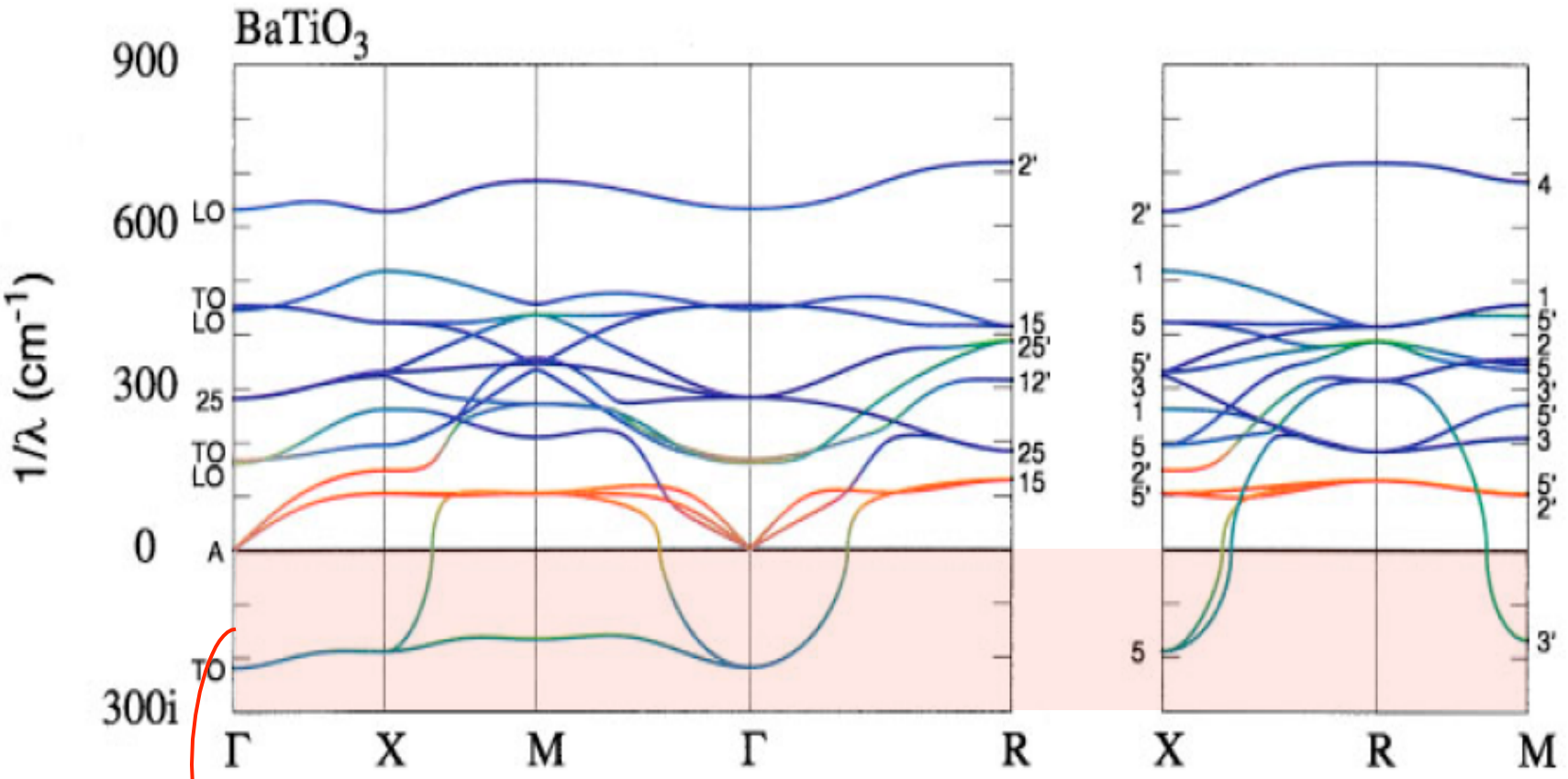
local polar distortion
associated to FE instability

simplified version of the
unit cell of our FE crystal

+ cell strains to capture ferroelastic & piezoelectric effects

Relevant degrees of freedom

Ghosez *et al.*, Phys. Rev. B 60, 836 (1999)



Our effective Hamiltonian should capture these soft distortions

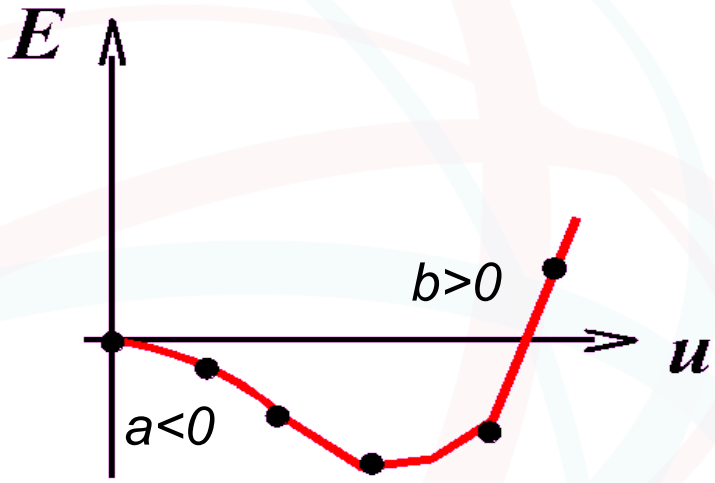
First-principles effective models for ferroelectrics

- Step 2: Simple parametric form of the energy

$$E[u] \rightarrow H_{eff}[u]$$

$$\langle P \rangle = \frac{1}{Z} \sum_{u} P[u] e^{-H_{eff}[u]/k_B T}$$

Simple parametrization of the energy



Ab initio calculation
for each value of ***u***

Compute once and for all:

$H_{eff}[\boldsymbol{u}] = E_0 + a\boldsymbol{u}^2 + b\boldsymbol{u}^4$

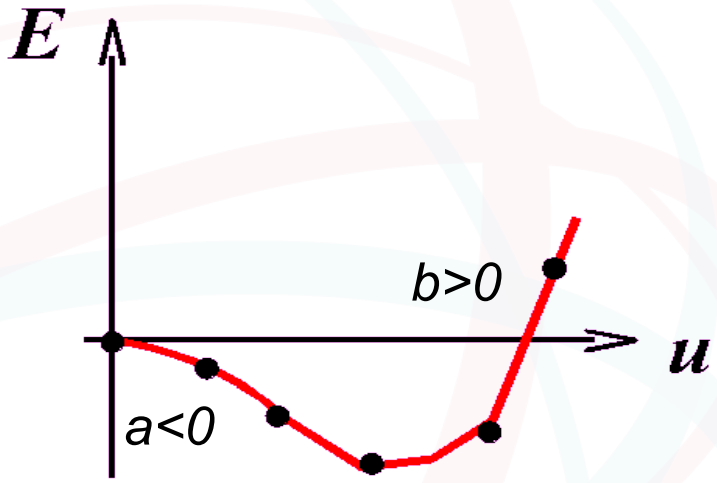
Effective Hamiltonian:

• Minimal Taylor expansion of the energy, as a function of $\{u\}$ and $\{\eta\}$, taking the high-symmetry cubic phase as reference (u=0, η=0).

$$H_{\text{eff}}(\{\boldsymbol{u}\},\{\boldsymbol{\eta}\}) = \sum \mathrm{K}_{ij}\, \boldsymbol{u}_i\, \boldsymbol{u}_j + \sum \Gamma_{ij}\, \boldsymbol{u}_i^2\, \boldsymbol{u}_j^2 + \sum \mathrm{C}_{lk}\, \boldsymbol{\eta}_l\, \eta_k + \sum \mathrm{B}_{lij}\, \boldsymbol{\eta}_l\, \boldsymbol{u}_i\, \boldsymbol{u}_j$$

• The tensors K, Γ, C and B calculated from first-principles

Simple parametrization of the energy



Ab initio calculation
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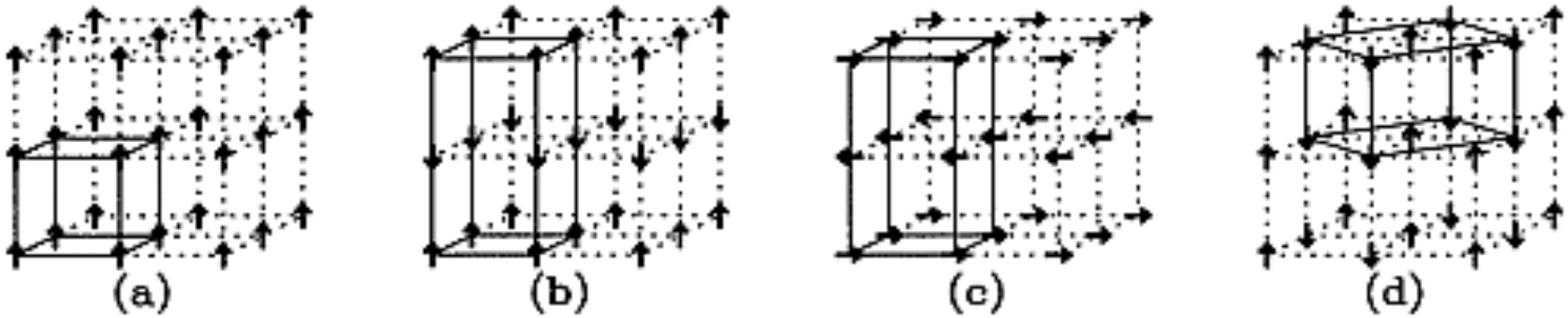


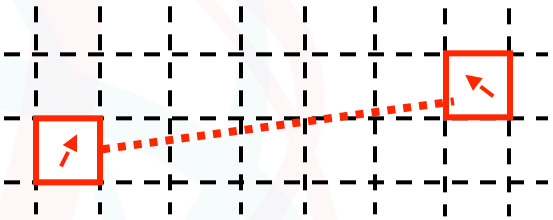
Parts of the Hamiltonian (I)

- Interactions between the local polar modes

Harmonic:

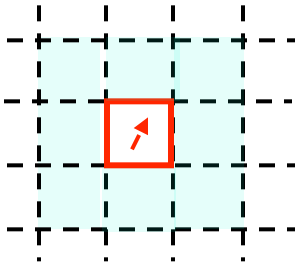
$$\frac{1}{2}\sum_{ij} K_{i\alpha j\beta} u_{i\alpha} u_{j\beta}$$

long-range "attracive"



$$Q_{i\alpha\, j\beta} \sim Z^*_{i\alpha} Z^*_{j\beta} / r^3$$

short-range "repulsive"

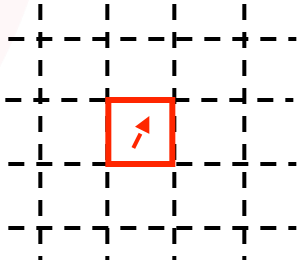


$$J_{i\alpha\, j\beta} \sim 3^{\text{rd}}\ \text{n.n.}$$

Anharmonic:

$$\frac{1}{4}\sum_{ijkl} \overleftrightarrow{\Gamma}_{ijkl} \vec{u}_i \vec{u}_j \vec{u}_k \vec{u}_l$$

on-site, ultra-localized in space



$$\overleftrightarrow{\Gamma}_{ijkl} \sim \overleftrightarrow{\Gamma} \delta_{ij} \delta_{ik} \delta_{il}$$

- In the spirit of the classic φ^4 models for studies of structural phase transitions

Parts of the Hamiltonian (II)

- Strains

  - Homogeneous: $\frac{1}{2}\vec{\eta}\,\overleftrightarrow{C}\,\vec{\eta}$

  - Inhomogeneous (crude approx. to acoustic phonon bands)

$$\frac{1}{2}\sum_i \vec{\eta}_i\,\overleftrightarrow{C}'\,\vec{\eta}_i \qquad \begin{cases} \overleftrightarrow{C}' : \text{trivially derived from } \overleftrightarrow{C} \\ \vec{\eta}_i : \text{local strain} \end{cases}$$

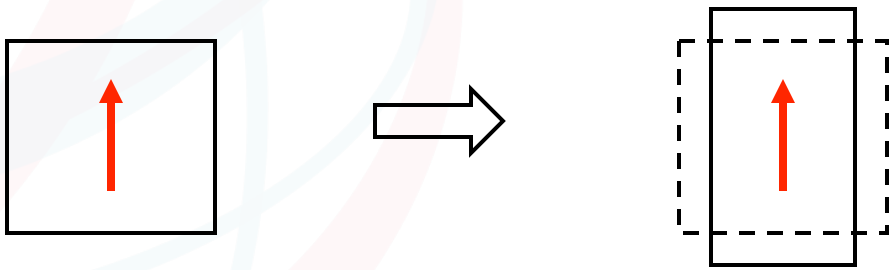
ultra-localized in space

Parts of the Hamiltonian (III)

- Coupling between polar local modes and strain

$$\sum_i \vec{\eta}\, \vec{u}_i \overleftrightarrow{B}\, \vec{u}_i$$

- lowest lying coupling allowed by symmetry in cubic perovskites
- ultra-localized in space



First-principles effective models for ferroelectrics

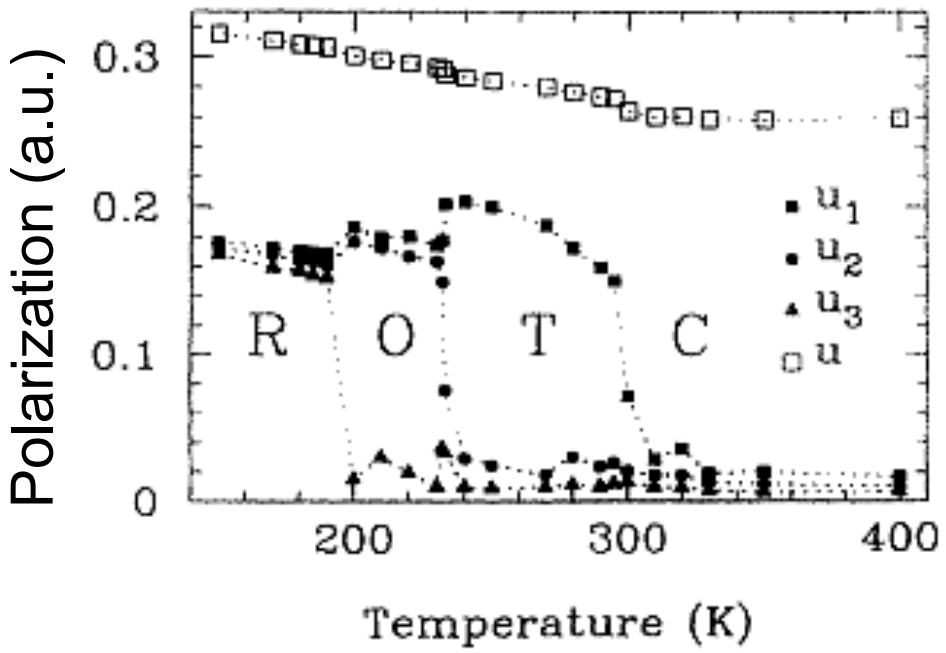
And once we have this....

$$\langle P \rangle = \frac{1}{Z} \sum_{u} P[u] e^{-H_{eff}[u]/k_B T}$$

- Step 3: Calculate the thermal average with the usual methods (e.g., Molecular dynamics or Monte Carlo)

It works!

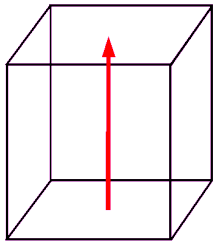
- Sequence of ferroelectric phase transitions of $BaTiO_3$



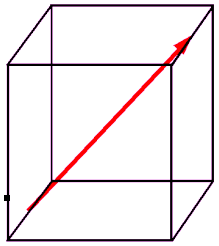
Calculated polarization (P_x, P_y, P_z) as a function of temperature

Zhong, Vanderbilt & Rabe, PRL 73, 1861 (1994)

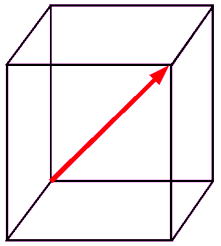
P || [001]
Tetragonal



P || [011]
Orthorhom.

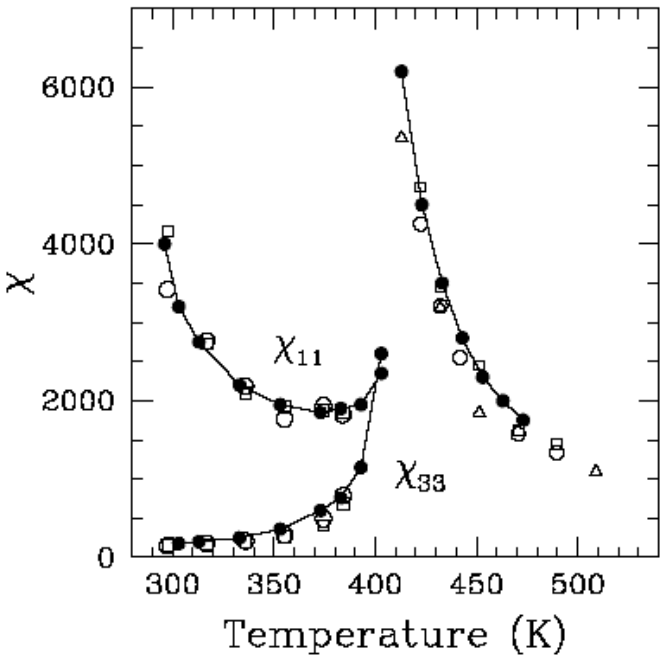


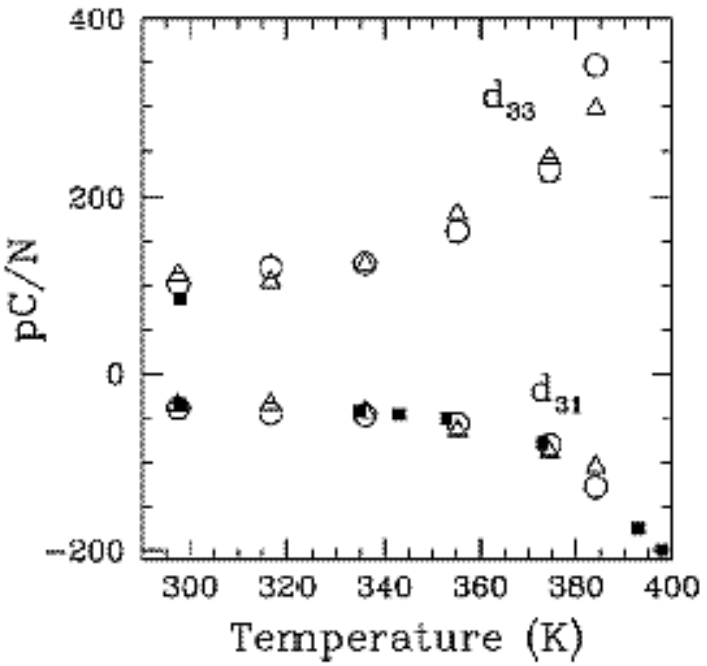
P || [111]
Rhombo.



It works!

- Dielectric and piezoeletric responses of $BaTiO_3$





Solid symbols stand for experimental values

García & Vanderbilt, APL 72, 2981 (1998)

"A 21st century version of a classic"

- **Systematic production of models retaining physical insight**

  - By removing non-essential approximations of the H_{eff} approach

Key references:

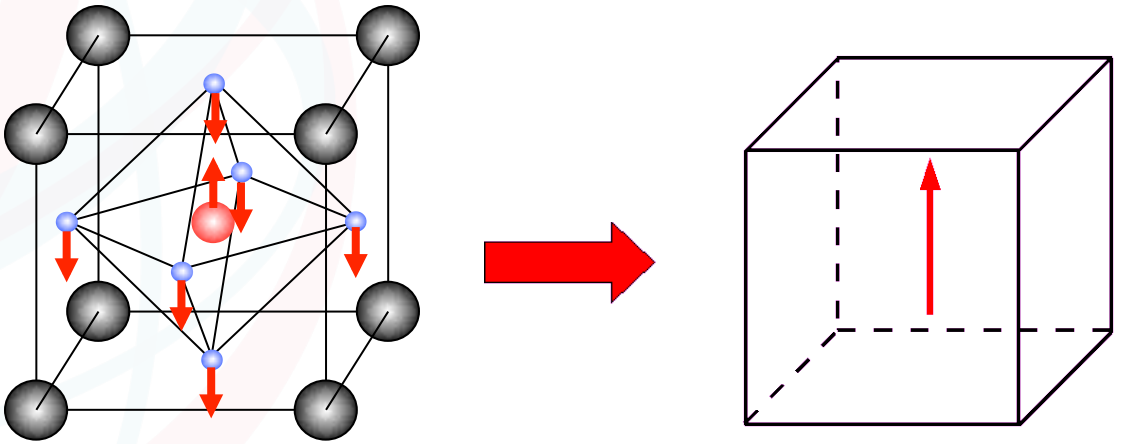
First-principles model potentials for lattice-dynamical studies
J.C. Wojdeł, P. Hermet, M.P. Ljungberg, P. Ghosez and J. Íñiguez
Journal of Physics: Condensed Matter 25, 305401 (2013)

Efficient scheme to construct systematically improvable second-principles lattice-dynamical models
C. Escorihuela-Sayalero, J.C. Wojdeł and J. Íñiguez
Phys. Rev. B 95, 094115 (2017)

Critique of the effective Hamiltonian approach

- Very nice! ... but has not become widely used
- Not optimal for difficult cases
  - → Inhomogeneities as in heterostructures, surfaces
  - → Many relevant degrees of freedom per unit cell
  - → Many polymorphs separated by small energies, not accurate enough

The problem:



The (our) solution: **Remove the problem!**

New model potentials

- For any material:

  Energy as a function of all distortions of a reference structure

$$E(\mathbf{u},\eta) = E_0 + \tag{1}$$

$$+\sum_{i,j,\alpha,\beta} {}^{2}K_{i\alpha j\beta} u_{i\alpha} u_{j\beta} + \sum_{i,j,k,\alpha,\beta,\gamma} {}^{3}K_{i\alpha,j\beta,k\gamma} u_{i\alpha} u_{j\beta} u_{k\gamma} + \ldots \tag{2}$$

$$+\sum_{l,m} {}^{2}C_{lm}\eta_l\eta_m + \sum_{l,m,n} {}^{3}C_{lmn}\eta_l\eta_m\eta_n + \ldots \tag{3}$$

$$+\sum_{i,\alpha,l} {}^{11}\Lambda_{i\alpha l} u_{i\alpha}\eta_l + \sum_{i,\alpha,j,\beta,l} {}^{12}\Lambda_{i\alpha j\beta l} u_{i\alpha} u_{j\beta}\eta_l + \sum_{i,\alpha,l,m} {}^{21}\Lambda_{i\alpha lm} u_{i\alpha}\eta_l\eta_m + \ldots$$

$$\tag{4}$$

Approximations: spatial cut-off for short-range interactions, cut-off for the polynomial expansion, restricted to a maximum number of bodies in interaction terms, linear approximation to dipole-dipole forces, **fixed bonding topology**, etc.

- Trivial to apply to any material; systematic improvement possible

New model potentials

- **"Displacement-differences representation"**

$$u_{i\alpha}u_{j\beta} \rightarrow (u_{i\alpha} - u_{j\alpha})(u_{i\beta} - u_{j\beta})$$

✓ automatically satisfies translational invariance

- Reduction of parameters by using symmetry of ref. structure
- Efficient scheme to impose boundedness from below

Much more on Wednesday

Model is linear in parameters: Trivial fitting!

$$G[\Theta, \mathrm{TS}] = \frac{1}{M_1} \sum_{s\tau} \left(f_\tau^{\mathrm{TS}}(s) - f_\tau[\Theta](s) \right)^2$$

$$G[\Theta, \mathrm{TS}] = \frac{1}{M_1} \sum_{s\tau} \left(f_\tau^{\mathrm{TS}}(s) - \sum_\lambda \theta_\lambda \bar{f}_{\lambda\tau}(s) - f_\tau^{\mathrm{fixed}}(s) \right)^2$$

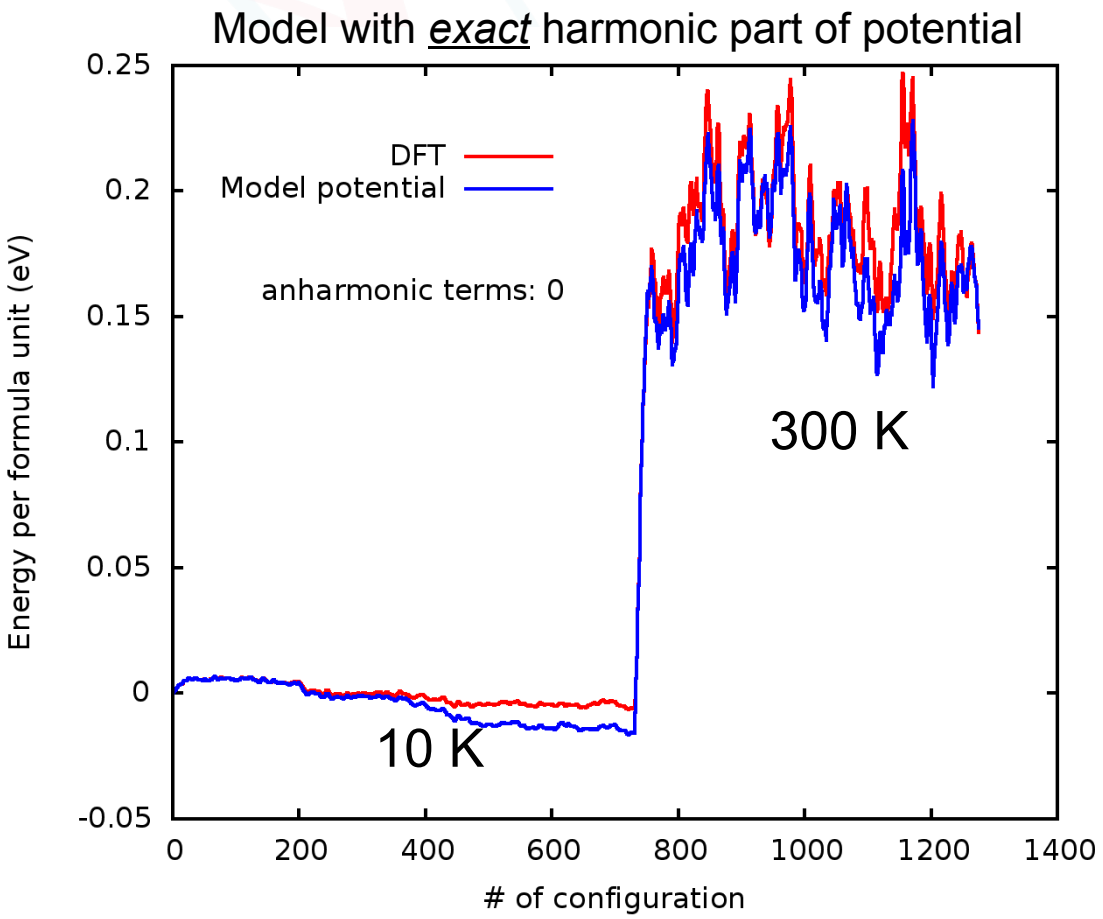
$$\partial G[\Theta, \mathrm{TS}]/\partial\theta_\lambda \quad = \quad 0 \quad \forall\, \lambda$$

$$\sum_\lambda \Delta_{\mu\lambda}\theta_\lambda = \Gamma_\mu$$

Much more on Wednesday

Models can be systematically improved!

$SrTiO_3$ simulated in a 2x2x2 (40 atom) box



ΔE

@ 10 K

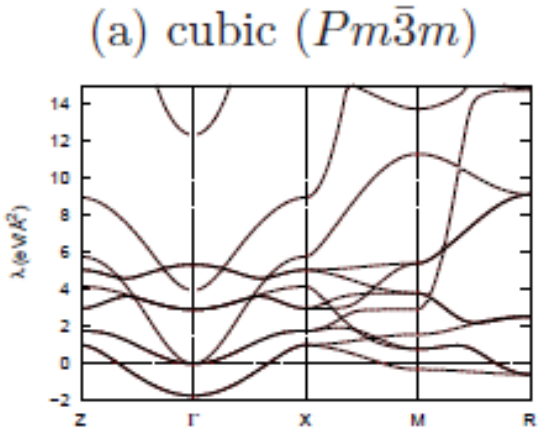
0.6 meV/fu

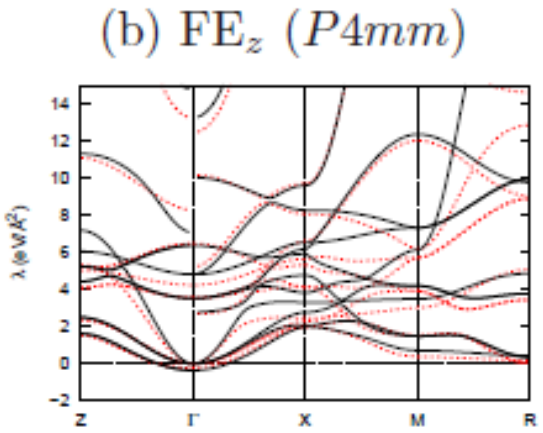
@ 300 K

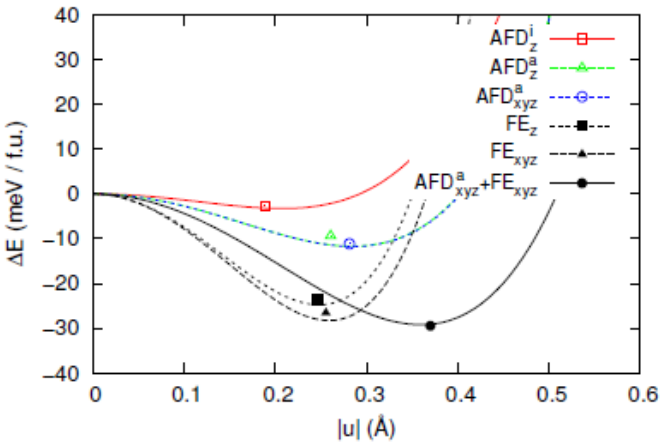
1.5 meV/fu

Much more on Wednesday

Example of application to $PbTiO_3$







Structure	Method	u^{Γ}_{Pbz}	u^{Γ}_{Tiz}	u^{Γ}_{O1z}	u^{Γ}_{O3z}	O_6 rot.	Energy
FE$_z$ ($P4mm$)	LDA	0.179	0.072	−0.104	−0.043	—	−23.7
	Model	0.180	0.073	−0.105	−0.043	—	−24.8
FE$_{xyz}$ ($R3m$)	LDA	0.104	0.048	−0.063	−0.027	—	−26.6
	Model	0.105	0.049	−0.063	−0.028	—	−28.3
AFD$_z^a$ ($I4/mcm$)	LDA	—	—	—	—	5.4	−9.4
	Model	—	—	—	—	5.9	−11.7
AFD$_{xyz}^a$ ($R\bar{3}c$)	LDA	—	—	—	—	3.4	−11.2
	Model	—	—	—	—	3.4	−11.7
AFD$_z^i$ ($P4/mbm$)	LDA	—	—	—	—	3.9	−2.7
	Model	—	—	—	—	4.3	−3.3
FE$_{xyz}$+AFD$_{xyz}^a$ ($R3c$)	LDA	0.096	0.047	−0.058	−0.026	2.8	−29.5
	Model	0.098	0.047	−0.060	−0.026	2.1	−29.5

Displacements: Angstrom

Rotations: degrees

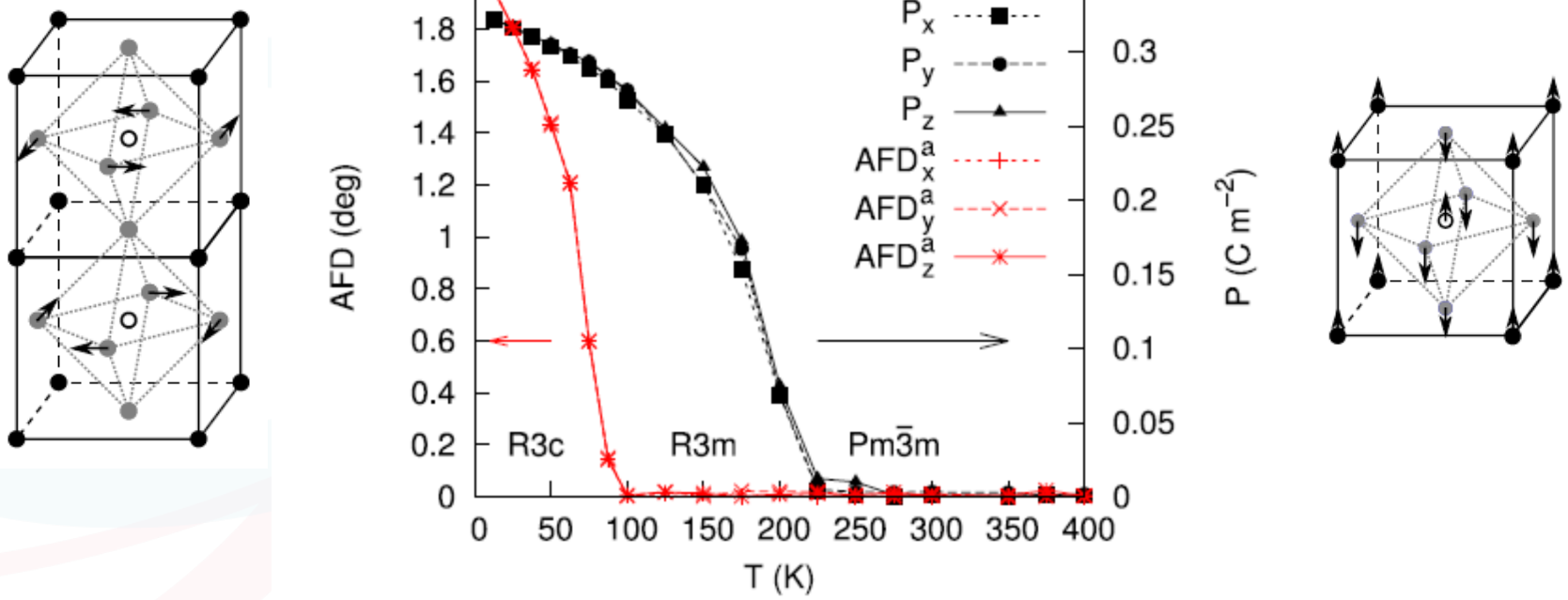
Energies: meV/f.u.

Excellent agreement!

Wojdeł, Hermet, Ljungberg, Ghosez & Íñiguez, JPCM 25, 305401 (2013)

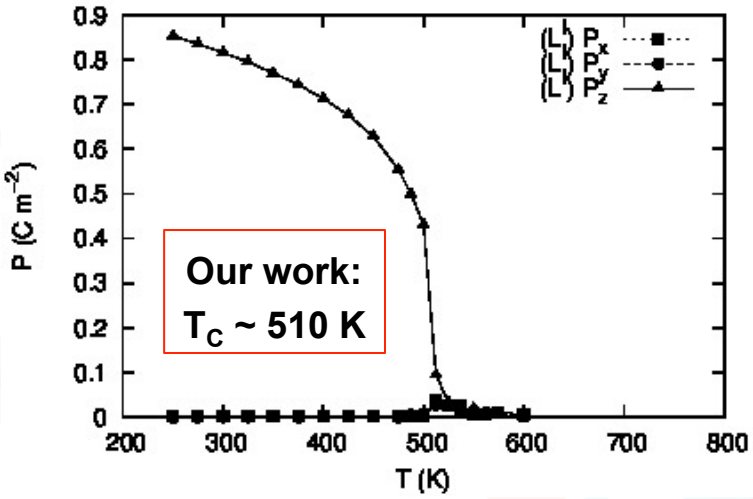
New microscope → New results!

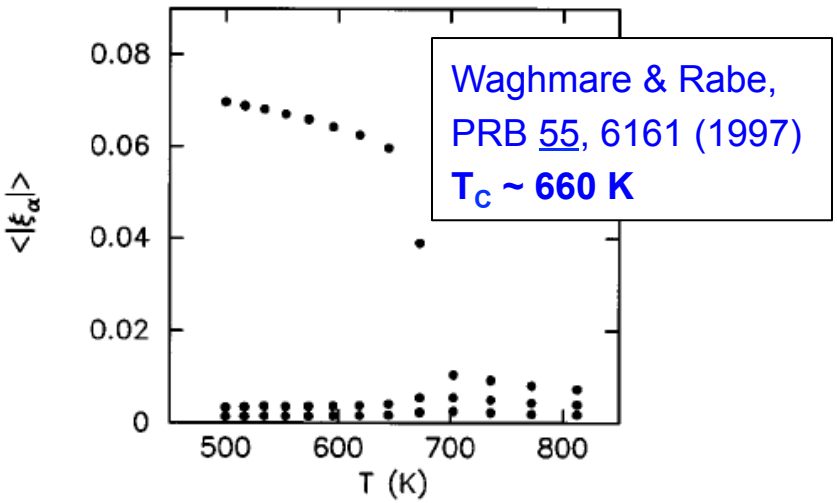
• During the development of the model for $PbTiO_3$, we ran simulations for a fixed cubic cell and found unexpected and novel transitions.



• We confirmed the correctness of the low-temperature phase, for a fixed cubic cell, by running direct first-principles simulations.

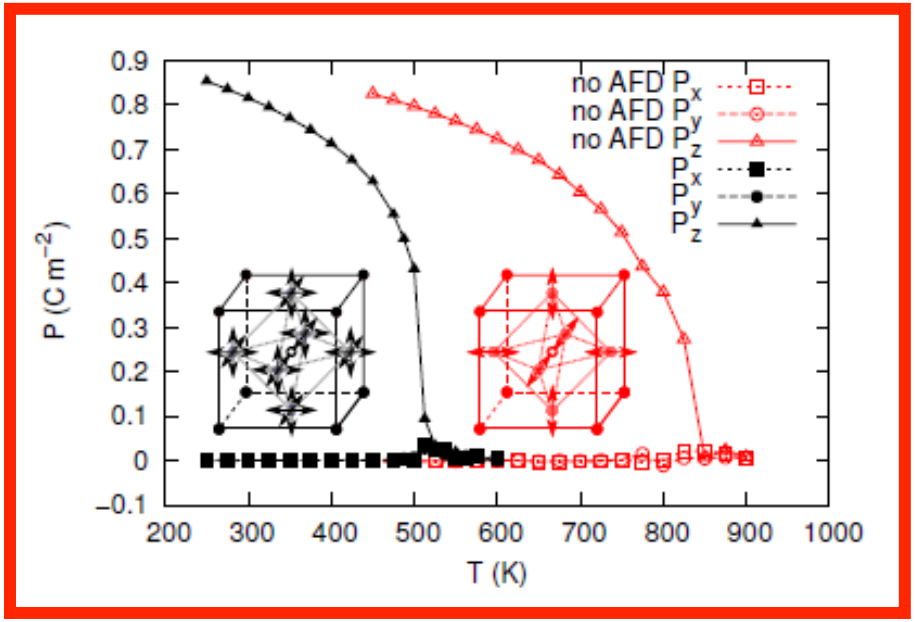
Competing instabilities in $PbTiO_3$



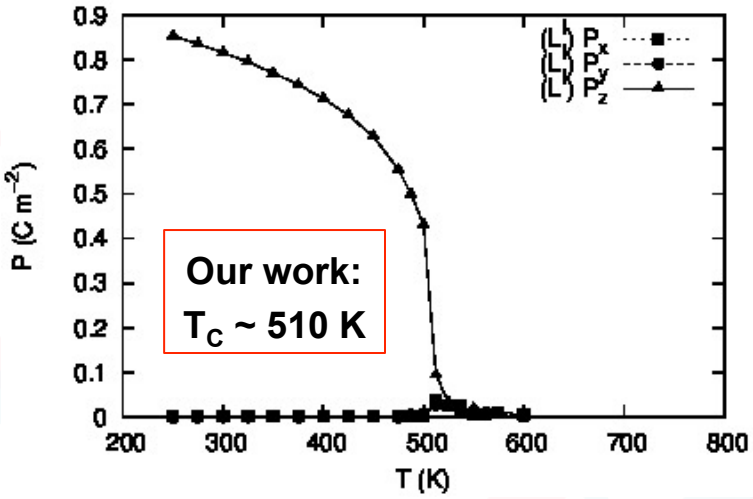


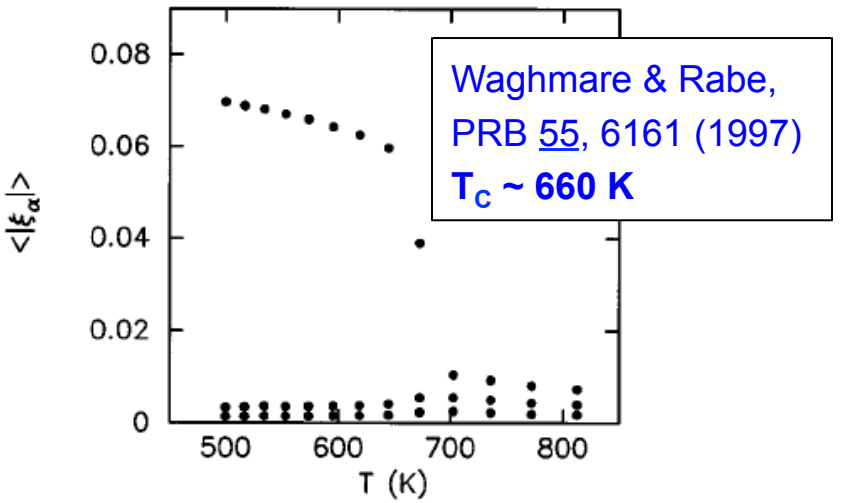
Experimental T_C : 760 K

- Our energy surface for the polar distortions is very similar to the one of Waghmare and Rabe
- NOTE: they only included polar distortions, leaving out everything else!
- In particular, they left out the O_6-octahedral rotations that are known to compete with the polar distortions...
- We can remove the O_6-rots by hand...



Competing instabilities in $PbTiO_3$

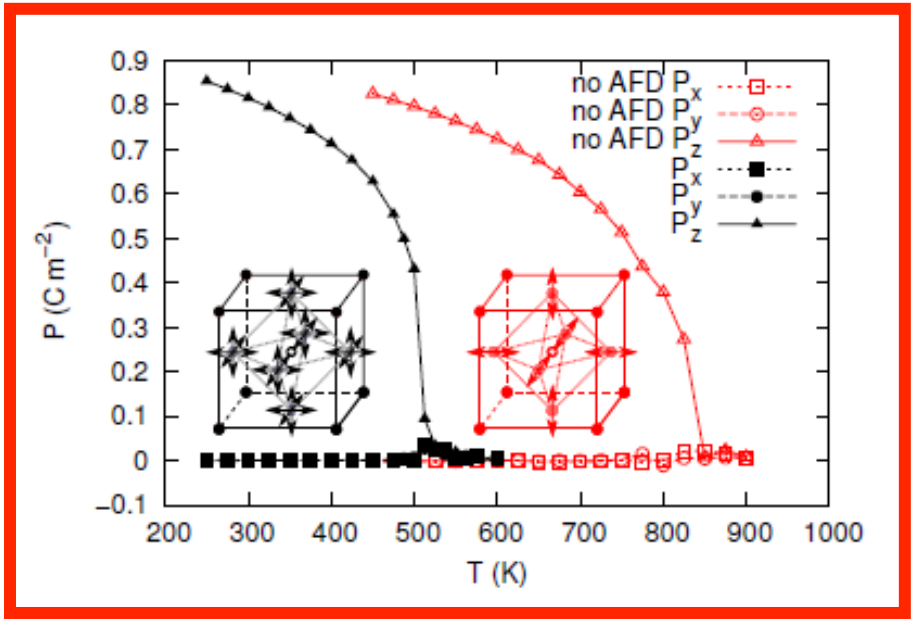




Experimental T_C : 760 K

HUGE competition between structural instabilities

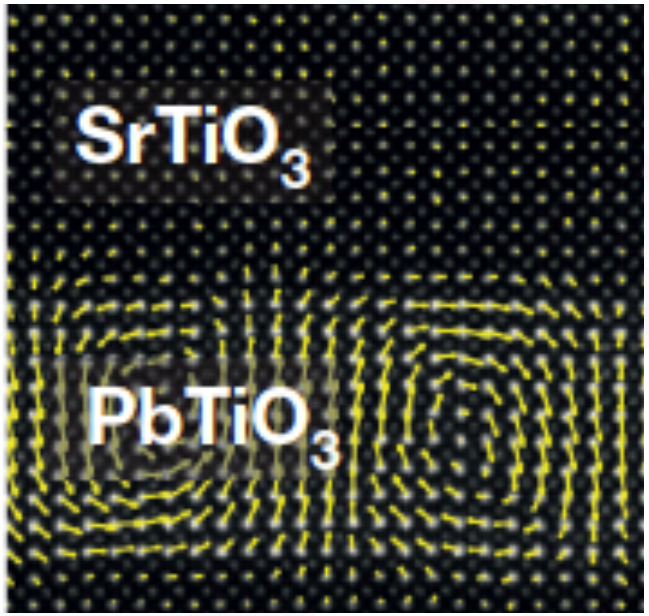
$$E \sim (-a + b\langle v^2 \rangle)\, u^2$$



- Previous, related:
  Kornev *et al.*, PRL 97, 157601 (2006)

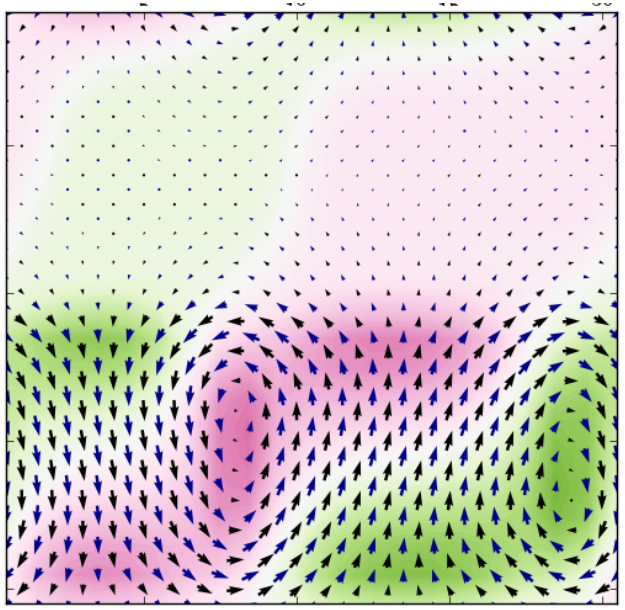
Recent applications: Complex orders

Yadav *et al*., Nautre 530, 198 (2016)



TEM image

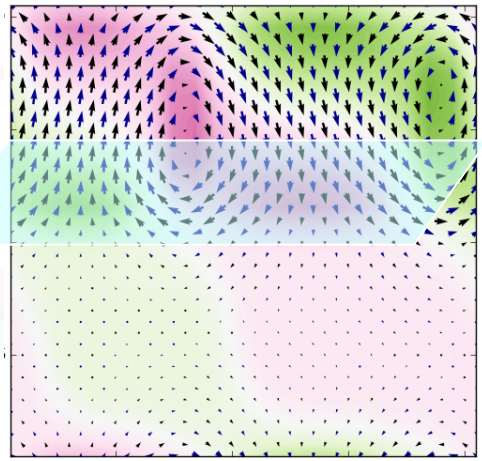
!! Chiral !!



second-principles simulation

"Emergent chirality in polar vortex superlattices", submitted.
Shafer, García-Fernández, Arenholz, Junquera, Ramesh *et al*.

Recent applications: Complex orders

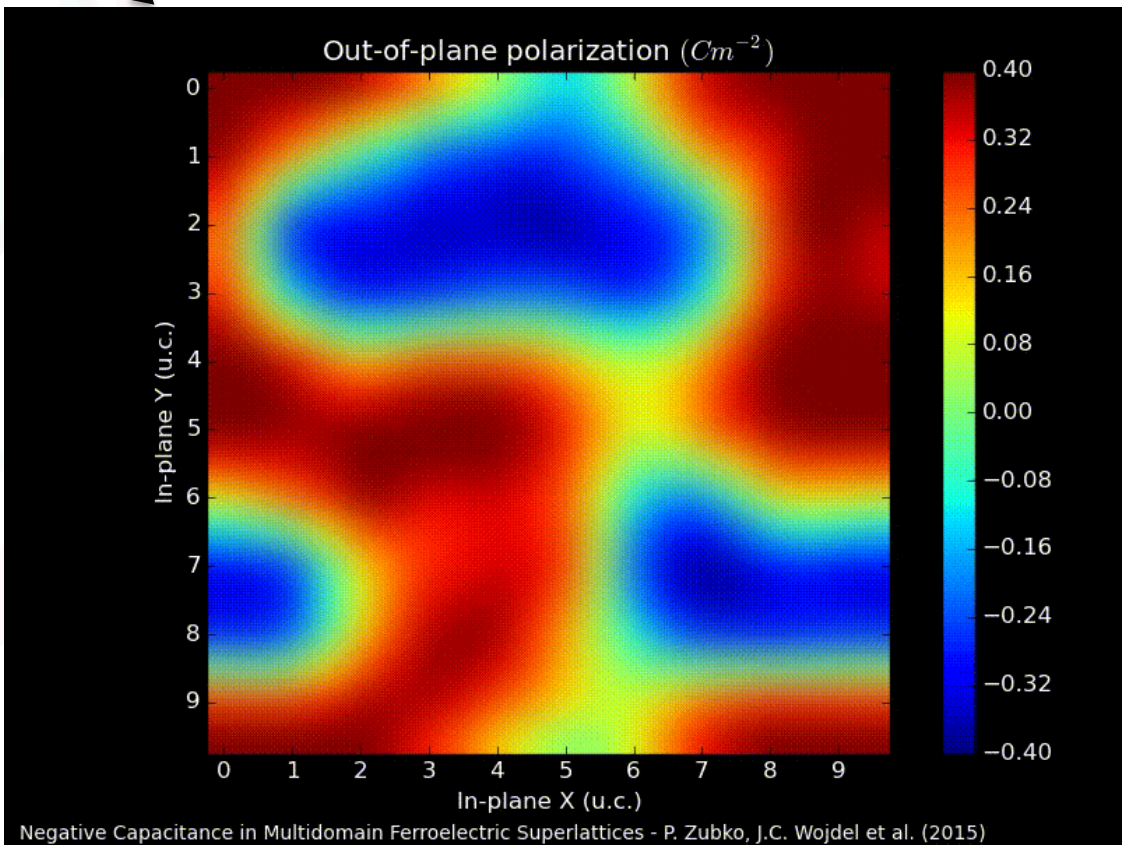


This is at 0 K.

Negative capacitance in multidomain ferroelectric superlattices

Zubko, Wojdeł, Hadjimichael, Fernandez-Pena, Sené, Luk'yanchuk, Triscone and Íñiguez

Nature 534, 524 (2016)



Domain liquid !

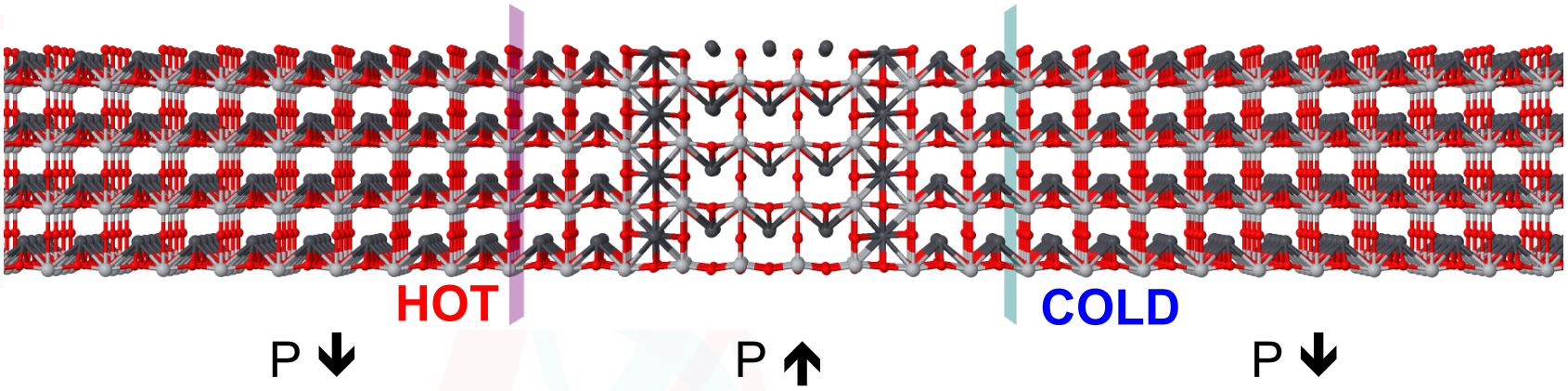
Mid-cut of a $PbTiO_3$ layer

inslde a $PbTiO_3/SrTiO_3$ superlattice.

T=400K

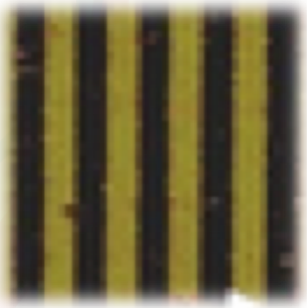
Recent applications: Heat currents

180º domain walls in $PbTiO_3$



Phonon in

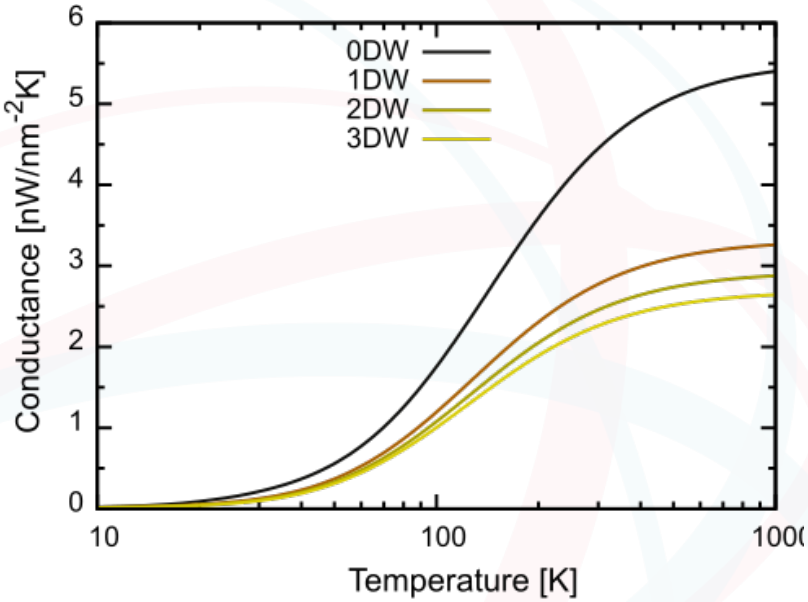
Phonon back-scattered

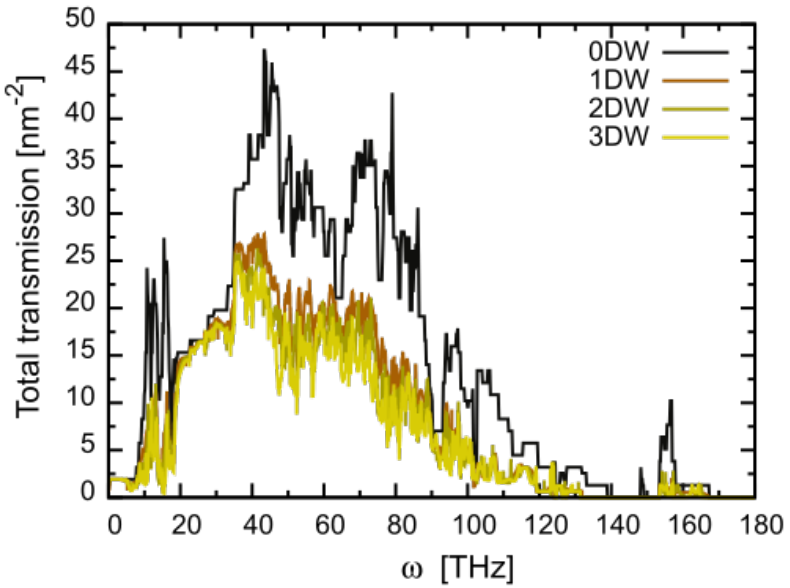


"DW obstacle" that we can write/erase

Phonon thru

Recent applications: Heat currents



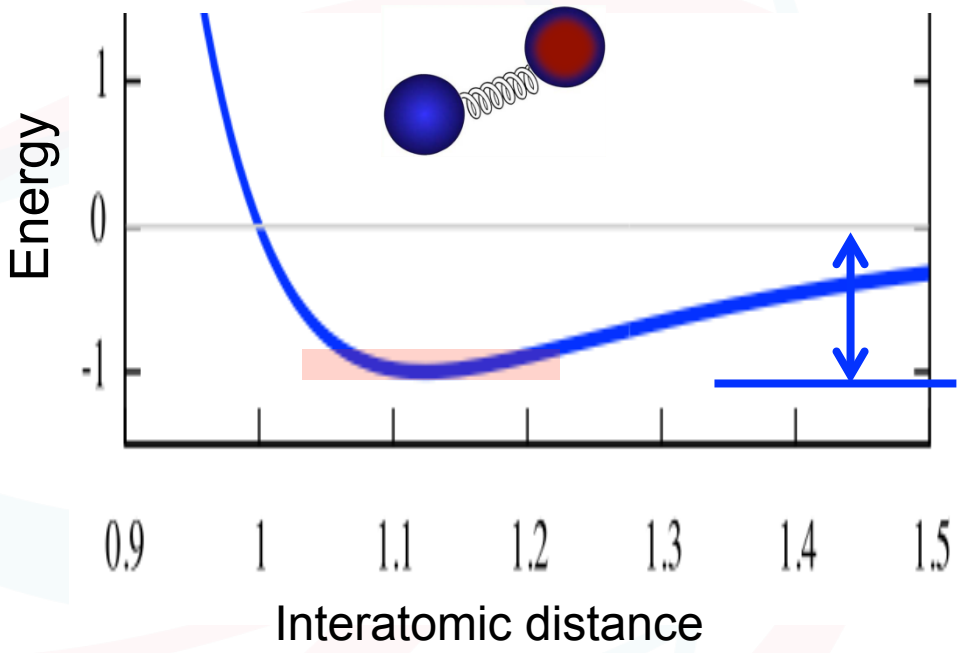


- We thought DWs will act as heat resistors in series ✖
- **Instead, DW acts as a phonon filter !!!** ✓
- T phonons almost fully blocked ; L phonons largely unaffected

Royo *et al.*, submitted

Very important to note!!

$$E = E_{RAG} + E(\{\eta_{\alpha\beta}\}, \{u_{l\kappa\alpha}\})$$



Cohesive energy: 1-10 eV/atom

Interactions controlling transitions, responses to perturbations:

1-100 meV/atom

In all these examples, we always respect our basic NO CHEMISTRY rule

SCALE-UP: Focus on the finer energy scale

→ quasi-perturbative conditions

→ cannot do chemistry

SCALE-UP: tools for lattice simulations

SPLD: Second-Principles Lattice Dynamics

Wojdel, Ljungberg, Íñiguez (ICMAB-CSIC), 2010--2013

SCALE-UP

García-Fernández, Junquera (Cantabria), Íñiguez (LIST), 2016--2017

- At this time, SCALE-UP implements only a fraction of the lattice simulation modes and features in SPLD.
- For the moment, the development of this part is centralized in… me (probably with contributions from Carlos & Mauro, soon)
- We are going to catch up with SPLD during the fall
- So, if you need something, or would like to do something, talk to me

SCALE-UP: tools for lattice simulations

- Run Metropolis Monte Carlo, at constant or varying temperature

- Run NVE and isokinetic molecular dynamics (at constant or varying temperature in the latter case)

  Note that varying temperature (simulated annealing) this is good enough to do most of the structural relaxations that you may need

- Run under external electric and stress fields

Exercises for lattice simulations

- Exercises **to learn**

Exercise #1: Relax the structure of $SrTiO_3$ by MC annealing

- Check the ultra-simple input, and understand what you are asking scale-up to do
- Run scale-up
- Check out the standard output, have a look at the energy
- Check out the resulting structure. Plot with xcrysden
- What has happened? How do the atoms look like in the ground state of $SrTiO_3$? Is the phase cubic?

Exercises for lattice simulations

- Exercises **to learn**

Exercise #2: Same as #1, but keeping the RAG cell

- Check the ultra-simple input, and understand what you are asking scale-up to do
- Run scale-up
- Check out the standard output, have a look at the energy. Compare with Exercise #1
- Check out the resulting structure. Compare with Exercise #1.
- What has changed?

Exercises for lattice simulations

- Exercises **to learn**

Exercise #3: Same as #2, but using an isokinetic MD

- Check the ultra-simple input, and understand what you are asking scale-up to do
- Run scale-up
- Check out the standard output, have a look at the energy. Compare with Exercise #2
- Check out the resulting structure. Compare with Exercise #2.
- For fun, repeat the calculation in a 1x1x1 supercell. What has changed?

Exercises for lattice simulations

- Exercises **to learn**

Exercise #4: Apply an external stress

- Check the ultra-simple input, and understand what you are asking scale-up to do
- Run scale-up
- Check out the standard output, have a look at the energy. Compare with Exercise #1
- Check out the resulting structure. Compare with Exercise #1.
- Any difference? Try to understand your result for the polarization.

Exercises for lattice simulations

- Exercises **to learn**

Exercise #5: Apply an external field

- Check the ultra-simple input, and understand what you are asking scale-up to do
- Run scale-up
- Check out the standard output, have a look at the energy. Compare with Exercise #1
- Check out the resulting structure. Compare with Exercise #1.
- Any difference? Try to understand your result for the polarization.

Exercises for lattice simulations

- Exercises **<u>to test</u>** that you have learn something ! ;)

Exercise #6: A susceptible material

- Study $SrTiO_3$ as a function of a applied electric field, and monitor the evolution of the electric polarization
- What is the value of the dielectric susceptibility at zero field?
- Do you understand the evolution of the polarization?
- Run the simulation for 2x2x2 and 1x1x1 cells. What are the differences?

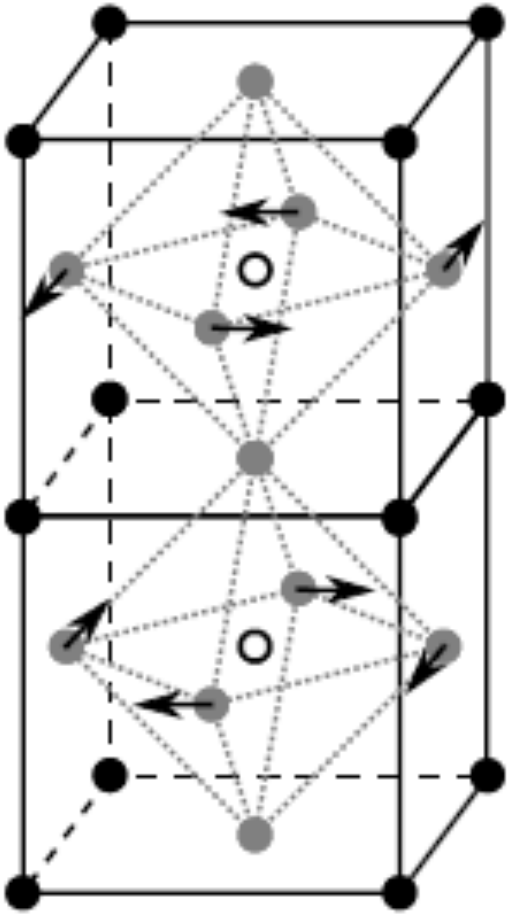
Exercises for lattice simulations

- Exercises **to test** that you have learn something ! ;)

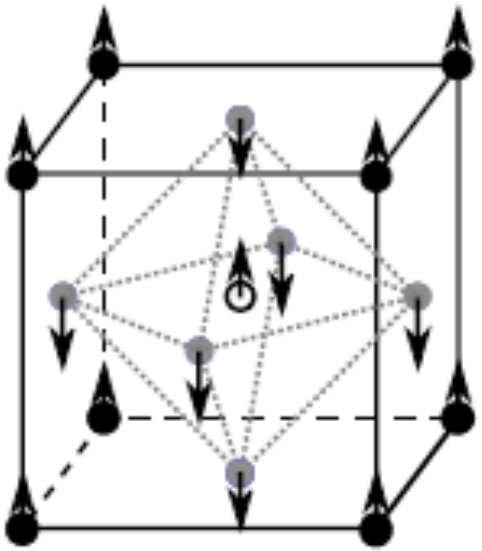
Exercise #7: Under stress

- Study $SrTiO_3$ as a function of a applied hydrostatic pressure, positive and negative
- Monitor the evolution of the structure. What are the main changes?
- If you dare, calculate the dielectric susceptibility as a function of pressure. What happens?
- Do the study for 1x1x1 and 2x2x2 supercells. Any differences?

Key distortions in $SrTiO_3$ (and all perovskites)



Rigid rotations of O_6 octahedra



Cations displace with respect to oxygens, leading to local electric dipoles and, eventually, macroscopic polarization