Functional Materials IV:
Ferroics and Multiferroics (contd)

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Collaborators

- Anil Kumar (JNCASR,Rutgers),
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- Jaita Paul (SNBNCBS)

- Experiments: A Shirin and CNR Rao.

Ferroelectrics: free energies from first-principles

Electronic Structure – atomistic simulations

E_{tot}

Bridge

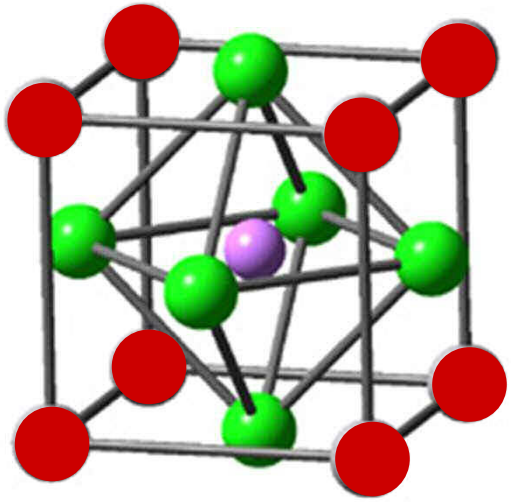
Phenomena at long length and time scales
in both extended and confined materials

➢Ferroelectric $BaTiO_3$

Ba

Ti

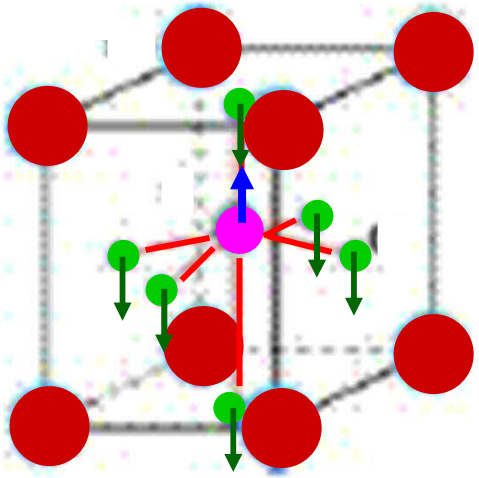
O



➢ High Temperature

➢ CUBIC Structure: PARAELECTRIC

➢ a = b = c



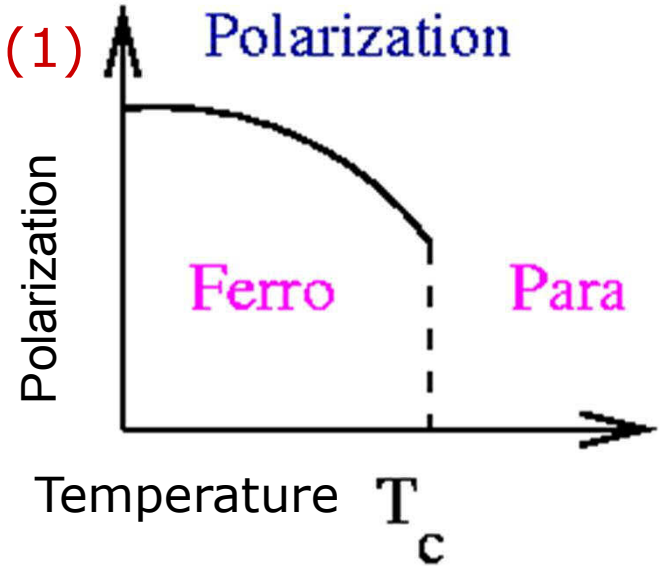
➢ Room Temperature

➢ TETRAGONAL Structure: FERROELECTRIC

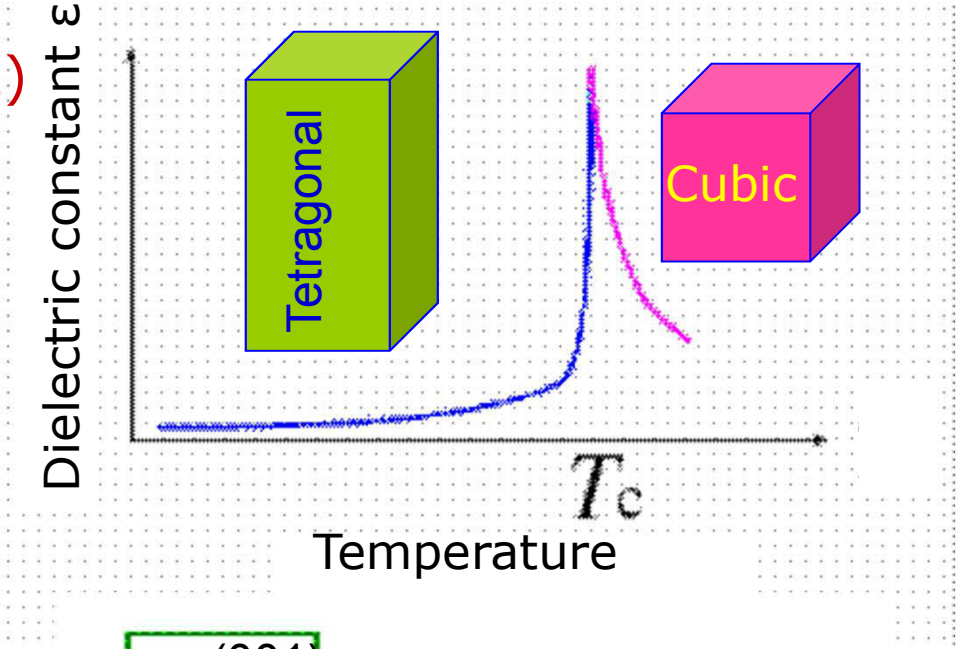
➢ a = b ≠ c: strain

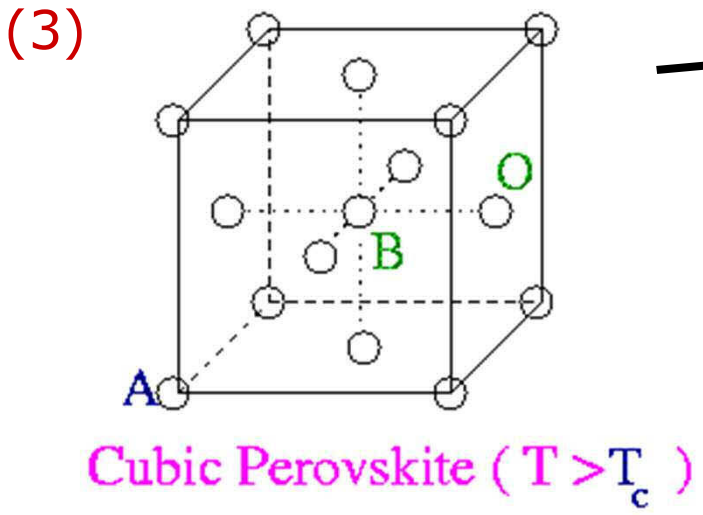
❖ Ti^{4+} and Ba^{2+} shifted wrt O^{2-} → finite dipole moment: polar phonon

➢ Ferroelectric Phase transition(s)

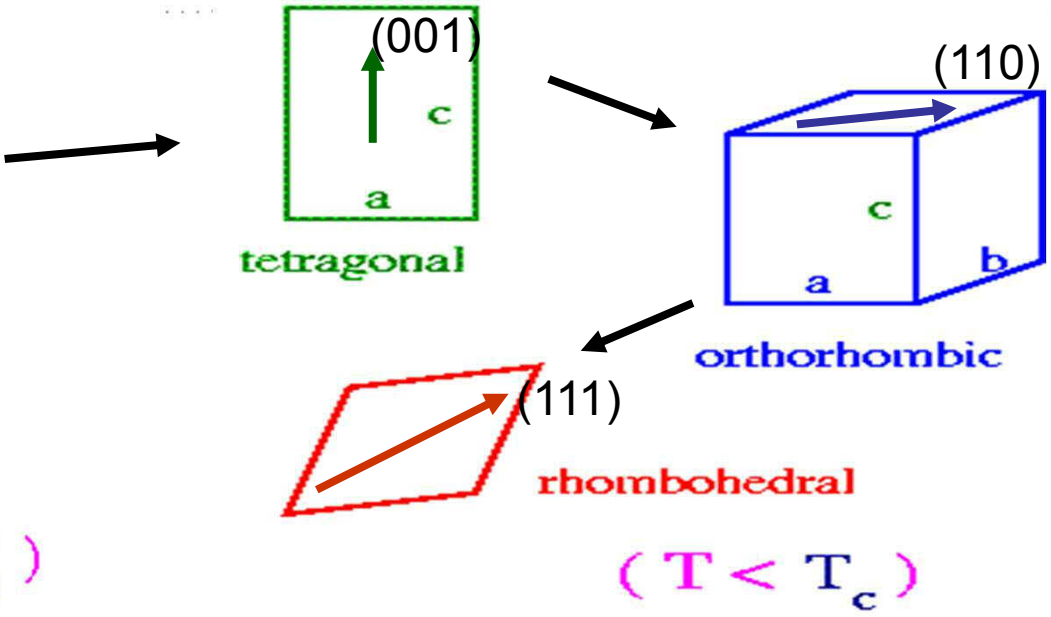


Perovskite Ferroelectrics





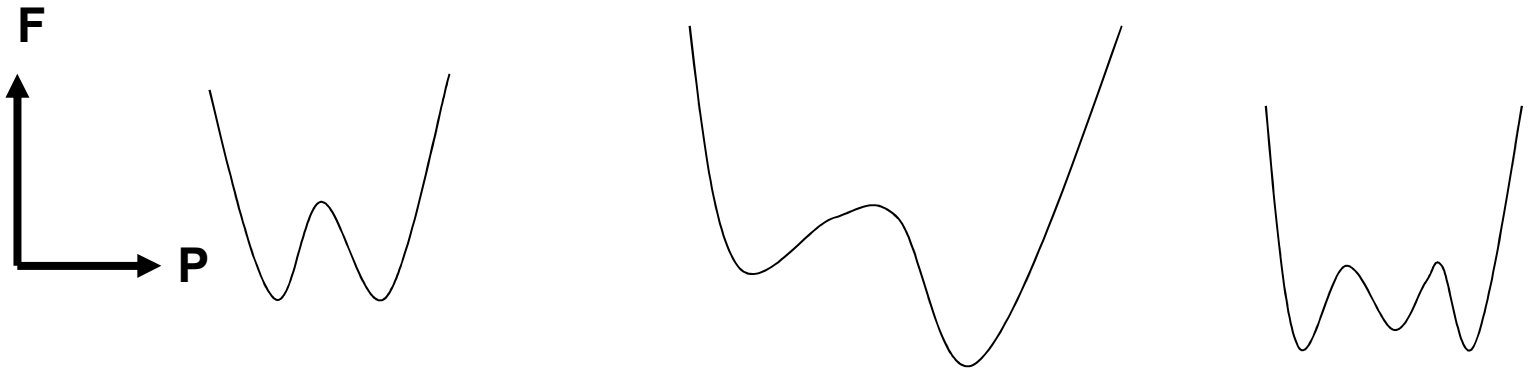
Cubic Perovskite ($T > T_c$)



($T < T_c$)

Why free energies (I)?

- Nature of the transition and its free energy land-scape:



MFT versus exact free energies:

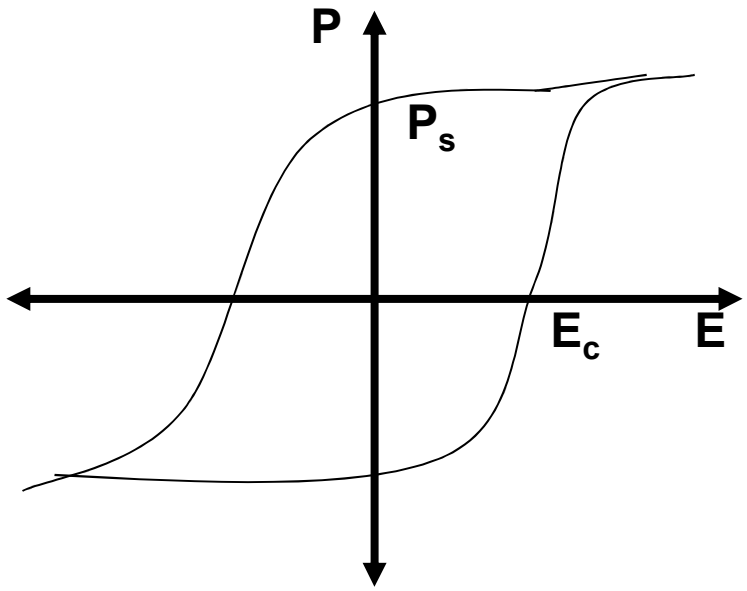
Work by Heine's group (90's): in "mean field" approach, F(P) is *non-analytic* near P=0.

Landau MFT: second order transition (Rabe and Waghmare (1996)).

First-order transition: driving mechanism?

Why free energies (II)?

Polarization Switching in ferroelectrics [thin films]:



Time-scales (> ns) and length-scales (domains > 10 nms)

Kay-Dunn scaling in FE films:

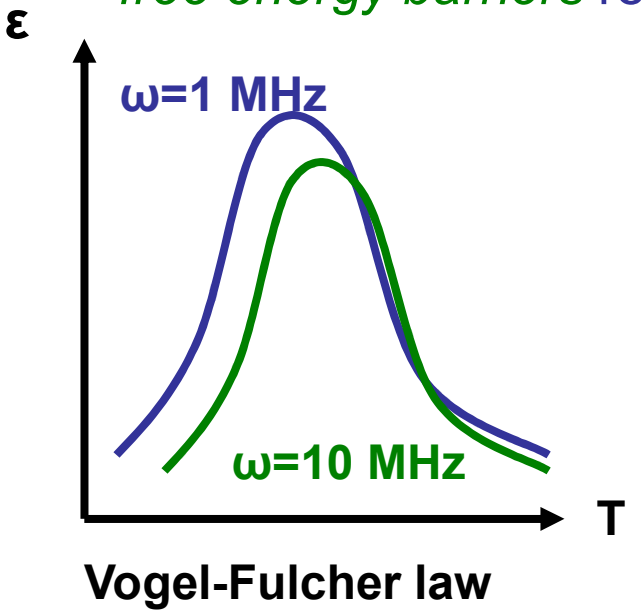
$E_c \sim d^{-2/3}$

[Heterogeneous Nucleation of Domains]

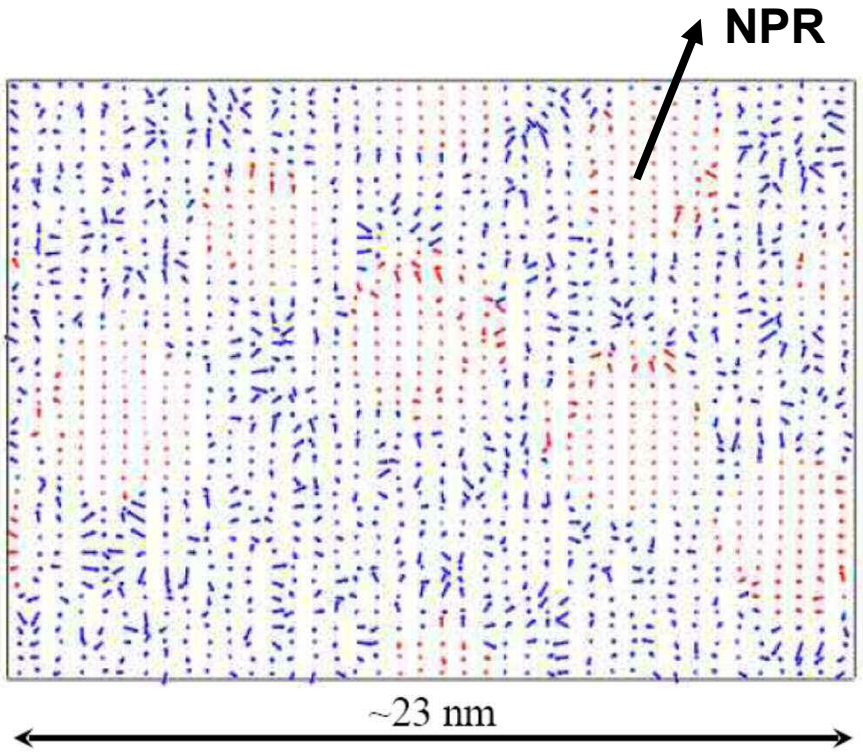
Details of the free energy land-scape (eg. barriers along the paths of formation and switching of domains) determine switching properties

Why free energies (III)?

- **Relaxor ferroelectrics** (eg. $PbMg_{1/3}Nb_{2/3}O_6$): Glassy Dynamics
  Nano-polar regions **[NPR]**
  free energy barriers relevant to their dynamics and flipping



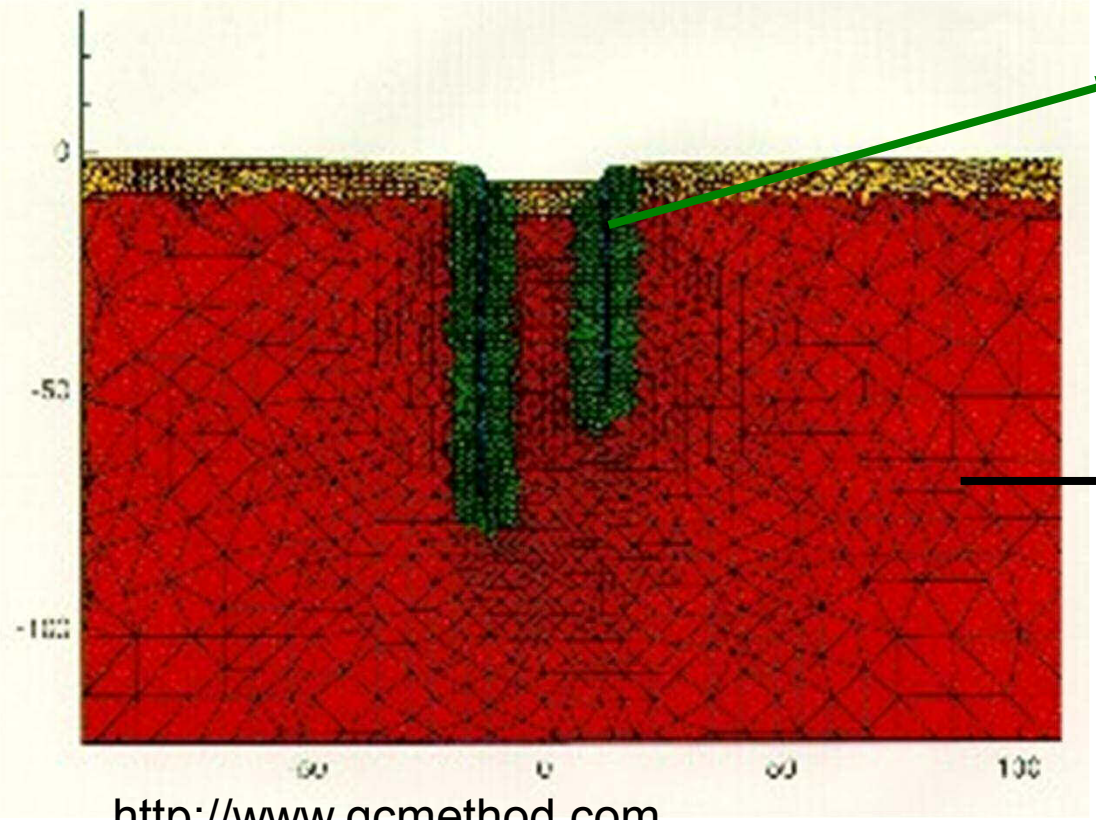
Vogel-Fulcher law



Need domain wall energies, associated free energy barriers

Why free energies (IV)?

- Simulation of FE devices at nano-scale
- Continuum + atomistic analysis: *quasi-continuum*



http://www.qcmethod.com

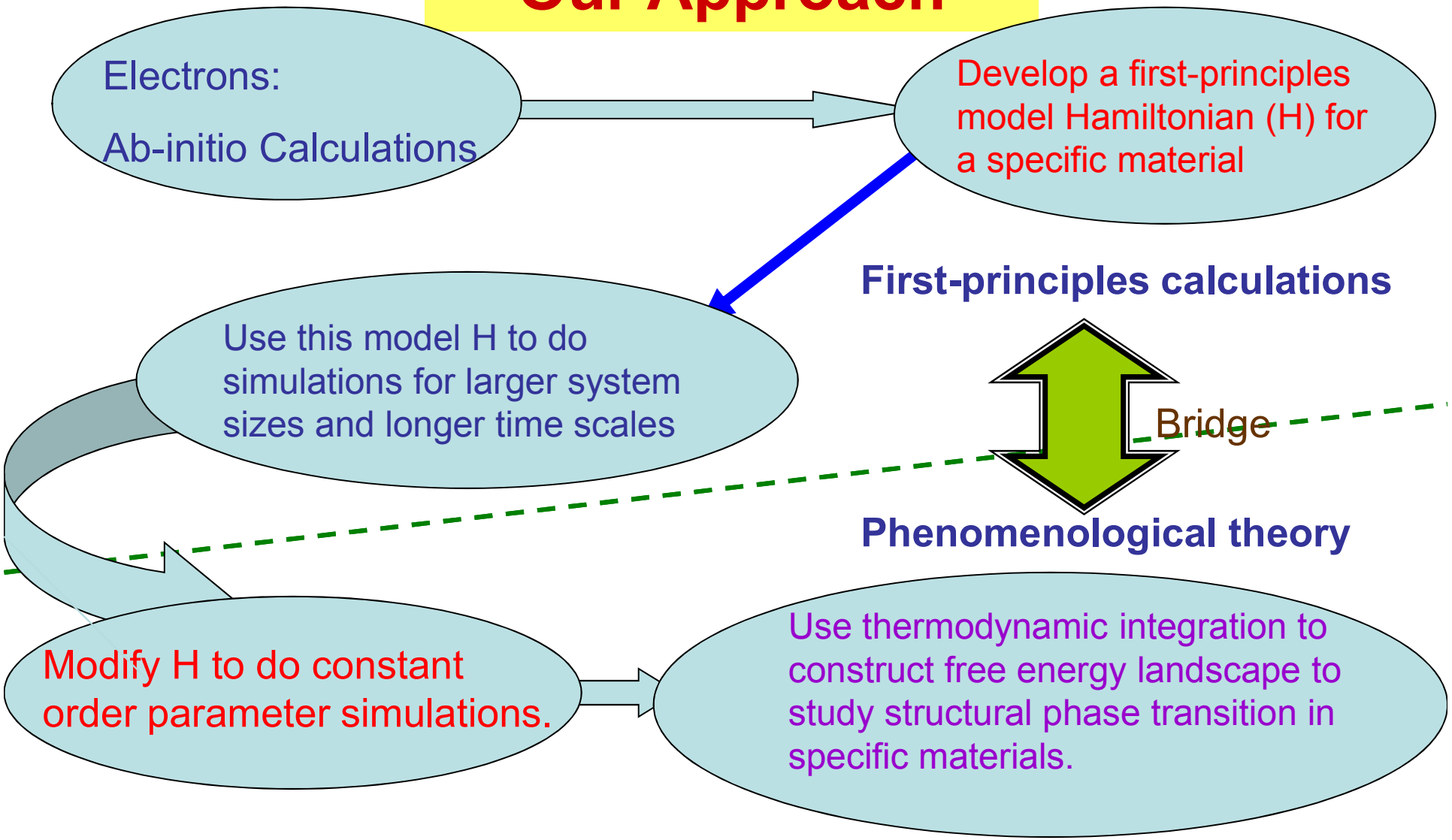
Atomistic MD

consistent

Landau-like theory
F(*T*, strain)

Expand the range of problems one can tackle.

Our Approach



We use this approach to study structural phase transitions and domains in $BaTiO_3$, which is a ferroelectric material.

$BaTiO_3$ Hamiltonian

$$H_0 = \frac{M^*_{dipole}}{2}\sum_{i,\alpha}\dot{\xi}^2_{i,\alpha} + \frac{M^*_{acoustic}}{2}\sum_{i,\alpha}\dot{\omega}^2_{i,\alpha} + V^{self}(\{\vec{\xi}\}) + V^{dipole}(\{\vec{\xi}\})$$
$$+ V^{short}(\{\xi\}) + V^{elastic,\text{homo}}(\eta_1,\ldots,\eta_6) + V^{elastic,in\,\text{homo}}(\{\vec{\omega}\})$$
$$+ V^{coup,\text{homo}}(\{\vec{\xi}\},\eta_1,\ldots,\eta_6) + V^{self}(\{\vec{\xi}\},\{\vec{\omega}\})$$

Parameters determined from first-principles

[BaTiO3: Nishimatsu et al (2010); PbTiO3: Waghmare et al (1997)].

ξ = Ti off-centering [3-D classical vector dof/cell]

ω = translational (acoustic) mode [3-D classical vector dof/cell]

→ inhomogeneous strain

η = homogeneous strain components [6 global dof]

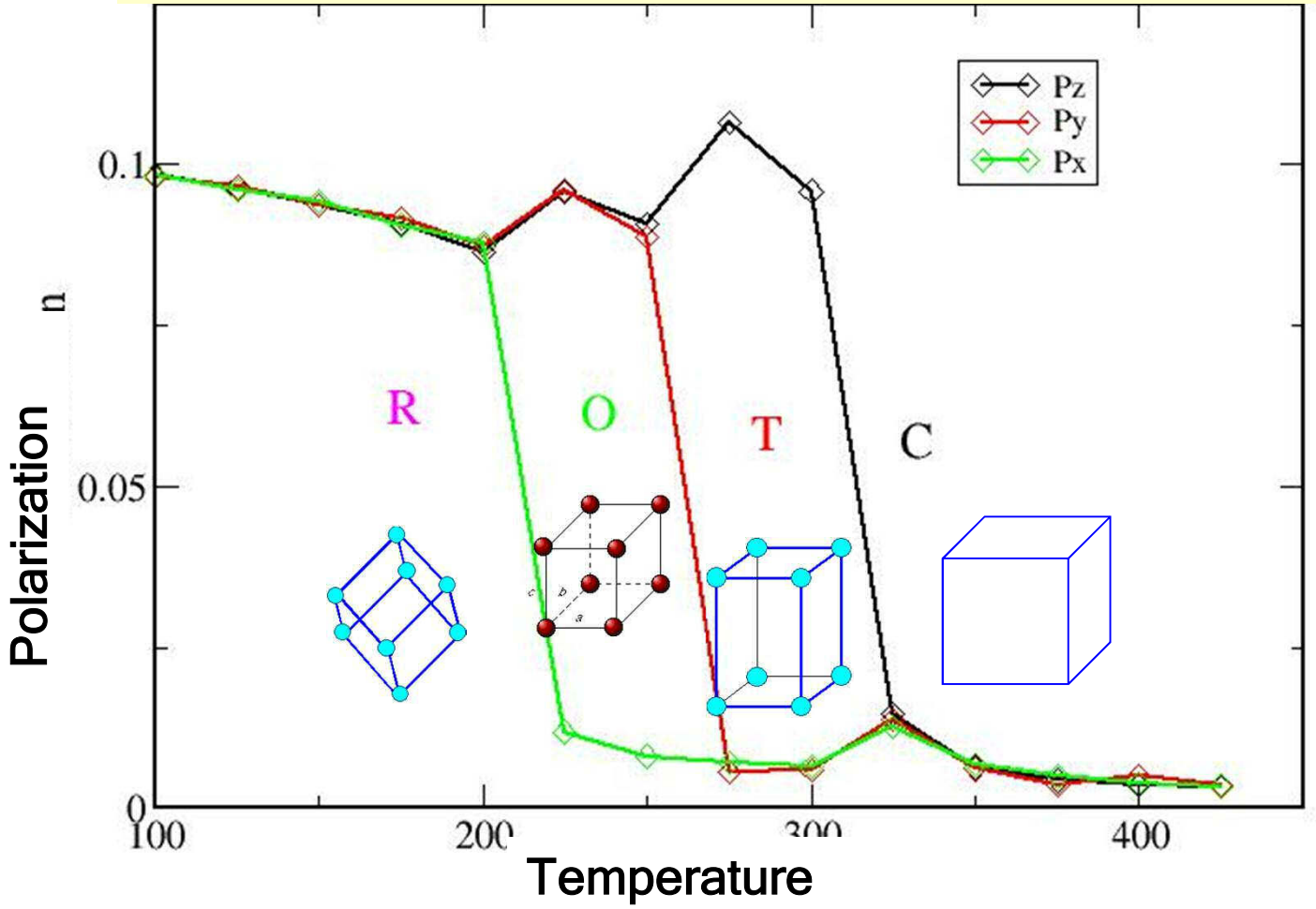
Molecular Dynamics:

FERAM code developed by

T Nishimatsu, U. V. Waghmare, Y. Kawazoe & Vanderbilt; PRB (2008).

http://loto.sourceforge.net/feram

Ferroelectric Phase Transition in *BULK* $BaTiO_3$: with first-principles model H_0



C: Cubic

T: Tetragonal

O: Orthorhombic

R: Rhombohedral

$T_c(1) = 225K$

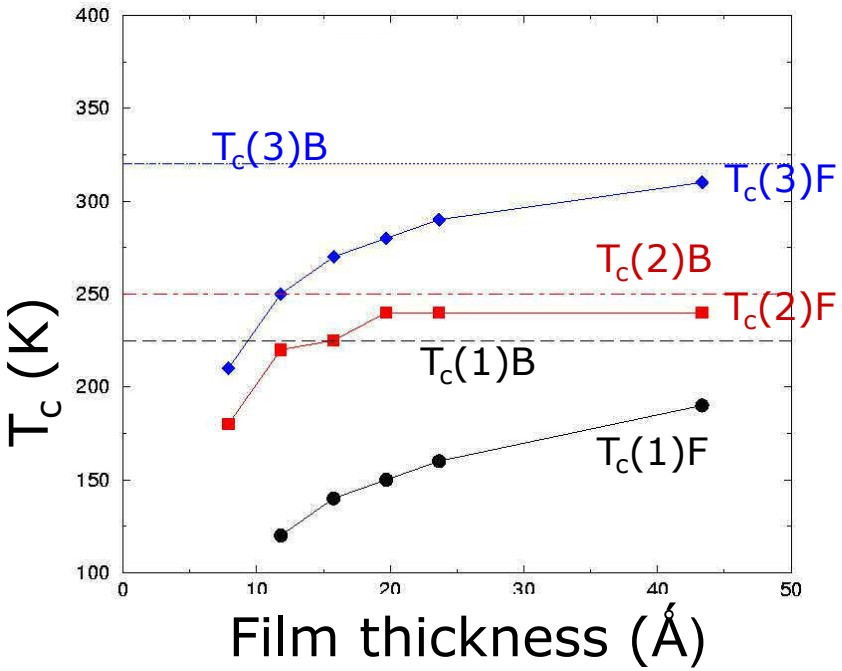
$T_c(2) = 250K$

$T_c(3) = 320K$

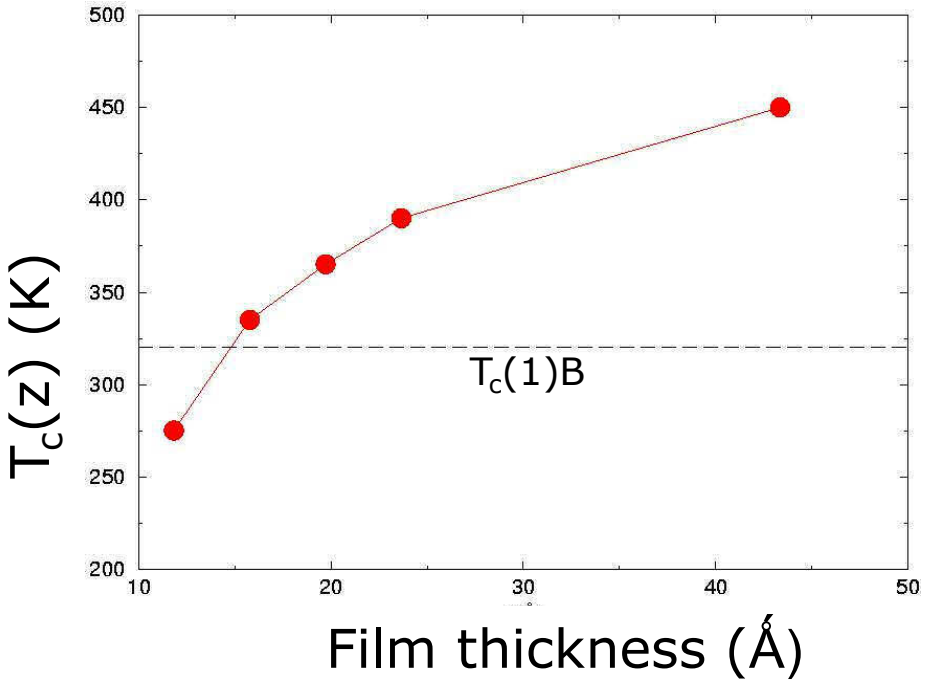
Nishimatsu, Iwamoto, Kawazoe, Waghmare, Phys Rev B **82, 134106 (2010)**

Transition Temperature as a Function of Film-Thickness: perfect electrodes

Without epitaxial strain



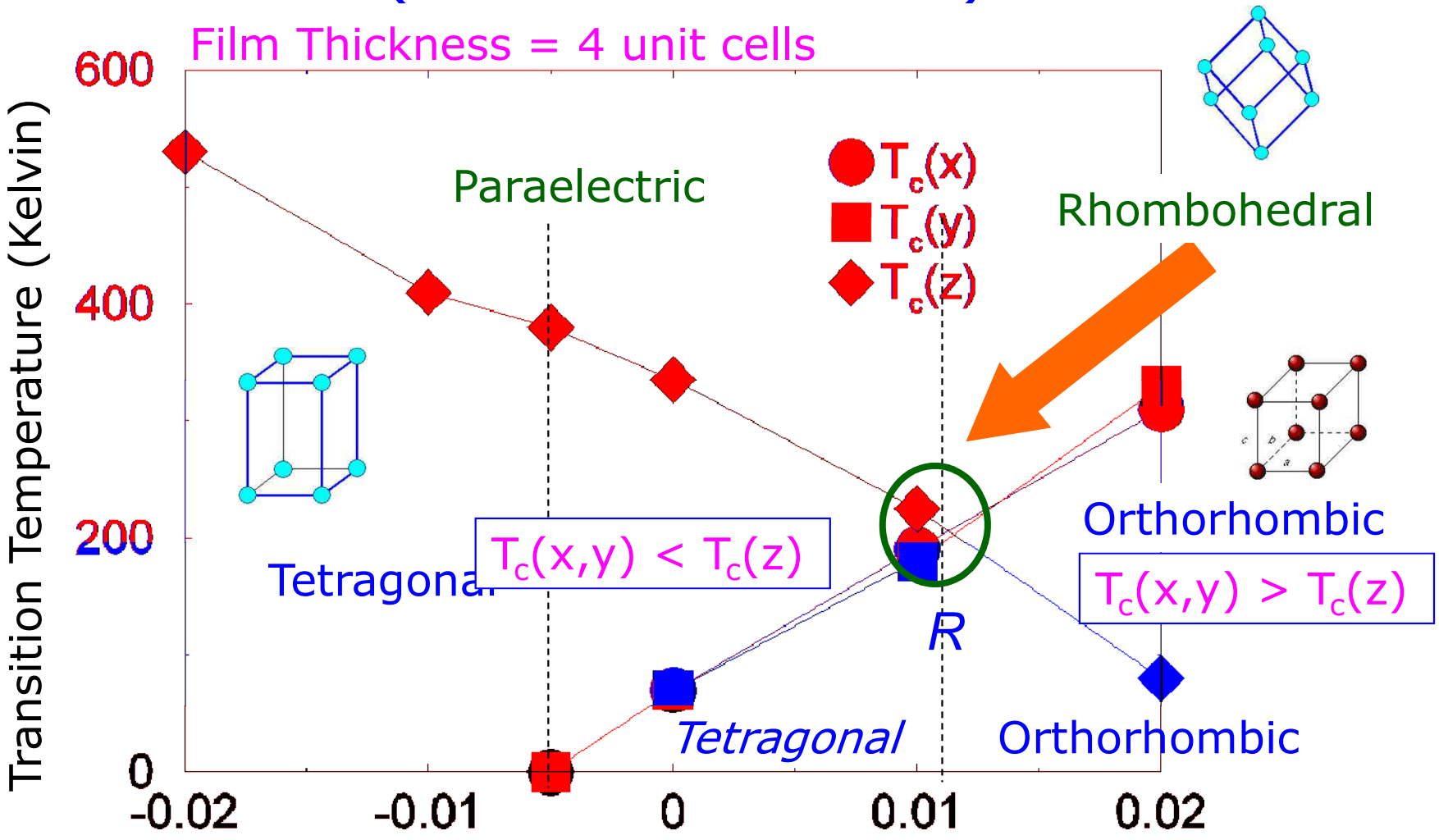
With epitaxial strain (-0.01)



- $T_c(x,y)$ also depends strongly on L
- **For Thin films with epitaxial strain, $T_c(z)$ is enhanced**

Paul, Nishimatsu, Kawazoe, Waghmare, PRL (07), APL (08), PRB (09).

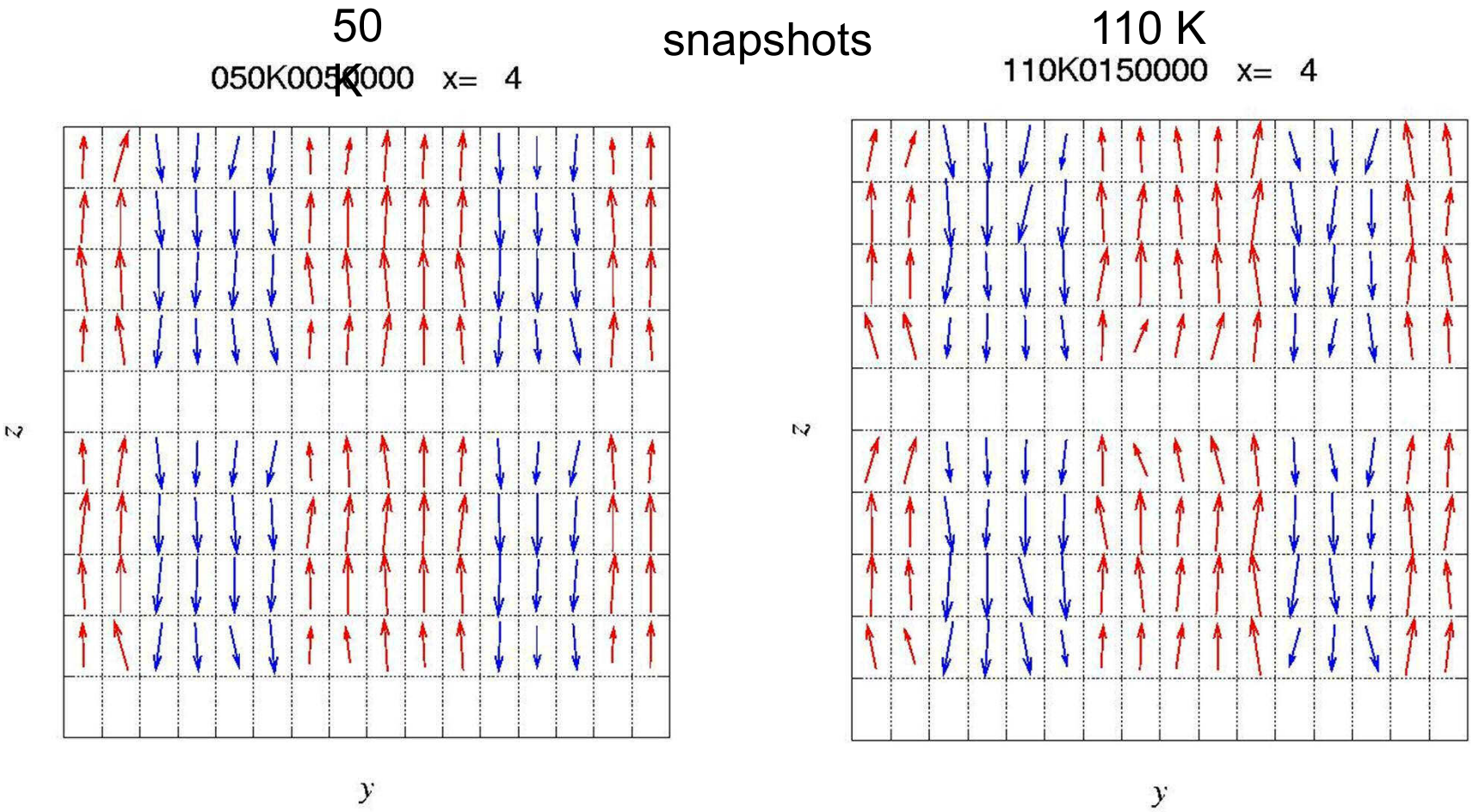
Effect of varying Strain: Phase Diagram (Perfect Electrodes)



Paul, Nishimatsu, Kawazoe, UVW, PRL (2007).

What is the nature of ferroelectric phase at low T?

(imperfect electrodes)



A clear indication of a phase with stripe-like domains

Experiments: Fong et al, Science 304, 1650 (2004).

Free Energy

- Thermodynamically, at a given temperature stability of the system is determined by the minimum of free energy.
- Dynamics of the system as function of temperature.
- Minimum Energy Pathways (MEP) and free energy barriers: events with long time-scale

$$F = -k_B T \ln \int \prod_i dr_i e^{-\beta E(r_1, r_2, .. r_N)}$$

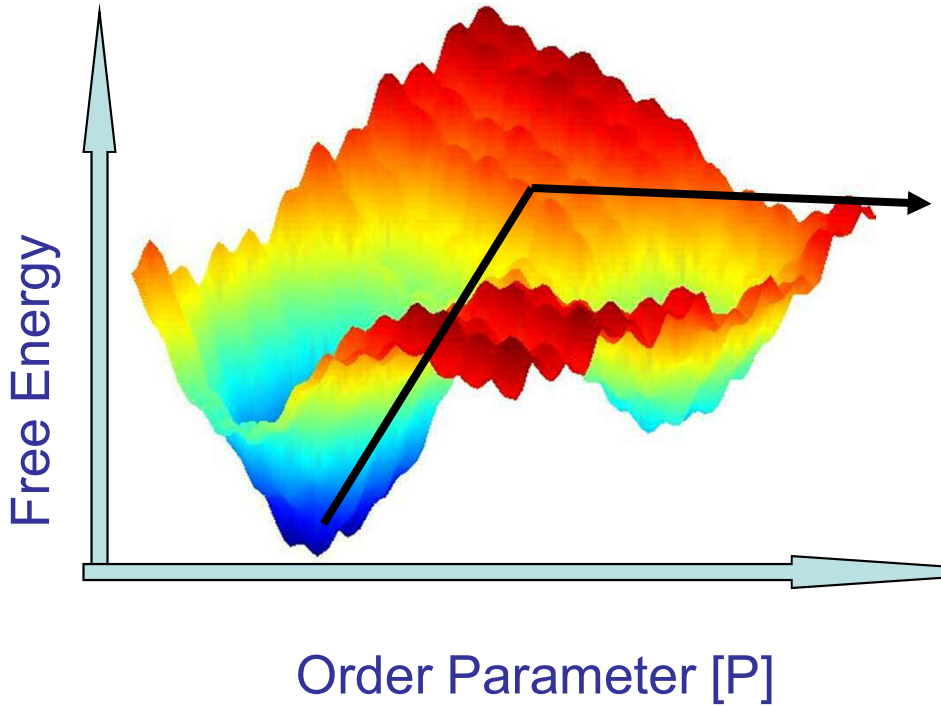
- Evaluation of free energy and determination of the MEPs are *quite hard* even on the most powerful computers.

Calculation of Free Energy

- *free energy differences* are accessible.

$$\frac{\partial F}{\partial P} = \frac{\int \prod_i dr_i \frac{\partial E}{\partial P} e^{-\beta E(r_1, r_2, \ldots, r_N)}}{\int \prod_i dr_i e^{-\beta E(r_1, r_2, \ldots, r_N)}} = \left\langle \frac{\partial E}{\partial P} \right\rangle$$

$$\Delta F = \int_{P1}^{P2} \left\langle \frac{\partial E}{\partial P} \right\rangle dP$$



Thermodynamic Integral.

Problem in doing this integral

A system prefers to stay at free energy minima; how to constrain it at arbitrary value of P?

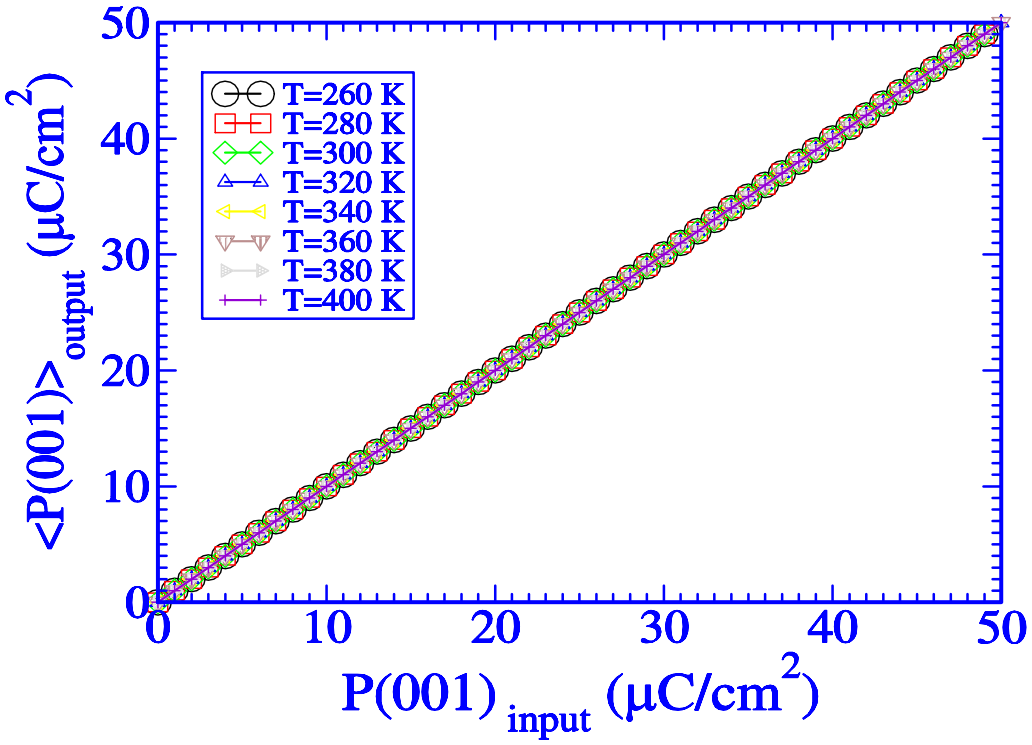
Solution: Constrained Order Parameter Simulations.

Constrained Polarization Simulations of $BaTiO_3$

Augmented first-principles Hamiltonian →

$$H = H_0 - Z^* \vec{E}.\sum_i \xi_i + \Omega \vec{P}.\vec{E} - \frac{\Omega(\varepsilon_\infty - 1)}{8\pi}\vec{E}^2$$

H optimized wrt *E* at each MD step



Thermodynamic Integration

$$H = H_0 - Z^* \vec{E}.\sum_i \xi_i + \Omega \vec{P}.\vec{E} - \frac{\Omega(\varepsilon_\infty - 1)}{8\pi}\vec{E}^2$$

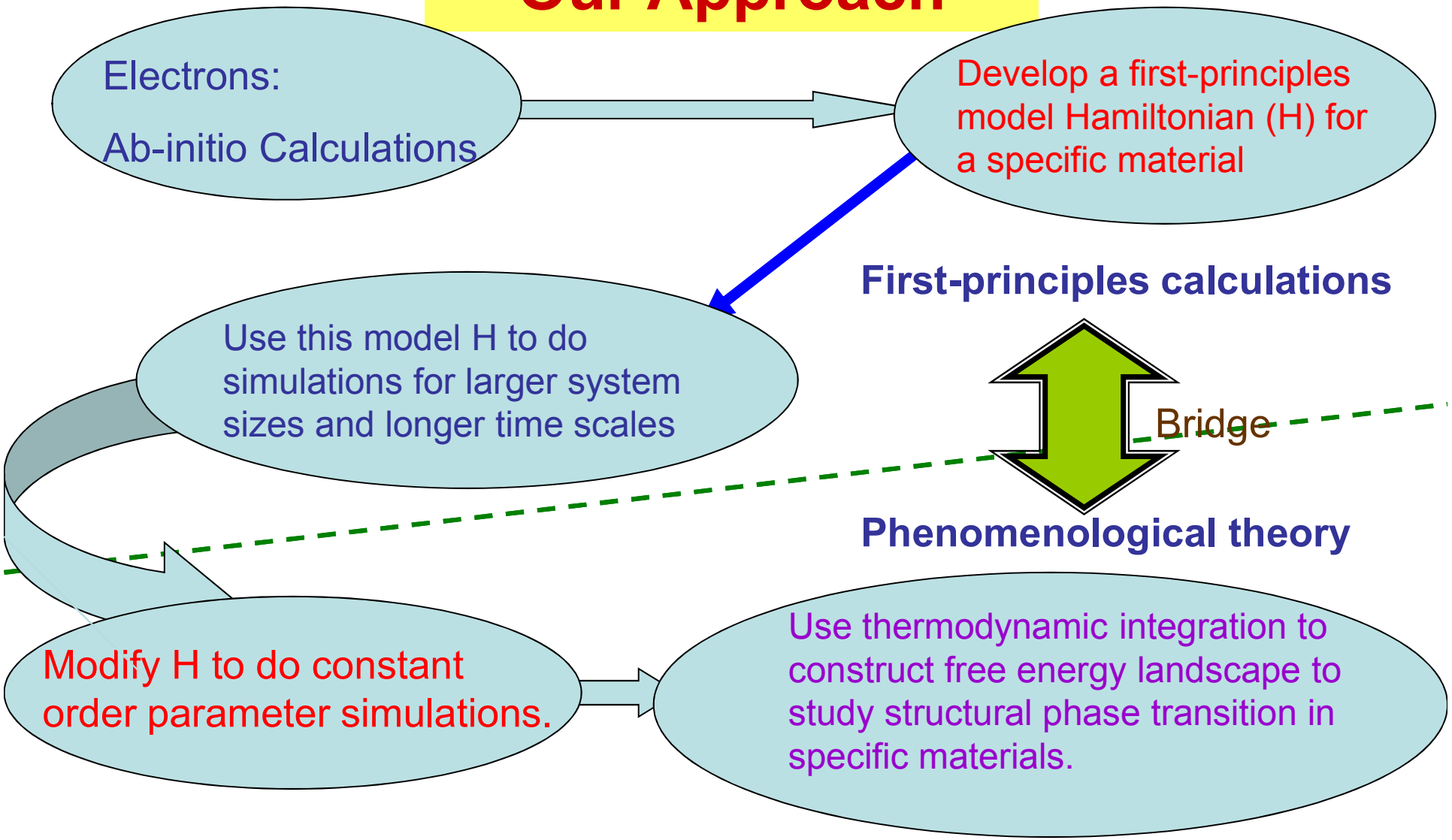
$$Z = \int d\xi_i . e^{-\beta H} \qquad \& \qquad F = -k_B T \ln Z$$

$$\frac{\partial F}{\partial P} = -k_B T . \frac{\int -\beta \Omega \vec{E} d\xi_i . e^{-\beta H}}{\int d\xi_i . e^{-\beta H}} \quad \Longrightarrow \quad \frac{\partial F}{\partial P} = \Omega \langle E \rangle$$

$$\partial F = \Omega \int_0^P \langle E(\vec{P}') \rangle d\vec{P}'$$

Electrical work done by average auxiliary field on P

Our Approach



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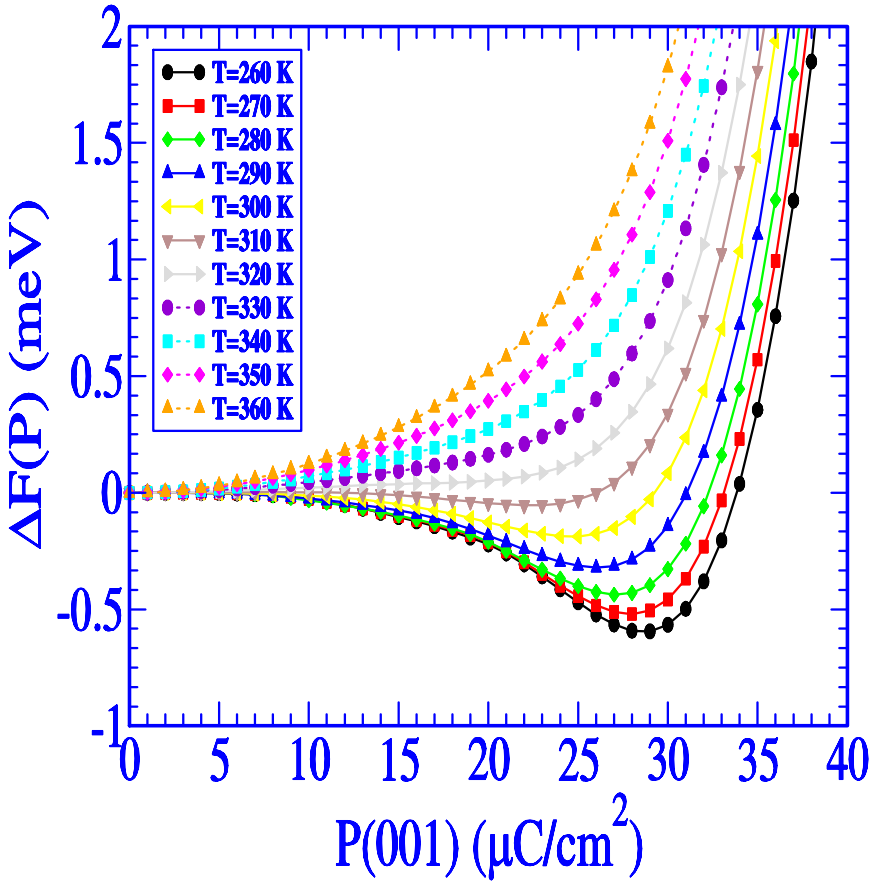
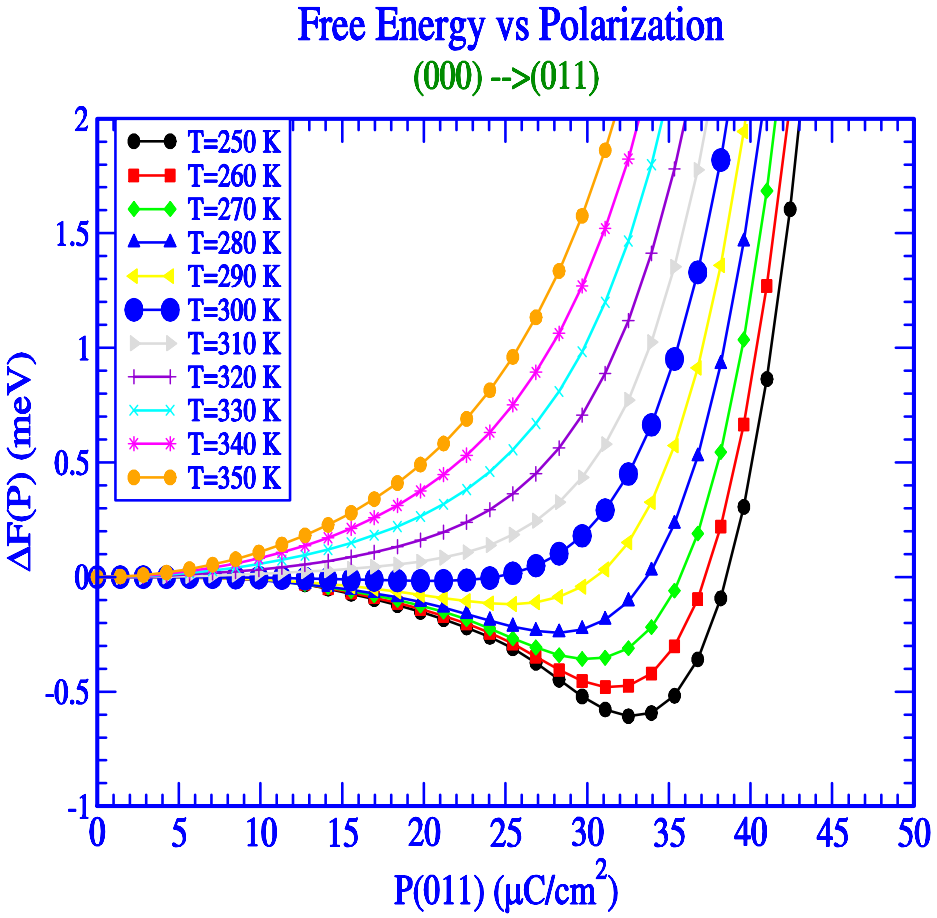
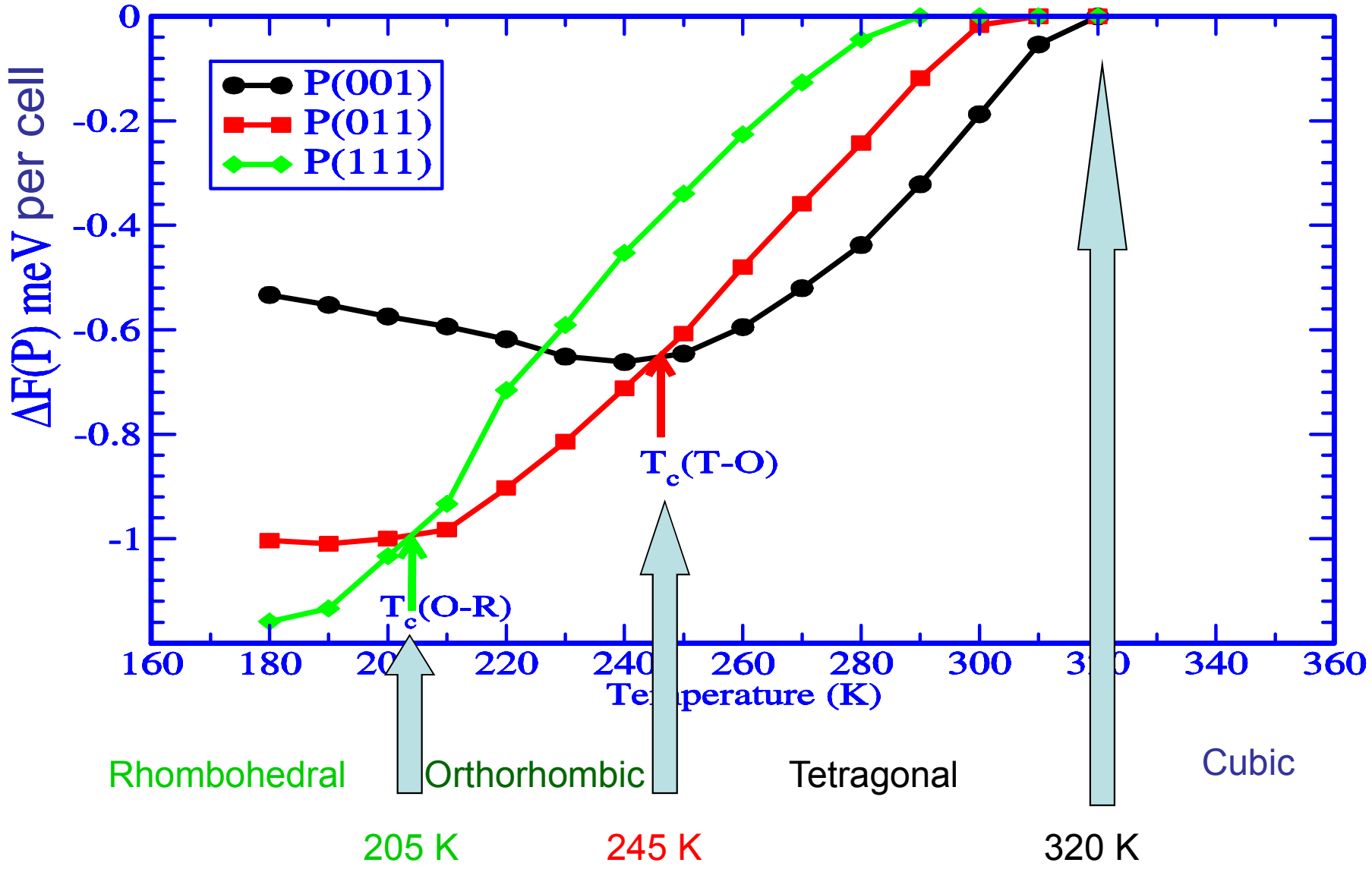
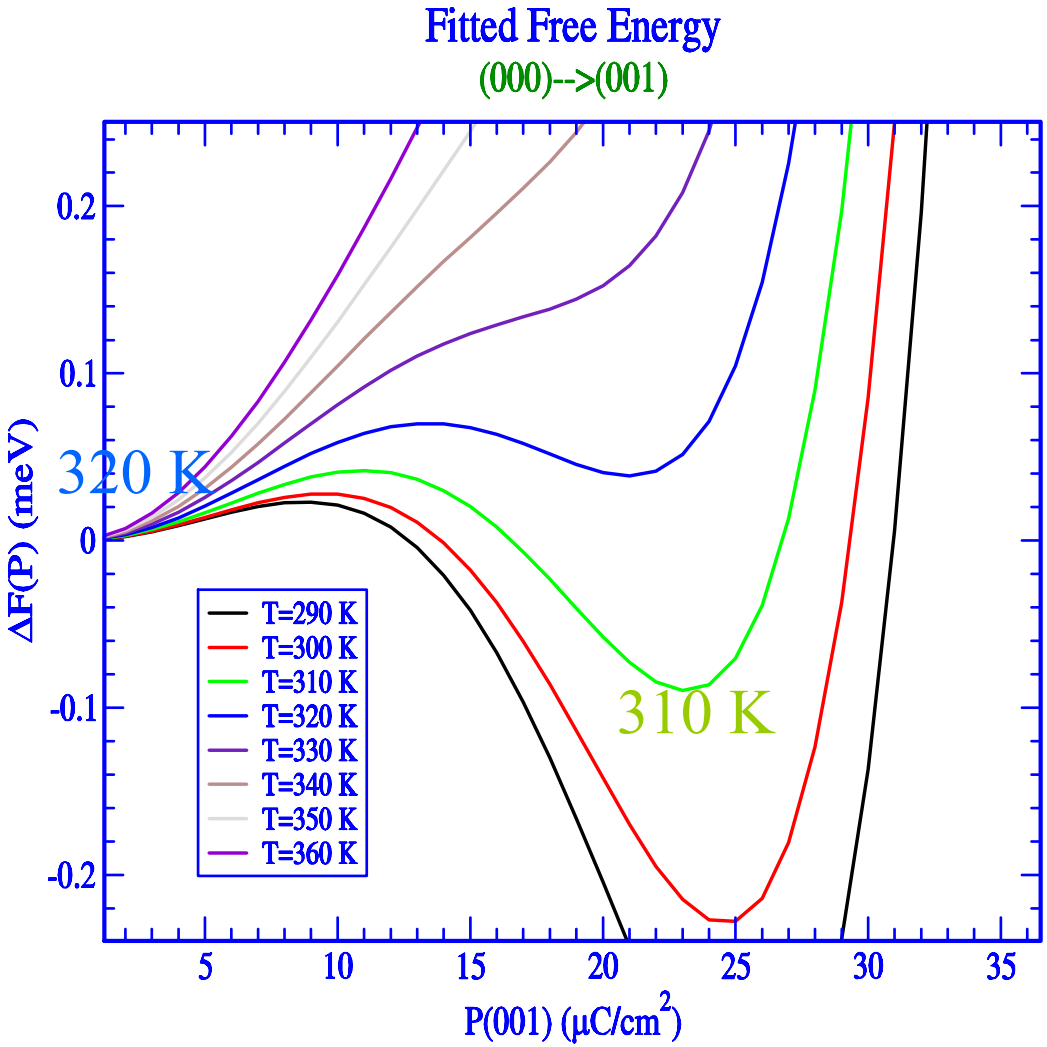




Free Energy for different phases of $BaTiO_3$



First-principles Landau-like Free Energy F(P): Order of the transition



$F(P)=F_0+A\,P^2+B_1\,P^4+$

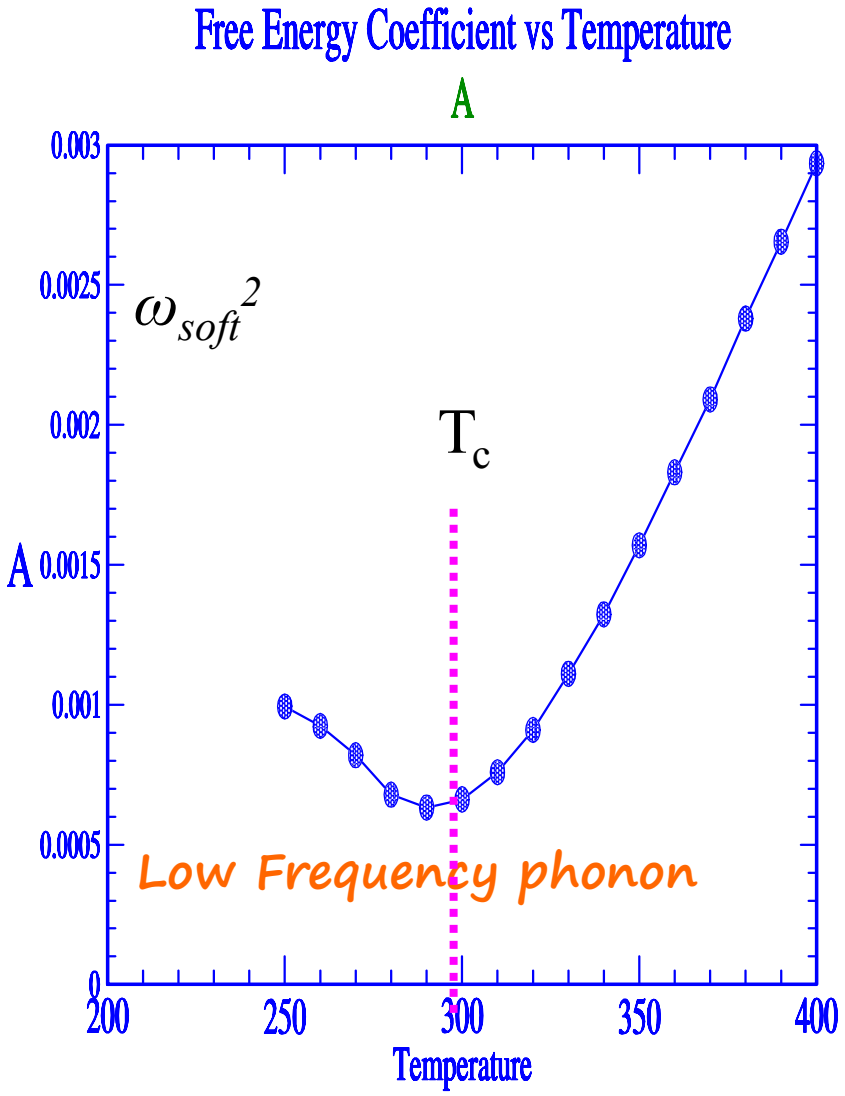
Coefficient

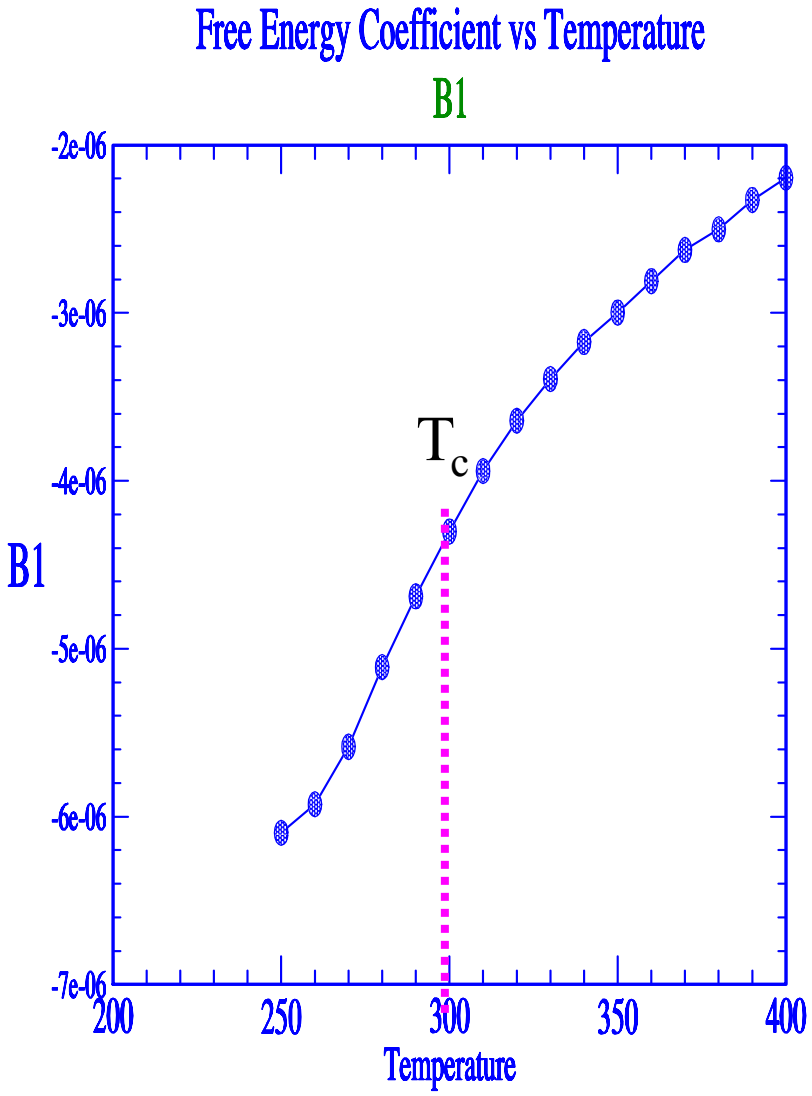
A α (soft mode frequency)^2

► First Order Transition

(with Anil Kumar, unpublished)

Free Energy Coefficients





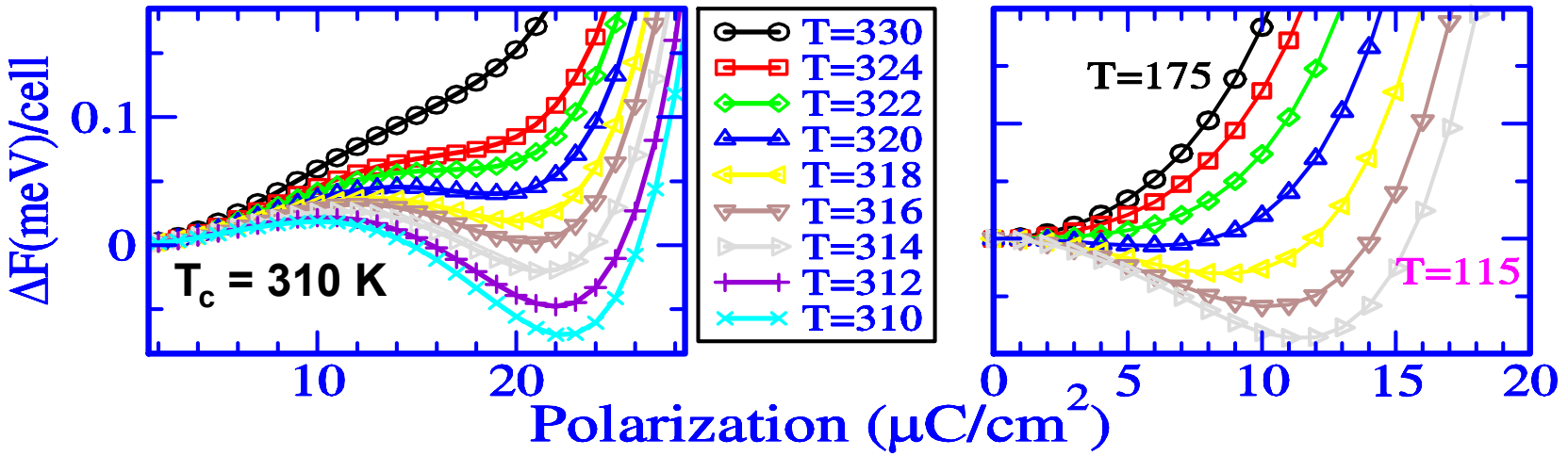
-ve Fourth order term of free energy drives the transition 1st order

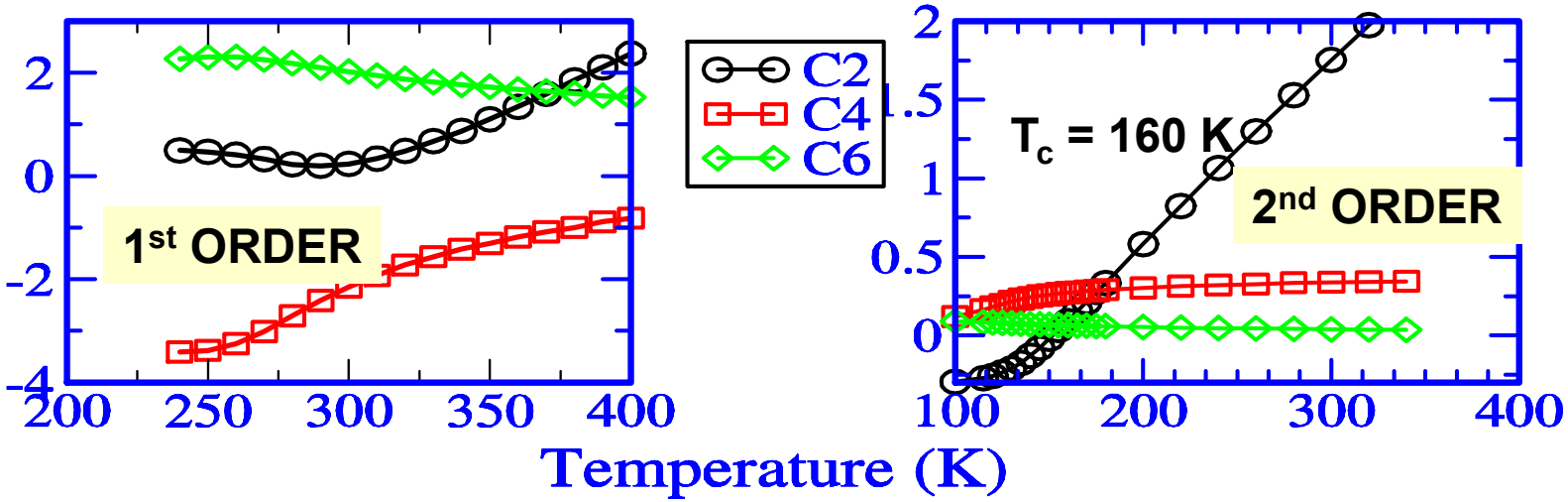
Which coupling gives 1st order?

$$\Delta F = C2\,P^2 + C4\,P^4 + C6\,P^6$$

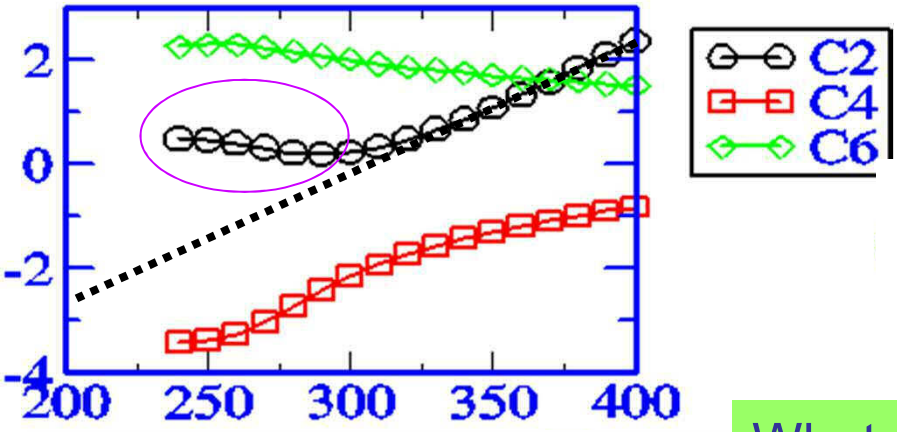
$$H_{sp} = g\,P^2\,\eta$$

Strain-P coupling *g* ON OFF





Fluctuation-driven 1st order phase transition

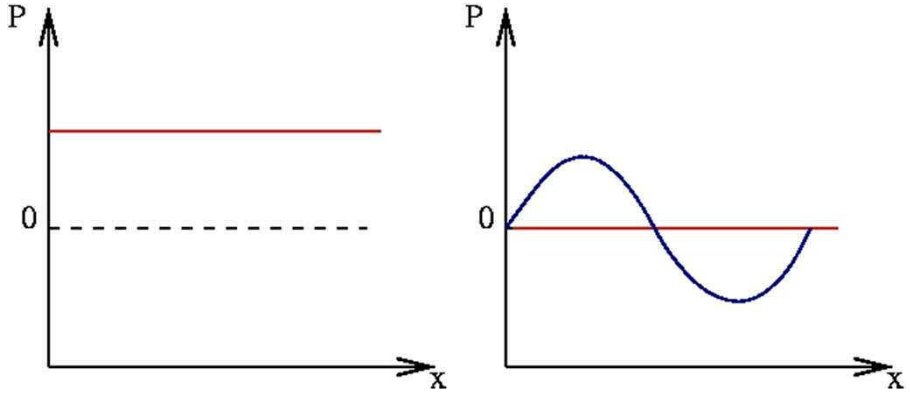


Second order coefficient
C2 > 0, even below T_c.
Cubic phase is *locally stable*?

What does our constraint on P do?

$$Z(P) = \int \Pi d\xi_i \delta(P - \frac{\sum_i \xi_i}{N}) e^{-\frac{H_0(\{\xi_i\})}{k_B T}}$$

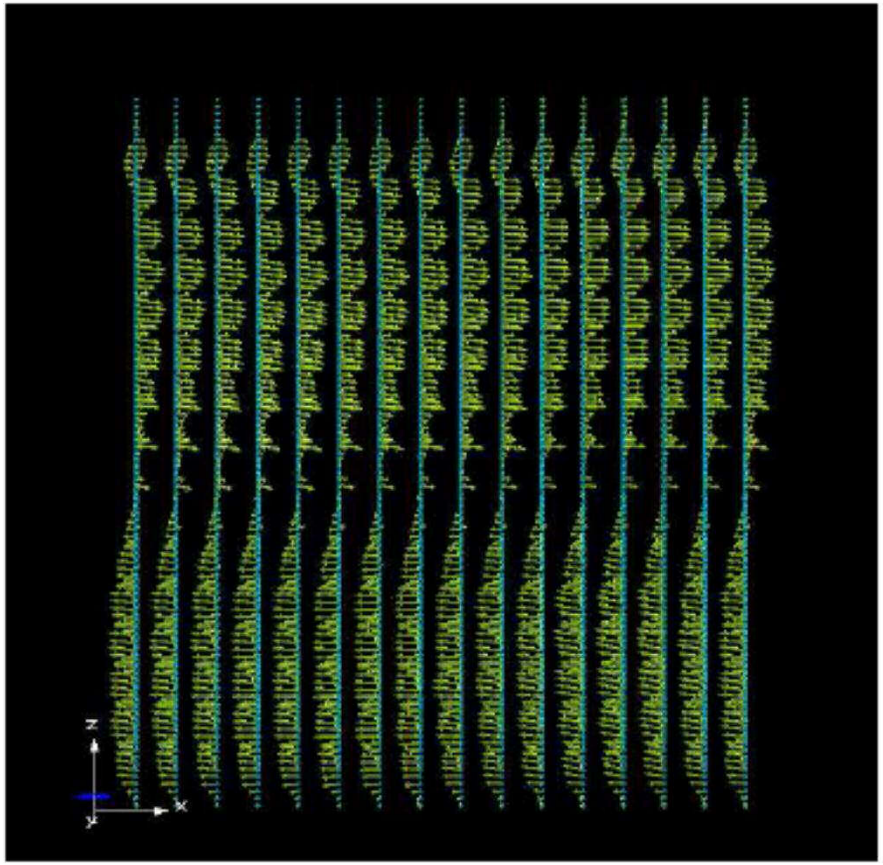
P (T < T_c) = 0 forces a state with long-wavelength fluctuation to be stable!

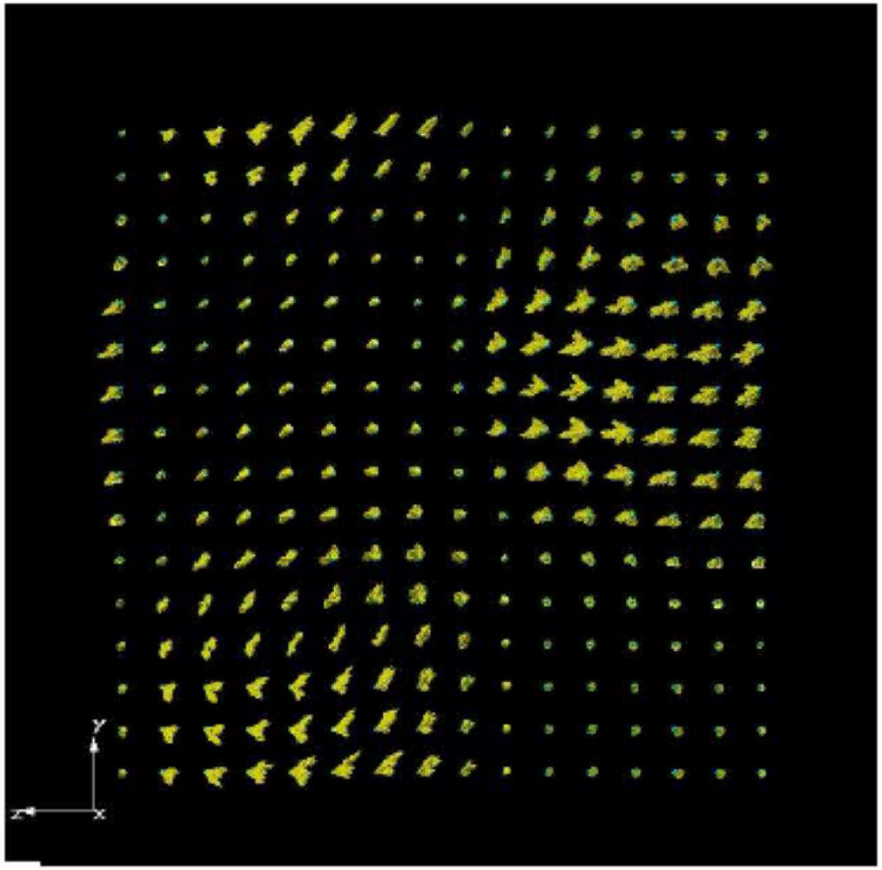


Fluctuation becomes a relevant DoF,
and can NOT be integrated out!

P=0 state of $BaTiO_3$ at T=280 K

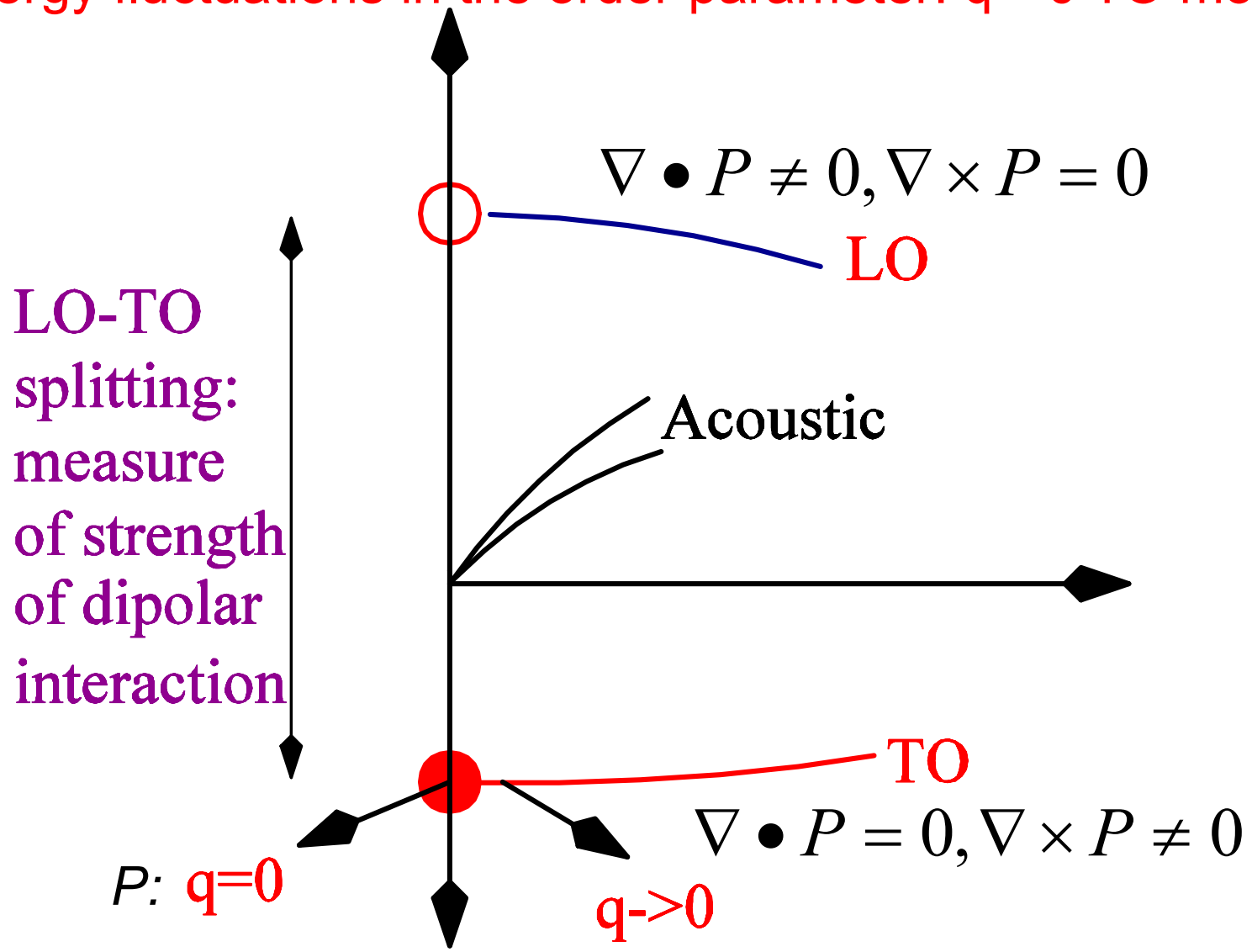
(A snapshot from a constrained P MD)





The reference configuration (P=0) at $T < T_c$ is not Paraelectric!

Low energy fluctuations in the order parameter: q→0 TO modes



Important Addition to Landau-Ginzburg Theory for Ferroelectrics

$$G(\vec{P},T) = G_0 + A(T)\int dr\,|\vec{P}(r)|^2 + B_1(T)\int dr\left[P_x^4(r)+P_y^4(r)+P_z^4(r)\right]$$

$$+ B_2(T)\int dr\,|\vec{P}(r)|^4 + C\int dr\,|\vec{P}(r)|^6 + D\int dr\,|\vec{P}(r)|^8$$

$$+ U\int dr\,|\nabla\bullet\vec{P}(r)|^2 + V\int dr\,|\nabla\times\vec{P}(r)|^2$$

$$+ \frac{1}{2\varepsilon^{\infty}}\int drdr'\frac{|\nabla\bullet\vec{P}(r)||\nabla'\bullet\vec{P}(r')|}{|r-r'|}$$

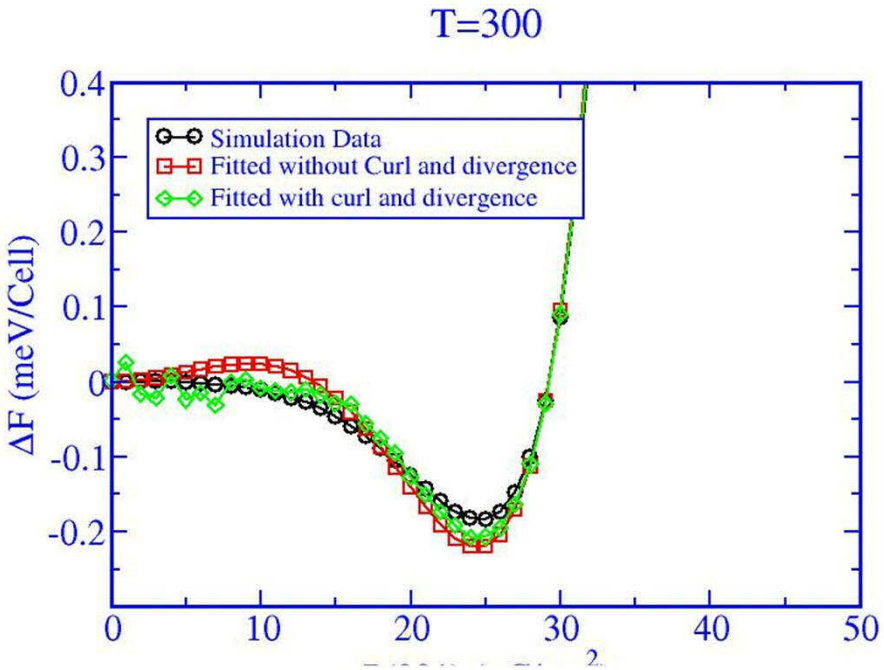
U and V: How the energetics of q→0 fluctuations in P differ from that of P

LO-TO splitting, long range interactions: parameter free

Effects of depolarization fields in finite systems, etc

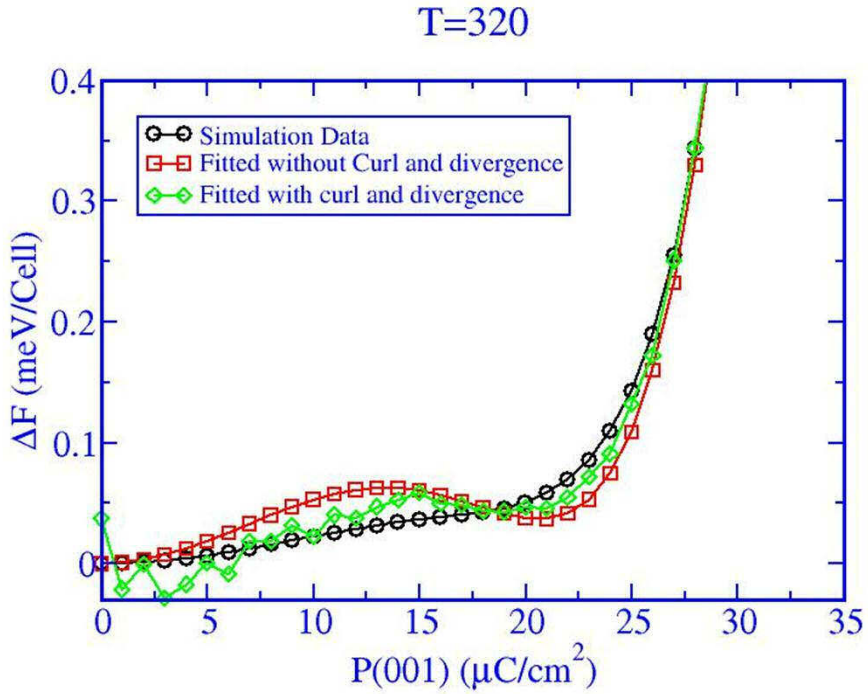
Guiding principle for continuum:

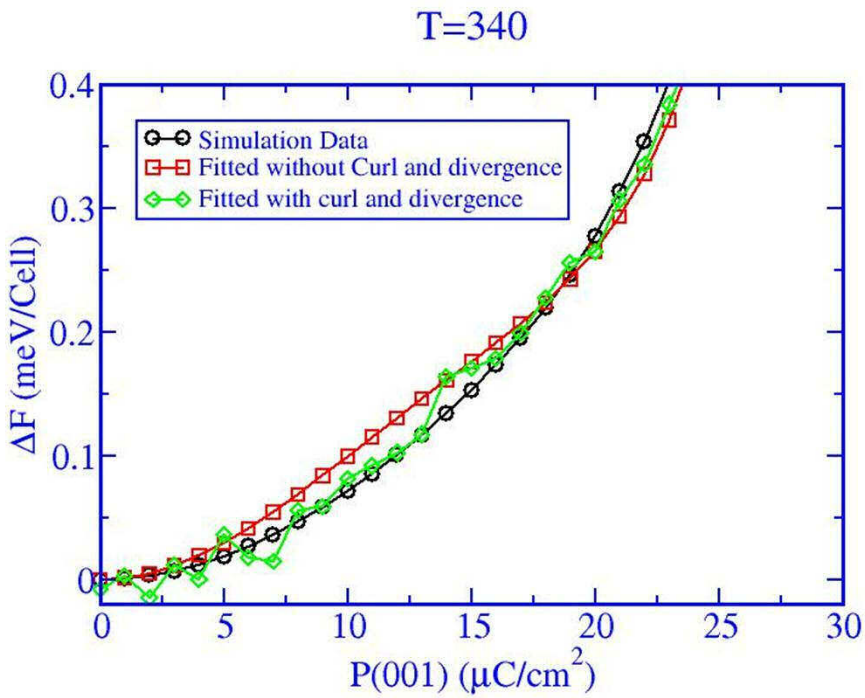
P(r) field favors to be divergence-free



Fitting Free energy with inhomogeneities in the order parameter:

- Improved quality
- Noise due to that in <div and curl terms>





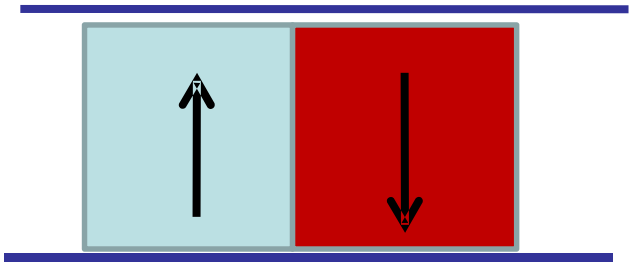
Implications of the Generalized Free Energy Functional

Polarization field should be divergence-free, as

$\nabla \bullet P$ costs energy!

Applicable to both *bulk* and *nano-scale* ferroelectrics

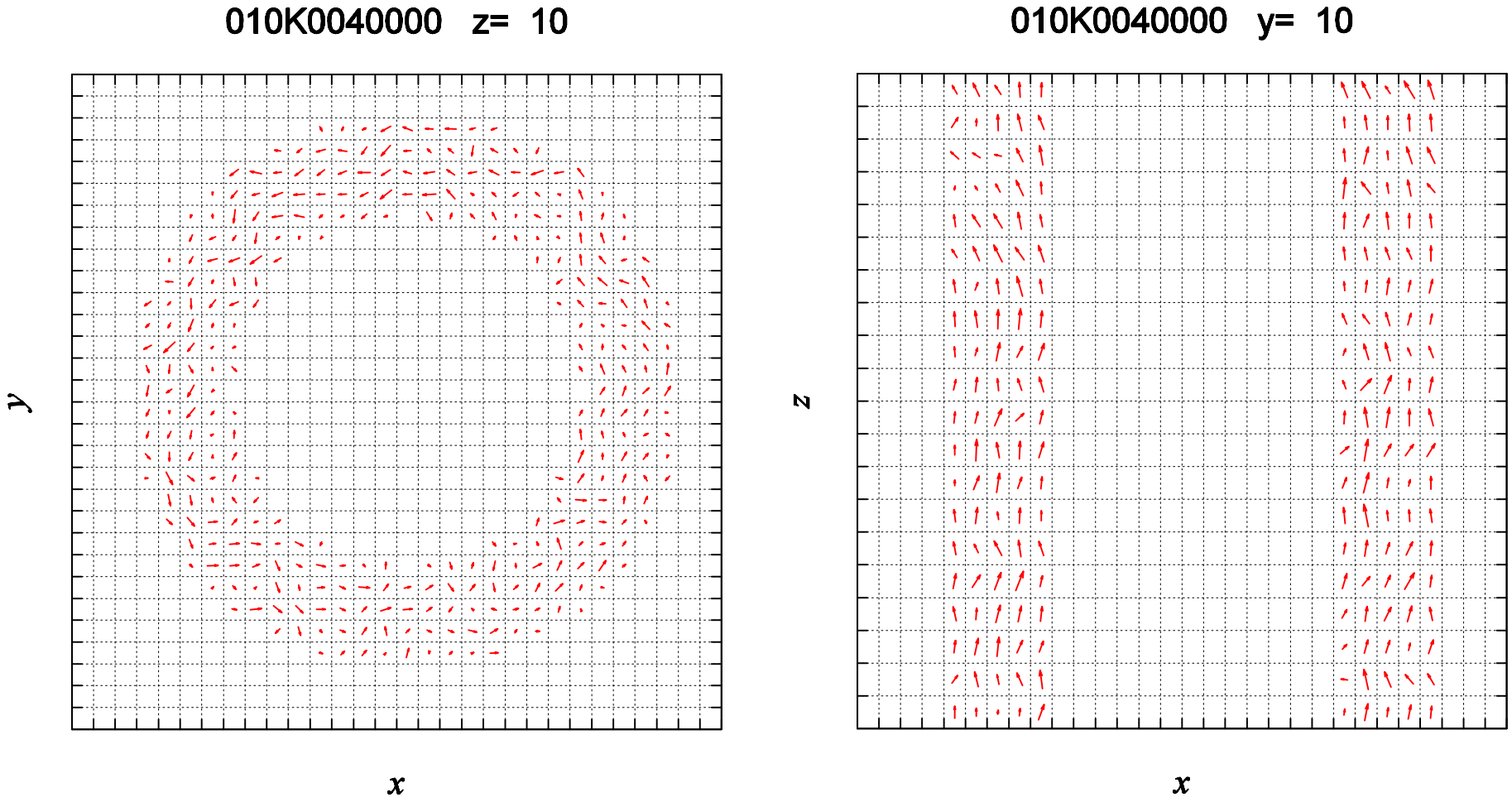
Example: nano-thin film of a FE



Effects of depolarization field included naturally.
Formation of domain: *curl P is nonzero*

Ferroelectric $BaTiO_3$ Nanotube of

Radii R_{in} = 3.2 nm; R_{out} = 5.2 nm

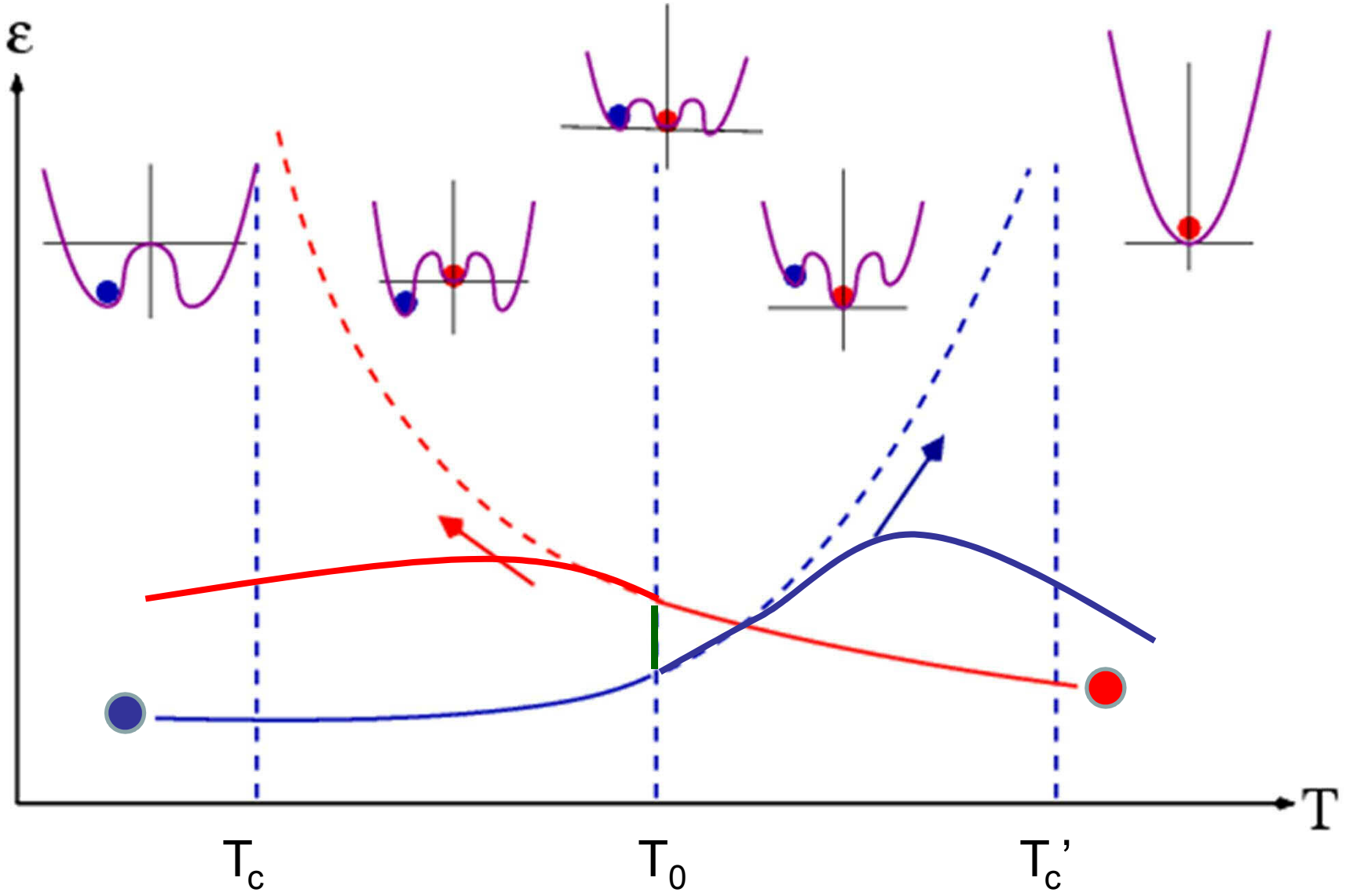


Cross section Vertical Section

Chiral ordering of dipoles

(With J Paul and T V Ramakrishnan, unpublished)

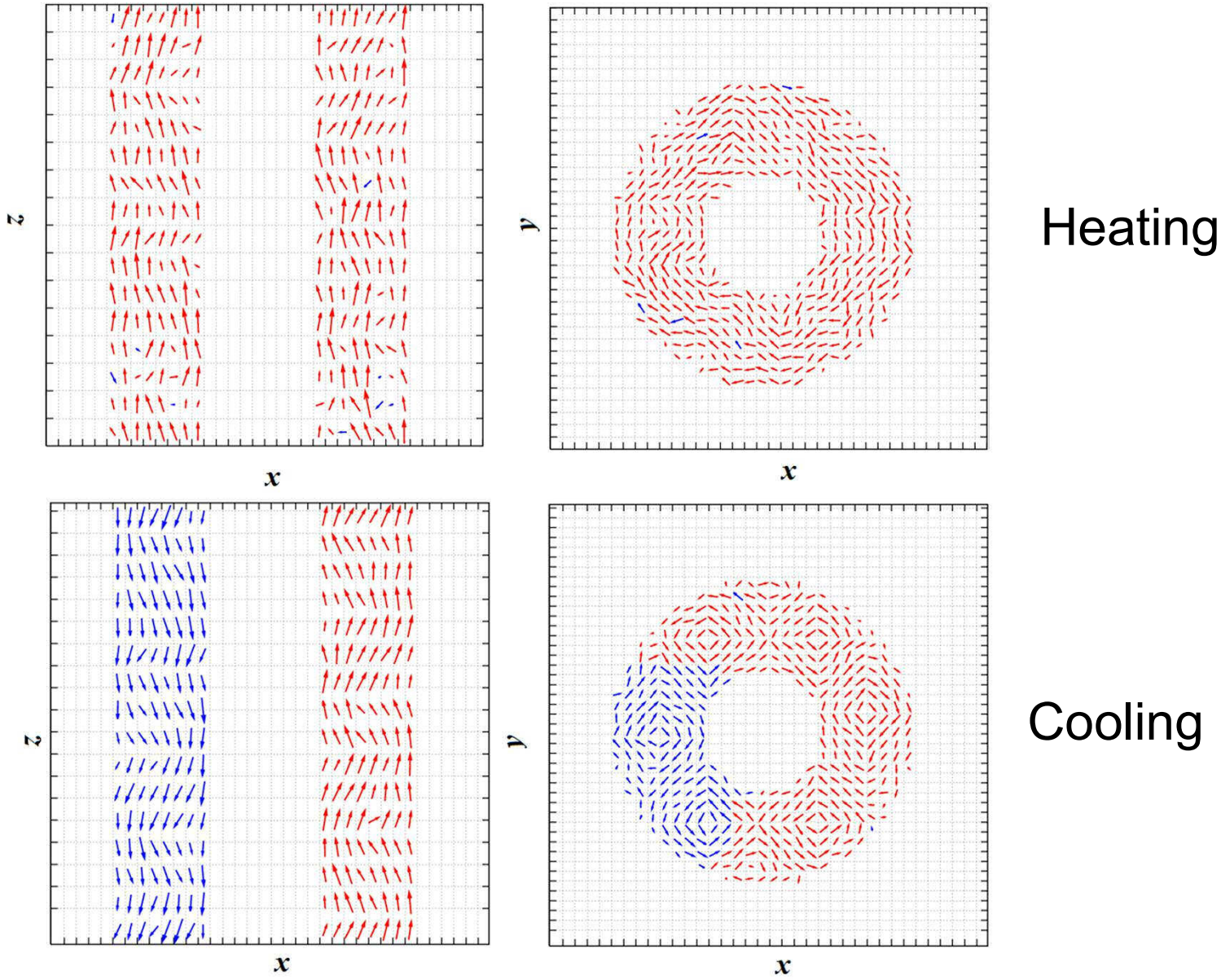
Landau Theory of 1st Order Ferroelectric Transition



Smoother (superheated and supercooled) curves

Hysteresis: Origin in Metastable Degenerate States

Nature of the low temperature phase



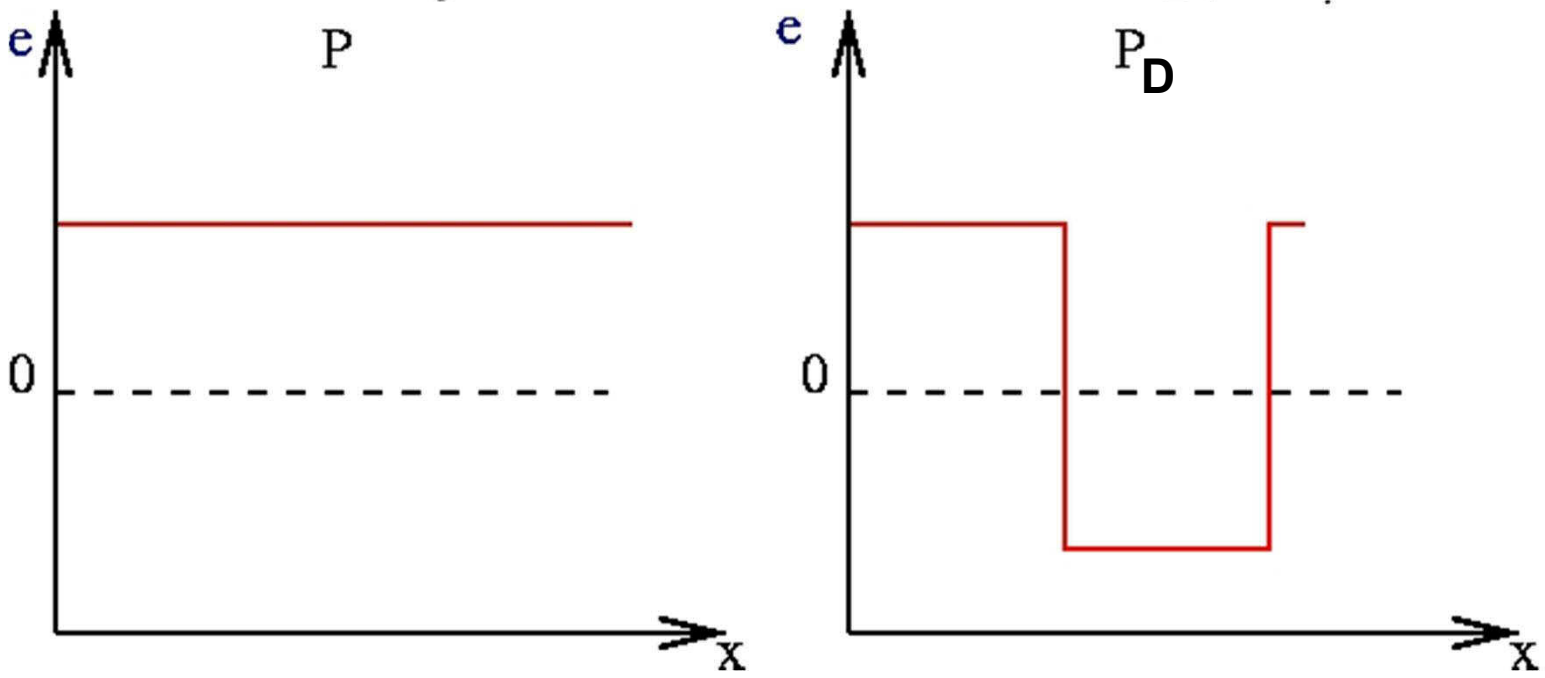
Heating

Cooling

Ferroelectric Domains:

free energy of inhomogeneous order parameter

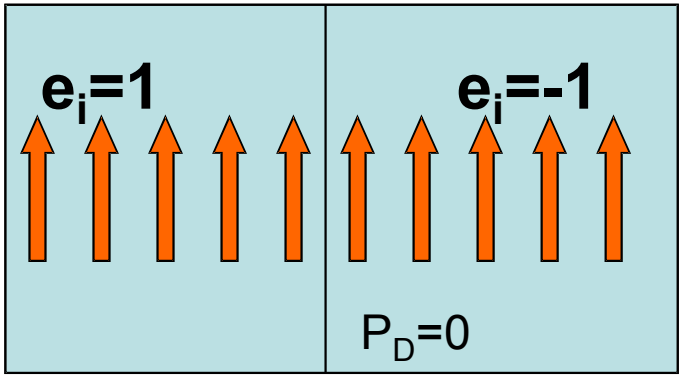
$$P = \frac{1}{N}\sum_i \xi_i \qquad P_D = \frac{1}{N}\sum_i \hat{e}_i \xi_i$$

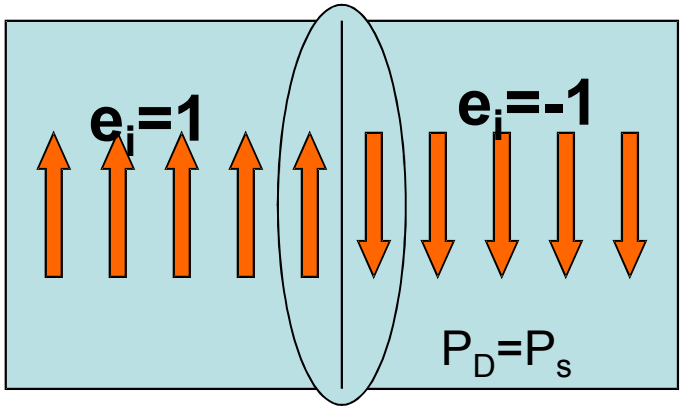


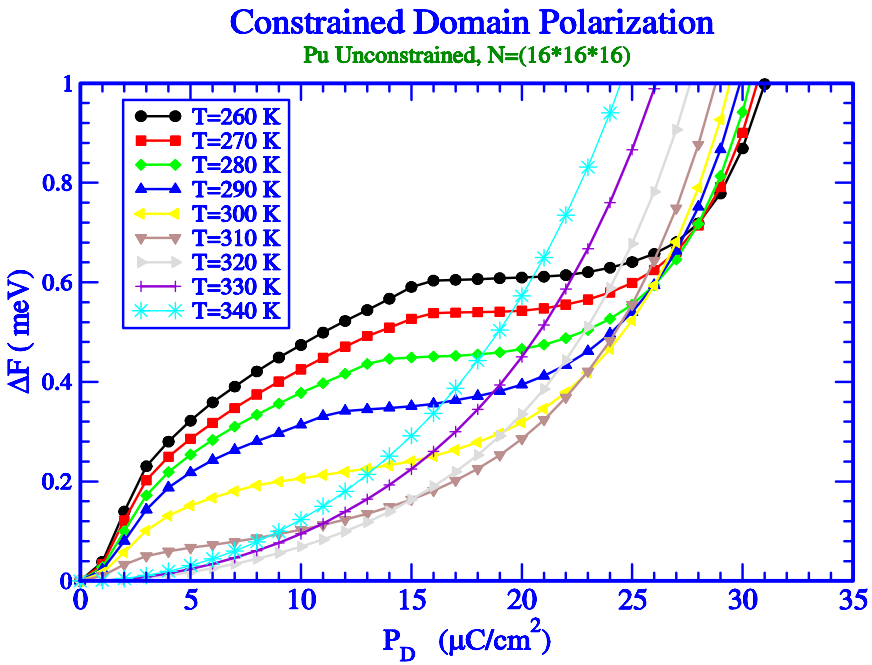
Augmented H remains the same formally:

Access to free energy of any inhomogeneous configuration of P!

Domain Wall Energy







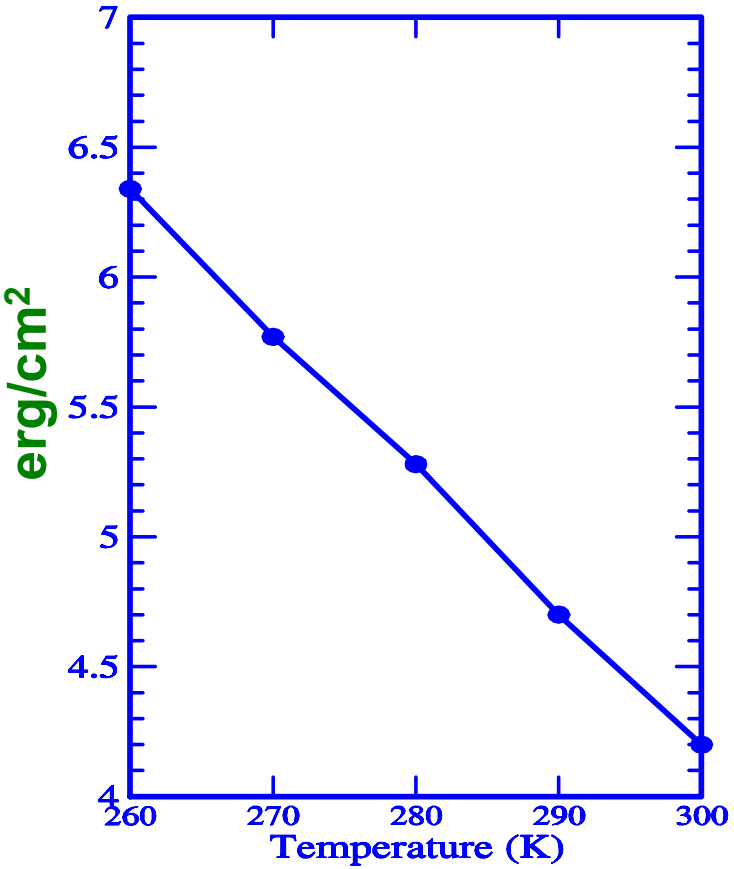
$$\vec{P}_D = \frac{(\varepsilon_\infty - 1)}{4\pi}\vec{E}_d + \frac{Z^*(\sum_{i=1}^{N/2} e_i.\vec{\xi}_i + \sum_{i=N/2+1}^{N} e_i.\vec{\xi}_i)}{\Omega}$$

Domain Wall Energy = $\Delta F\big|_{P_D=P_s}$

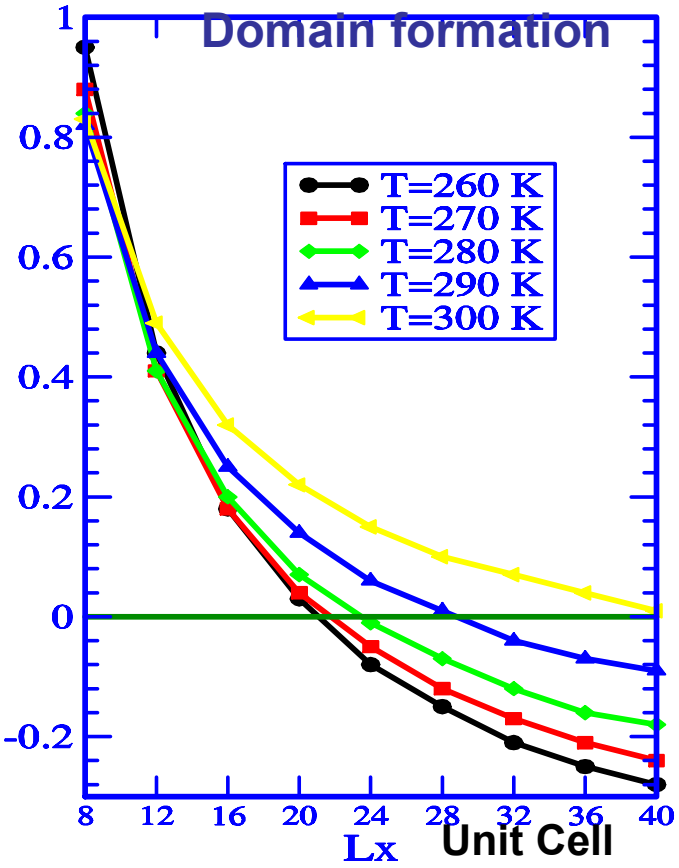
Free energy difference of the two configuration shown above can be used to calculate domain wall energy.

Stability of Domains with system size

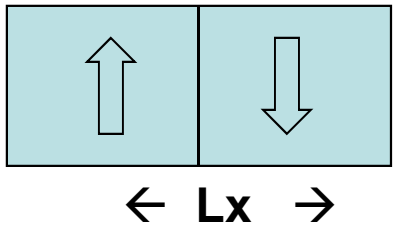
Domain Wall Energy



Gain in Energy wrt PE phase with Domain formation



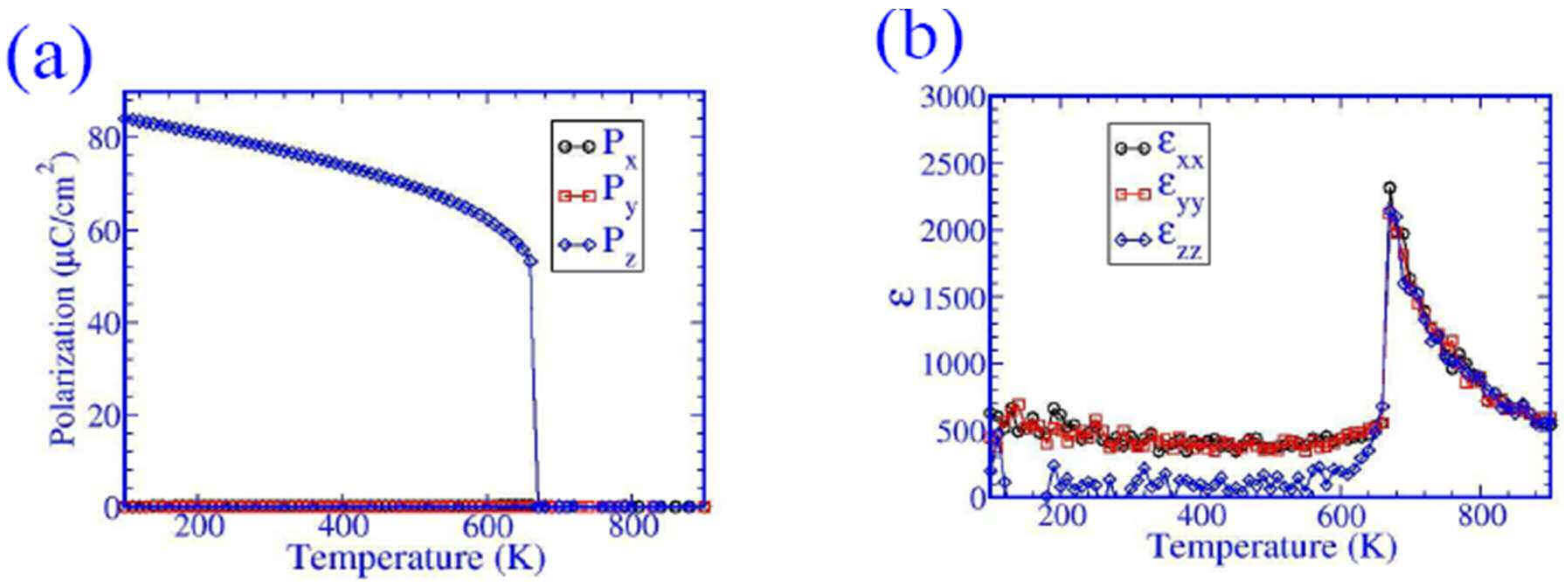
Ly= Lz =16 Unit Cell



Domain is stable if $\Delta F(\uparrow\uparrow) + Domain\ \ Wall\ Energy < 0$

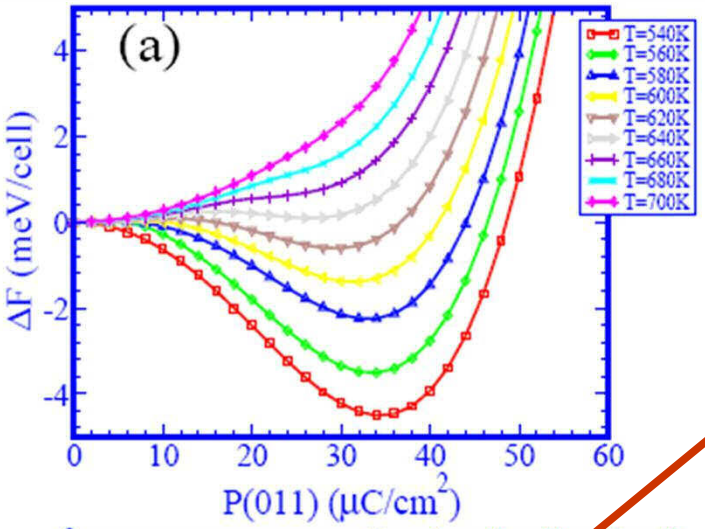
Domain is stable if system size > a critical size [> 8nm] for a given temp.

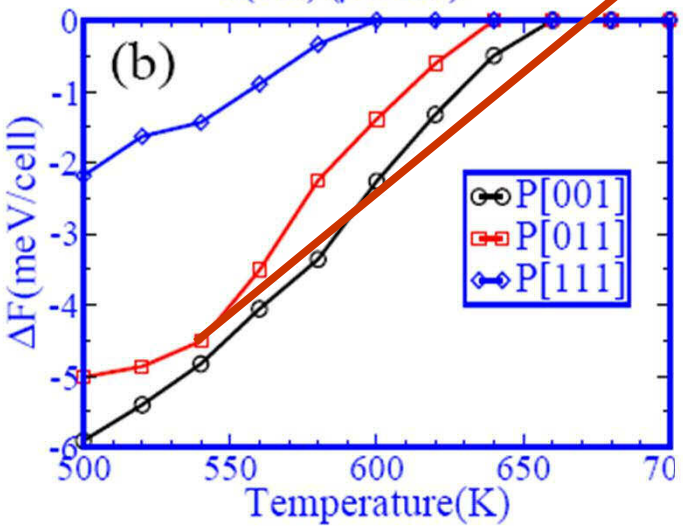
$PbTiO_3$

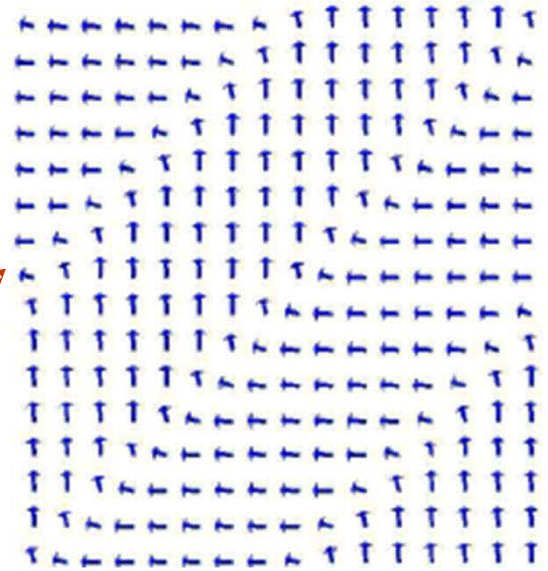


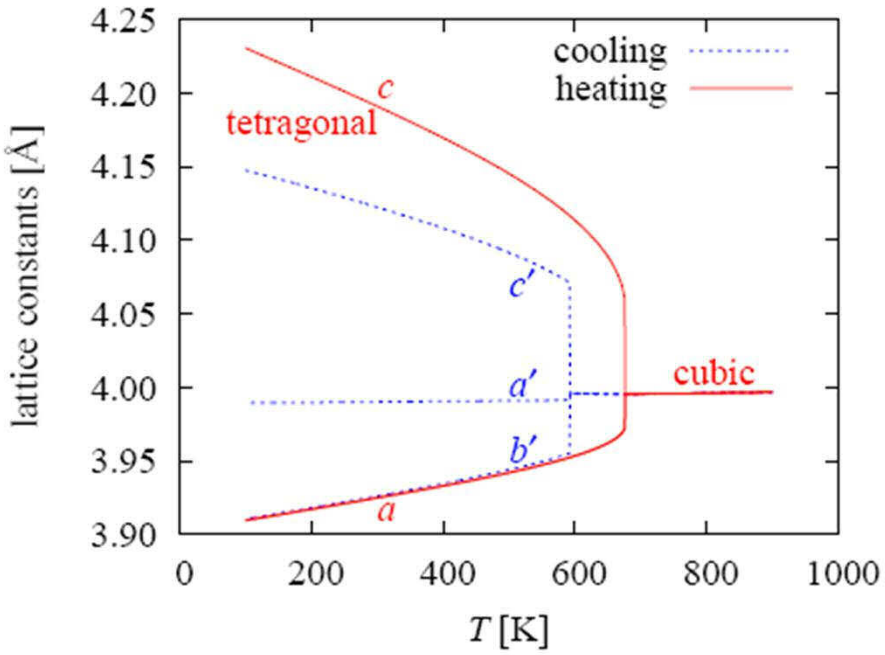
Only one transition: Cubic to tetragonal P(001)

Free Energies: $PbTiO_3$



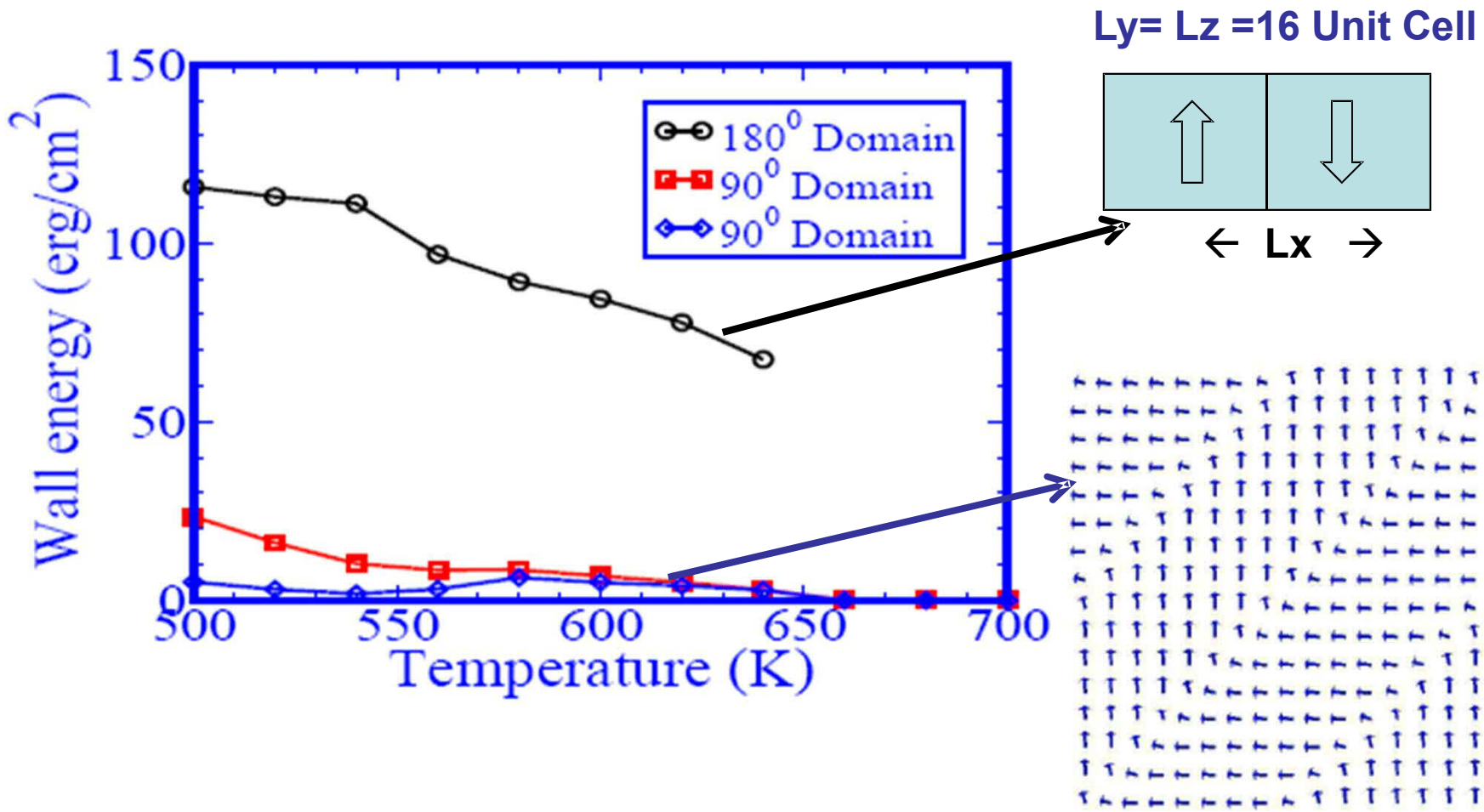






Inhomogeneous Ordering:
T-hysteresis

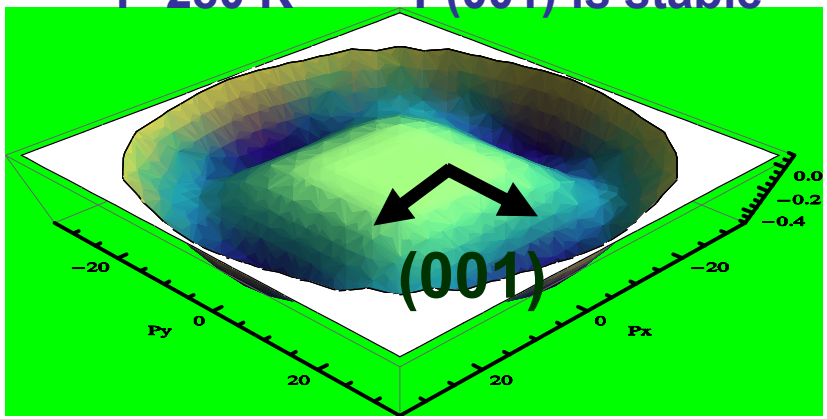
90° vs 180° Domains in $PbTiO_3$



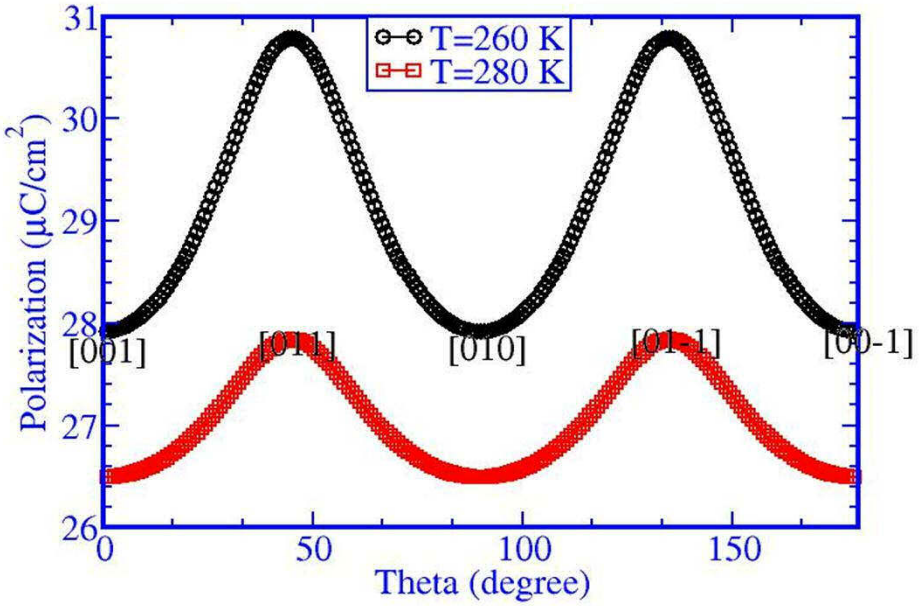
180°: An order of magnitude larger than that of $BaTiO_3$!

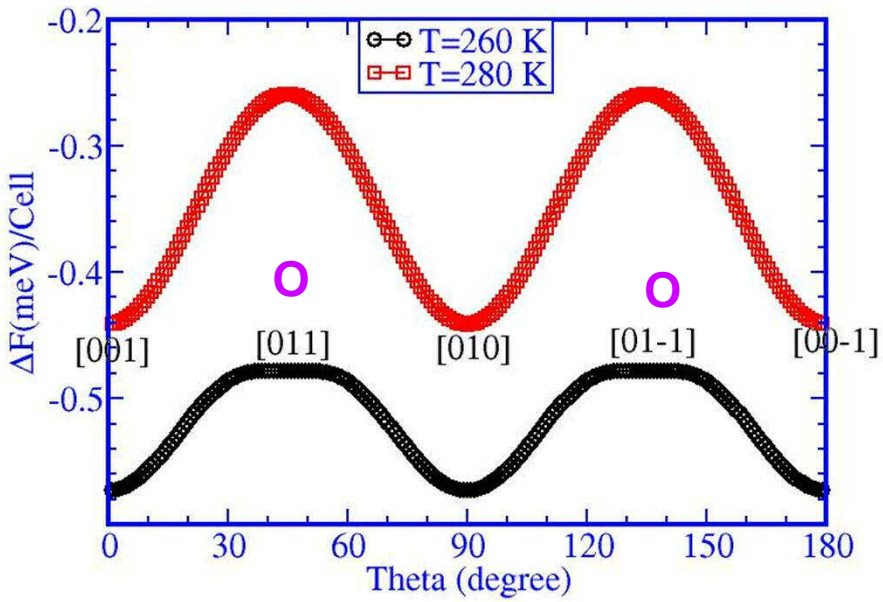
90° : More stable

Minimum Free Energy Pathway for Polarization Switching: P(001) to –P(001)



	Temp.	Energy Barrier
Red	T=280	0.18 meV/cell
Black	T=260	0.10 meV/cell





Lower barrier at 260 K due to vicinity to T-O phase transition

Conclusions

- Method for first-principles free energies of structural phase transitions:
  constrained MD + thermodynamics integration

- Clarified the nature of *fluctuation driven 1st order FE transitions.*

- Addition to Landau free energy functional:

  Polarization field should be divergence-free

- Spatial fluctuations: Hysteretic ε(T) of $BaTiO_3$ nanotubes

- Contrast between $BaTiO_3$ and $PbTiO_3$

Many applications of the method are possible
(eg extension to shape memory alloys) and planned.

Thank You!