Zentropy Theory for Ferroelectrics: A Case Study of PbTiO$_3$

Zi-Kui Liu,* Shun-Li Shang, Jinglian Du,† and Yi Wang

Department of Materials Science and Engineering, The Pennsylvania State University,
University Park, Pennsylvania 16802, USA

† Current address: State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi’an, Shaanxi 710072, China

* Corresponding author: prof.zikui.liu@psu.edu

ORCID: 0000-0003-3346-3696 (Zi-Kui Liu); 0000-0002-6524-8897 (Shun-Li Shang); 0000-0001-6154-945X (Yi Wang)

Abstract

Thermodynamics of ferroelectric to paraelectric (FE-PE) transitions is commonly described by the phenomenological Landau theory and more recently by effective Hamiltonian. Here we show that the zentropy theory, which considers the total entropy of a macroscopic system (macrostate) as a weighted sum of entropies of representative microscopic configurations (microstates) and the configurational entropy among the microstates, can predict the FE-PE transition without fitting parameters. In PbTiO$_3$, the microstates are FE states with or without domain walls. With the energetics of microstates determined from first-principles calculations, the FE-PE transition for PbTiO$_3$ is predicted showing remarkable agreement with experiments, unveiling the microscopic fundamentals of the transition.
Main Text

It is challenging to computationally predict the macroscopic functionalities of materials because only one or a few configurations can be considered in a typical computational approach, whereas the macroscopic functionalities stem from sampling all possible configurations at all scales simultaneously. This challenge becomes acute for systems with multiple phase transitions, which is often where the most fascinating properties exist such as ferroelectric materials discussed in the present work. Ferroelectric materials are with two or more discrete states of different nonzero electric polarization in zero applied electric field, referred to as “spontaneous” polarization, and can switch between these states with an applied electric field, stress, or temperature [1]. These effects are maximal near the boundary between polar ferroelectric (FE) and macroscopical non-polar paraelectric (PE) phases [2], commonly called a morphotropic phase boundary (MPB). They are traditionally described by the phenomenological Landau-Ginsburg-Devonshire theory (LGDT) [3] with the systematic modeling work reported by Cross and co-workers [4] by fitting model parameters to experimental observations.

Even though the LGDT formalism describes the FE and PE behaviors well macroscopically, it does not correctly describe the microscopic features, such as the domain walls (DWs) [5,6]. As a symmetry-based analysis of equilibrium behavior near a phase transition, LGDT postulates that the macroscopic polarization changes smoothly from a finite value in the FE phase to zero in the PE phase in accordance with macroscopic experimental measurements. On the other hand, the microscopic theory of polarization developed more recently [1,7] focuses on differences in polarization between two different states, which is what actually measured in a polarization-reversal experiment. Therefore, the macroscopic polarization in the macroscopic FE phase
(termed as macrostate in the present work), defined as the sum of the dipole moments in a given cell divided by the cell volume in the LGDT formalism, does not reflect the realistic microscopic states (termed as microstates in the present work) with a sizeable fraction of the electronic charge being shared among ions in a delocalized manner.

One critical result of the modern theory of polarization (MTP) is that the microscopic polarization does not necessarily vanish for a centrosymmetric phase, i.e., the PE phase. The constraint of PE centrosymmetry with the polarization mapped onto itself by the inversion operation can be realized by lattice vector values [1,7]. It has been demonstrated that the MTP together with first-principles calculations based on density functional theory (DFT) [8] is able to provide quantitative understanding of key quantities of ferroelectrics, e.g., the spontaneous polarization, the Born effective charges, the piezoelectric response, and the DW structures and energies [9].

In efforts to predict the FE-PE transitions at finite temperatures, effective Hamiltonian approaches have been developed with model parameters fitted to DFT-based first-principles calculations followed by Monte Carlo or molecular dynamic simulations [10,11]. The effective Hamiltonians are constructed by representing the energy surface in terms of a Taylor expansion around the high-symmetry cubic PE structure. The predictions from those simulations presented a remarkable agreement with experimental observations in terms of the phase stability sequence, transition temperatures, latent heats, and spontaneous polarizations, providing insights into the order-disorder versus displacive character of the transitions and the importance of various interaction terms in the effective Hamiltonians. It is particularly significant that the magnitude of local mode of polarization is significantly nonzero in the cubic PE state for both BaTiO₃ [10] and
PbTiO$_3$ [12]. It is also striking to observe that in BaTiO$_3$, the local mode was close to that of its ground state, i.e., the rhombohedral structure; while for PbTiO$_3$, the orthorhombic-like 90° DW was observed [11]. The predicted nonzero local polarizations from the above simulations are in excellent agreement with a range of experimental observations in the literature for ABO$_3$ perovskites, particularly PbTiO$_3$ [13]. But the fitting of the energy surface in terms of a Taylor expansion and the to-be-predicted structure reduces the predictability of the approach.

PbTiO$_3$ is a simple ferroelectric material with a phase transition from the FE tetragonal structure to the PE cubic structure at about 763 K without external stress and electric field based on the X-Ray diffractions [14], and the cubic structure is unstable at 0 K [15]. The volume of the tetragonal structure decreases with the increase of temperature, and the volume of the cubic structure increases with temperature [14]. However, when both Pb and Ti edges were measured via XAFS (X-ray-absorption fine structure) analysis with the time and spatial resolutions being $\sim 10^{-16}$ sec (0.1fs) and 1$^{st}$ to 4$^{th}$ nearest neighbor shells, it was found that the displacements of both Pb and Ti atoms within the unit cell vary little with temperature below the transition and decrease only slightly above the transition temperature [13].

Fang et al. [16] performed ab initio molecular dynamics (AIMD) simulations for PbTiO$_3$ using the macroscopic lattice parameters measured by X-ray in the literature [14]. In contrast to the conventional molecular dynamics (MD) analyses where results are averaged over time, Fang et al. [16] categorized the atomic configurations as a function of time in terms of the Ti-O bond lengths within the nearest-neighboring shell. It was shown that an appreciable amount of cubic configuration, i.e., equal length of all Ti-O bonds, exists at temperatures about 300 K, much lower
than its FE-PE transition temperature of 763 K, even though the time-averaged overall atomic configuration is tetragonal. By following the time evolution of each Ti-O bond (see the video in the supplemental information), it is observed that the cubic configuration originates from the switch of the c-axis of the tetragonal configuration from z direction to x or y direction through thermal fluctuations and vice versa. As the temperature increases, the switch becomes more frequent, resulting in an increase of thermal population of the cubic configuration and a decrease of macroscopic tetragonality, signifying that the FE-PE transition is intrinsically second-order [16].

It is striking to see that all local Ti-O environments are tetragonal except those that are switching from one tetragonal orientation to another tetragonal orientation, even above the FE-PE transition with the macroscopic lattice in the AIMD simulations fixed to the experimentally measured cubic lattice parameter [14], resembling the polar clusters discussed in the literature [17]. At the same time, these tetragonal orientation fluctuations generate local DWs. The simulated local lattice parameters and Ti displacements are in excellent agreement with those measured experimentally [13]. It is thus evident that the phenomenological LGDT formalism does not capture the fundamental physics behind the FE-PE transition in PbTiO₃, i.e., the switch between FE configurations that results in the macroscopic PE cubic structure characterized by the X-ray scattering with its time resolution much lower than the switch between the FE configurations.

In the present work, we apply our zentropy theory [18] to predict the FE-PE transition of PbTiO₃. The zentropy theory stipulates that the total entropy of a macrostate is a combination of the
weighted sum of individual microstates and the configurational entropy among microstates in terms of the Gibbs-Boltzmann distribution as follows

\[ S = \sum_{k=1}^{N} p_k S_k - k_B \sum_{k=1}^{N} p_k \ln p_k = S_{0K} + \int_{0}^{T} \frac{C}{T} dT \]  \hspace{1cm} \text{Eq. 1} \]

where \( S_k \) and \( p_k \) are the entropy and probability of microstate \( k \), respectively, \( N \) is the total number of microstates including multiplicity of each microstate, \( C \) is the heat capacity, and \( S_{0K} \) is the entropy at \( 0 \) \( K \) which equals to zero under the convention of the third law of thermodynamics. The first and second summations in Eq. 1 denote the contributions from quantum mechanics and statistical mechanics of microstates, respectively, while the integration in Eq. 1 represents the experimentally measured macroscopic properties. \( S_k \) and \( Z_k \) (partition function of the microstate \( k \)) can be predicted by DFT-based calculations and used to calculate \( p_k = Z_k / Z \) with \( Z = \sum_{k=1}^{N} Z_k \) being the partition function of the macrostate [18]. In the canonical (NVT) ensemble, the partition function is written as follows [18],

\[ Z = e^{-\frac{F}{k_B T}} = \sum_{k=1}^{N} Z_k = \sum_{k=1}^{N} e^{-\frac{F_k}{k_B T}} \]  \hspace{1cm} \text{Eq. 2} \]

where \( F \) and \( F_k \) are the Helmholtz energies of the macrostate and the microstate \( k \), respectively.

We utilized the zentropy theory to predict critical phenomena in Ce and Fe\(_3\)Pt due to their magnetic transitions, demonstrating remarkable agreement with available experimental data, particularly the positive and negative divergences of thermal expansion for Ce and Fe\(_3\)Pt at their critical points, respectively [19].

The above discussion indicates that the microstates of PbTiO\(_3\) include the FE ground state and two FE nonground states with 90° and 180° DWs, denoted by FEG, 90DW and 180DW in the present
work, respectively, as shown in Fig. 1. The 90° and 180° DWs can be regarded as twins on the (101) and (100) planes, respectively [5]. The polarizations on either side of the DW are almost perpendicular to one another in the 90° DW, and parallel with opposite orientation in the 180° DW due to the additional constraint that the normal component of the polarization should be continuous across the DW so that no net interface charge is present [5]. The highly charged head-to-head or tail-to-tail 180° DWs due to surface or other defects [20,21] are not considered in the present work due to their high DW energies [21], thus vanishing thermal probabilities.

*Fig. 1. Domain wall (DW) structures: (a) 180° DW and (b) 90° DW from [5].*

For the FEG microstate, the first domain has six energetically equivalent orientations with the c-axis direction along the ±x, ±y, or ±z axes, while the second domain can be placed on one of the two sides of the remaining two axes with its polarization in the same direction as the first domain, resulting in a total of $6 \times 2 \times 2 \times 1 = 24$ equivalent microstates. The same number of equivalent microstates exists for the 180° DWs except the polarization of the second domain in the opposite direction of the first domain, i.e., $6 \times 2 \times 2 \times 1 = 24$ microstates. For the 90° DWs, there are four additional degrees of freedom for the polarization direction in the second domain, i.e., two directions along each of the two remaining axes, resulting in $6 \times 2 \times 2 \times 4 = 96$ microstates. It is noted that the DW orientation in the 90° DWs changes when the polarization direction of the second domain changes in order to keep the DW free of net interface charge. Considering that there is only one ground state at 0 K fully defined by its electron density distribution in accordance with DFT [8], the multiplicity ratio of the FEG, 90DW and 180DW microstates is 1:4:1.
The properties of ferroelectric DWs have been extensively studied in the literature [22]. The 90° DW energy in PbTiO₃ was predicted to be 35 and 29 mJ/m² using ultrasoft pseudopotentials (USPP) [5] and the projector augmented wave (PAW) method as implemented in VASP [23], respectively, both with the exchange-correlation functional being the local density approximation (LDA). It was pointed out that the PAW method slightly underestimates the spontaneous polarization compared with the USPP method [24], thus probably lower DW energies. The 180° DW can be Pb or Ti centered with the latter being unstable at a saddle point [5,25]. The Pb-centered 180° DW energy is predicted to be 150 or 270 mJ/m² using the norm-conserving non-local Troullier–Martins type pseudopotentials with or without inversion symmetry, respectively [25], 132 mJ/m² in terms of the high-symmetry centrosymmetric structure with inversion symmetry [5], and 128 or 114 mJ/m² with atomic relaxations in the z-axis direction only or in all the three spatial directions, respectively [26], using the LDA and PAW methods as implemented in VASP.

In the present work, two sets of 90° and 180° DW energies are used, i.e., (I) 35 and 132 mJ/m² from [5] with the interfacial areas in the supercell being $a^2\sqrt{1 + (c/a)^2}$ and $ca$ with lattice parameters $a = 3.86\text{Å}$ and $c = 4.04\text{Å}$, respectively; and (II) 29 and 114 mJ/m² from [24] and [26] with $a = 3.8731\text{Å}$ and $c = 3.9990\text{Å}$, respectively. It should be noted that there are two DWs in the supercells used for calculating the DW energies. The predicted probability of microstates using the two sets of DW energies is plotted in Fig. 2 with the multiplicity taken into account, i.e., $4p_{90DW} = 4 Z_{90DW}/Z$ for the probability of the 90DW microstate, and the data file
used for the calculations is provided in the supplementary information. Using 50% probability of the FEG microstate as the criterion based on our previous predictions for magnetic transitions [27–30] and the AIMD simulations [16], the predicted FE-PE transition temperatures are 776 K and 645 K for the dataset (I) and (II), respectively, which are 13 K above and 118 K below the experimental value of 763 K [14]. Considering that only the DW energies at 0 K from DFT-based first-principles calculations in the literature are used, the present predictions without fitting parameters are remarkable.

Fig. 2. Probability of microstates plotted as a function of temperature using datasets (I) and (II) with different combinations of DW energies: (a) 35 mJ/m$^2$ (90DW) and 132 mJ/m$^2$ (180DW) and (b) 29 mJ/m$^2$ (90DW) and 114 mJ/m$^2$ (180DW). The $T_c$ values are the predicted FE-PE transition temperatures.

Since the DW energies at 0 K from the literature are used in the present work, only the configuration entropy among microstates in Eq. 1 can be evaluate as follows

$$S^{\text{conf}} = -k_B(p_{\text{FEG}} \ln p_{\text{FEG}} + 4p_{90\text{DW}} \ln p_{90\text{DW}} + p_{180\text{DW}} \ln p_{180\text{DW}}) \quad \text{Eq. 3}$$

The configurational entropies for the two datasets are plotted in Fig. 3, showing higher values with the dataset (II) than those with the dataset (I), and thus the lower transition temperature with the dataset (II) than that with the dataset (I).

Fig. 3. Configurational entropy plotted as a function of temperature using datasets (I) and (II) with different combinations of DW energies.
In summary, the zentropy theory is applied to predict the FE-PE transition in PbTiO$_3$ with the $90^\circ$ and $180^\circ$ DW energies determined by DFT-based first-principles calculations in the literature without fitting parameters, demonstrating remarkable agreement with experimental results. The present prediction from the zentropy theory captures the fundamental physics behind the FE-PE transitions in terms of thermal fluctuation of polarization directions and thus provides a theoretical guidance for the discovery and design of FE materials with emergent functionalities. Future work on PbTiO$_3$ includes the predictions of free energies of the FEG, 90DW, and 180DW microstates, and other properties such as heat capacity and negative thermal expansion of PbTiO$_3$ using our mixed-space approach for phonon calculations of polar materials [31]. Qualitatively, the negative thermal expansion in PbTiO$_3$ can be explained from the increased probability of the 90DW microstate which has its volume smaller than that of the FEG microstate [32].

**Acknowledgements**

The authors acknowledge the support from the Endowed Dorothy Pate Enright Professorship at the Pennsylvania State University. JLD is financially supported by the China Scholarship Council. The authors thank Huazhi Fang for providing the video from the AIMD simulations for PbTiO$_3$. 
References

[1] K. M. Rabe, C. H. Ahn, and J. Triscone, *Physics of Ferroelectrics: A Modern Perspective* (Springer, Berlin, Heidelberg, 2007).

[2] M. Ahart, M. Somayazulu, R. E. Cohen, P. Ganesh, P. Dera, H. Mao, R. J. Hemley, Y. Ren, P. Liermann, and Z. Wu, *Origin of Morphotropic Phase Boundaries in Ferroelectrics*, Nature **451**, 545 (2008).

[3] A. F. Devonshire, *Theory of Barium Titanate I*, Philos. Mag. **40**, 1040 (1949).

[4] M. J. Haun, E. Furman, S. J. Jang, H. A. McKinstry, and L. E. Cross, *Thermodynamic Theory of PbTiO3*, J. Appl. Phys. **62**, 3331 (1987).

[5] B. Meyer and D. Vanderbilt, *Ab Initio Study of Ferroelectric Domain Walls in PbTiO3*, Phys. Rev. B - Condens. Matter Mater. Phys. **65**, 104111 (2002).

[6] J. F. Scott, *Electrocaloric Materials*, Annu. Rev. Mater. Res. **41**, 229 (2011).

[7] R. Resta, *Theory of the Electric Polarization in Crystals*, Ferroelectrics **136**, 51 (1992).

[8] W. Kohn and L. J. Sham, *Self-Consistent Equations Including Exchange and Correlation Effects*, Phys. Rev. **140**, A1133 (1965).

[9] R. Resta and D. Vanderbilt, *Theory of Polarization: A Modern Approach*, in *Physics of Ferroelectrics: A Modern Perspective*, edited by K. M. Rabe, C. H. Ahn, and J.-M. Triscone (Springer, Verlag Berlin Heidelberg, 2007), pp. 31–68.

[10] W. Zhong, D. Vanderbilt, and K. M. Rabe, *Phase-Transitions in BaTiO3 From First Principles*, Phys. Rev. Lett. **73**, 1861 (1994).

[11] A. Kumar, K. M. Rabe, and U. V. Waghmare, *Domain Formation and Dielectric Response in PbTiO3: A First-Principles Free-Energy Landscape Analysis*, Phys. Rev. B **87**, 024107 (2013).
[12] U. V Waghmare and K. M. Rabe, *Ab Initio Statistical Mechanics of Ferroelectric Phase Transition in PbTiO₃*, Phys. Rev. B **55**, 6161 (1997).

[13] N. Sicron, B. Ravel, Y. Yacoby, E. A. Stern, F. Dogan, and J. J. Rehr, *The Ferroelectric Phase Transition in PbTiO₃ from a Local Perspective*, Phys. B Condens. Matter **208–209**, 319 (1995).

[14] G. Shirane and S. Hoshino, *On the Phase Transition in Lead Titanate*, J. Phys. Soc. Japan **6**, 265 (1951).

[15] H. Fu and R. E. Cohen, *Polarization Rotation Mechanism for Ultrahigh Electromechanical Response in Single-Crystal Piezoelectrics*, Nature **403**, 281 (2000).

[16] H. Z. Fang, Y. Wang, S. L. Shang, and Z. K. Liu, *Nature of Ferroelectric-Paraelectric Phase Transition and Origin of Negative Thermal Expansion in PbTiO₃*, Phys. Rev. B **91**, 24104 (2015).

[17] M. E. Manley, J. W. Lynn, D. L. Abernathy, E. D. Specht, O. Delaire, A. R. Bishop, R. Sahul, and J. D. Budai, *Phonon Localization Drives Polar Nanoregions in a Relaxor Ferroelectric*, Nat Commun **5**, 3683 (2014).

[18] Z.-K. Liu, Y. Wang, and S.-L. Shang, *Zentropy Theory for Positive and Negative Thermal Expansion*, J. Phase Equilibria Diffus. (2022), https://doi.org/10.1007/s11669-022-00942-z.

[19] Z. K. Liu, Y. Wang, and S. Shang, *Thermal Expansion Anomaly Regulated by Entropy*, Sci. Rep. **4**, 7043 (2014).

[20] K. Moore, M. Conroy, E. N. O’Connell, C. Cochard, J. Mackel, A. Harvey, T. E. Hooper, A. J. Bell, J. M. Gregg, and U. Bangert, *Highly Charged 180 Degree Head-to-Head Domain Walls in Lead Titanate*, Commun. Phys. **3**, 231 (2020).
[21] J. Sifuna, P. García-Fernández, G. S. Manyali, G. Amolo, and J. Junquera, First-Principles Study of Two-Dimensional Electron and Hole Gases at the Head-to-Head and Tail-to-Tail 180° Domain Walls in PbTiO3 Ferroelectric Thin Films, Phys. Rev. B 101, 174114 (2020).

[22] D. Meier and S. M. Selbach, Ferroelectric Domain Walls for Nanotechnology, Nat. Rev. Mater. 7, 157 (2022).

[23] G. Kresse, J. Furthmüller, J. Furthmüller, J. Furthmueller, J. Furthmüller, J. Furthmüller, J. Furthmüller, J. Furthmüller, J. Furthmüller, J. Furthmüller, and J. Furthmü, Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set, Phys. Rev. B 54, 11169 (1996).

[24] T. Shimada, Y. Umeno, and T. Kitamura, Ab Initio Study of Stress-Induced Domain Switching in PbTiO3, Phys. Rev. B 77, 094105 (2008).

[25] S. Pöykkö and D. Chadi, Ab Initio Study of Dipolar Defects and 180° Domain Walls in PbTiO3, J. Phys. Chem. Solids 61, 291 (2000).

[26] R. K. Behera, C.-W. Lee, D. Lee, A. N. Morozovska, S. B. Sinnott, A. Asthagiri, V. Gopalan, and S. R. Phillpot, Structure and Energetics of 180° Domain Walls in PbTiO3 by Density Functional Theory, J. Phys. Condens. Matter 23, 175902 (2011).

[27] Y. Wang, L. G. Hector Jr, H. Zhang, S. L. Shang, L. Q. Chen, and Z. K. Liu, A Thermodynamic Framework for a System with Itinerant-Electron Magnetism, J. Phys. Condens. Matter 21, 326003 (2009).

[28] Y. Wang, S. L. Shang, H. Zhang, L.-Q. Chen, and Z.-K. Liu, Thermodynamic Fluctuations in Magnetic States: Fe3Pt as a Prototype, Philos. Mag. Lett. 90, 851 (2010).

[29] S. L. Shang, Y. Wang, and Z. K. Liu, Thermodynamic Fluctuations between Magnetic States from First-Principles Phonon Calculations: The Case of Bcc Fe, Phys. Rev. B 82,
[30] Y. Wang, S. L. Shang, L. Q. Chen, and Z. K. Liu, *Magnetic Excitation and Thermodynamics of BaFe2As2*, Int. J. Quantum Chem. **111**, 3565 (2011).

[31] Y. Wang, J. J. Wang, W. Y. Wang, Z. G. Mei, S. L. Shang, L. Q. Chen, and Z. K. Liu, *A Mixed-Space Approach to First-Principles Calculations of Phonon Frequencies for Polar Materials*, J. Phys. Condens. Matter **22**, 202201 (2010).

[32] S. Stemmer, S. K. Streiffer, F. Ernst, and M. Rüuhle, *Atomistic Structure of 90° Domain Walls in Ferroelectric PbTiO3 Thin Films*, Philos. Mag. A Phys. Condens. Matter, Struct. Defects Mech. Prop. **71**, 713 (1995).
Fig. 1
Fig. 2

(a) 35, 132 mJ/m²

- FEG
- 90DM
- 180DM
- 90DW + 180DW

$T_c = 776$ K

(b) 29, 114 mJ/m²

- FEG
- 90DM
- 180DM
- 90DW + 180DW

$T_c = 645$ K
Fig. 3