

Unraveling Hidden Order and Dynamics in a Heterogeneous Ferroelectric System Using Machine Learning

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Challenge Science Domain: Material Science

Ferroelectrics are materials that have spontaneous electric polarization – which characterizes a well-defined state of the material system, that can be switched by an applied external electric-field. Existence of a spontaneous polarization implies that the ferroelectric material shows a hysteretic response to the applied field, ideal for use as a memory function, in a ferroelectric random-access memory (FeRAM) device. Real materials are not pure – they have point-and extended-defects, buried-interfaces as well as domain-walls (i.e. spatial discontinuity in the local polarization vector). In the presence of heterogeneities, in addition to the global order-parameter (i.e overall spontaneous polarization of the material) there are additional manifestations on the local order-parameter (local polarization), that lead to ‘hidden’ order in the material. As an example, interfaces of different ferroelectric thin-films can show chiral polarization loops, whose formation, stability and motion are not only governed by material properties, but also topological properties. We find that the shape as well as the area of the hysteresis loops are strongly modified by such ‘hidden’ order. Further, the dynamics of ferroelectric switching are also significantly modified in the presence of such ‘hidden’ order in heterogeneous ferroelectrics. We are specifically interested in discovering such ‘hidden’ order from molecular dynamics simulations and correlate them with the type of heterogeneities present in the simulation, and ascertain how this order influences not just the memory function, but also its ‘dynamics’ under externally applied field. Dynamic control of memory is the basis of ferroelectric based neuromorphic materials.

We provided the files with local polarization for a length of time for all datasets:
Local polarization P_u of each unit cell (shown in figure below) was calculated using:

$$P_u(t) = 1/V_u(Z_{Ti}^*r_{Ti}(t) + \frac{1}{8}Z_{Ba}^* \sum_{i=1}^8 r_{Ba,i}(t) + \frac{1}{2}Z_O^* \sum_{i=1}^6 r_{O,i}(t))$$

where V_u is the volume of the unit cell, Z_{Ti}^* , Z_{Ba}^* , Z_O^* are the charges of the Ti, Ba and O atoms obtained using the Electron Equilibration Method (EEM) approach using a reactive force field (ReaxFF), and $r_{Ti}(t)$, $r_{Ba,i}(t)$, $r_{O,i}(t)$ are the positions of the Ti, Ba and O atoms of each unit cell at time t [1].

A)

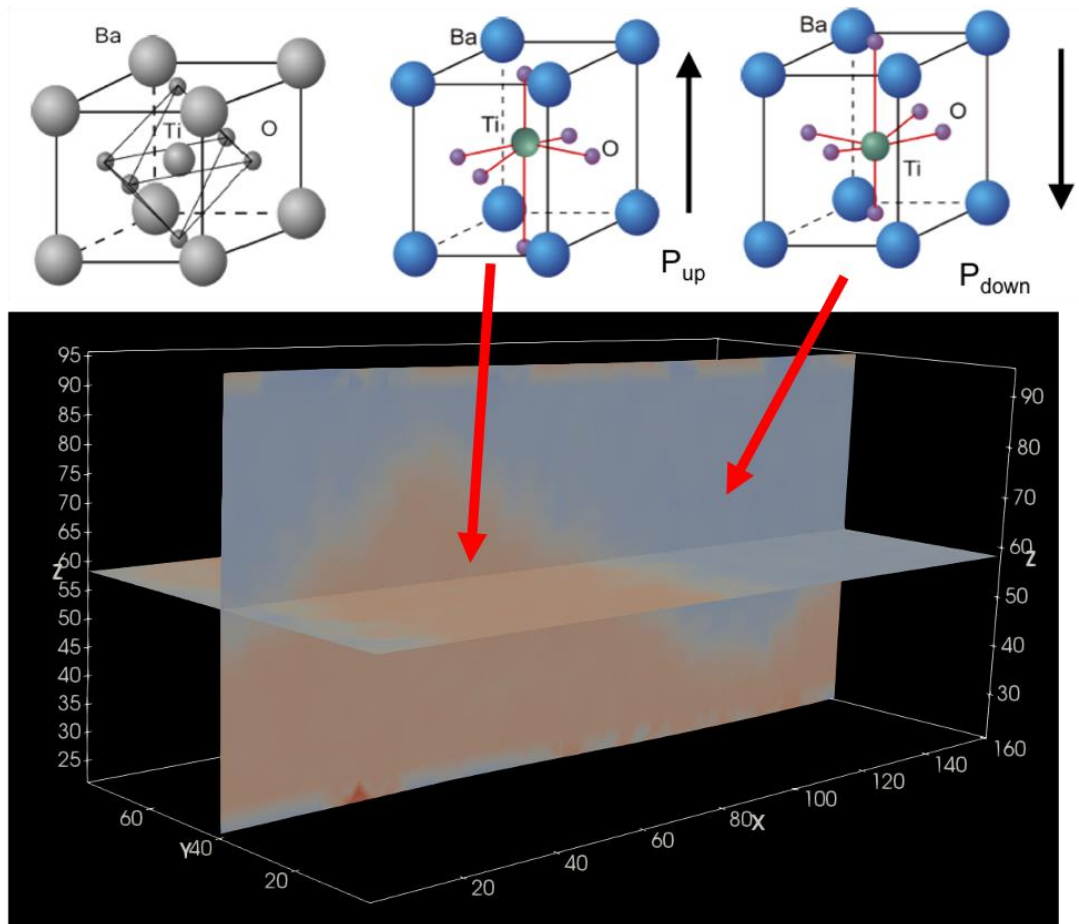


Figure A Unit cell schematic of the BaTiO₃ (top), for the case with zero-polarization, polarization pointing UP and polarization pointing DOWN, respectively. The bottom figure, generated by PARAVIEW, is a snapshot from the molecular dynamics (i.e. time-series data of local polarization), where the UP regions show up as orange, and DOWN regions as blue. The domain-wall i.e. the interface between the UP/DOWN region should have different dynamics than the rest [2]

B)

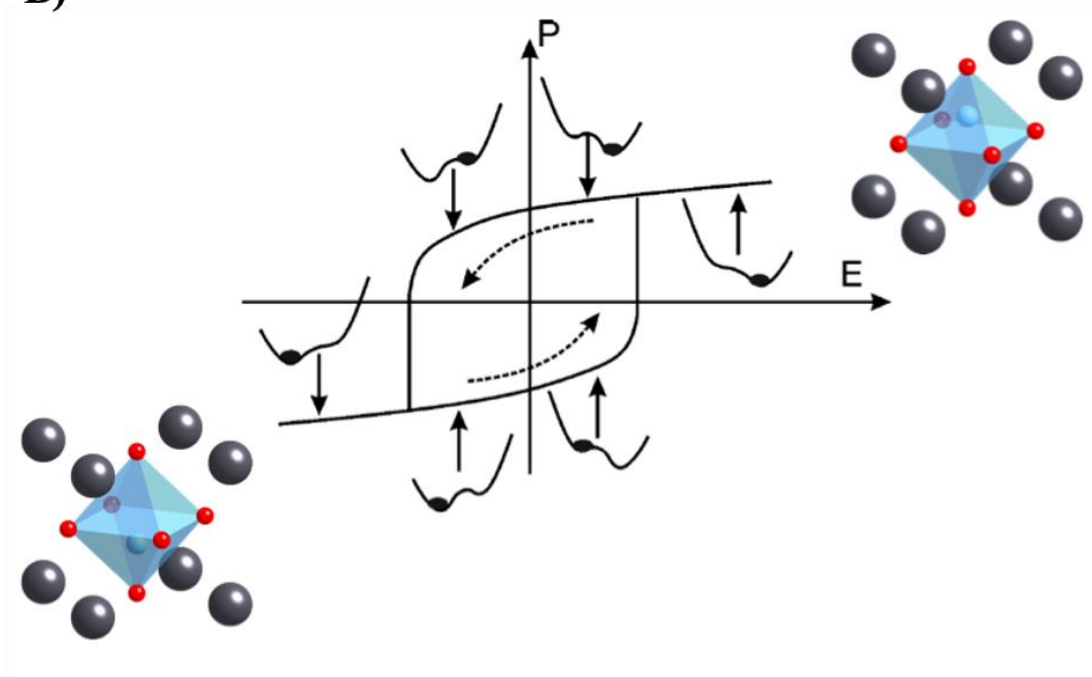


Figure B shows the hysteric response of BaTiO_3 to an applied electric field. It is not clear how domain wall dynamics differ for different heterogeneities, and control the shape of this loop [2]

The relative atomic motion of Ti-atom as shown in fig. (A) determines the unit cell's local polarization for a given system. Orange and blue regions are two different symmetric ‘domains’ – domain with P_{up} and P_{down} respectively, with a domain-wall between them. Under an electric-field, say one pointing up, the domain-wall moves so as to increase the fraction of UP domains. At a particular electric-field, all domains (or almost all) will be converted to a single UP domain. Reversal of the electric-field will result in an increase in the DOWN domain fraction, and the total polarization pointing up will reduce in magnitude till the macroscopic polarization is flipped. Interestingly, a plot of the total polarization of the box, when as a function of the electric-field, does not show perfect reversible motion – one sees a so-called hysteresis loop, as shown in fig. (B) – where a change in the total polarization depends on which state it started from, and in which direction the field was applied. This motion (i.e., kinetics and dynamics) of domain walls under fields can be different heterogeneities, such as defects, are present. While in a static snapshot of the local polarization at an instant in time, as shown in fig. (A) above, one only sees two domains, different parts of the same domain could show different dynamics as well as kinetics. We want to identify how many different such ‘dynamical’ states (i.e., regions with different dynamics) exist in our MD simulation when it is in equilibrium? How do these dynamical states evolve under an applied electric-field? How are these dynamical states modified in the presence of heterogeneities thereby leading to a change in the hysteric response?

The current state-of-the-art methods to extract dynamical information from molecular dynamics simulations combine Koopman’s operator theory of dynamical systems [3] or methods such as dynamic mode decomposition (DMD) [4] with Variational autoencoders (VAEs) and Time-lagged

independent component analysis (TICA)[5]. We are interested in extending the current state-of-the-art approaches to identify dynamical states in hysteretic solids.

Datasets:

DATASET LINK : https://drive.google.com/drive/folders/1W62AFI-q-xC_aTkJeh1RxGt3-MHBXEN?usp=sharing

We uploaded two batches of datasets: Batch-a) Equilibrium dynamics at a constant temperature at zero electric-field, with one trajectory each for 4-different defect structures (i.e. SETs 1 to 4). Each trajectory has a time-step of 0.25 fs, and is run for 7775000 time-steps, with snapshots written out every 4 time-steps (i.e. every 1fs); and Batch-b) Non-Equilibrium dynamics at a constant temperature with the same 0.25 fs time-step, but data dumped every 500 times-steps (i.e. every 125fs) for each of the SETs. The total trajectory of each defect structure (i.e. each SETs 1 to 4) is 2800000 time-steps (5600 snapshots), with stepping of electric-field by 0.01 V/Å, after every 100,000 time-steps (i.e. every 200 snapshots), from E=0 to E=0.05 V/Å to E = -0.05 V/Å to E=0.05 V/Å.

Datasets divided into two subsets (a) and (b), each contains different types of defects:

(a) Equilibrium Dynamics	SET1 (no defects)	VTKFILES, LOCAL_DIPOLE_FILES
	SET2 (with Ov defect)	VTKFILES, LOCAL_DIPOLE_FILES
	SET3 (with Bav defect)	VTKFILES, LOCAL_DIPOLE_FILES
	SET4 (with (Ba-O)v defect)	VTKFILES, LOCAL_DIPOLE_FILES
(b) Non-Equilibrium Dynamics	SET1 (no defects)	VTKFILES, LOCAL_DIPOLE_FILES
	SET2 (with Ov defect)	VTKFILES, LOCAL_DIPOLE_FILES
	SET3 (with Bav defect)	VTKFILES, LOCAL_DIPOLE_FILES
	SET4 (with (Ba-O)v defect)	VTKFILES, LOCAL_DIPOLE_FILES

One can visualize the dynamics of the given dataset by using the uploaded VTKFILES using the PARAVIEW software.

LOCAL_DIPOLE_FILES snippet below contains co-ordinate of Ti atoms and local polarization for each snapshot.

```
# TIMESTEP 250000 0.000000 0.000000 0.000000 162.462759 81.229598 120.800000
2.079 2.043 20.809 0.00505805 -0.00416993 -0.00028926
2.059 2.028 25.018 -0.00045007 -0.00058029 0.00758195
2.085 2.019 29.146 0.00016893 0.00004470 0.00600944
```

First line, is header contains #TIMESTEP <timestep> <xlow> <ylo> <zlow> <xhigh> <yhigh> <zhigh>

Where unit of timestep is (fs), xlow-xhigh determine the cartesian min/max of the simulation box along the x-direction. Similarly, for y- and z-directions.

Second line onwards, first three columns (column wise) are cartesian co-ordinates of Ti atoms (in Å) while next three columns are the cartesian coordinates of the local polarization vector (in micro-Coulomb/cm²).

The challenge questions are:

- 1) How to extract and represent dynamical states from a molecular dynamics simulation using graph-based methods?
- 2) How do these dynamical states evolve under an applied electric-field?
- 3) How are these dynamical states modified in the presence of heterogeneities thereby leading to a change in the hysteretic response?

Notes:

- 1) ML algorithms to be implemented in one of the following languages: Python, C/C++, Julia.
- 2) Preference for ML framework : PyTorch/PytorchGeometric, Tensorflow

References:

1. Akbarian, D., Yilmaz, D.E., Cao, Y., Ganesh, P., Dabo, I., Munro, J., Van Ginhoven, R. and Van Duin, A.C., 2019. Understanding the influence of defects and surface chemistry on ferroelectric switching: a ReaxFF investigation of BaTiO₃. *Physical Chemistry Chemical Physics*, 21(33), pp.18240-18249.
2. <http://mini.physics.sunysb.edu/~mdawber/research.htm>
3. Brunton, S.L., Budišić, M., Kaiser, E. and Kutz, J.N., 2021. Modern Koopman Theory for Dynamical Systems. arXiv preprint arXiv:2102.12086.
4. Demo, N., Tezzele, M. and Rozza, G., 2018. PyDMD: Python dynamic mode decomposition. *Journal of Open Source Software*, 3(22), p.530.
5. Pérez-Hernández, G., Paul, F., Giorgino, T., De Fabritiis, G. and Noé, F., 2013. Identification of slow molecular order parameters for Markov model construction. *The Journal of chemical physics*, 139(1), p.07B604_1.

GITLAB LINK:

<https://code.ornl.gov/3sd/smc-datachallenge2021/>