# Topological orders in ferroelectrics

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## **Before we begin / disclaimer**

 If you are interested in topology in ferroelectrics, you may want to look at the literature by (at least) the following authors:

#### **Experiment:**

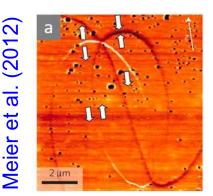
- R. Ramesh, L.W. Martin (Berkeley  $\rightarrow$  Rice)
- N. Valanoor (New South Wales)
- D. Muller (Cornell), X. Pan (UC Irvine)
- X.L. Ma (Chinese Ac. Sci. -- Shenyang), ...

#### Theory:

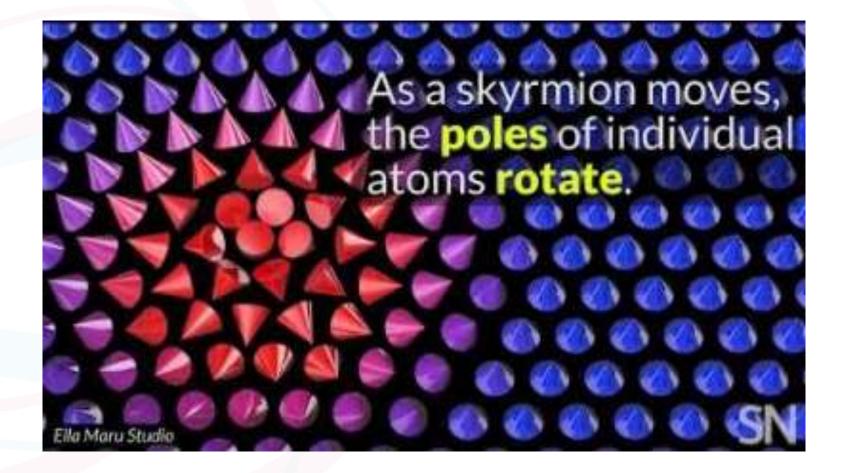
- L. Bellaiche, S. Prokhorenko (Arkansas)
- I. Luk'yanchuk (Picardie)
- L.Q. Chen (Penn State)
- J. Junquera (Cantabria), ...

#### <u>Plus:</u>

- S.-W. Cheong
- M. Fiebig
- D. Meier
- N. Spaldin
- M. Mostovoy
- A. Cano

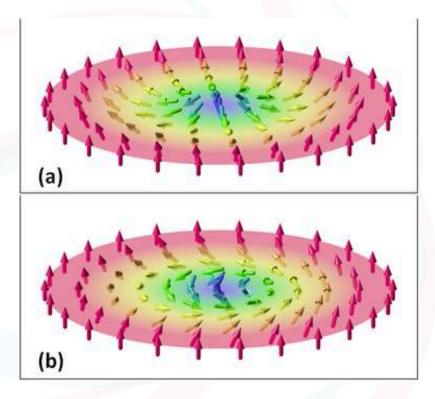


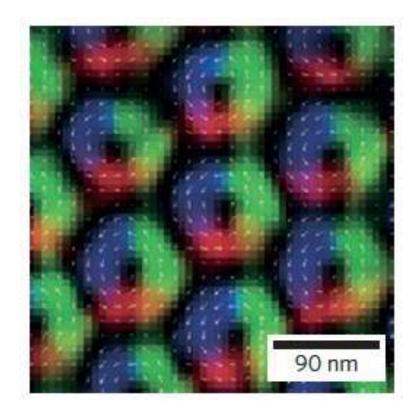
#### What strikes you about these images?



https://www.youtube.com/@ScienceNewsMag

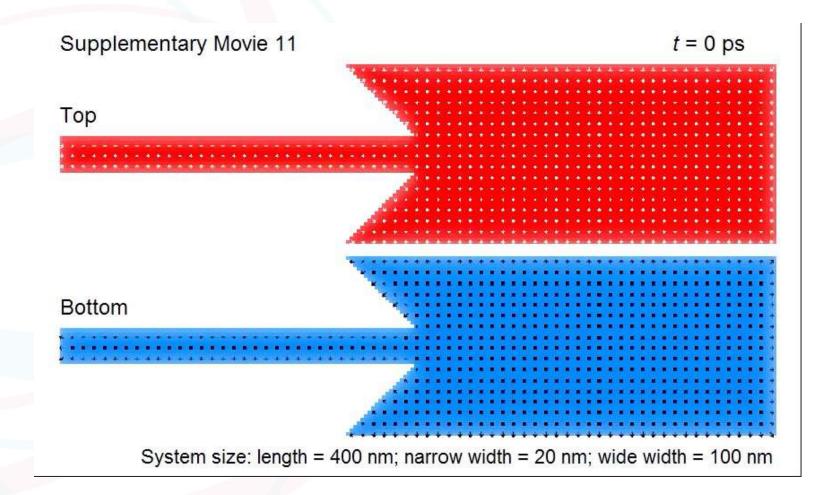
#### What strikes you about these images?





https://en.wikipedia.org/wiki/Magnetic\_skyrmion Yu *et al.*, Nature <u>465</u>, 901 (2010)

#### What strikes you about these images?



Zhang et al., Nature Communications 7, 10293 (2016)

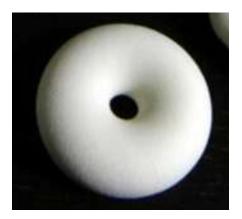
# What about topology?



Image from <a href="https://www.shapeways.com/shops/henryseg">https://www.shapeways.com/shops/henryseg</a>

#### What about topology?





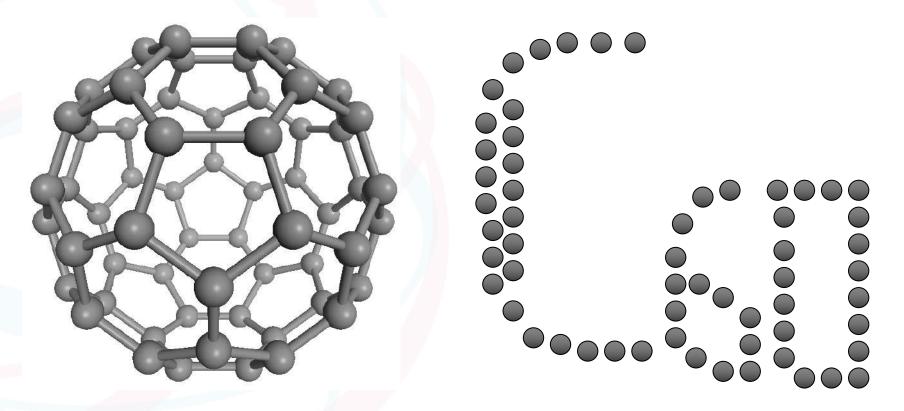
OK, great, they are topologically equivalent. Yet, everything else is pretty much <u>inequivalent</u> between these two.

( If you want to have a cup of coffee, which one would you use? :)

Image from <a href="https://www.shapeways.com/shops/henryseg">https://www.shapeways.com/shops/henryseg</a>

#### To bring the point home...

What is the difference between these two configurations of 60 carbon atoms?



What's more important, topology or energy?

#### My personal interest in skyrmions

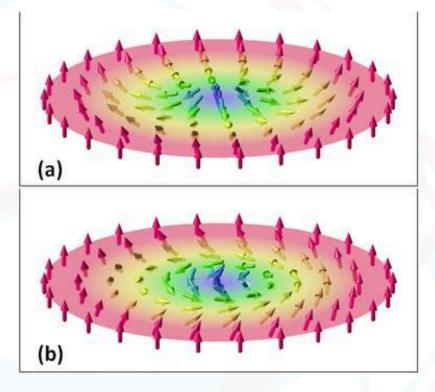
- **Particle-like nature**, diffusive and driven dynamics
- Possibility to create them, erase them, move them, count them, make them interact, …
- Topology will usually be present, but I am not really planning to "use it" (for the moment, at least)

#### On topology vs symmetry:

At a minimum, homotopy theory provides *the* natural language for the description and classification of defects in a large class of ordered systems. Whether it will eventually gain as wide a currency among condensed matter physicists as, for example, the language and theorems of the theory of group representations, depends both on how large that class of systems proves to be, and on how many of the *nontrivial* topological insights turn out to have direct manifestations in the laboratory.

N.D. Mermin, Rev. Mod. Phys. <u>51</u>, 591 (1979)

## Can we have stable "electric skyrmions"?



#### Basics of magnetic skyrmions:

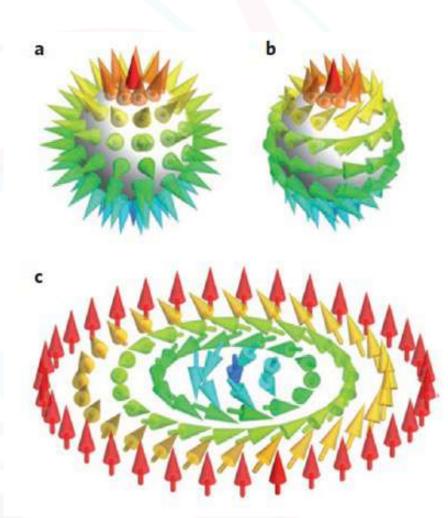
- Non-collinear structures
- (Essentially,) Skyrmions display spins in every possible orientation
  Source of non-collinearity: Something called Dzyaloshinskii-

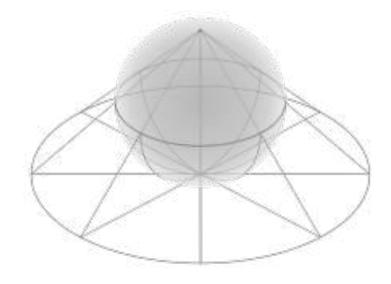
Moriya interaction (DMI), which occurs in many magnets

 While not the only possible "driving force" for magnetic skyrmions, DMI is a very frequent one and very important historically, so let's stop for a second here.

For more, see e.g. Nagaosa & Tokura, Nature Nanotechnology <u>8</u>, 899 (2013).

#### [Every possible orientation...]





https://en.wikipedia.org/wiki/ Stereographic\_projection

Pfleiderer, Nat. Phys. 7, 673 (2011)

#### **Basic spin Hamiltonian and spin orders**

$$H = -\sum_{i \neq j} J \overrightarrow{S_i} \cdot \overrightarrow{S_j} - \sum_i K S_{i,z}^2 + \sum_{i \neq j} \overrightarrow{D} \cdot \overrightarrow{S_i} \times \overrightarrow{S_j} + \cdots$$

• Symmetric exchange *J*: favors collinear orders, FM or AFM

E.g., for J > 0 we have  $\uparrow \uparrow \uparrow \uparrow \circ -$ 

- On-site anisotropy K: defines easy magnetic axis or plane
  - E.g., for K < 0 we have

• Anti-symmetry exchange  $\vec{D}$  (DMI): favors <u>non-collinear spins</u>

[DMI: spin-orbit contribution to exchange, second-order perturbation]

#### So, is there a DMI for electric dipoles?

TABLE I. Orders of magnitude of the most relevant magnetic and electric interactions in typical magnetic and ferroelectric materials.

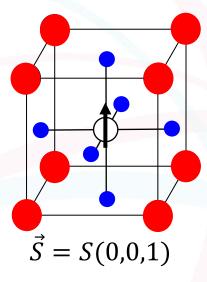
	Magnetic (J)	Electric (J)
Dipolar (at 1 nm)	$5 \times 10^{-26}$	$1 \times 10^{-20}$
Short-range	$1 \times 10^{-21}$	$5 \times 10^{-21}$
Anisotropy	$5 \times 10^{-25}$	$5 \times 10^{-21}$
DMI	$5 \times 10^{-22}$	$5 \times 10^{-22}$

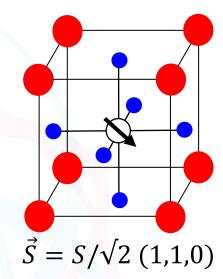
• We can have a non-zero "electric DMI", but it seems relatively small

- On the other hand, the <u>anisotropy energy</u> in ferroelectrics is (typically) much greater than in ferromagnets, and greater than the DMI
- Hence, a priori, non-collinear electric dipoles seem unlikely

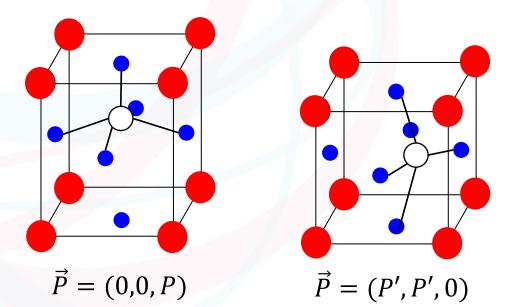
Zhao *et al.*, Nature Materials <u>20</u>, 341 (2021) Junquera *et al.*, Reviews of Modern Physics <u>95</u>, 025001 (2023)

#### A word about the anisotropy energy





On-site magnetic anisotropy comes from the spin-orbit interaction → relatively small



Polarization anisotropy comes from changes in chemical bonds & cell deformations

 $\rightarrow$  relatively large

#### So, is there a DMI for electric dipoles?

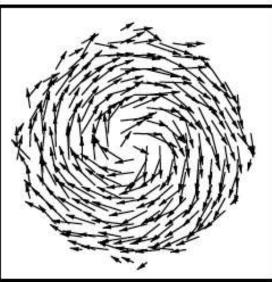
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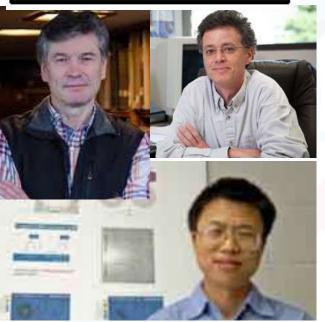
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- There is indeed a non-zero "electric DMI", but it seems relatively small
- On the other hand, the <u>anisotropy energy</u> in ferroelectrics is (typically) much greater than in ferromagnets, and greater than the DMI
- Hence, a priori, non-collinear electric dipoles seem unlikely

Zhao *et al.*, Nature Materials <u>20</u>, 341 (2021) Junquera *et al.*, Reviews of Modern Physics <u>95</u>, 025001 (2023)

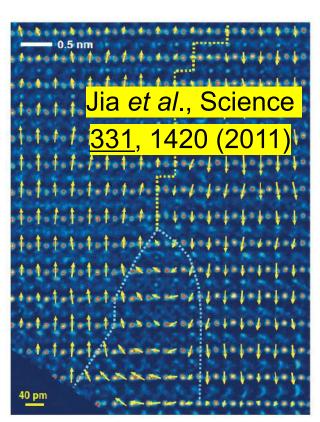
# And yet...





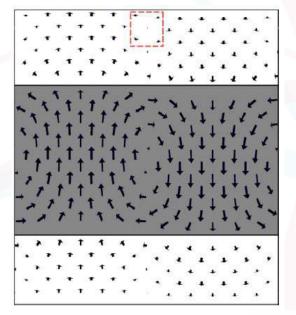
In 2004: Naumov *et al.* predicted <u>dipole</u> vortexes in ferroelectric nanorods ! In 2008: Aguado-Puente and Junquera (PRL <u>100</u>, 177601) predicted <u>closure</u> domains in ferroelectric ultrathin films

In 2011: Related experimental evidence from STEM !



# Then, PbTiO<sub>3</sub>/SrTiO<sub>3</sub> entered the picture

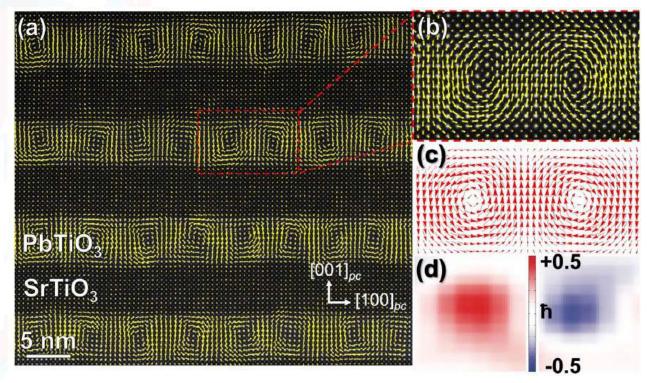
#### DFT prediction (2012)



Aguado-Puente & Junquera, PRB <u>85</u>, 184105 (2012)

consistent with experiments by Zubko *et al.* (e.g., Phys. Rev. Lett. 104, 187601 (2010))

#### Very famous experimental demonstration (2016)



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

#### So, how can we have non-collinear order after all...?

TABLE I. Orders of magnitude of the most relevant magnetic and electric interactions in typical magnetic and ferroelectric materials.

	Magnetic (J)	Electric (J)
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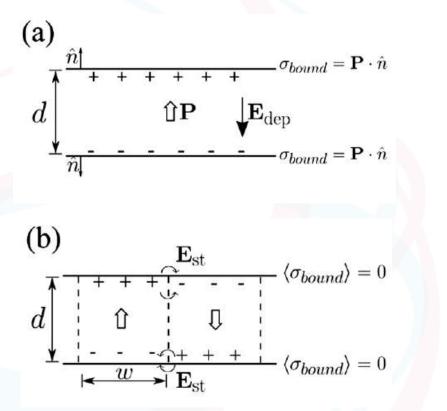
• Electrostatic dipole-dipole interactions dominate

• Everything else "adapts" in order to minimize electrostatic energy

• <u>Note:</u> By contrast, "magnetostatic" couplings are very weak. They play no significant role as regards skyrmion stabilization (usually, at least).

Junquera et al., Reviews of Modern Physics <u>95</u>, 025001 (2023)

#### Electrostatics in ferroelectrics, well known!



The "depolarizing field" (E<sub>dep</sub>) will typically "kill" the homogeneous polarization

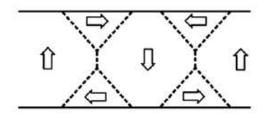
However,  $E_{dep}$  can be drastically reduced if the ferroelectric breaks into domains, so that only small "stray fields" ( $E_{st}$ ) remain

[Where the thickness of the domains (*w*) depends on the thickness of the layer (*d*) according to Kittel's law (Physical Review 70, 965 (1946))]

Junquera et al., Reviews of Modern Physics <u>95</u>, 025001 (2023)

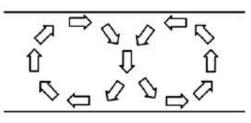
#### What about ultrathin ferroelectric films?

(c)



The stray fields can be further reduced by forming flux-closure domains

#### (d)

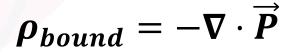


If the thickness of the layer is <u>very small</u>, we can even obtain dipole vortexes !

No polarization at the center of the domain wall / vortex !!

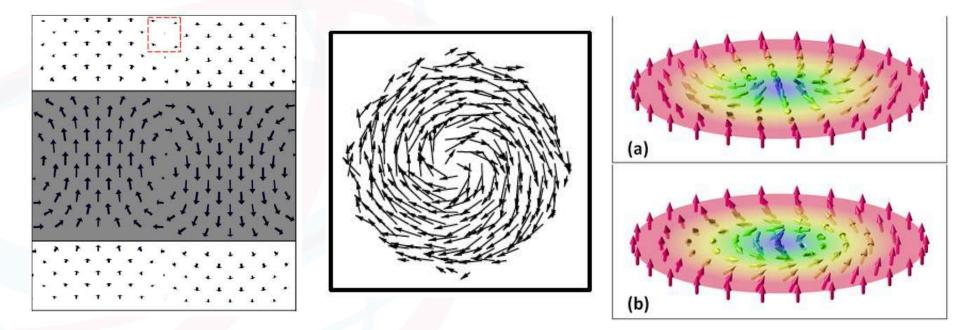
Junquera et al., Reviews of Modern Physics <u>95</u>, 025001 (2023)

#### [A word about these domains and domain walls]



#### This is great, but...

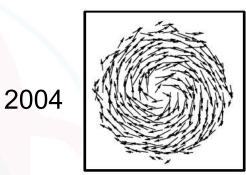
#### ... is there a skyrmion here?



(If not, what are we missing?)

# Theory → Experiment

Non-collinear electric dipoles



Vortex-like domain walls 2012

?

2011

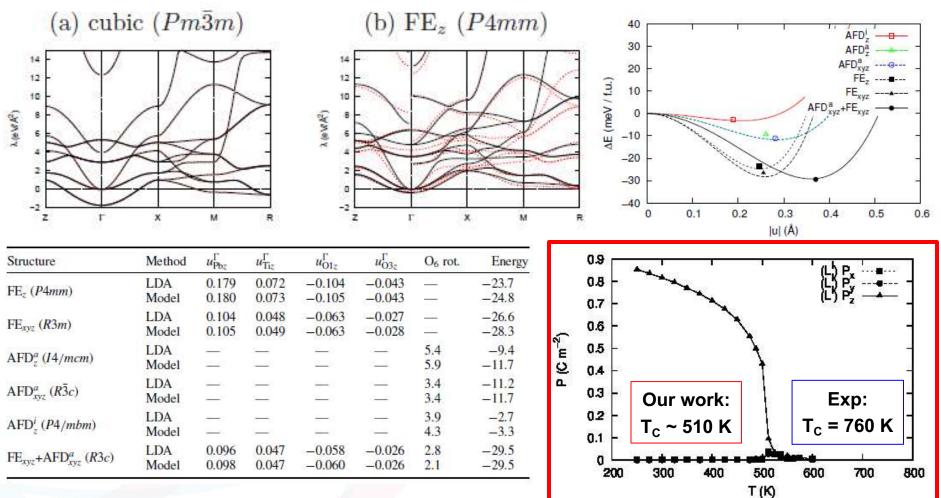
2016

?

Electric skyrmion



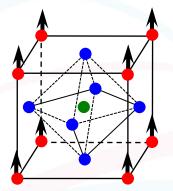
#### Second principles model for PbTiO<sub>3</sub> (and SrTiO<sub>3</sub>)



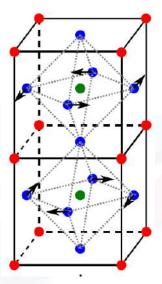
Displacements: Angstrom ; Rotations: degrees ; Energies: meV/f.u. **Excellent accuracy reproducing first-principles data** 

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

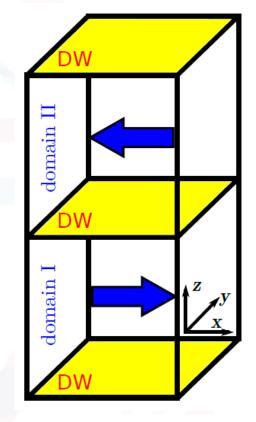
# Ferroelectric walls, expectations circa 2010

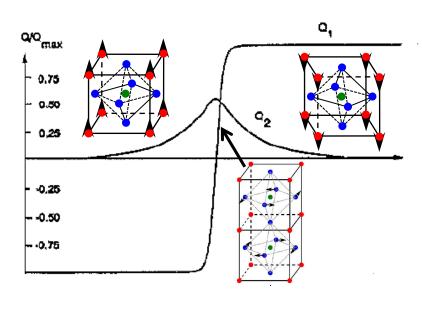


Ferroelectric polarization



Rotations of the O<sub>6</sub> octahedra

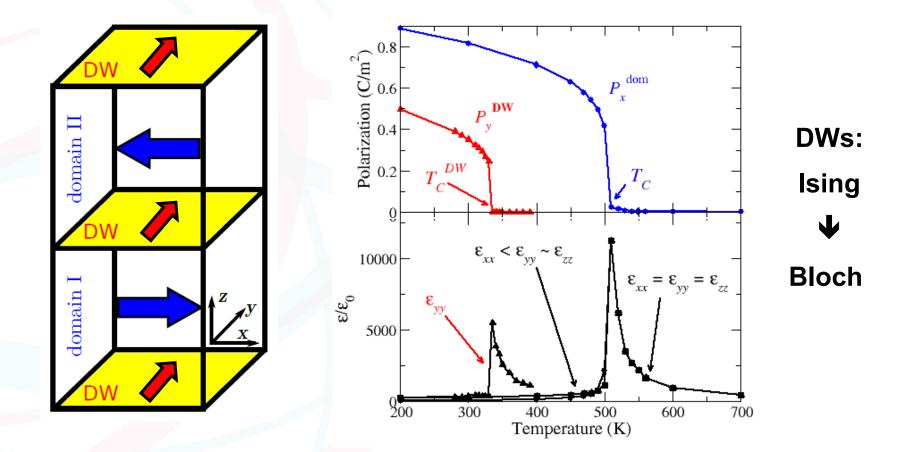




 $G = \frac{1}{2}\gamma_1 (\nabla Q_1)^2 + \frac{1}{2}\gamma_2 (\nabla Q_2)^2 + \frac{1}{2}A_1Q_1^2 + \frac{1}{4}B_1Q_1^4 + \frac{1}{2}A_2Q_2^2 + \frac{1}{4}B_2Q_2^4 + \lambda Q_1^2Q_2^2.$ 

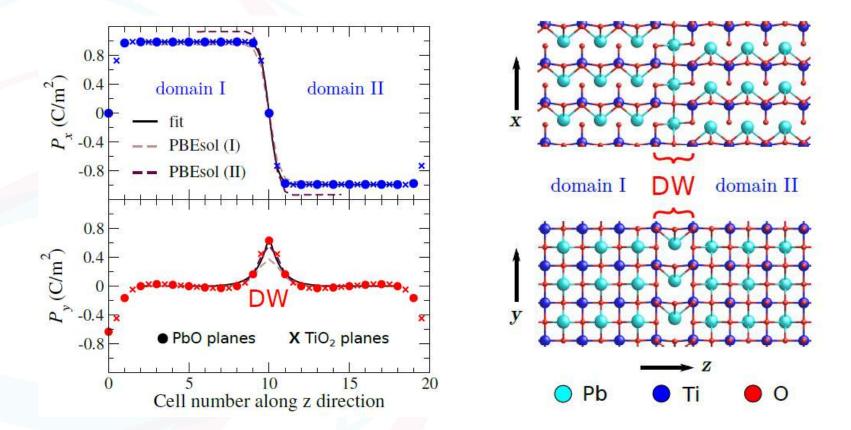
- Houchmandzadeh, Lajzerowicz & Salje, JPCM <u>3</u>, 5163 (1991).
- Lajzerovicz & Niez, J. Phys. Lett. <u>40</u>, L165 (1979).
- Tagantsev, Cross & Fousek, *Domains in Ferroic Crystals and Thin Films* (Springer, 2010).
- Taherinejad et al., Phys. Rev. B 86, 155138 (2012).
- Marton, Stepkova & Hlinka, Phase Transit. <u>86</u>, 103 (2013).

#### Ferroelectricity at ferroelectric domain walls



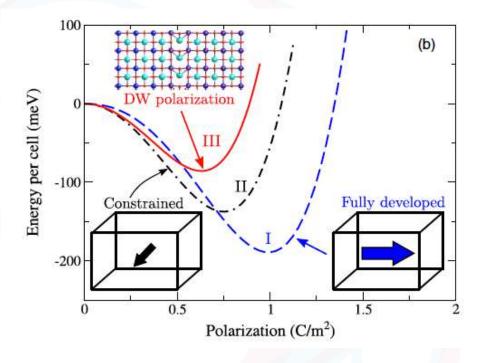
Wojdeł & Íñiguez, Phys. Rev. Lett. <u>112</u>, 247603 (2014)

# **Bloch DW, explicitly confirmed from DFT**



- Confirmed independently by other authors via DFT studies
- → Wang et al., JAP <u>116</u>, 224105 (2014); Liu & Cohen, JPCM <u>29</u>, 244003 (2017)
- Very similar to behavior predicted for DWs in BaTiO<sub>3</sub> [DFT, Phys. Rev. B <u>86</u>, 155138 (2012)] and SrTiO<sub>3</sub> [phenomenology, PRB <u>64</u>, 224107 (2001)]

# Why a DW polarization



- (I) Polarization well in bulk PbTiO<sub>3</sub>
- (II) Bulk-like polarization with unfavorable c/a (as at DW)
- (III) Polarization well at DW

In spite of unfavorable constraints (strain, dimensionality) PTO's ferroelectric instability active at DW

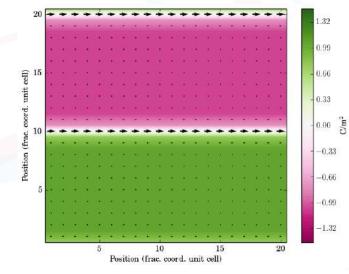
Phenomenological interpretation

 $G = \frac{1}{2}\gamma_1(\nabla Q_1)^2 + \frac{1}{2}\gamma_2(\nabla Q_2)^2 + \frac{1}{2}A_1Q_1^2 + \frac{1}{4}B_1Q_1^4 + \frac{1}{2}A_2Q_2^2 + \frac{1}{4}B_2Q_2^4 + \lambda Q_1^2Q_2^2.$ 

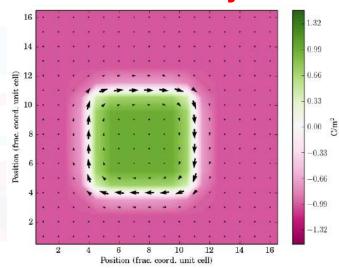
- $\blacktriangleright$  We usually think of Q<sub>1</sub> and Q<sub>2</sub> are two different distortions.
- > Here we have equivalent  $Q_1 = P_z$  and  $Q_2 = P_y$ ; they compete ( $\lambda > 0$ )
- Once Q<sub>1</sub> condenses to form domains, Q<sub>2</sub> effectively becomes the "weaker" order and occurs only at the walls

#### You can't always get what you want...

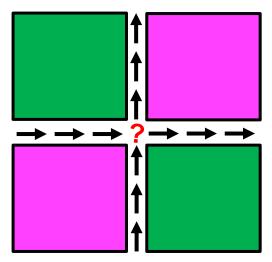
#### Ideal planar 180° DW in PbTiO<sub>3</sub>



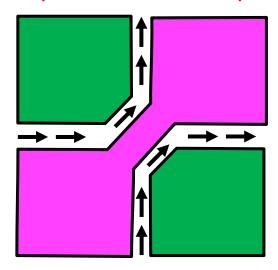
#### closed DW → skyrmion!



#### What happens in this case?



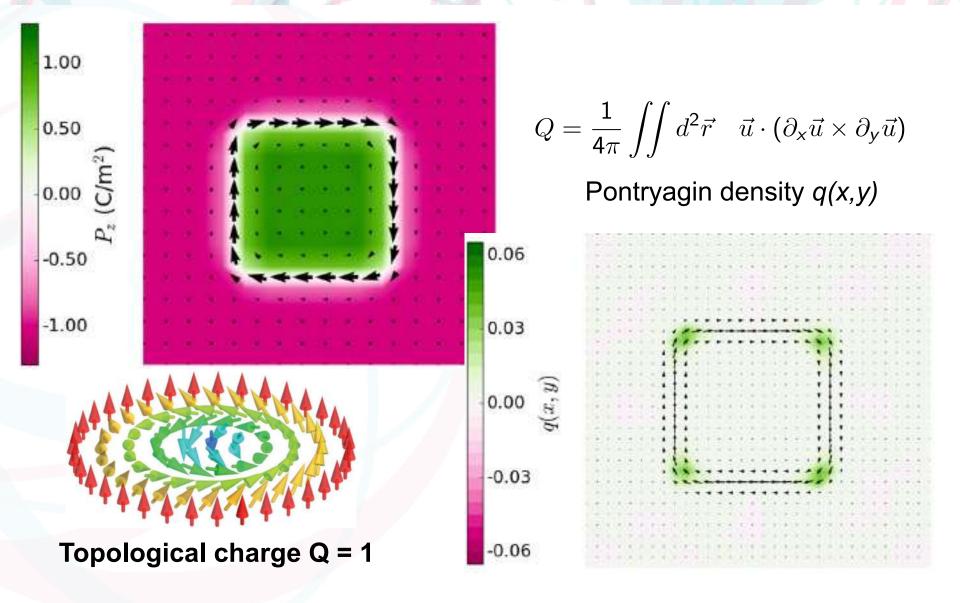
relaxes to... M



# **PRL (2014)**

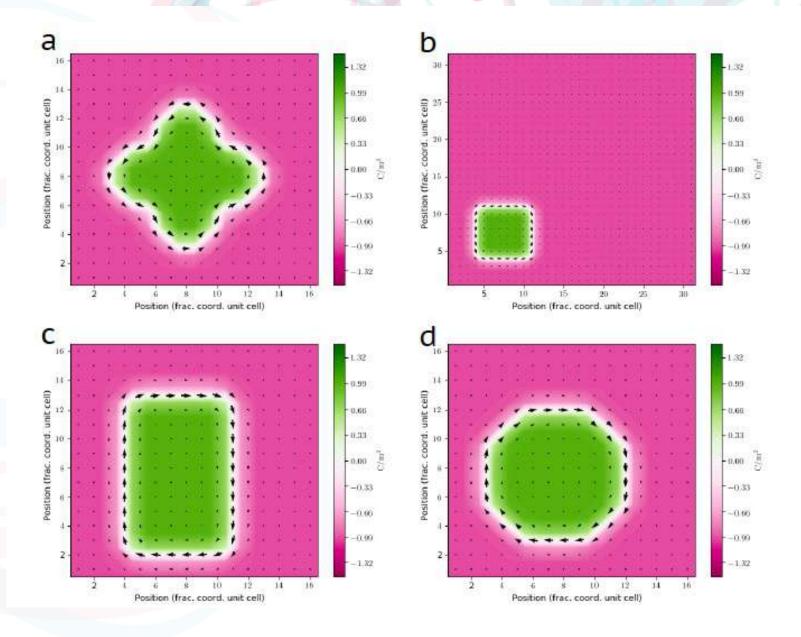
# Sci. Adv. (2019)

## It is a stable Bloch "skyrmion bubble"



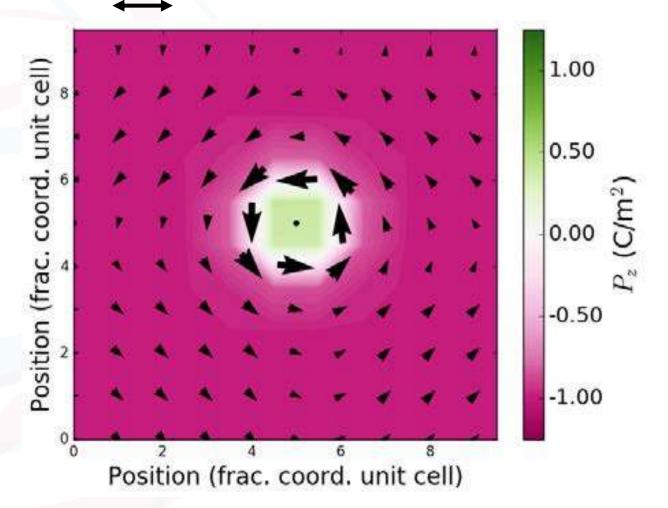
Gonçalves et al., Sci. Adv. 5, eaau7023 (2019)

# It is a stable Bloch "skyrmion bubble"

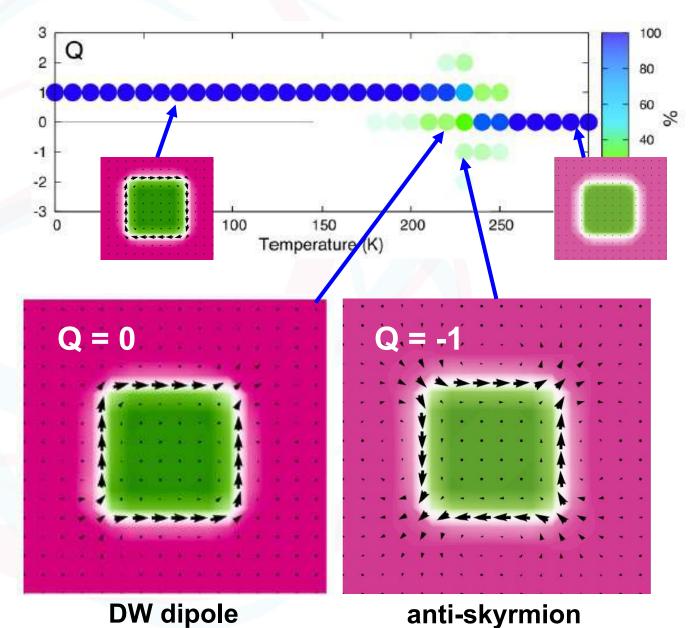


#### And it can be really very small !

~ 0.4 nm

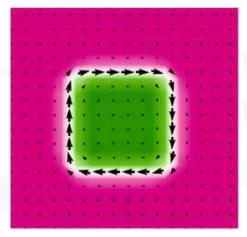


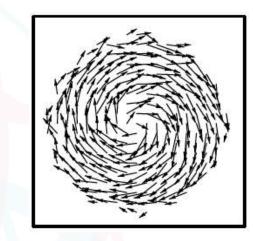
# Upon heating: $Q = 1 \rightarrow Q = 0$



- 1. Run Monte Carlo
- 2. Take snapshots
- 3. Cut 2D slice
- 4. Compute Q
- 5. Construct histogram

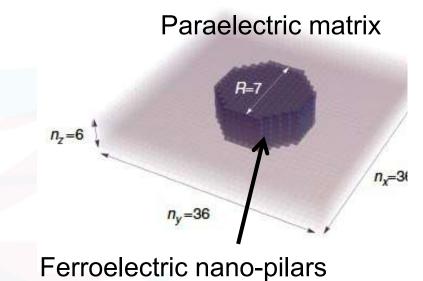
#### **Topologically equivalent to...**

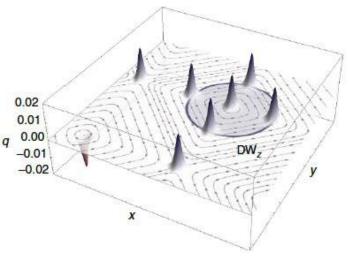




#### + out-of-plane polarization

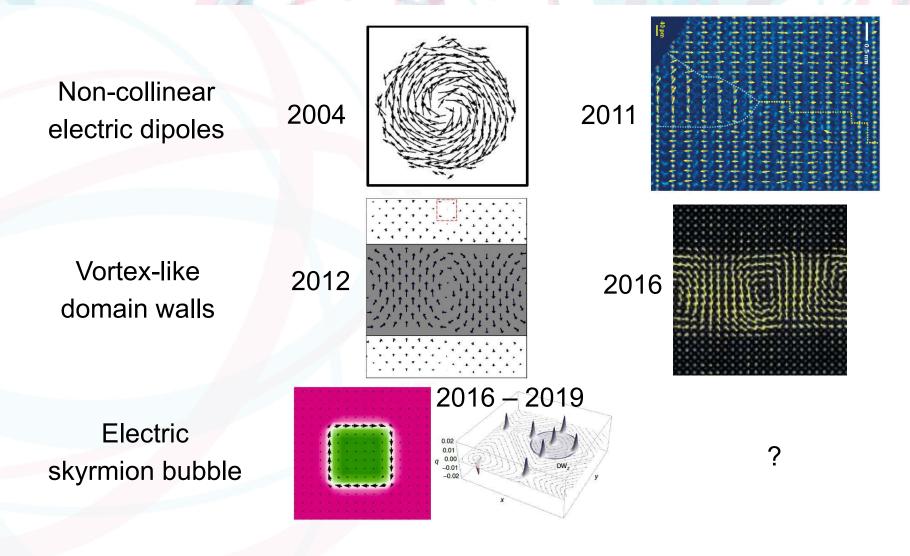






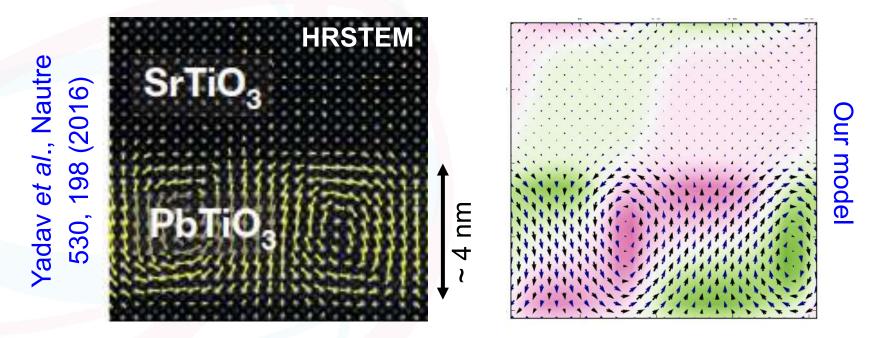
**Topological charge** 

#### **Theory vs Experiment**



#### Any experimental evidence for DW polarization?

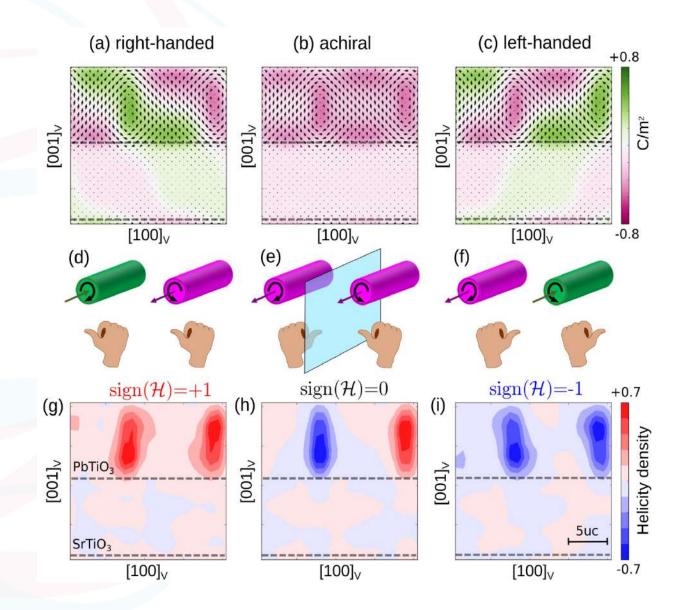
- Key feature (polarization at DWs of PbTiO<sub>3</sub>) is solid from first principles
- Temperature scale: main issue with our predictions
- Very difficult to measure directly



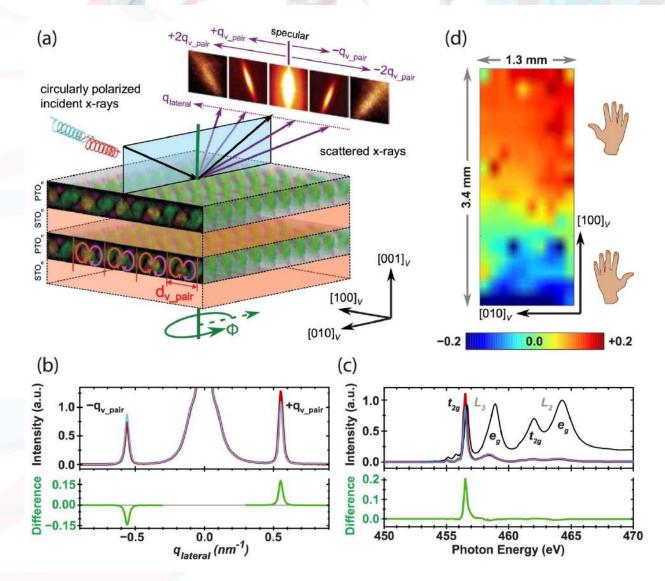
*Emergent chirality in the electric polarization texture of titanate superlattices,* Shafer *et al.*, PNAS <u>115</u>, 915 (2018)

- Damodaran *et al.*, Nat. Mats. <u>16</u>, 1003 (2017)
- Zubko *et al.*, PRL <u>104</u>, 187601 (2010); Aguado-Puente *et al.*, PRB <u>85</u>, 184105 (2012)

# Chirality in PbTiO<sub>3</sub>/SrTiO<sub>3</sub> superlattices



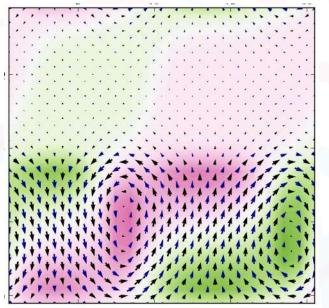
# **Chirality in PbTiO<sub>3</sub>/SrTiO<sub>3</sub> superlattices**

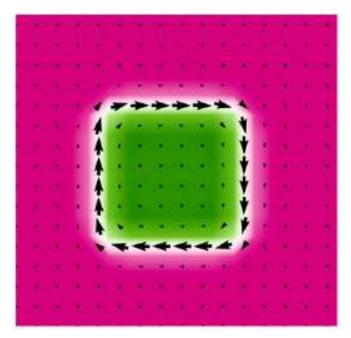


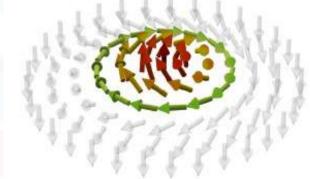
Experimental evidence of from resonant soft x-ray diffraction

## We are almost there, but...

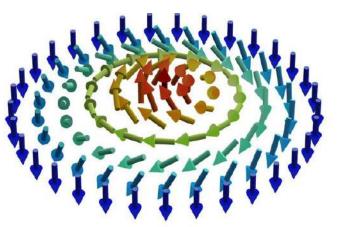
#### Is there a skyrmion here?







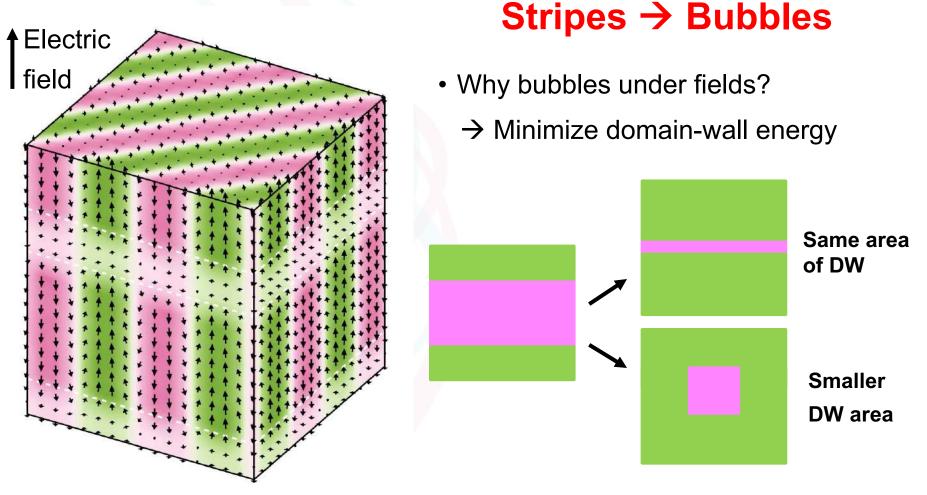
In fact, the "polarized vortexes" are "<u>merons</u>" with Q=1/2



[Meron figure taken from Shao et al., Nat. Comm. 14, 1355 (2023)]



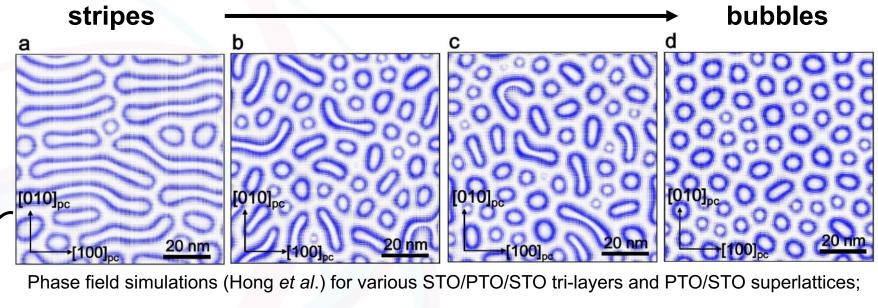
## The last step: breaking the stripes



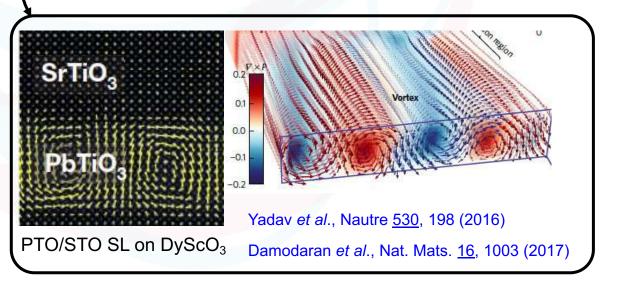
(Plus: bubbles favored by entropy)

Aramberri & Íñiguez (2023), https://arxiv.org/abs/2308.01716

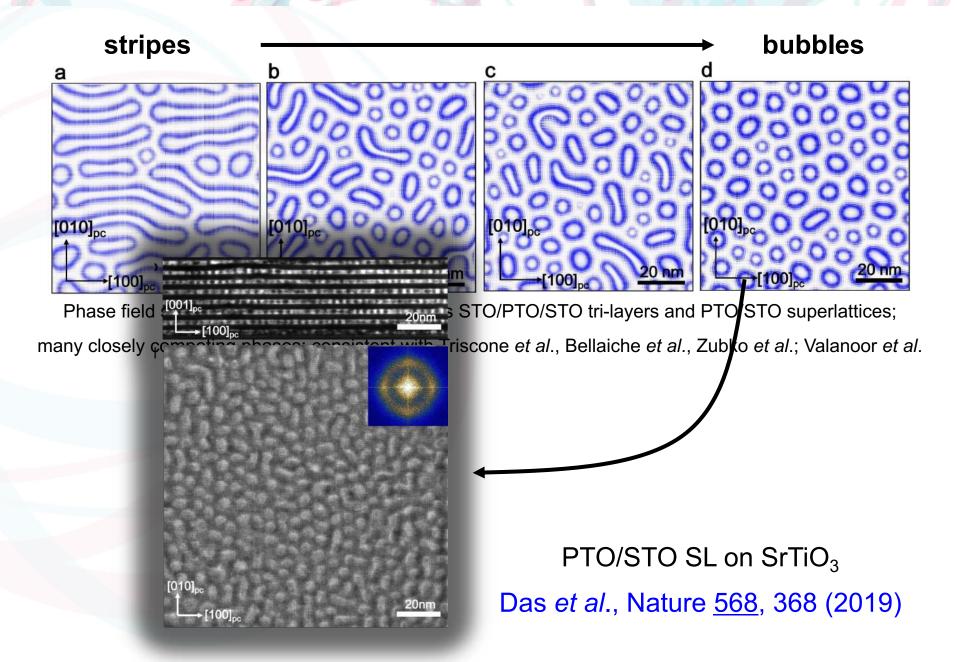
## A jungle of states to explore



many closely competing phases; consistent with Triscone et al., Bellaiche et al., Zubko et al.; Valanoor et al.

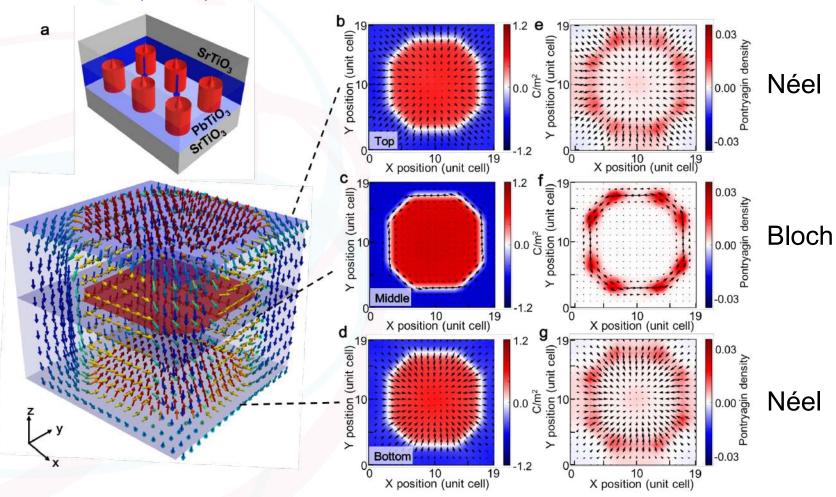


## A jungle of states to explore



#### **Second-principles simualtions**

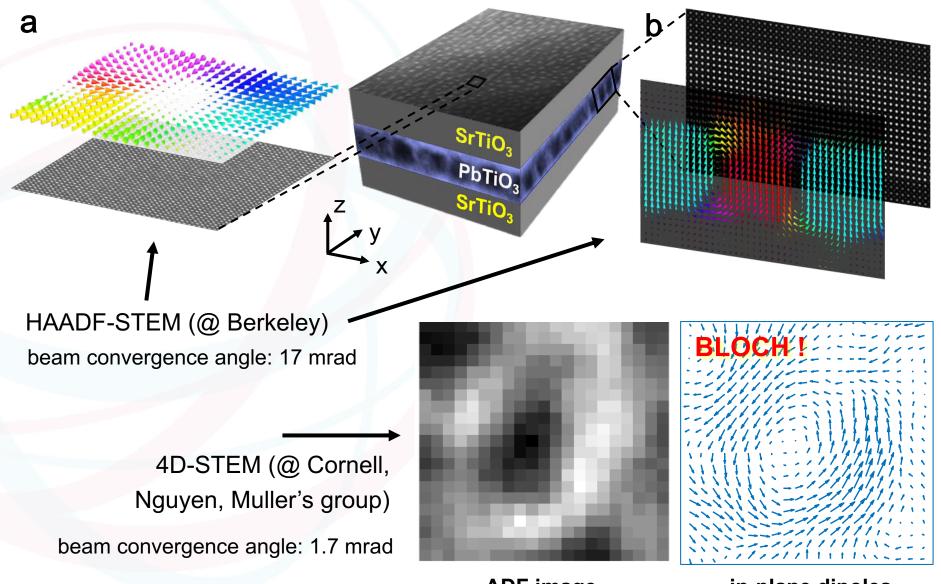
#### Das et al., Nature (2019)



- Topological number is Q=1 all along the column domain
- Character varies (Néel → Bloch → Néel) as we move along

# **STEM studies of PTO/STO on STO**

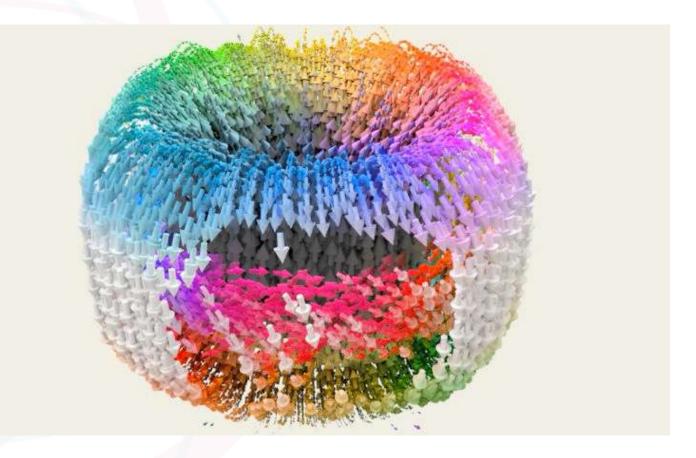
#### Das et al., Nature (2019)



**ADF** image

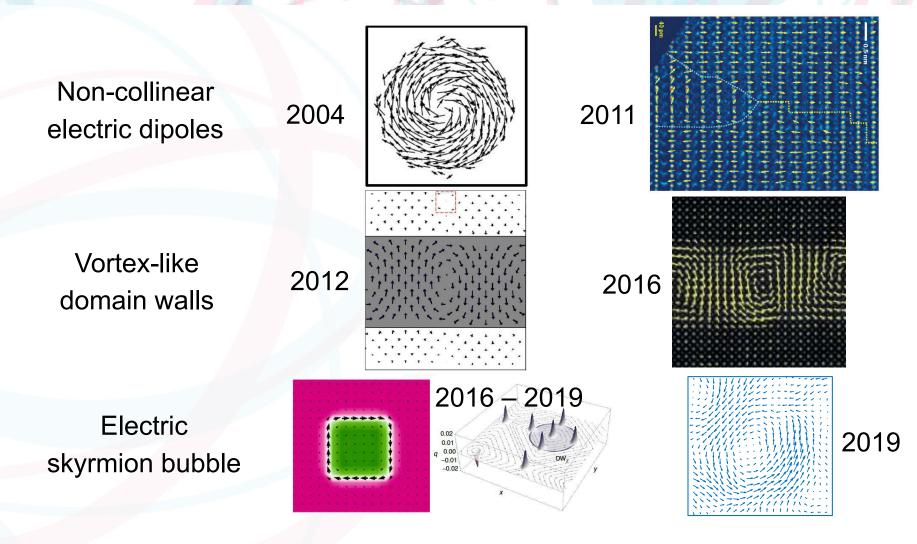
in-plane dipoles

# A little movie from the simulation data



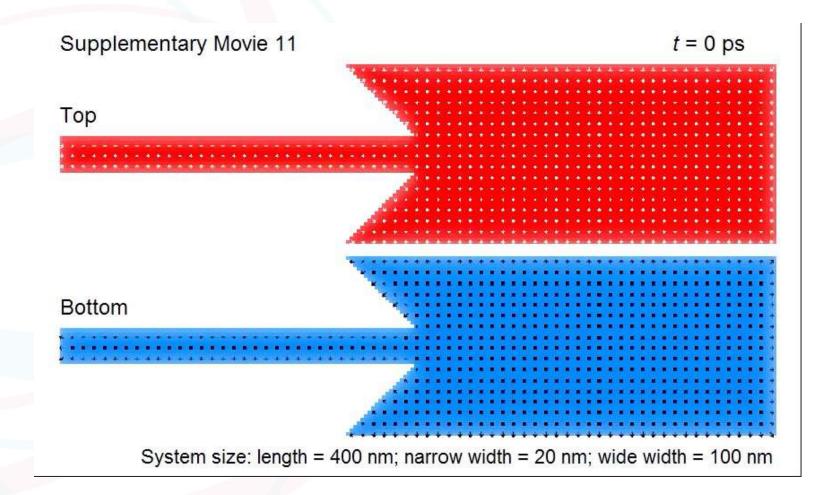
Das et al., Nature (2019)

# **Theory vs Experiment**

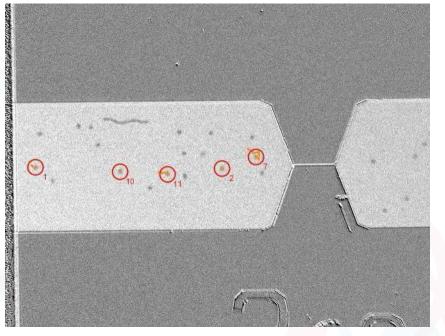




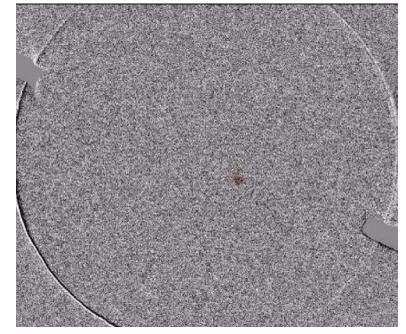
## What strikes you about these images?



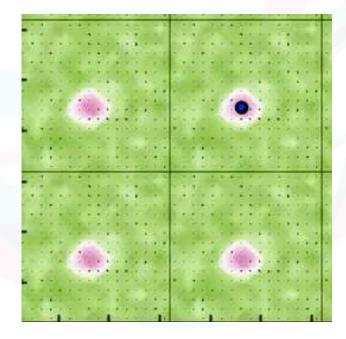
Zhang et al., Nature Communications 7, 10293 (2016)

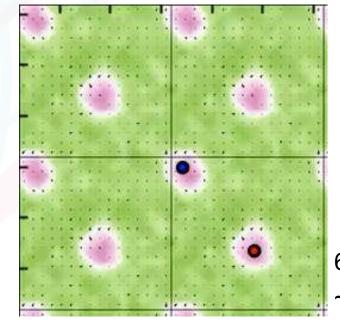


Zázvorka et al., Nat. Nano <u>14</u>, 658 (2019)



Zhao et al., PRL <u>125</u>, 027206 (2020)

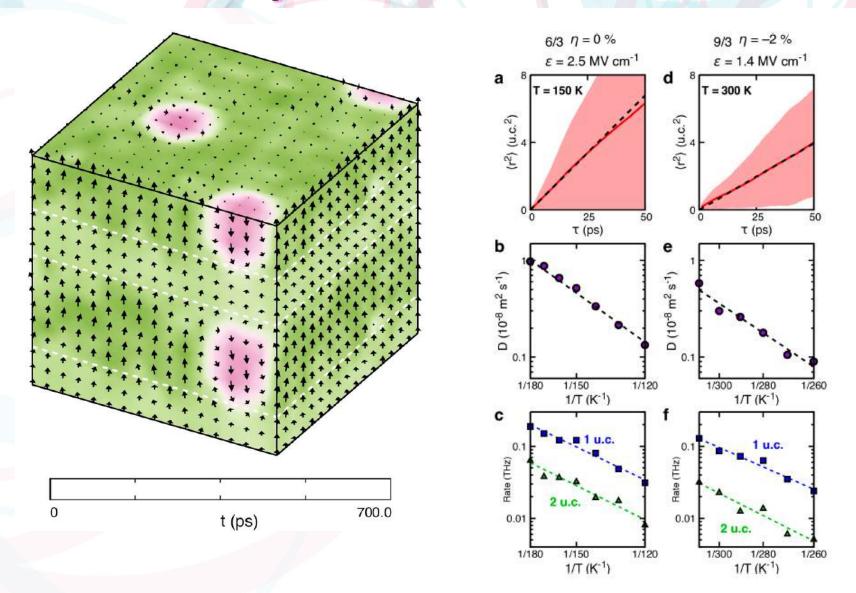




Aramberri & Íñiguez, arXiv (2023)

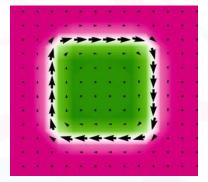
6/3 SL @ 150 K ~ 2 MV/cm

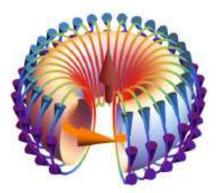
#### **Brownian dynamics of electric bubbles**



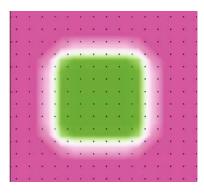
Aramberri & Íñiguez (2023), https://arxiv.org/abs/2308.01716

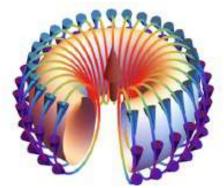
# Are these particles "topological"?





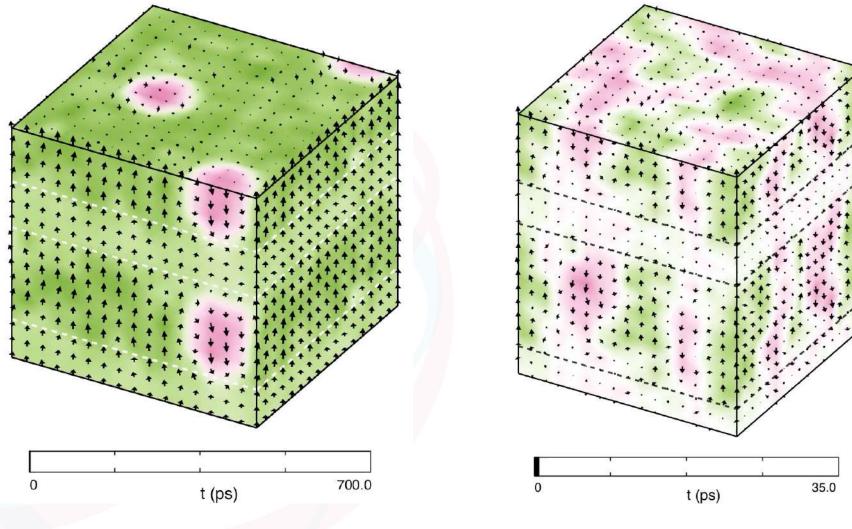
Low temperature Static Bloch & Nèel features





<u>High temperature</u> Mobile Only Nèel features

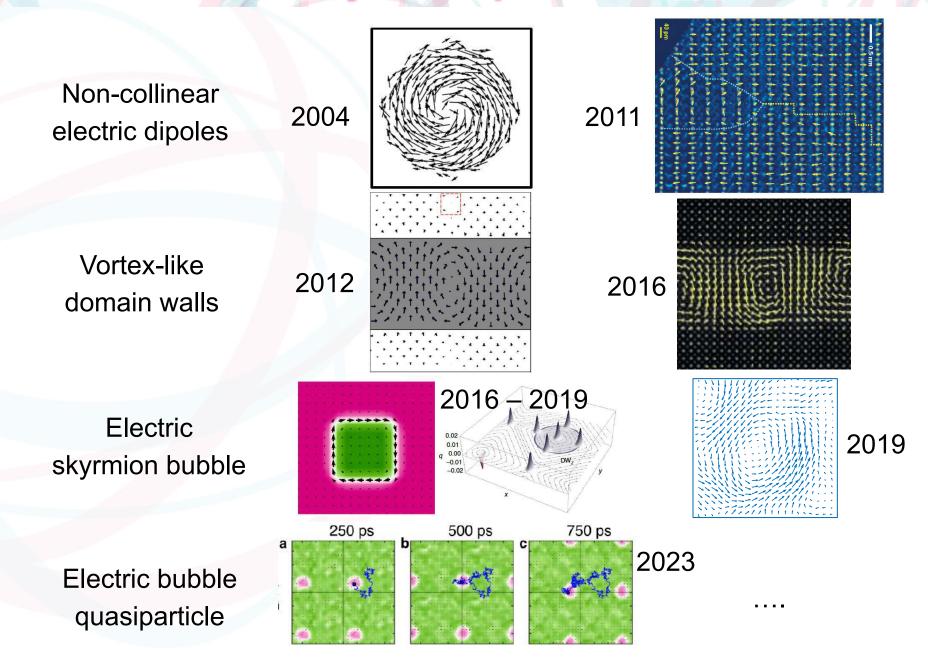




Aramberri & Íñiguez (2023)

Zubko et al. (2016)

## **Theory vs Experiment**



# So, how big a deal is this?

#### • If you are interested in chirality, toroidicity, etc.

- → Require arrangements typical of skyrmions, vortices (topological)
- → Although similar non-topological arrangements (merons) can also present such properties.
  Shafer (2018) Das (2019)
- If you are interested in (other) functional properties...

→ Negative capacitance: both topo and non-topo

Zubko (2016) Das (2021)

→ Tunable ~ THz: non-topo ✓ ; topo <sup>(1)</sup> Li (2021)

#### If you are interested in the particle-like behavior

→ You definitely want skyrmion-like (i.e., bubble-like) objects...

 $\rightarrow$  ... which may well be topological

Aramberri (2023)



# Word on the street !

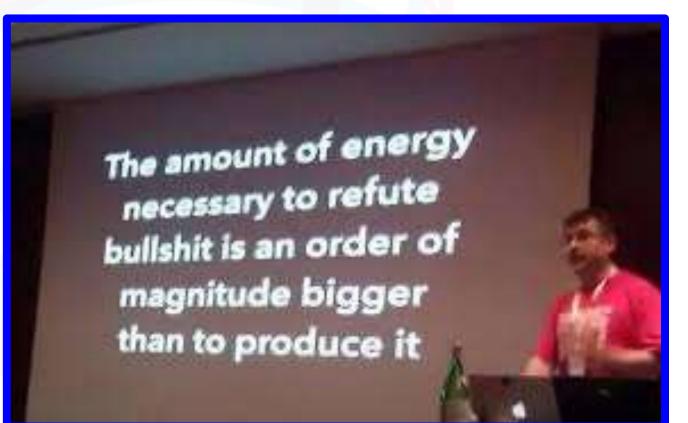
- "All phase transitions involve a change in topology"
- "Skyrmions are very stable because they are topologically protected"
- "Non-topological states cannot be stable"
- "The occurrence of skyrmions requires interactions of the Dzyaloshinsky-Moriya type"
- "All topological states are chiral"
- "All chiral states are topological"
- "Skyrmions and anti-skyrmions cannot coexist (for long times) because they annihilate each other"
- "We can expect many functional properties to be exclusive of electric skyrmions"

# Bastiat (1845), Brandolini (2013)

"[...] nos adversaires dans la discussion ont sur nous un avantage signalé. Ils peuvent en quelques mots exposer une vérité incomplète ; et, pour montrer qu'elle est incomplète, il nous faut de longues et arides dissertations."

Frédéric Bastiat, Sophismes Économiques (1845)

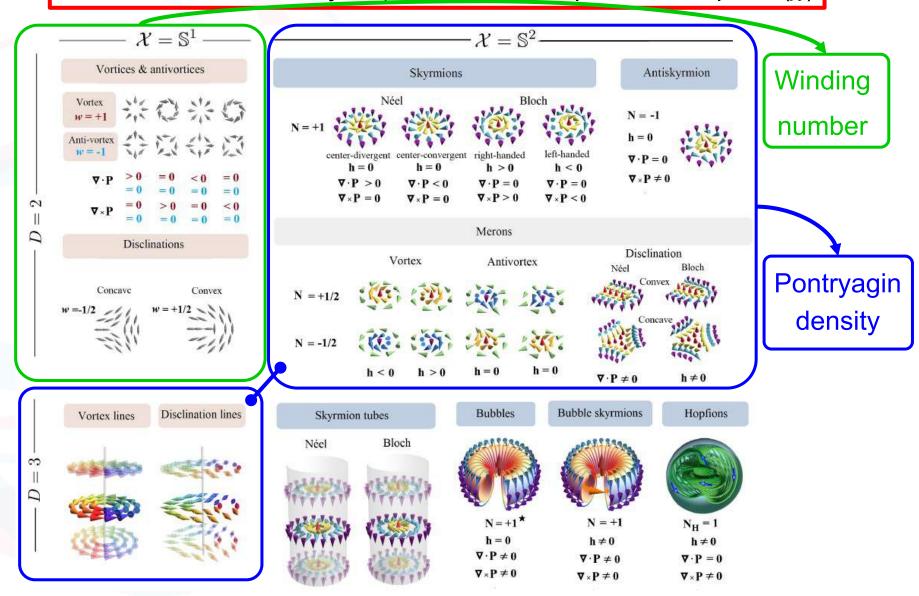
Reported independently in 2013 as the "bullshit asymmetry principle"



https://en.wikipedia. org/wiki/Brandolini% 27s\_law

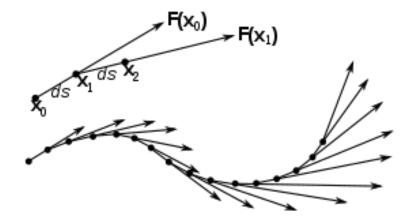
# How to chose your topological invariant?

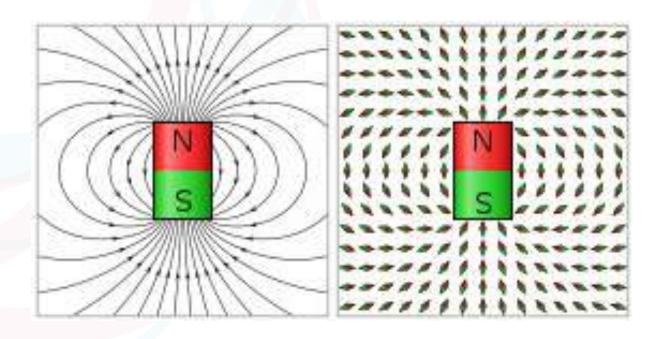
Dimension of the object (D), of the order parameter space ( $\chi$ )



#### **Topology: counting and describing singularities**

First, a word about "field lines"





#### https://en.wikipedia.org/wiki/Field\_line

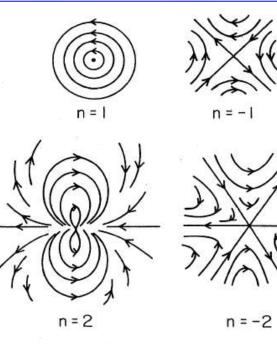


FIG. 1. Point singularities of planar spins in two dimensions with winding numbers  $\pm 1$  and  $\pm 2$ .

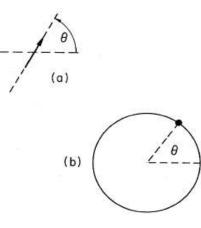
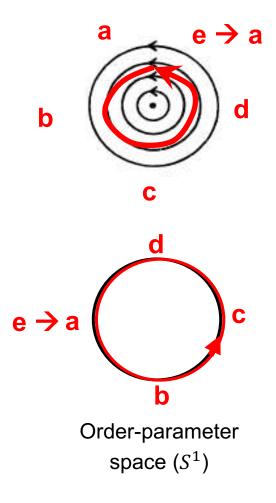


FIG. 3. (a) A planar spin in a given orientation. (b) The representation of that orientation by a point in the order-parameter space.



$$w = \frac{1}{2\pi} \oint d\theta = +1$$

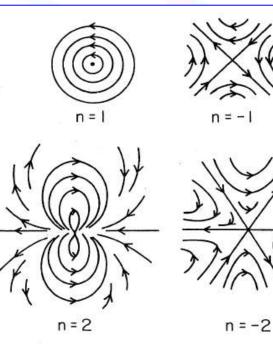


FIG. 1. Point singularities of planar spins in two dimensions with winding numbers  $\pm 1$  and  $\pm 2$ .

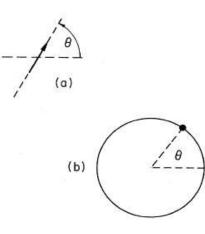
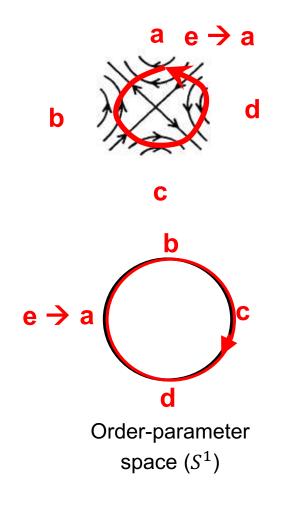
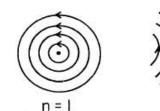


FIG. 3. (a) A planar spin in a given orientation. (b) The representation of that orientation by a point in the order-parameter space.

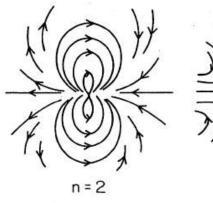


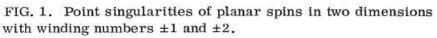
$$w = \frac{1}{2\pi} \oint d\theta = -1$$





n = -2





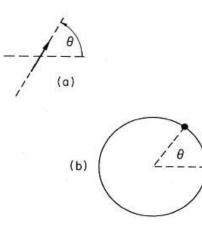
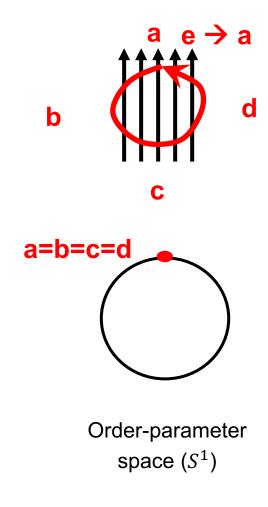
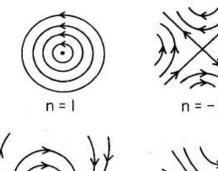


FIG. 3. (a) A planar spin in a given orientation.(b) The representation of that orientation by a point in the order-parameter space.



$$w = \frac{1}{2\pi} \oint d\theta = 0$$



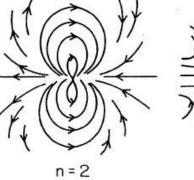


FIG. 1. Point singularities of planar spins in two dimensions with winding numbers  $\pm 1$  and  $\pm 2$ .

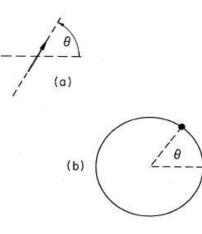


FIG. 3. (a) A planar spin in a given orientation.(b) The representation of that orientation by a point in the order-parameter space.

n = -2

Order-parameter space (S<sup>1</sup>)

$$w = \frac{1}{2\pi} \oint d\theta = 0$$

## The "defect" is always detected

Provided we have a well-behaved field, we get the same winding number for <u>any</u> path circling the singularity(ies).

 $\rightarrow$  The field "remembers" the singularity even very far from it.

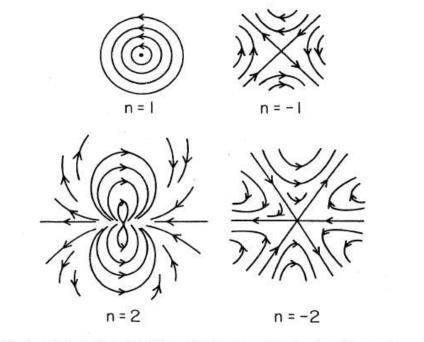
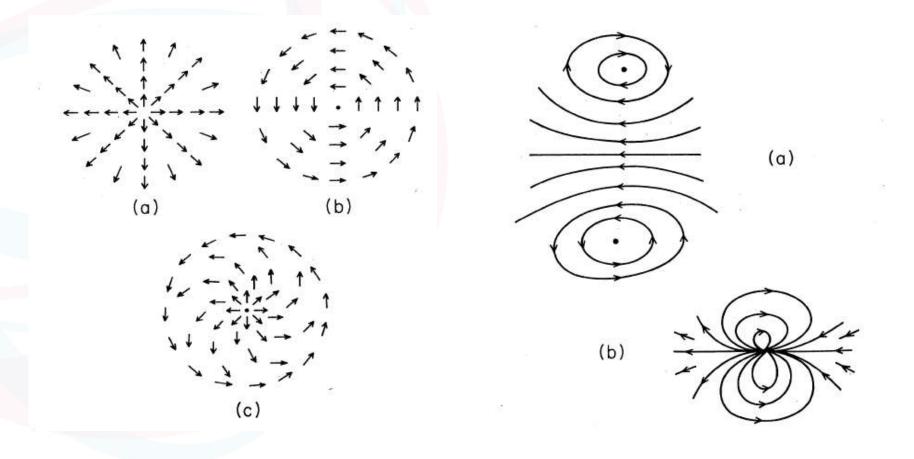


FIG. 1. Point singularities of planar spins in two dimensions with winding numbers  $\pm 1$  and  $\pm 2$ .

# **Topological equivalence**

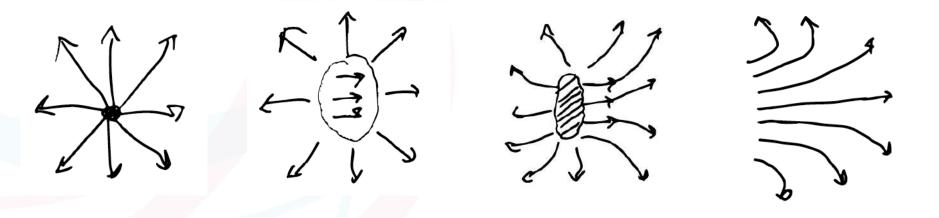
Singularities with the same topological number can be deformed into each other while the topological number stays the same at all times  $\rightarrow$  They belong to the same "homotopy class".



# **"Topological protection" (I)**

In contrast: a singularity Q cannot be removed without altering the field at distances arbitrarily remote from original Q

- $\rightarrow$  We can safely assume that such a situation will cost some energy
- → Topological protection !



w = +1

w = 0

# "Topological protection" (II)

#### **Topology does not know anything about interactions / energy**

(1) "All topological states are topologically protected" ???

(2) "... An energy barrier needs to be overcome in order to eliminate a topological state."

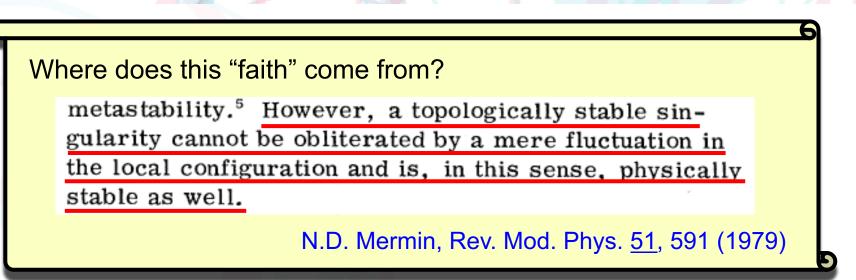
(3) "... This implies that all topological states are minima of the energy"

**Counter-example**: whenever the anisotropy energy  $(K > 0, |K| \gg |D|)$ dominates, skyrmion-like arrangement is a local maximum of energy.

Not true!

 $\uparrow \longrightarrow \downarrow$  $E \approx -2KS^2$  $E \approx -3KS^2$  $E \approx -2.5KS^2$ 

# **"Topological protection" (III)**

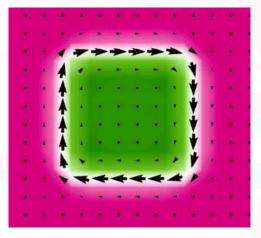


#### A safer (though hardly impressive) statement:

"Provided a (stable) topological singularity exist as a (meta)stable state, we will need to overcome an energy barrier in order to obliterate it and eliminate the topology."

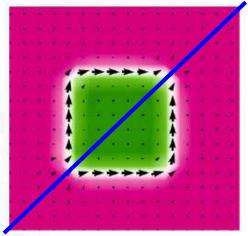
**<u>Bottomline</u>**: stability is all about the interactions, energy...

# **Topology** → Chirality ?



Bloch skyrmion

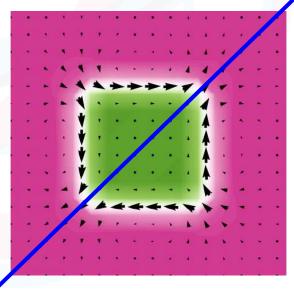
Topological and chiral



mirror plane

"polar bubble"

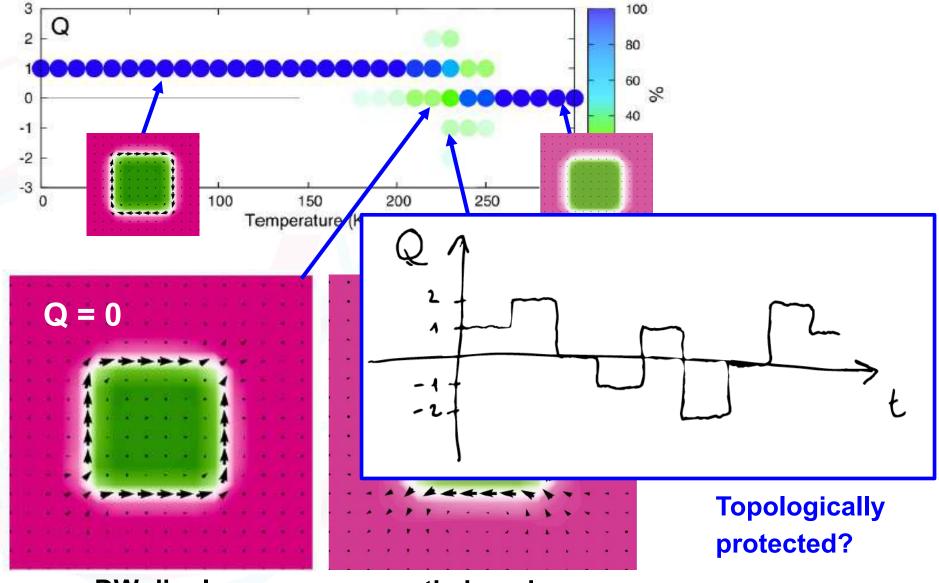
Non-topological and non-chiral



What about this anti-skyrmion?

**Topological and non-chiral** 

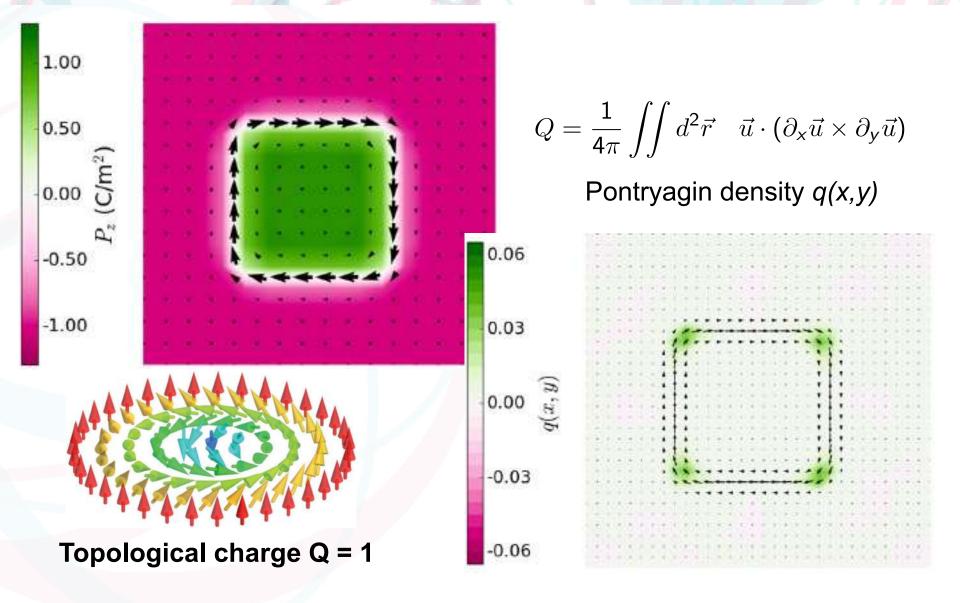
## **Specific of ferroelectrics: protection?**



**DW** dipole

anti-skyrmion

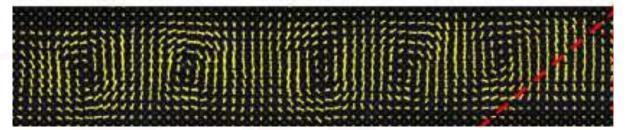
#### **Specific of ferroelectrics: quantized?**

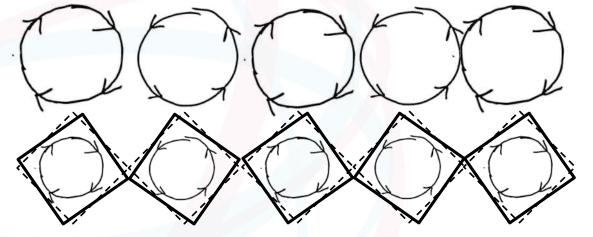


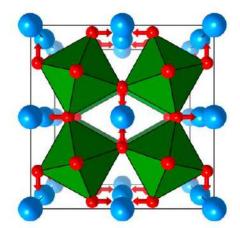
Gonçalves et al., Sci. Adv. 5, eaau7023 (2019)

# **Specific of ferroelectrics: quantized?**

# Is there a DMI in perovskite oxides?



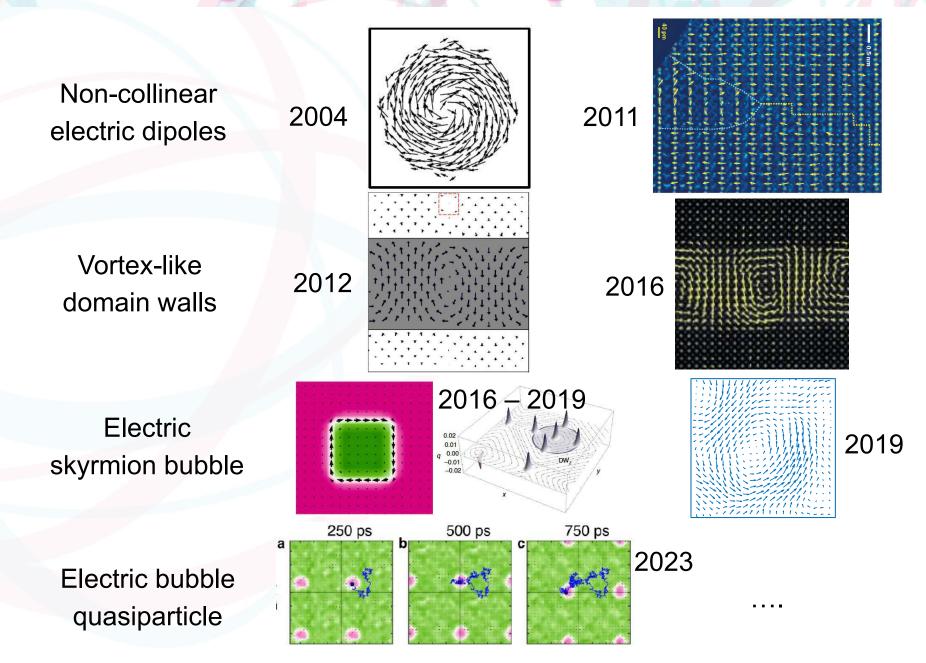


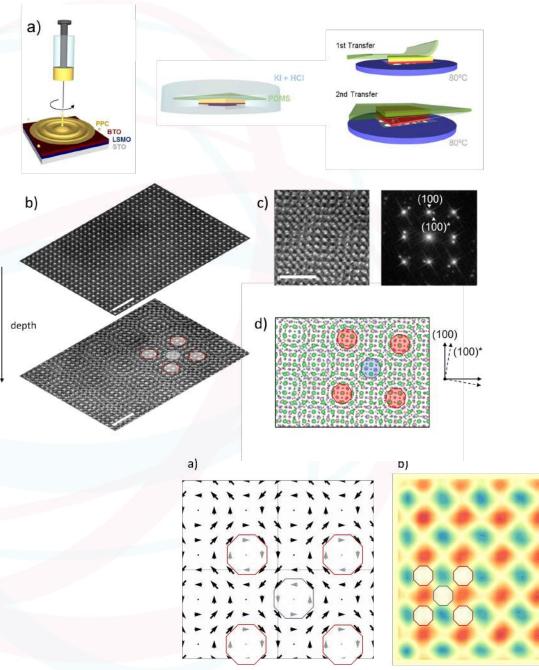




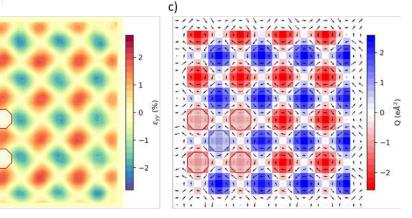


## Can't get more exciting than this !!





#### Sánchez-Santolino et al., https://arxiv.org/abs/2301.04438



# Thank you for your attention!