Theoretical Methods II

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- DFT studies of magnetoelectric effects
- **Simulations at larger length and time scales:**
  - Effective atomistic potentials
  - Continuum models
- A word on Machine Learning to construct effective potentials
- Some final comments…

Magnetism within DFT

- **"Collinear magnetism"** (LSDA or equivalent): independent treatment of up and down spins, scalar magnetization density.

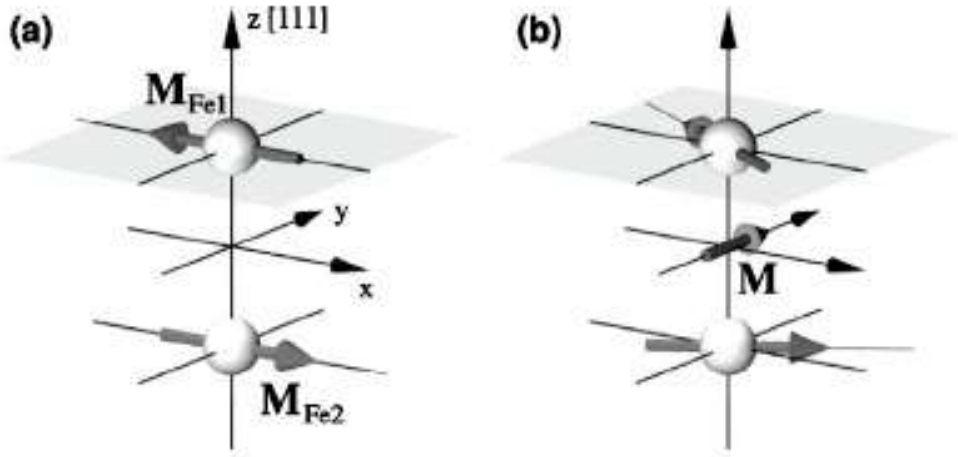
  The vast majority of magnetic calculations are collinear

- **Non-collinear magnetism:** three-dimensional magnetization density using spinor-like wavefunctions

  Not so frequently applied, but mandatory to reproduce the weak ferromagnetism (canting) and full magnetoelectric response tensors

Weak ferromagnetism in $BiFeO_3$

Ederer and Spaldin, PRB 71, 060401 (2005)



A more general definition of “ME effects”

Action: Application of an electric field → **Magnetoelectric Material** → Reaction: Change in magnetic state or properties

ME effects according to the nature (magnitude) of the reaction

“small”

Magnetic response to a small perturbation

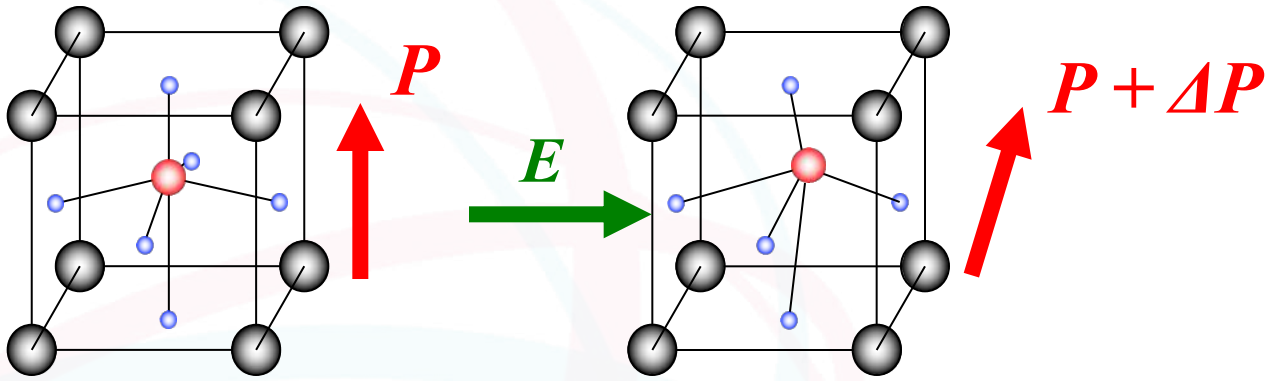
“medium”

Coupled ferroelectric and magnetic domains

“large”

E-field drives magnetic phase transition

(Lattice-mediated) magnetoelectric response



state at zero field

under applied field

- Structural response to an electric field:

$$E = E_{eq} + \frac{1}{2}\kappa u^2 - Z^* u\mathrm{E}$$

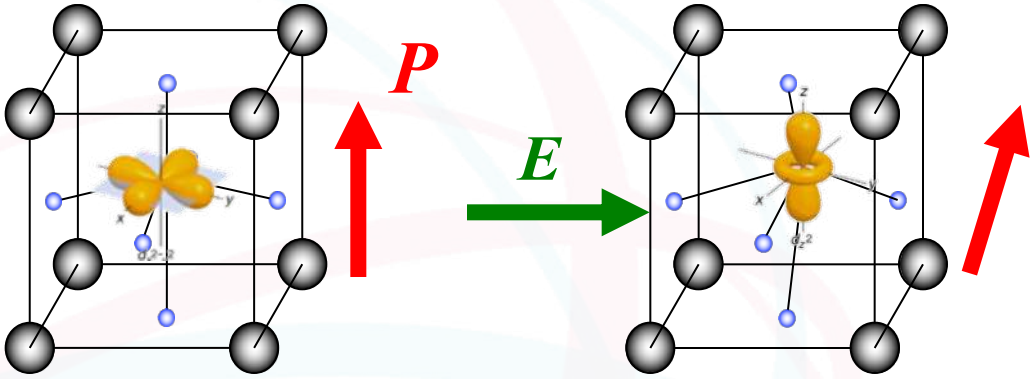
- u = atomic displacement from eq.
- κ = force constant or *mode stiffness*
- Z^* = ionic charge (dynamical)

$$\left.\frac{dE}{du}\right|_{\mathrm{E}} = 0 \rightarrow u = \frac{Z^*}{\kappa}\mathrm{E}$$

$$\Delta P = \frac{1}{\Omega} Z^* u = \frac{1}{\Omega}\frac{Z^* Z^*}{\kappa}\mathrm{E}$$

dielectric susceptibility

(Lattice-mediated) magnetoelectric response



state at zero field

under applied field

Dielectric response

$$\Delta P = \frac{1}{\Omega}\frac{Z^* Z^*}{\kappa}\mathrm{E}$$

change in orbital occupation ⇨ change in magnetic easy axis ⇨

Magnetoelectric response

$$\Delta M = \frac{1}{\Omega}\frac{Z^* \zeta}{\kappa}\mathrm{E}$$

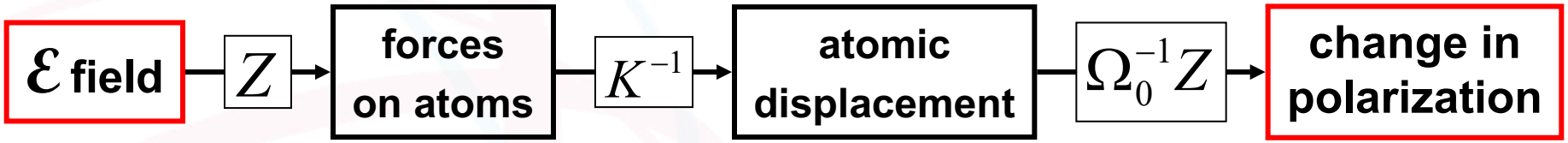
α

spin-orbit coupling

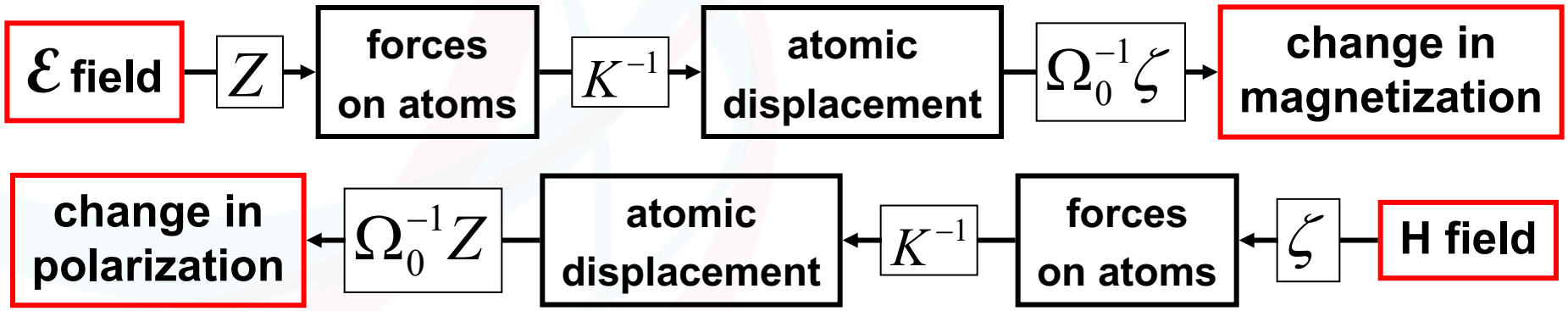
ζ : magnetostructural coupling

Dielectric *vs* ME response, lattice-mediated part

$$\chi_{\alpha\beta} \propto \Omega_0^{-1} Z_{m\alpha} K^{-1}_{mn} Z_{n\beta}$$



$$\alpha_{\alpha\mu} \propto \Omega_0^{-1} Z_{m\alpha} K^{-1}_{mn} \zeta_{n\mu}$$



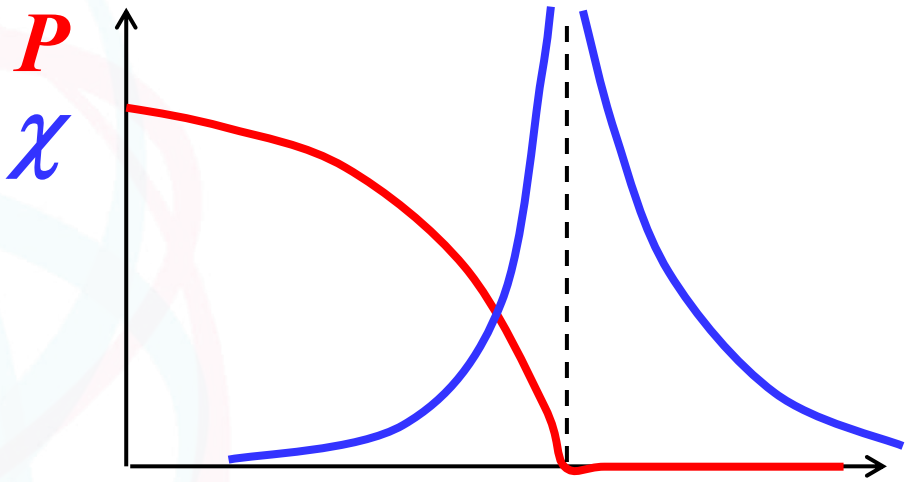
Theory developed in:

- **J. C. Wojdeł and J. Íñiguez, Phys. Rev. Lett. 103, 267205 (2009)**
- J. Íñiguez, Phys. Rev. Lett. 101, 117201 (2008)
- Extension to mag. case of Wu, Vanderbilt and Hamann, PRB 72, 035105 (2005)

How to get a large ME response at T_{room}?

- Good dielectrics & piezoelectrics: **small κ associated to a soft mode**

$$\chi = \frac{1}{\Omega}\frac{Z^* Z^*}{\kappa}$$



Temperature / Composition / Epitaxial strain

Can we do the same for the ME coupling $\alpha = \frac{1}{\Omega}\frac{Z^* \zeta}{\kappa}$?

Proof of Concept: $BiFeO_3$'s thin films

- One of the very few **magnetoelectric multiferroics at room temperature**

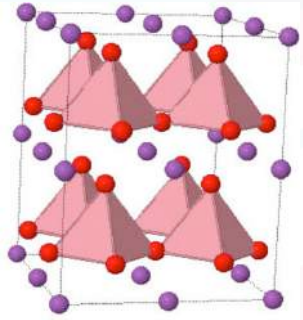
- G-type anti-ferromagnet
  - Neel temperature ~ 650 K
  - Bulk: spin cycloid
  - Films: canted AFM, net mag. moment

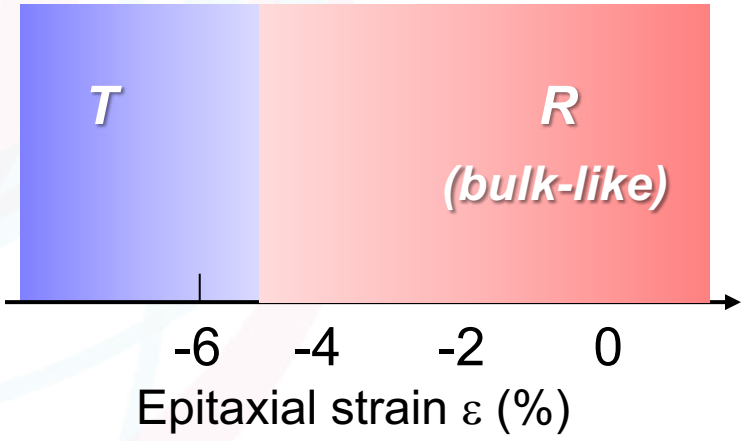
- Ferroelectricity
  - Transition temperature ~ 1100 K
  - Large polarization || [111] ($P \sim 0.9$ C/m^2)
  - Dominated by Bi's lone pair

- Epitaxial strain allows us to induce structural phase transition:

Super-Tetragonal

Very large P || [001]
Very large c/a ≈ 1.27

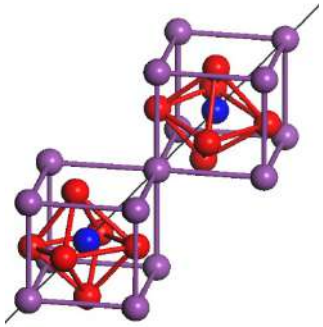




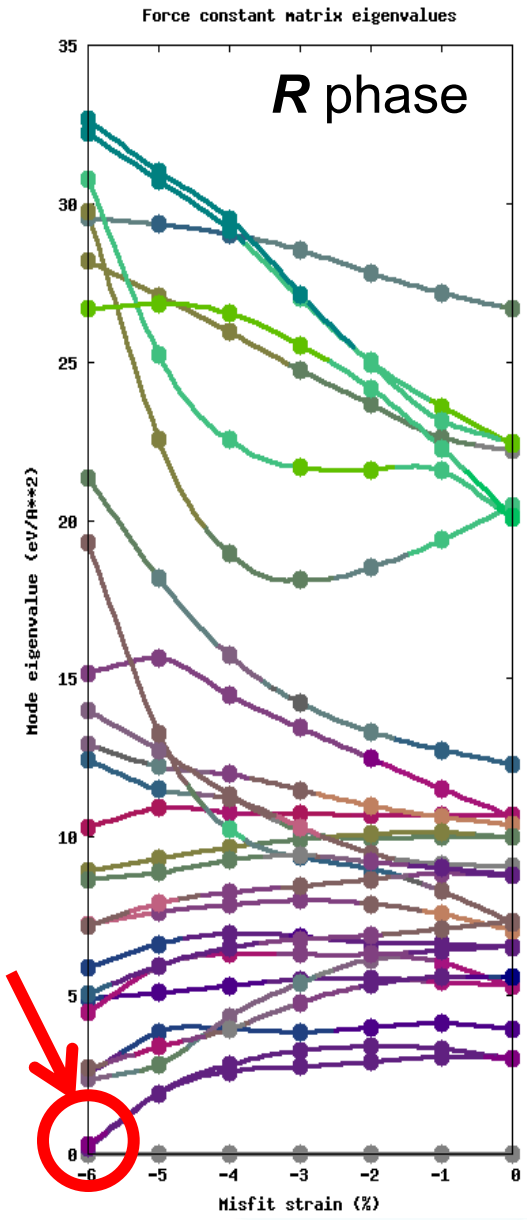
- H. Béa et al., PRL 102, 217603 (2009)
- R.J. Zeches *et al.*, Science 326, 977 (2009)

Rhombohedral

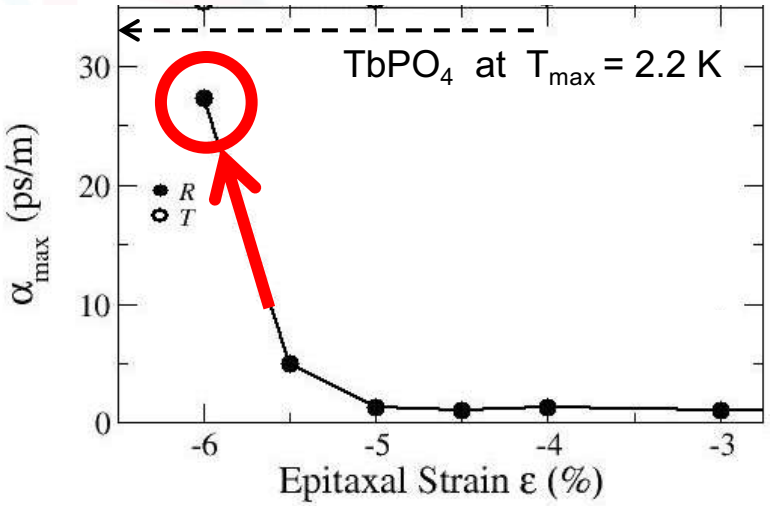
Large O_6 rotations
Large P || [111]



Soft-mode mechanism → Giant ME response!



$$\chi \sim Z^*_{soft} Z^*_{soft} \Big/ \kappa_{soft} \qquad \alpha \sim Z^*_{soft} \zeta_{soft} \Big/ \kappa_{soft}$$



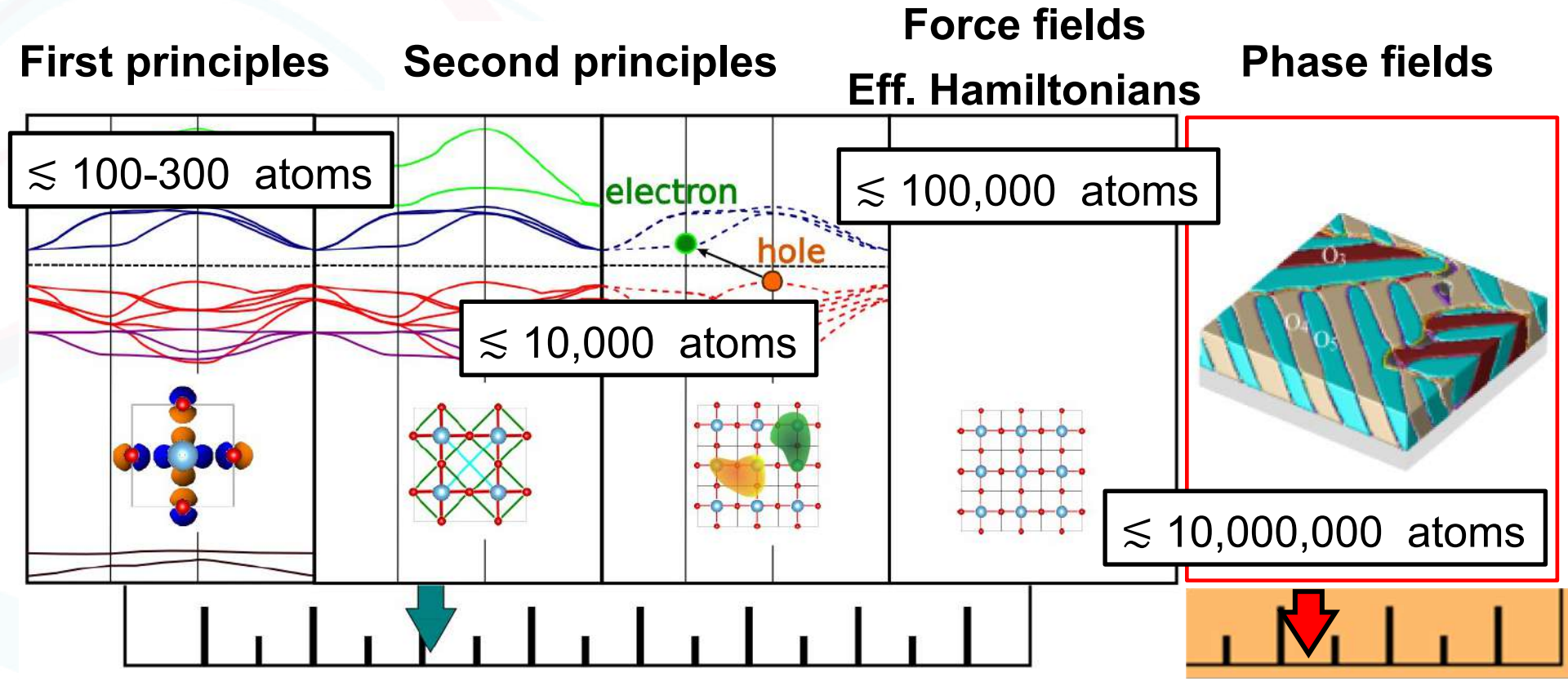
Proof of concept: First-principles investigation of $BiFeO_3$ under epitaxial strain

- **Computed ME responses comparable with greatest ones ever measured !**
- Mechanism active at room temperature!

J. C. Wojdeł and J. Íñiguez, PRL 105, 037208 (2010)

Questions?

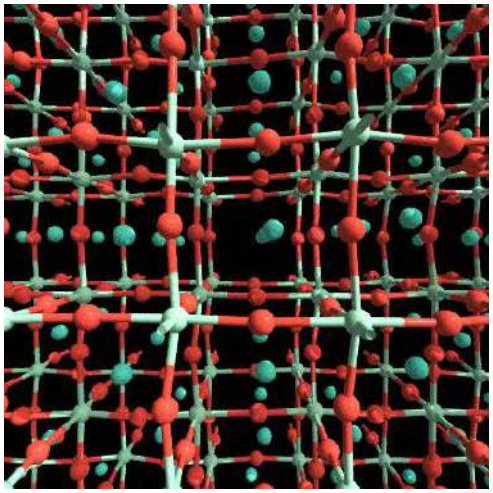
Graphical abstract



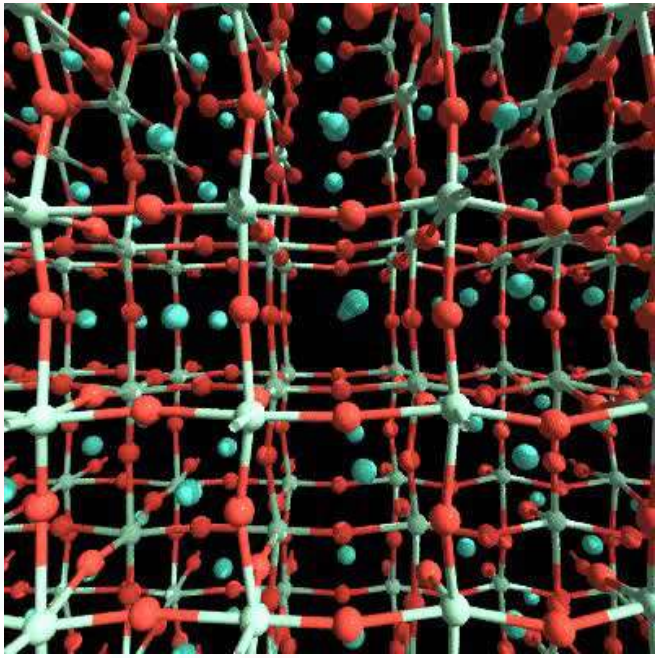
Atomistic part: Courtesy of J. Junquera & P. García-Fernández

We need to go beyond DFT…

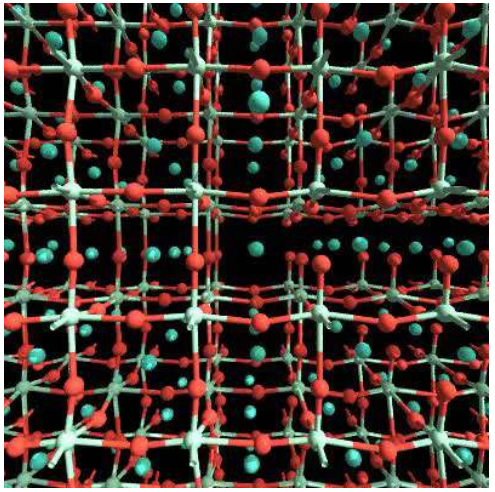
$T > T_C$



$T \sim T_C$



$T < T_C$



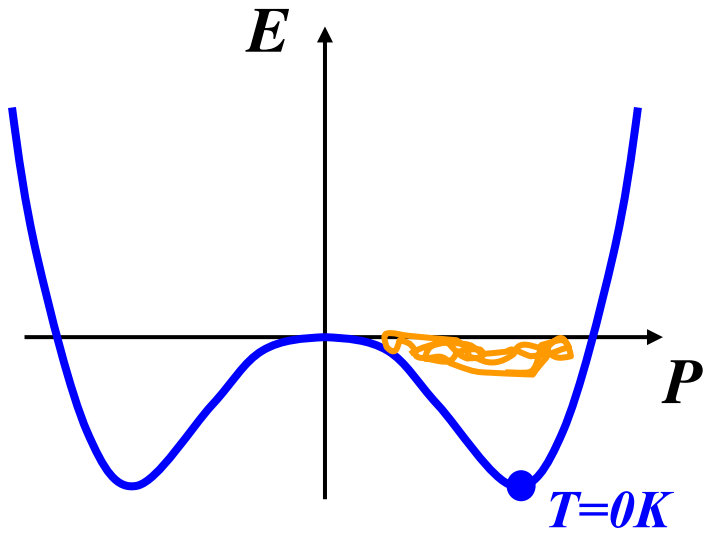
We want to move beyond T = 0 K !!!

Can we study phase transitions from DFT?

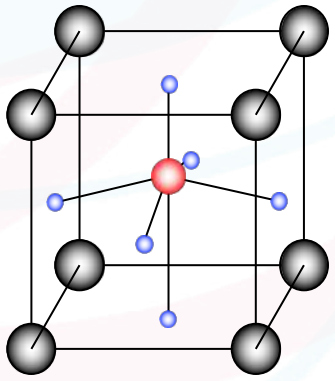
- We want to compute:

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

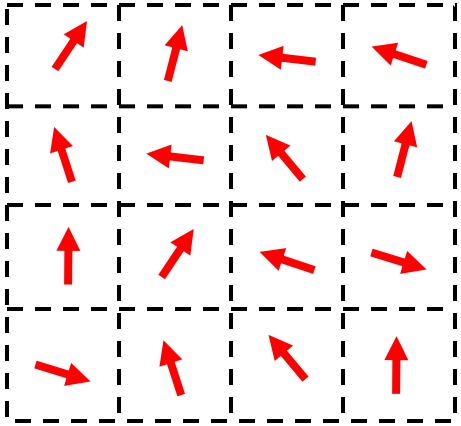
- The equilibrium value of P is a *thermal average* over all accessible states i



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

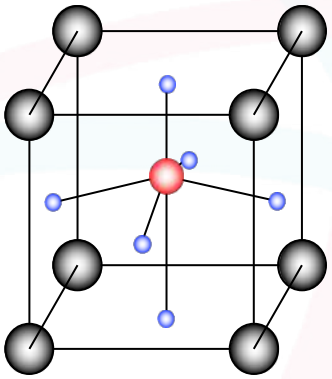


At ***finite temperatures*** **many** states are accessible:



Can we study phase transitions from DFT?

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



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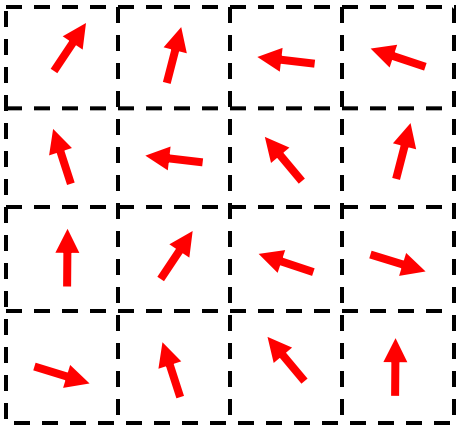
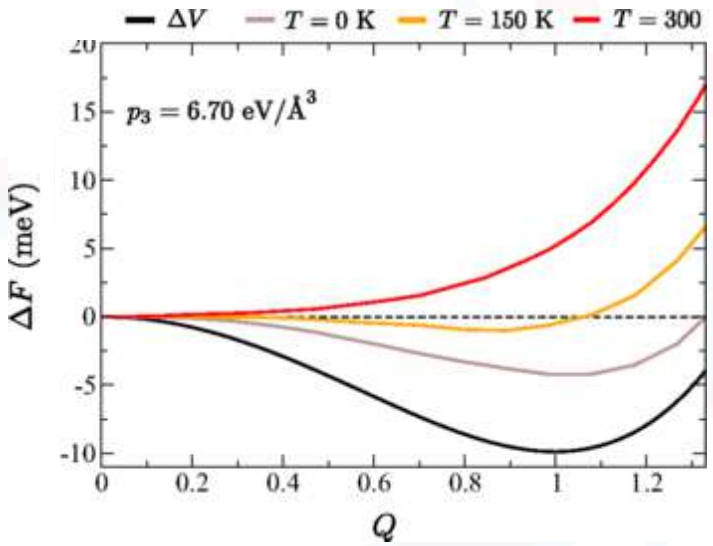


- Possible in principle, but there is a problem of computational cost

	# calcs	size	CPU time per calc	total CPU time
T = 0 K	100	40 atoms	1 hour	100 hours
T = 300 K	100,000	5000 atoms	10^{10} sec	10^{8} years

Can we study phase transitions from DFT?

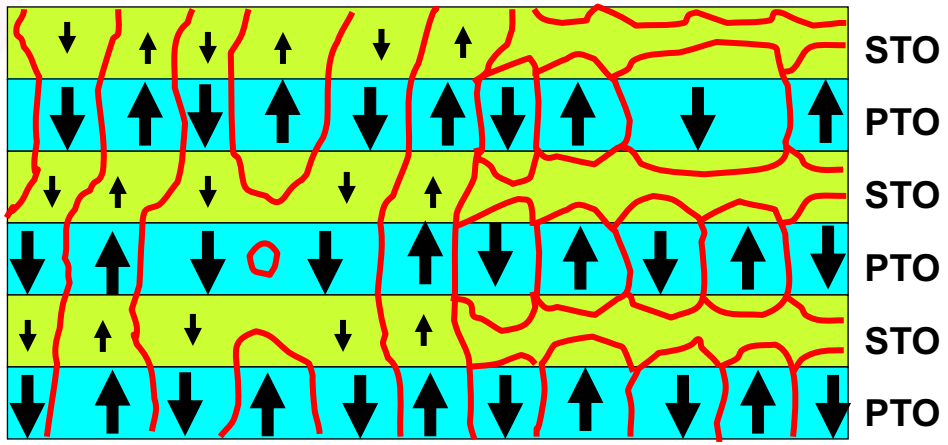
NOTE: Clever approximations allow us to study non-trivial phase transitions using Density Functional Theory…



Adapted from Blanco et al., PRB 96, 014111 (2017).

However, when the relevant "unit cell" is large, we stil have a problem !!

ferroelectric-paraelectric superlattice



First-principles effective models for ferroelectrics

- **The genesis of first-principles 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)

In more recent times:

- "Second-principles" methods
  Wojdel *et al.*, JPCM 25, 305401 (2013).
- Machine-Learned potentials

First-principles effective models for ferroelectrics

- We want to compute:

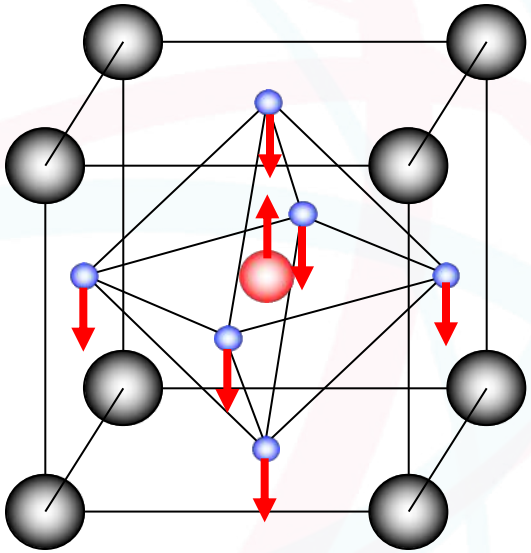
$$\langle P \rangle = \frac{1}{Z} \sum_{x} P[x] e^{-E[x]/k_B T}$$

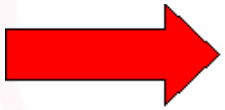
- Step 1: Identify *relevant* degrees of freedom

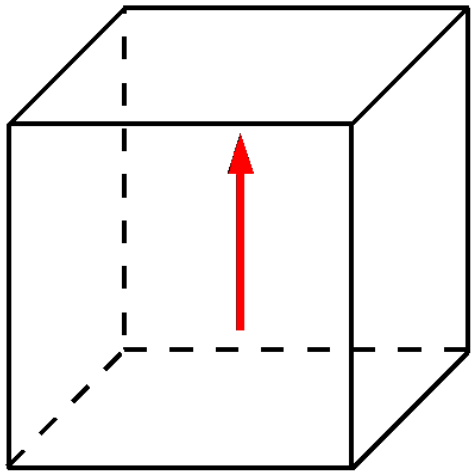
$$\{x\} \rightarrow \{u\} \subset \{x\}$$

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

Relevant degrees of freedom







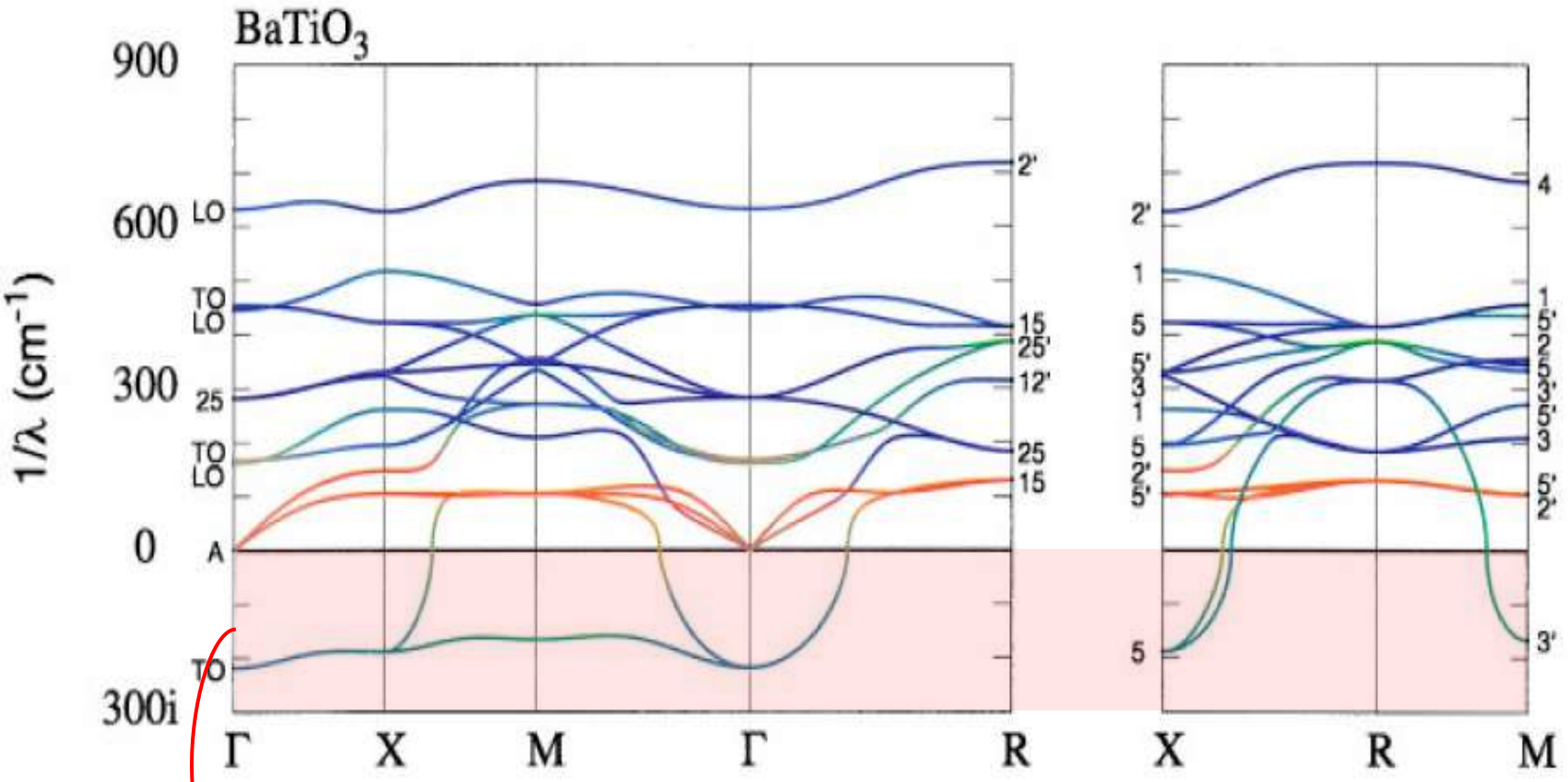
local polar distortion
associated to FE instability

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

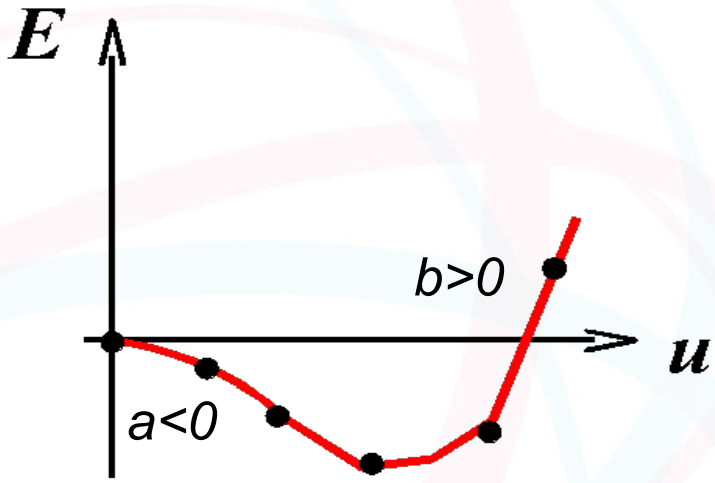
First-principles effective models for ferroelectrics

- 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:

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

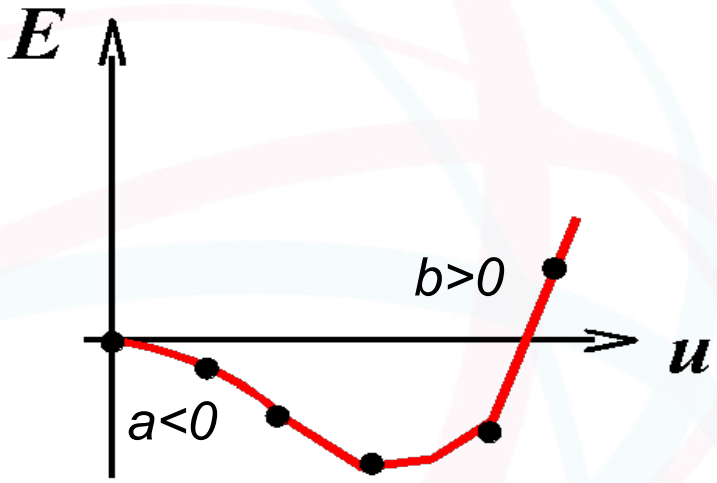
Effective Hamiltonian:

• 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



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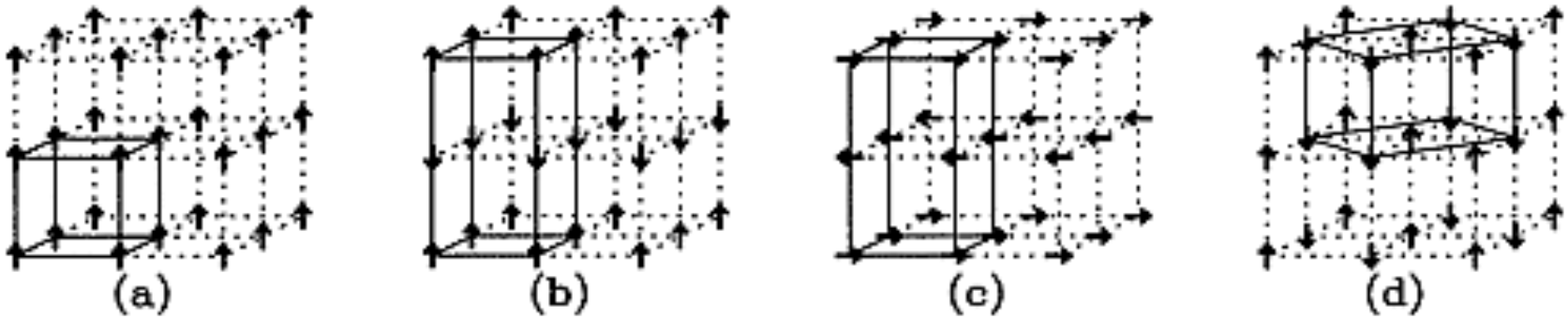


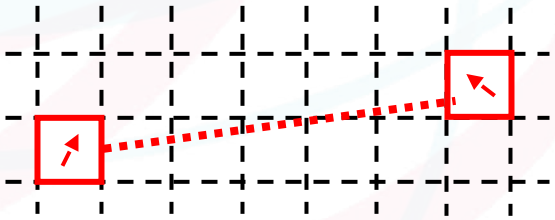
Detail: Long-range vs. short-range interactions

- Two types of harmonic interactions between the local polar modes

Harmonic enegy term:

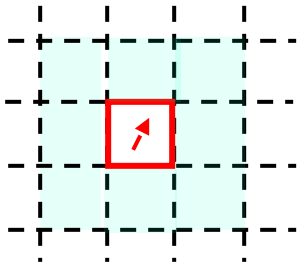
$$\frac{1}{2}\sum_{i\alpha j\beta} K_{i\alpha j\beta}\, u_{i\alpha} u_{j\beta} \qquad \text{where} \quad K_{i\alpha j\beta} = Q_{i\alpha j\beta} + J_{i\alpha j\beta}$$

long-range "attracive"



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

short-range "repulsive"



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

First-principles effective models for ferroelectrics

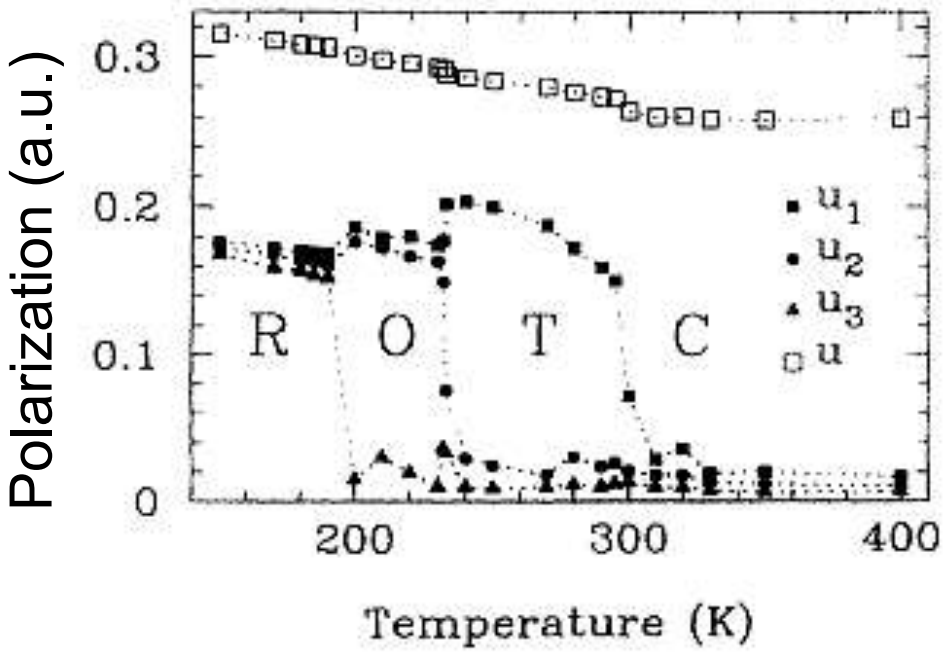
And once we have this....

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

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

It works!

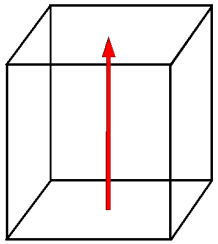
- Sequence of ferroelectric phase transitions of $BaTiO_3$



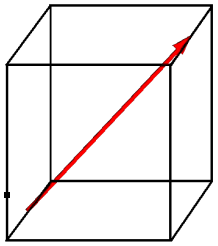
Calculated polarization (P_x, P_y, P_z) as a function of temperature

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

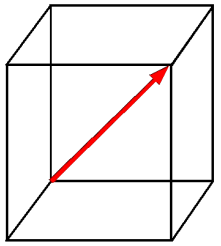
P || [001]
Tetragonal



P || [011]
Orthorhom.

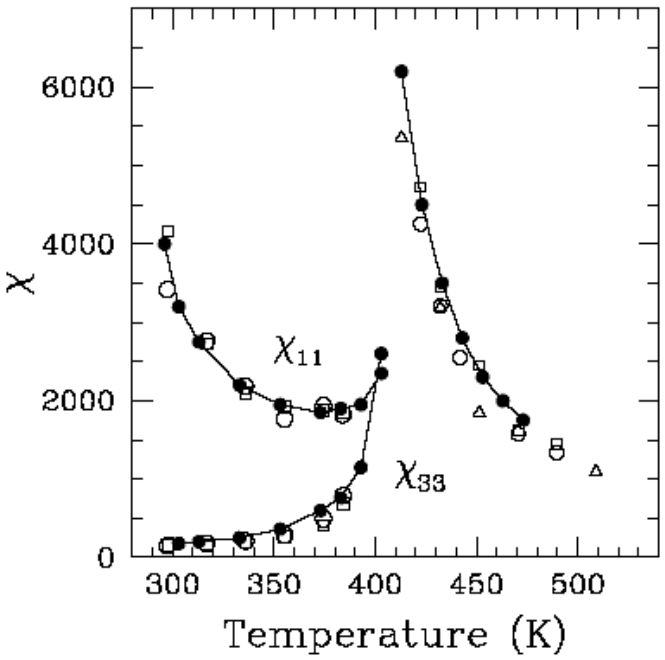


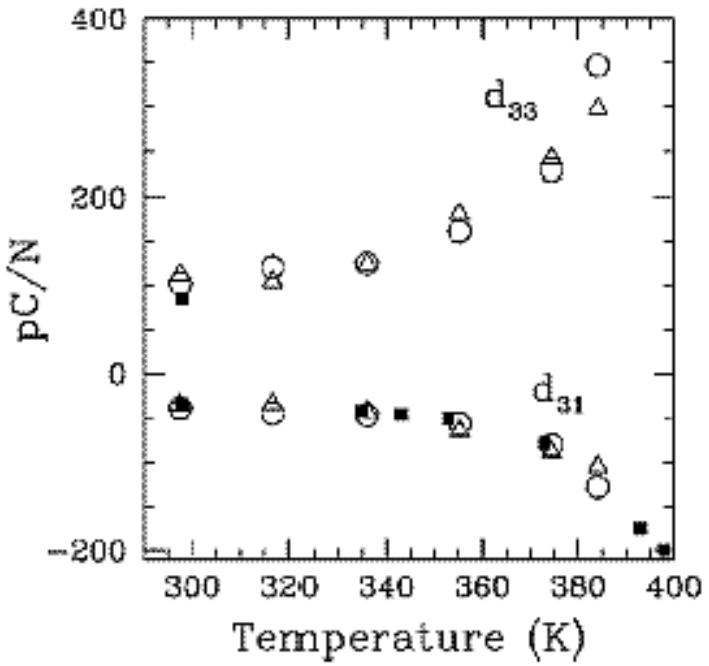
P || [111]
Rhombo.



It works!

- Dielectric and piezoeletric responses of $BaTiO_3$

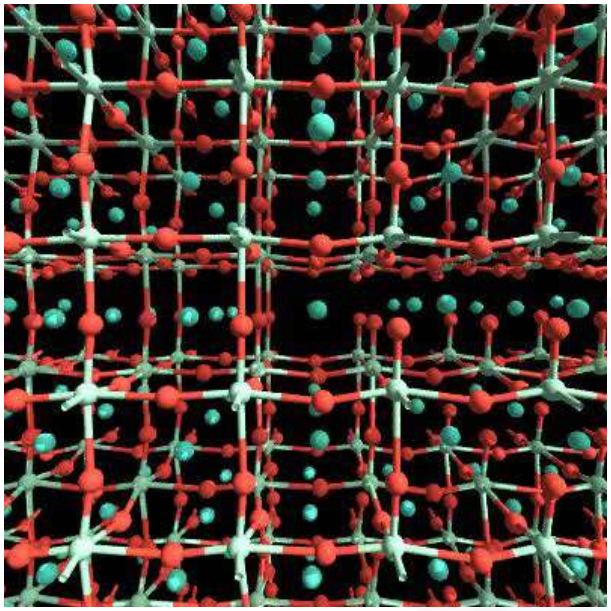




Solid symbols stand for experimental values

García & Vanderbilt, APL 72, 2981 (1998)

[About "Statistical Simulations"]



1) For a given state $\{\vec{x}_i(t), \vec{v}_i(t)\}$, compute the forces on the atoms $\{\vec{f}_i(t)\}$.

2) Update velocities and positions:

$$\vec{v}_i(t+dt) = \vec{v}_i(t) + \frac{1}{m_i}\vec{f}_i(t)dt$$

$$\vec{x}_i(t+dt) = \vec{x}_i(t) + \vec{v}_i(t)dt$$

3) Go back to 1) until we have enough data

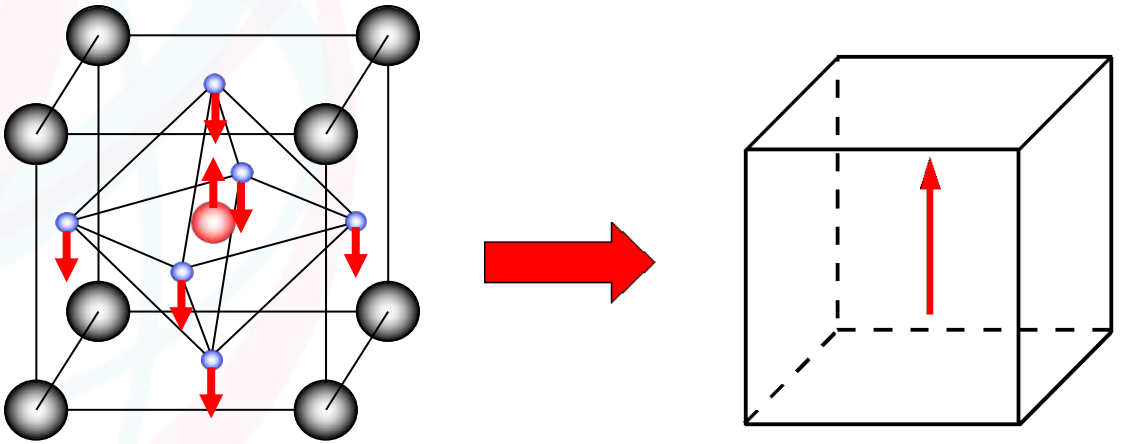
- From the positions we can compute quantities like $\vec{P}(t) = \vec{P}(\{\vec{x}_i(t)\})$
- Hence, for example, we obtain statistical averages by integration:

$$\langle \vec{P} \rangle = \frac{1}{t_f - t_i}\int_{t_i}^{t_f} \vec{P}(t)dt$$

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

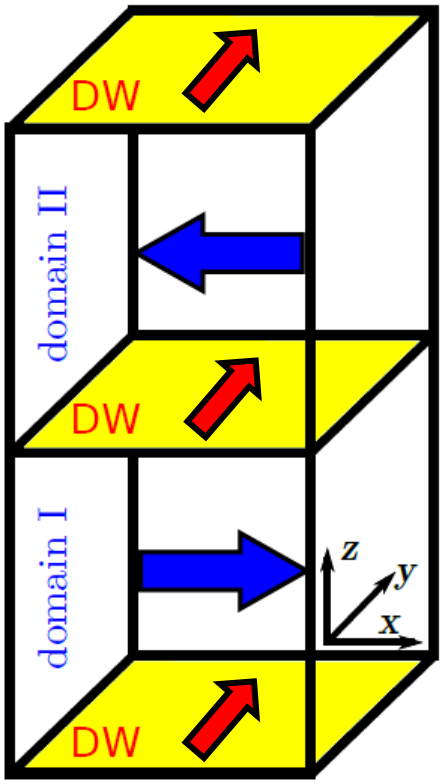
The problem:

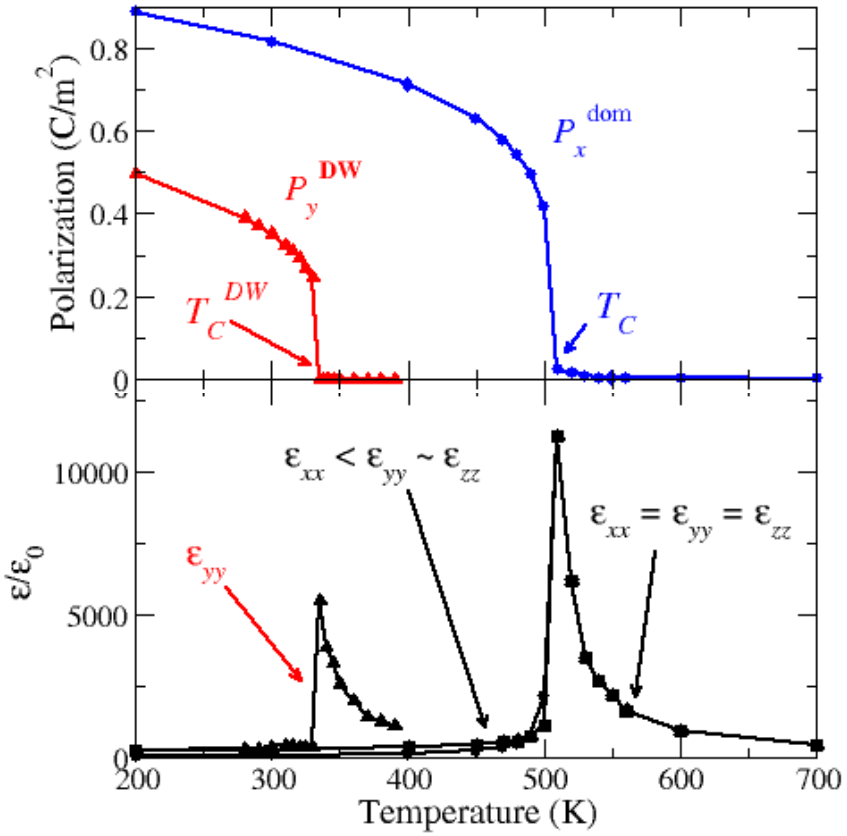


The (our) solution: **Remove the problem!**

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

Ferroelectricity at ferroelectric domain walls





DWs:

Ising

⬇

Bloch

Wojdeł & Íñiguez, Phys. Rev. Lett. 112, 247603 (2014)

Recap, effective potentials

• They give us the ability to predict dynamical response properties, structural phase transitions of systems up to 10,000 – 20,000 atoms.

• Can we always trust the predictions of these models?

- ❖ The simpler the model, the more robust
- ❖ For surprising predictions: Try to check using DFT !
- ❖ Beware: You get the physics you put in. Do not use as a black box.

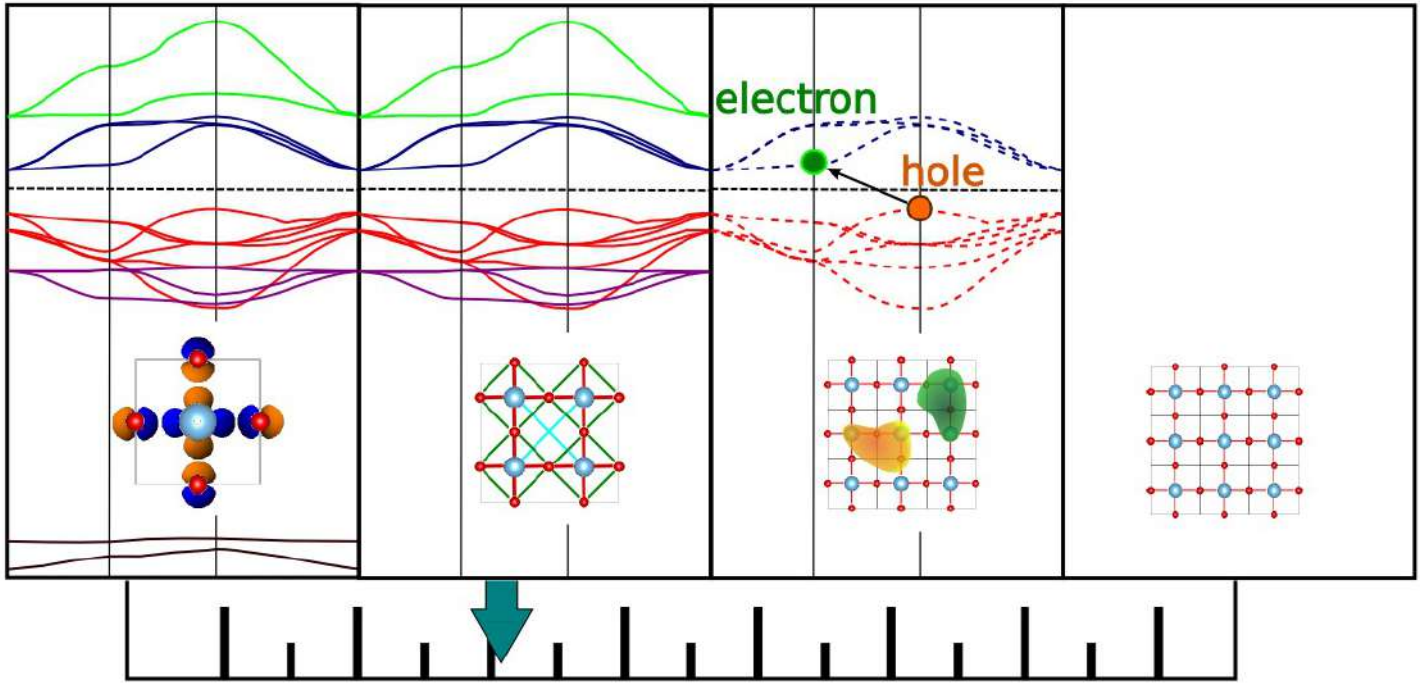
• When do we need other methods?

- ❖ If things get electronically/structurally non-trivial (defects, surfaces) → need to go back to DFT, maybe extend the models
- ❖ If things get even bigger (μm/μs) → need further simplifications!

Questions?

Graphical abstract

First principles | **Second principles** | **Force fields Eff. Hamiltonians** | **Phase fields**



all electrons … → … some electrons … … … → … … no electrons

all atoms …. …. … → … … … all cells

some fields

Atomistic part: Courtesy of J. Junquera & P. García-Fernández

Going continuum, field theory of ferroelectrics

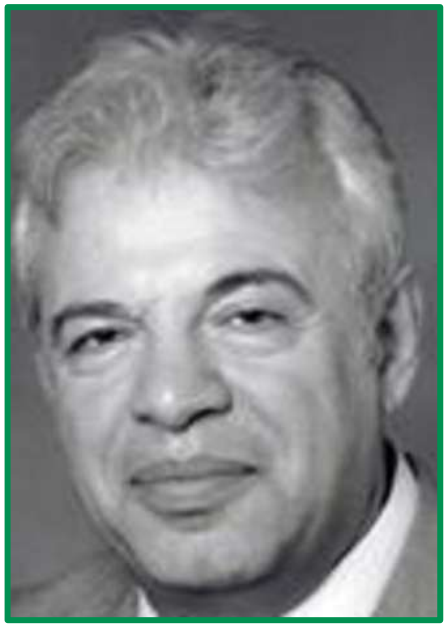
- Phase-Field Method of Phase Transitions/Domain Structures in Ferroelectric Thin Films: A Review

  L.-Q. Chen, J. Am. Ceram. Soc. 91, 1835 (2008).

- The Theory of Structural Transformations in Solids,

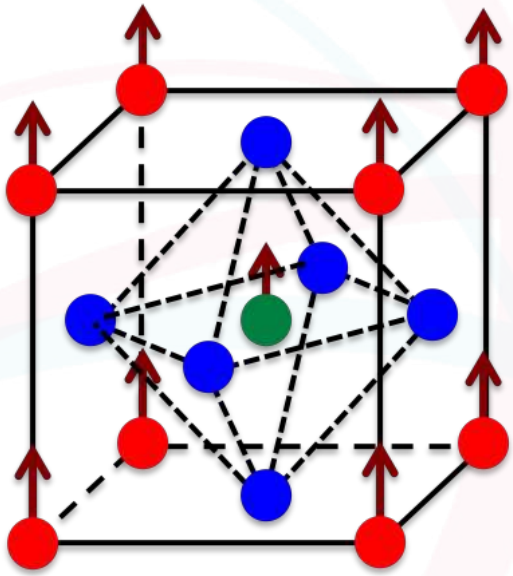
  A.G. Khachaturyan, Dover (1983, 2008).

Long Qing Chen



Armen G. Khachaturyan

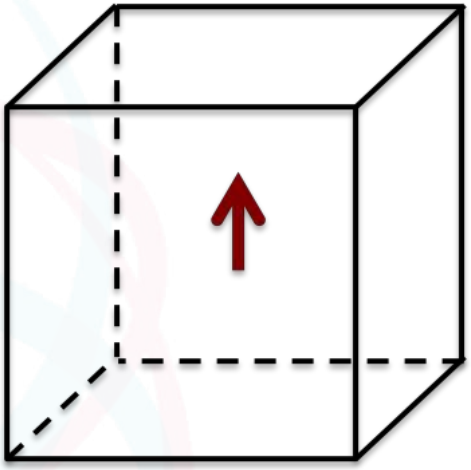
Continuum approach, coarse graining



First principles

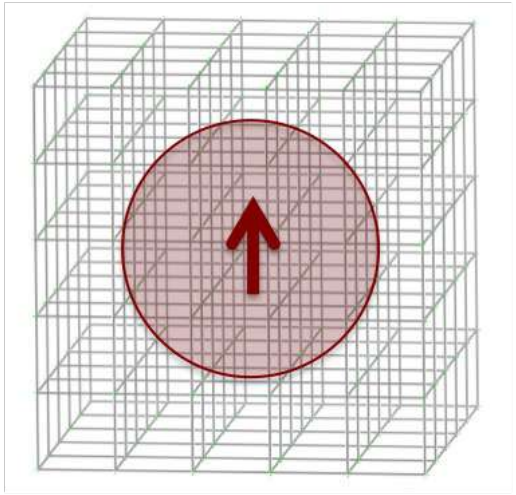
(also second princ.)

All the atoms



Effective Hamiltonians

Dipoles and strains in every unit cell

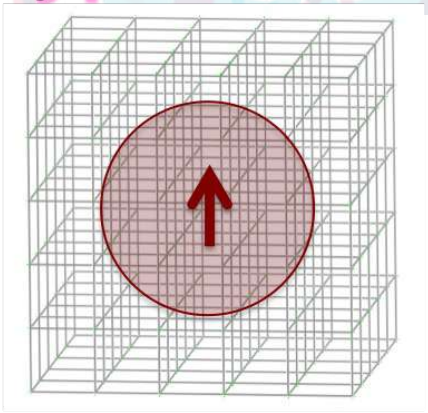


Phase-field Ginzburg-Landau models

Dipoles and strains in "*regions*"

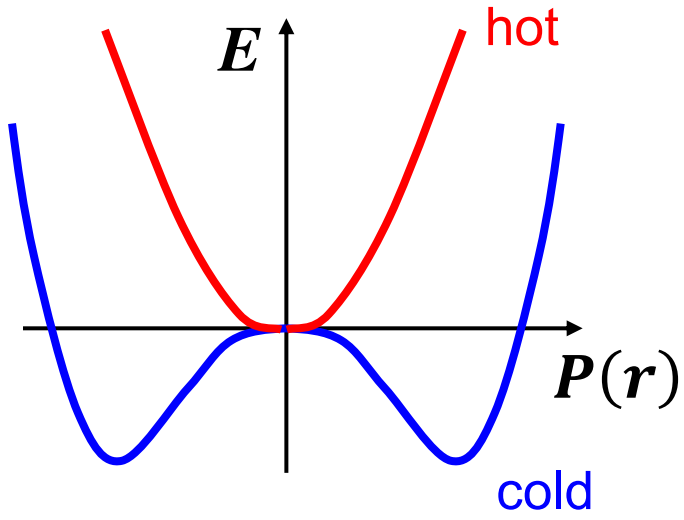
"Landau potential" hypothesis

Basic quantity: polarization field $\boldsymbol{P}(\boldsymbol{r})$



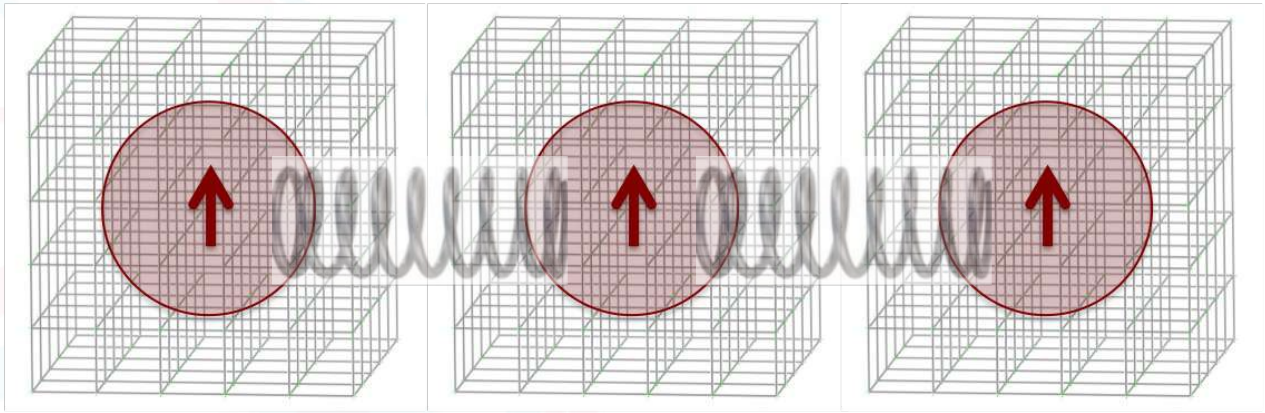
Big assuption: At every point $\boldsymbol{r}$ the polarization field $\boldsymbol{P}(\boldsymbol{r})$ "feels" a simple ***T-dependent Landau potential***

→ This local polarization can develop spontaneously



- The "regions" have to be ***large enough*** for this to actually happen.
- For typical ferroelectric peroskites: 1 region ~ 4x4x4 unit cells.

“Ginzburg-Landau” hypothesis



Besides electrostatics, the interactions between local polarizations are fully captured by the polarization gradient $\boldsymbol{\nabla} \cdot \boldsymbol{P}(\boldsymbol{r})$

The energy associated to the gradient is described by the lowest-order couplings allowed by symmetry:

- Often you will find: $\mathrm{E}_{\mathrm{grad}} = \frac{1}{2}\mathrm{G}\left(\boldsymbol{\nabla} \cdot \boldsymbol{P}(\boldsymbol{r})\right)^2$
- More general: $\mathrm{E}_{\mathrm{grad}} = \frac{1}{2}\sum_{ijkl} G_{ijkl} \frac{\partial P_i(\boldsymbol{r})}{\partial r_j} \frac{\partial P_k(\boldsymbol{r})}{\partial r_l}$

→ **Energy associated to the occurrence of domain walls !**

The basic phase-field scheme

- Phenomenological free-energy functional:

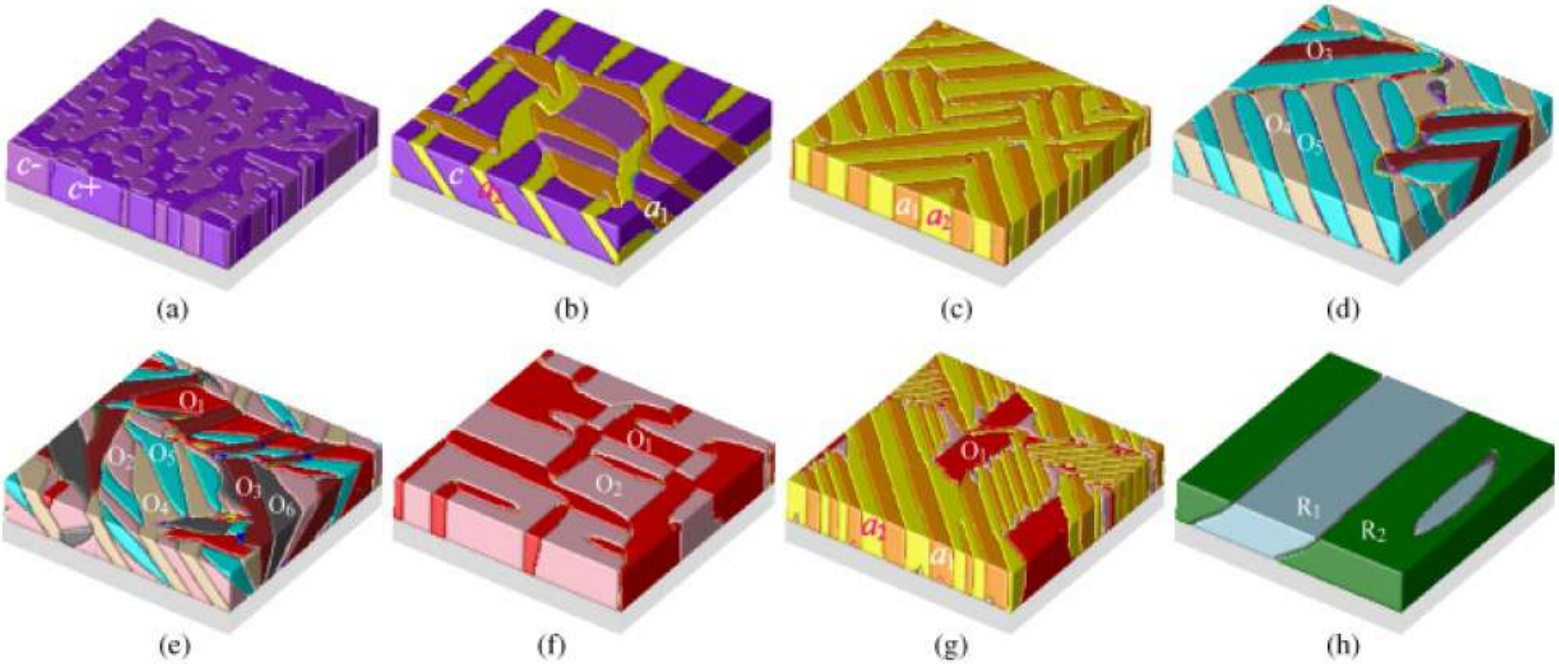
$$F = \int_V [\, f_{\text{bulk}}(P_i) + f_{\text{grad}}(\partial P_i / \partial x_j) + f_{\text{elast}}(P_i, \varepsilon_{ij}) + f_{\text{elec}}(P_i, E_i)]\, \mathrm{d}^3 x$$

- Equations of motion, in the relaxational limit:

$$\frac{\partial P_i(x,t)}{\partial t} = -L \frac{\delta F}{\delta P_i(x,t)}$$

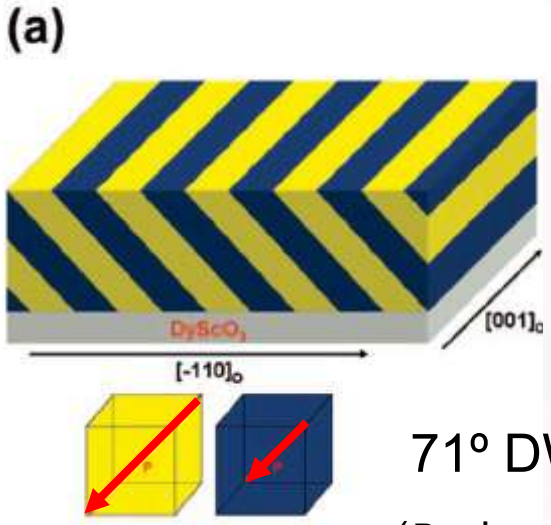
- Usual approach:
  1. Start from suitable (often random) $\boldsymbol{P}(\boldsymbol{r})$
  2. Apply elastic and electric boundary conditions and *T* of interest
  3. Simulate time evolution towards equilibrium configuration $\boldsymbol{P}_{eq}(\boldsymbol{r})$
  4. **Analyze and *understand* the result !! (physically transparent!)**

Multidomain structures, many successful applications!



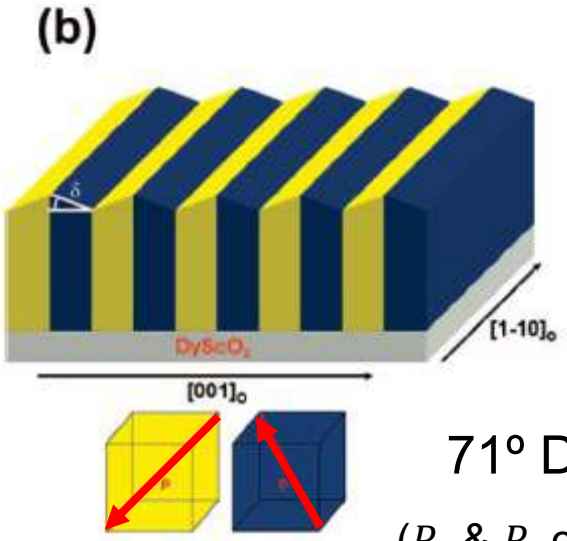
Multi-domain configurations in $BaTiO_3$ films, for different temperatures and epitaxial strains [Li et al., APL 88, 072905 (2006); JAP 98, 064101 (2005)]

Multidomain structures, many successful applications!



71º DWs

(P_x changes)

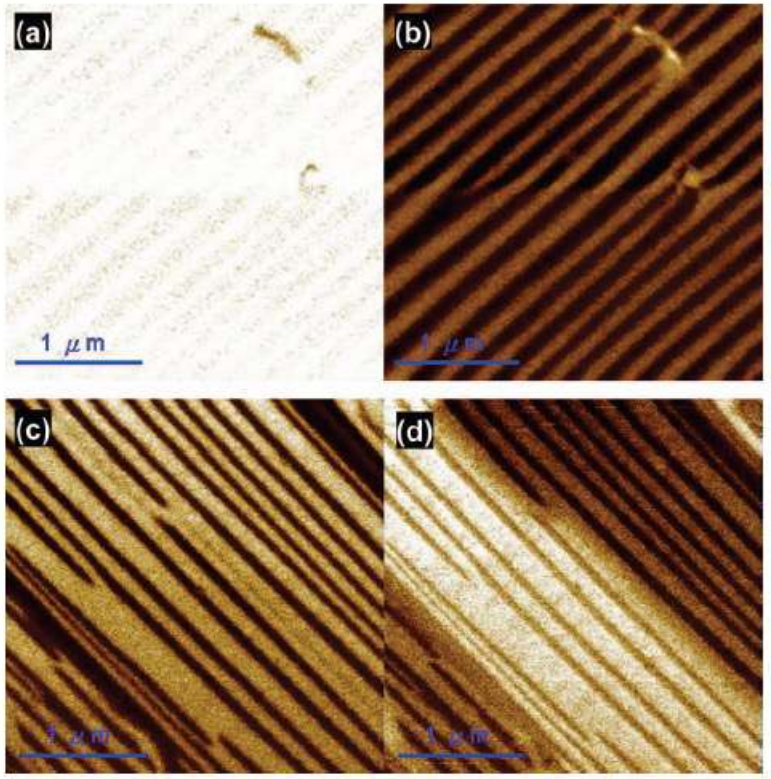


71º DWs

(P_x & P_z change)

Tailoring the multidomain ferroelectric state of $BiFeO_3$ films grown on $DyScO_3$ substrates

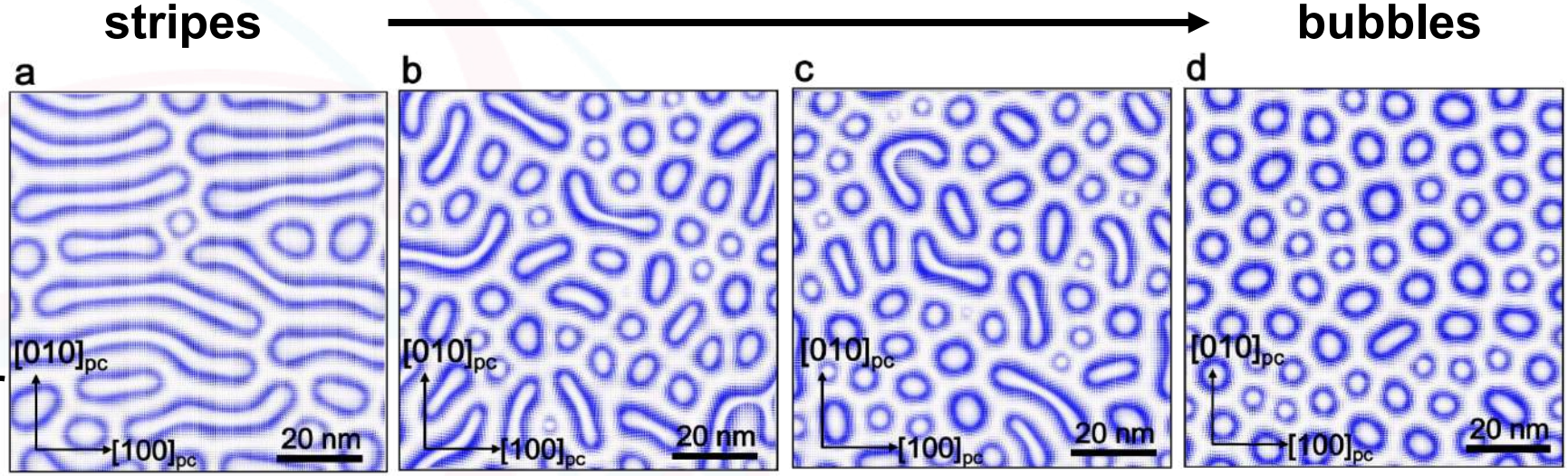
[Chu, Ramesh *et al*., NanoLetters 9, 1726 (2009)]



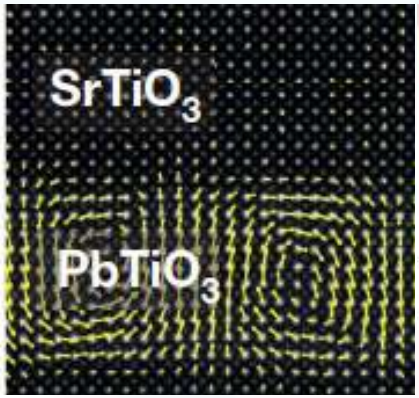
71º DWs

109º DWs

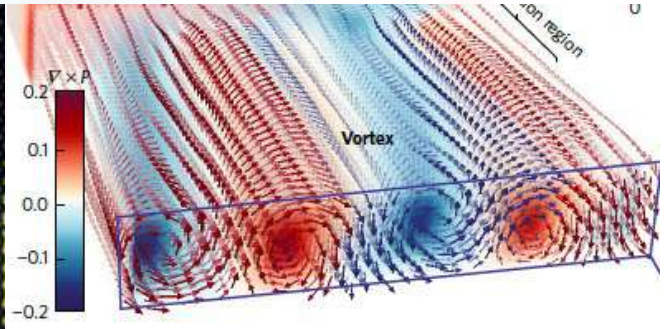
Competing states in PTO/STO superlattices



Phase field simulations (Hong *et al*.) for various STO/PTO/STO tri-layers and PTO/STO superlattices; many closely competing phases; consistent with Triscone *et al*., Bellaiche *et al*., Zubko *et al*.; Valanoor *et al*.



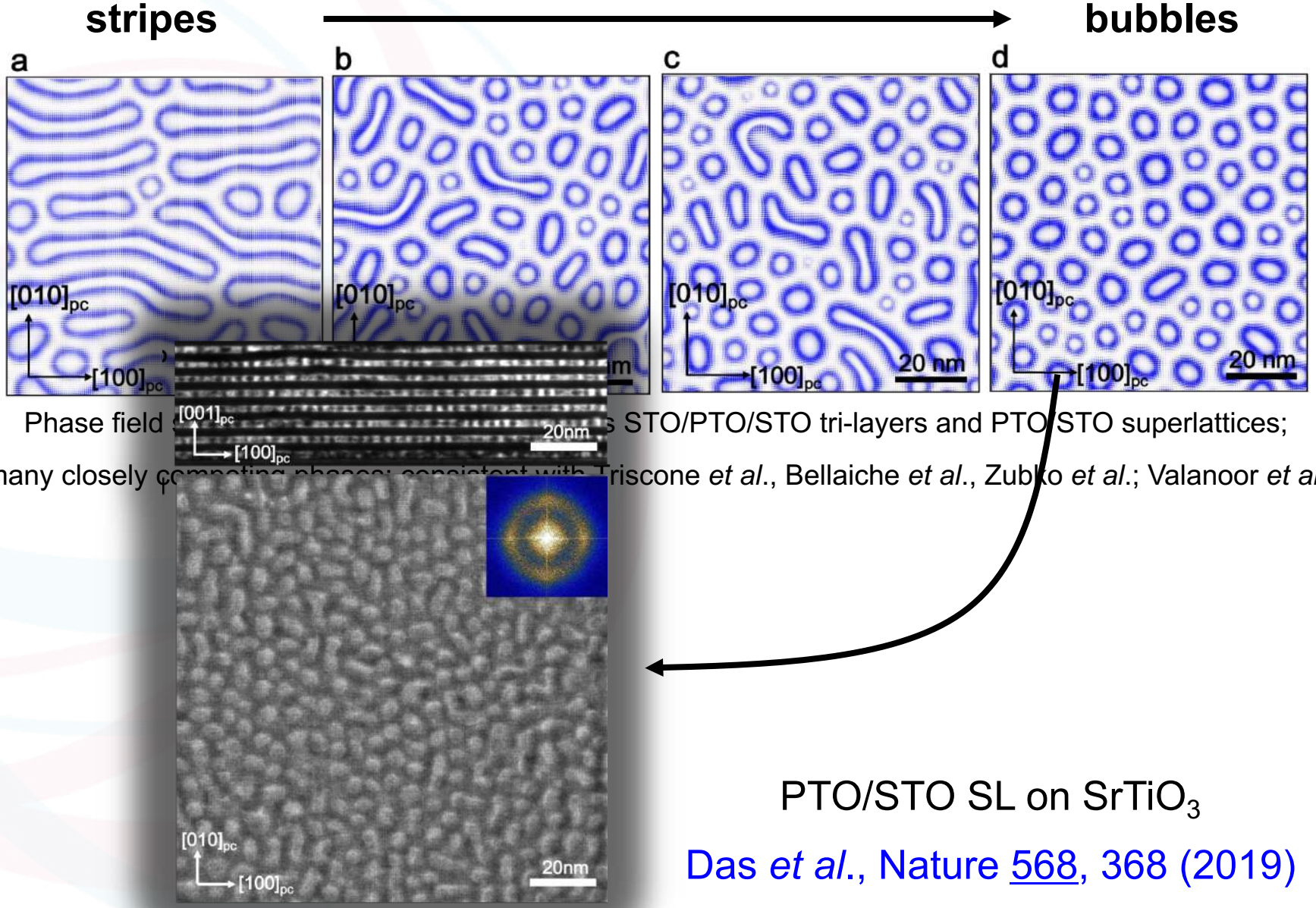
PTO/STO SL on $DyScO_3$



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

Damodaran *et al*., Nat. Mats. 16, 1003 (2017)

Competing states in PTO/STO superlattices

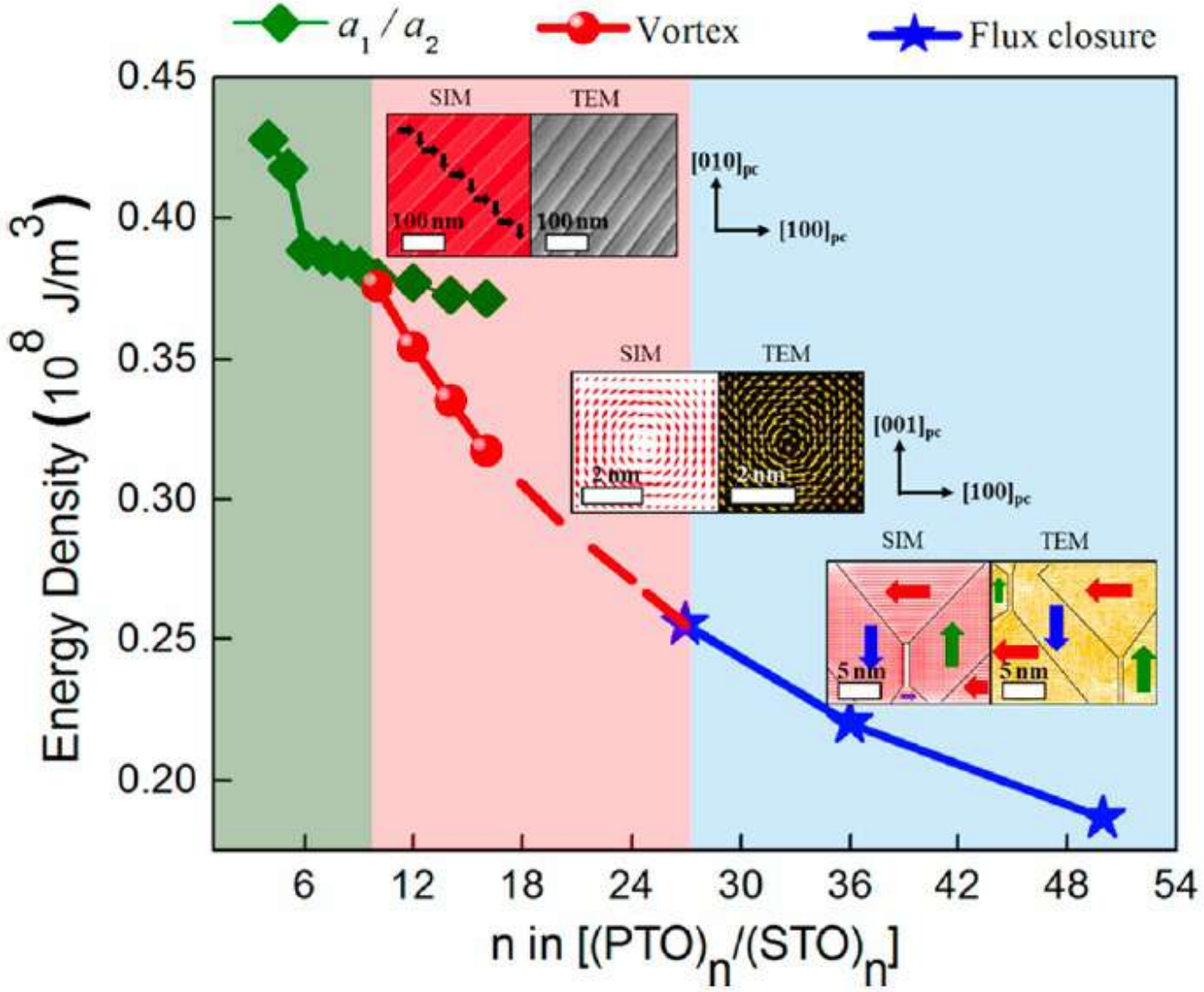


Phase field [illegible] STO/PTO/STO tri-layers and PTO/STO superlattices; many closely competing phases; consistent with Triscone *et al*., Bellaiche *et al*., Zubko *et al*.; Valanoor *et al*.

PTO/STO SL on $SrTiO_3$

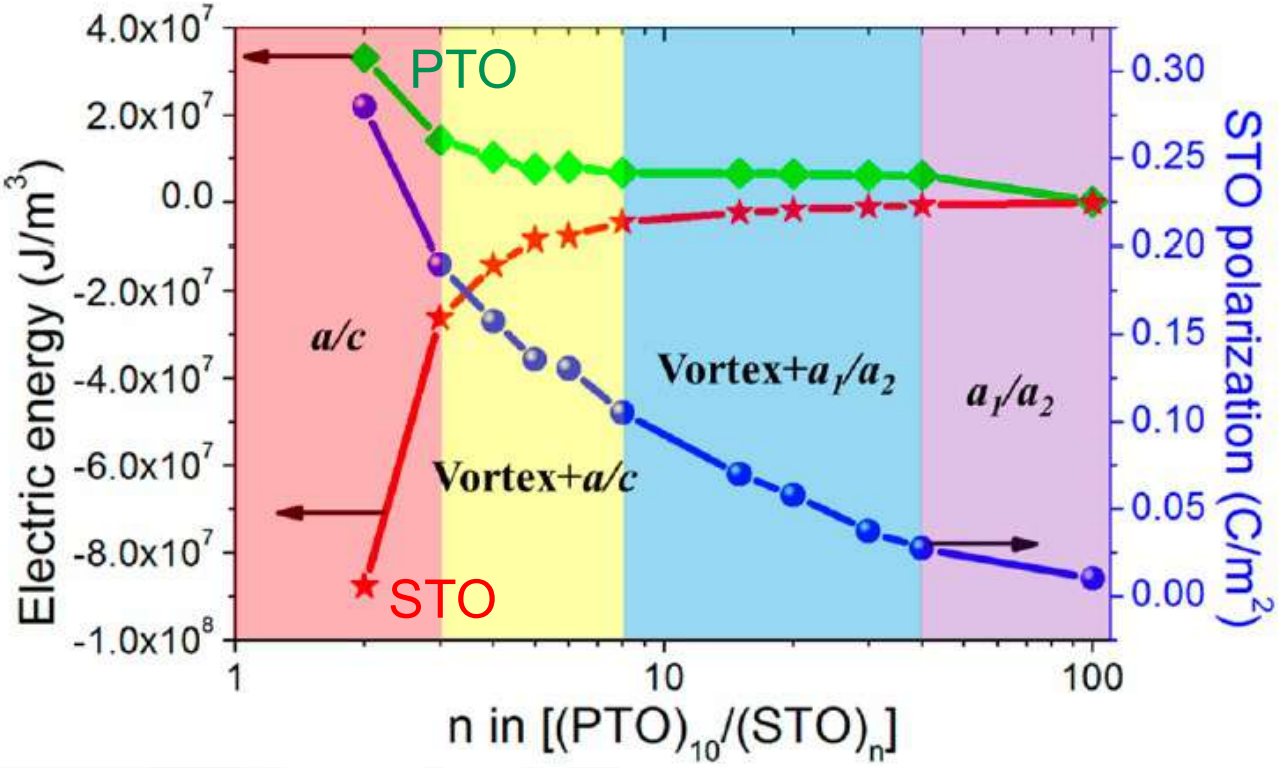
Das *et al*., Nature 568, 368 (2019)

Before the experiment: phase field predictions!



Z. Hong, … & L.-Q. Chen, NanoLetters 17, 2246 (2017)

Phase field → Understanding!



- Phase field approach: allows us to partition the energy and identify trends (gain understanding) in a precise and powerful way
- Here: polarizability of STO layer is critical to determine the PTO state

Z. Hong, … & L.-Q. Chen, NanoLetters 17, 2246 (2017)

Limits of the phase field approach

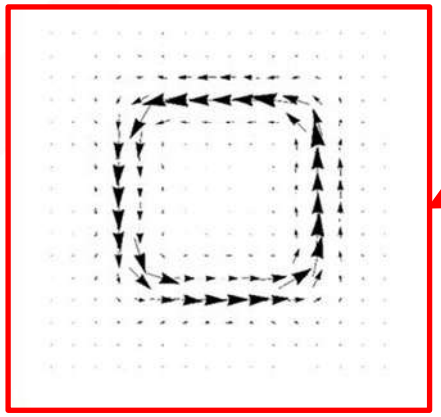
- Connection with first (or second) principles, not well explored yet
- At present, ultimate (sole) validation: **agreement with experiment**

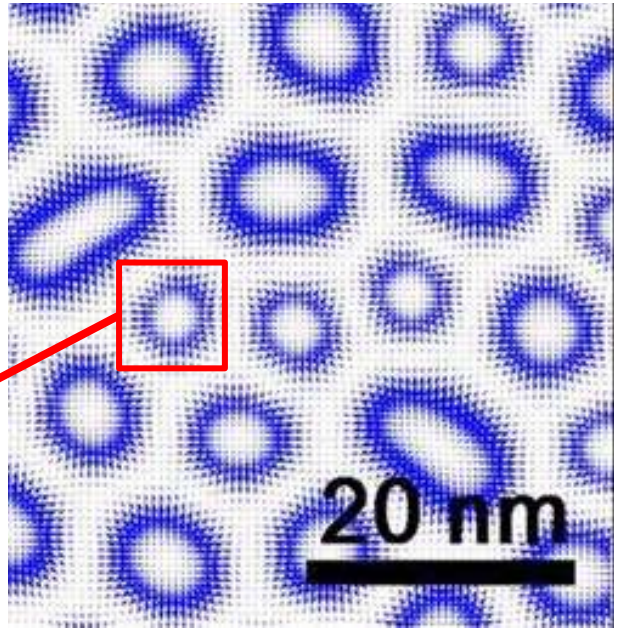
Where does it work well?

- Multidomains under various elastic/electric conditions
- Large characteristic lenghts (so local Landau energy is valid)
- Quantitative dynamics not important (long times, equilibration)

Where do we have to be careful?

- Internal domain wall struct., interfaces (< 2 nm)
- Fast dynamics (sub-THz), inertial effects



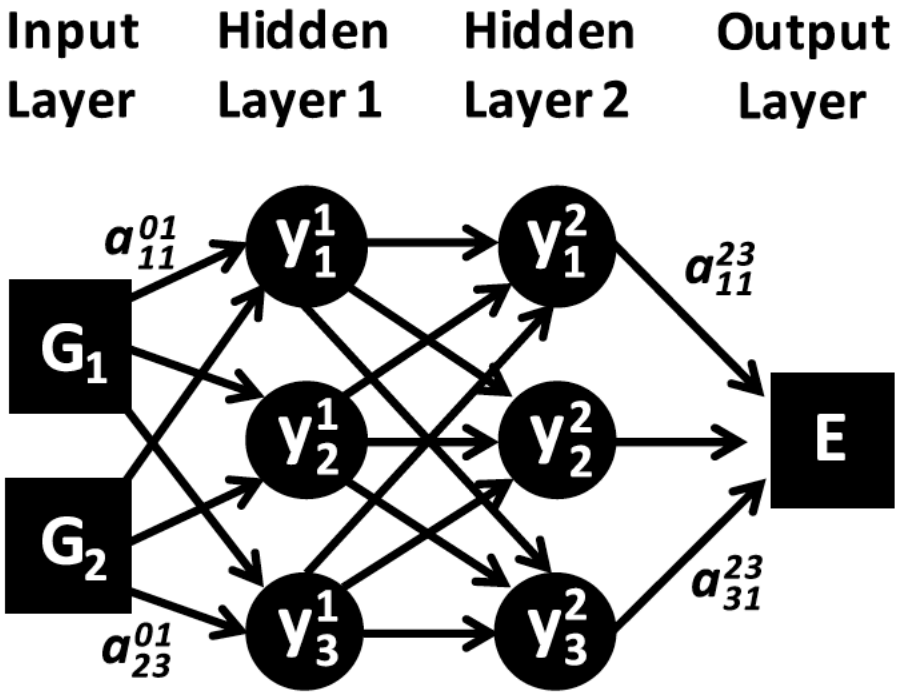


Skyrmions in PTO/STO

Das *et al.*, Nature 568, 368 (2019)

Questions?

Soon we will be (very) old…



Descriptors

(a convenient way to describe any state of our system of interest)

Outputs

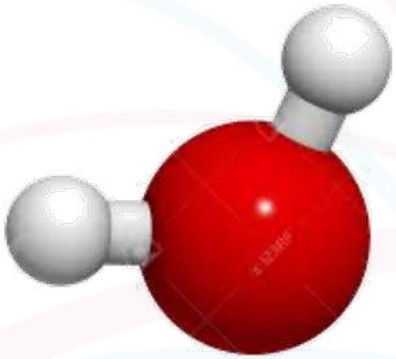
(e.g., total energy, force on an atom, polarization, …)

$$E = f\left(b_1^3 + \sum_{k=1}^{3} a_{k1}^{23} \cdot f\left(b_k^2 + \sum_{j=1}^{3} a_{jk}^{12} \cdot f\left(b_j^1 + \sum_{i=1}^{2} G_i \cdot a_{ij}^{01}\right)\right)\right).$$

Behler, J. Chem. Phys. 145, 170901 (2016)

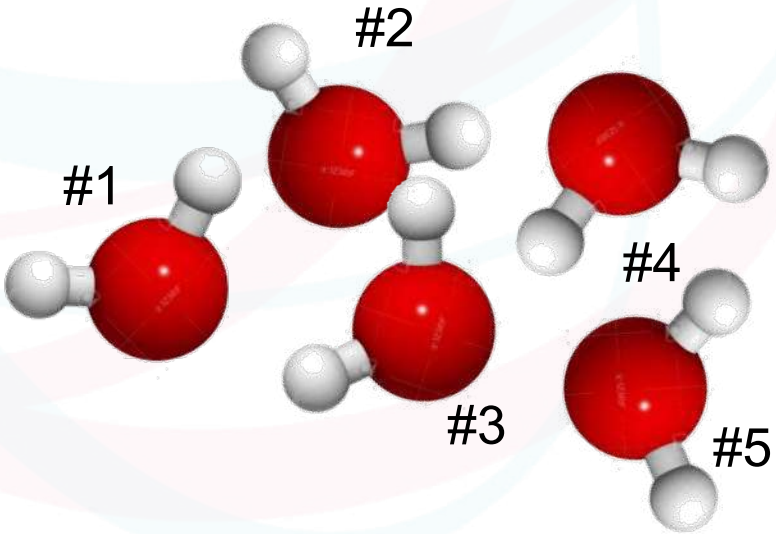
Behler & Csányi, Eur. Phys. J. B 94, 142 (2021)

The challenges of ML



How would you describe the state of this H_2O molecule as a list of numbers?

- Do you get a different list of numbers if we simply displace the molecule?
- Do you get a different list of numbers if we swamp the H atoms?



What is the range of the interactions in this system?

ML: Status and outlook

- Not so long ago, ML methods used to be a very inefficient black box, totally useless to handle something like a ferroelectric or a multiferroic
- However, advances in descriptors and in ML potentials – so that e.g. they incorporate basic symmetries of the system (spatial translation, equivalent atoms) – have resulted in a drastic improvement

- However, there is still a lot of room for development
  - **Physically informed models** that, e.g., capture correctly long-range interactions (electrostatic, vdWs) instead of describing in an approximate and ultimately incorrect way.
  - **Interpretable** potentials that are (more) physically transparent
  - **Hopefully:** Simpler potentials tailored to materials classes

  (Goes against the ”ML purity” but I think could be super-useful!)

Great opportunities for collaboration between ML and topical experts !!

Questions?

Advice to young experimentalists

- Never start a conversation like this:

  "We are finishing a paper on […] and would like to include a theory figure that supports our amazing results and interpretation. How can you help?"

- When talking to theorists / simulators, remember:

  * (Good) theory takes time (even in the ML era)

  * The results from theory may or may not agree with your experimental data or your interpretation of it. Be ready for that!

  * That's OK because (good) theory (and its comparison with experiment) will allow you to learn about your problem

  * And you can publish that (even in "fancy magazines")

Information for both young experimentalists and theorists (I)

- We cannot simulate real **samples** in the computer
- Most often, a quantitative comparison of experiment and theory is not warranted.
- If you ever meet a theorist who claims they can compute a complex quantity (ferroelectric transition temperature, coercive field, band gap, …) of a complex sample with great accuracy, **run**!

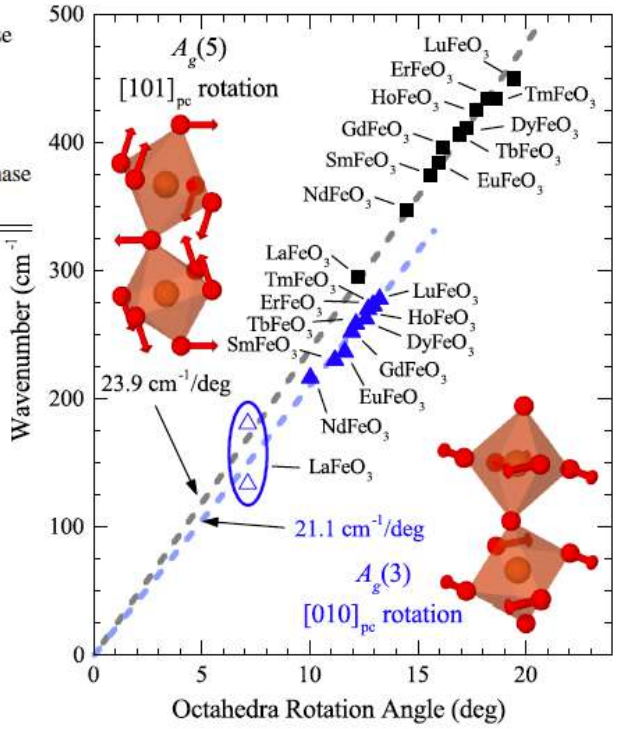
Information for both young experimentalists and theorists (II)

- So… what can a (good) theorist do ? Anything at all ?
- Of course, relatively simple properties of very good samples can be computed with good quantitative accuracy

Example: Spectroscopies

	$LaFeO_3$		$SmFeO_3$		$EuFeO_3$		$GdFeO_3$		$TbFeO_3$		$DyFeO_3$		
Symmetry	80 K	calc.	80 K	calc.	80 K	calc.	80 K	calc.	80 K	calc.	80 K	calc.	Main atomic motion
$A_g(1)$	84.5	89	109.5	109	110.9	112	111.1	111	112.5	112	113.3	112	$R(x)$, in-phase in x-z, out-of-phase in y
$A_g(2)$	135.3	127	144.2	138	140.7	140	140.4	137	143.9	136	140.5	135	$R(z)$, out-of-phase
$A_g(3)$	186.6	183	223.9	244	235.1	252	253.2	255	261.9	259	261.5	262	$[010]_{pc}$ FeO_6 rotation, in-phase
$A_g(4)$	274.2	273	319.1	320	323.2	325	329.9	330	334.5	330	341.1	332	O(1) x-z plane
$A_g(5)$	302.8	306	379.5	383	387.8	397	399.4	405	410.9	410	422.4	422	$[101]_{pc}$ FeO_6 rotation, in-phase
$A_g(6)$	449.8	433	420.7	413	419.6	414	420.9	416	420.1	416	417.3	415	Fe-O(2) stretching, in-phase
$A_g(7)$	433.3	413	470.7	468	474.0	476	483.6	480	490.1	484	496.8	490	O(1)-Fe-O(2) scissor-like bending
$B_{1g}(1)$		169	160.7	151		149		143		139		135	$R(y)$ in-phase in x-z, out-of-phase in y
$B_{1g}(2)$		148	238.7	233	236.4	243	247.1	244	251.9	248		250	$[010]_{pc}$ FeO_6 rotation, out-of-phase
$B_{1g}(3)$	338.1	328	353.3	352	350.0	356	357.0	356	359.2	356	360.9	359	$[010]_{pc}$ FeO_6 rotation, out-of-phase
$B_{1g}(4)$	442.3	425	426.4	422	425.8	424	428.8	426	427.7	425	427.4	427	Fe-O(2) stretching, out-of-phase
$B_{1g}(5)$	560.9	584		594		597		595		592		593	Fe-O(1) stretching
$B_{2g}(1)$	105.5	103	109.8	109	110.9	111	111.1	109	107.7	109	110.6	109	$R(z)$, in-phase in x-z, out-of-phase in y
$B_{2g}(2)$	143.0	144	157.4	159	159.3	163	159.9	161	160.1	161	162.8	161	$R(x)$, out-of-phase
$B_{2g}(3)$	166.5	172	255.0	278	271.1	291	289.3	299	302.7	305	324.9	311	$[101]_{pc}$ FeO_6 rotation, in-phase
$B_{2g}(4)$		329		346		348		349		349		351	O(1) x-z plane
$B_{2g}(5)$	416.8	401	462.8	460	468.2	469	478.9	474	485.6	478	493.7	482	O(1)-Fe-O(2) scissor-like bending
$B_{2g}(6)$		481	521.5	513	524.5	521	531.7	528	535.8	528		534	O(2)-Fe-O(2) scissor-like bending, in-phase
$B_{2g}(7)$	625.1	622	640.5	610	638.1	613	640.5	612		611	624.2	612	Fe-O(2) stretching, in-phase
$B_{3g}(1)$		137	145.0	135	133.6	134	132.2	129		126		123	$R(y)$ out-of-phase in x-z, y
$B_{3g}(2)$	316.8	300	322.8	313		315		312		311		311	O(1)-Fe-O(2) in-phase
$B_{3g}(3)$	436.0	425	432.7	424	429.9	424	431.5	426	433.3	422	433.1	424	octahedra squeezing in y
$B_{3g}(4)$	428.6	408	455.9	447	456.7	452	465.0	455	468.8	457	473.7	460	O(2)-Fe-O(2) scissor-like bending, out-of-phase
$B_{3g}(5)$	641.9	650		641		643		640		637	639.4	637	FeO_6 breathing

PRB'16



- Predicted: Raman frequencies for family of orthoferrites (pervoskite oxides)
- Able to explain experimental observations, visualize Raman vibrations modes
- **Available for Raman, IR, neutrons, etc.**
- **Available for crystals, molecules, etc.**

Information for both young experimentalists and theorists (II)

- But if your sample is complicated…

  - polycrystalline, with grain boundaries (HfO_2, ZrO_2, …)
  - presenting a complex multidomain structure (all nano-ferroics)
  - with unknown interactions across interfaces…
  - … that are not perfect (inter-diffusion, rugosity)
  - in presence of defects (extended & local), built-in fields
  - maybe intrinsically disordered (LSMO vs. $LaNiO_3$)
  - at room temperature, under inhomogeneous external fields

… and your properties of interest are non-trivial, then…

Information for both young experimentalists and theorists (III)

- The main job of the theorist is to **think** and figure out how to transform a complex unsolvable problem into well-defined solvable problems that give relevant information.

  - "Can the behavior be explained by the intrinsic properties of an ideal bulk-like version of your ferroelectric layer?"
  - "If we assume that the effect of the substrate is purely elastic (fixing the in-plane lattice constants of a perfect crystal), can we explain the results?"
  - "Is your complex sequence of temperature-drive phase transitions reflected in the potential energy landscape that we can compute at 0 K?"
  - "Can we reproduce the effect you see upon switching by working with a single domain?"
  - "Can we explain the stabilization of that phase by mere doping? By "chemical pressure"?"

Hypothesis validation

Information for young theorists (I)

- Your other main job of the theorist is to consider situations that have never been tested experimentally, and identify new effects and trends

    - Magnetic and electric skyrmions
    - Strain engineering
    - Strategies to electromechanical responses
    - Hyperferroelectrics
    - Switchable ferroelectric metals
    - …

- This is great fun!, just remember: focus on realistic materials

Information for young theorists (II)

- In case you have not noticed: You work on an experimental science
- Most of your chances to make a difference will involve experiment (and the people running them)

- They don't bite…
- … but you will need to learn (a bit about) what they can and cannot do, what's hard and what's easier
- … and educate them (a bit) about what you can and cannot do, what's hard and what's easier

- Practice the following sentences / constructions in front of the mirror:

"No" *"I cannot do that"* *"Maybe we can learn something if…"*

"The values will not match exactly, but we may be able to compare trends…"

"We may be able to help, but it would be a full project of its own. Maybe we could apply for funding together…"

So, remember…

The main job of the theorist is to **think**

(Besides the "thinking" part, your activity is relatively easy to automatize…)

From this:

"We are finishing a paper on […] and would like to include a theory figure that supports our amazing results and interpretation. How can you help?"

To this:

"We may be able to help, but it would be a full project of its own. Maybe we could apply for funding together…"

Thank you for your attention!