Karlsruhe Institute of Technology

Phase-field modeling of ferroelectric materials in the context of a multiscale simulation chain

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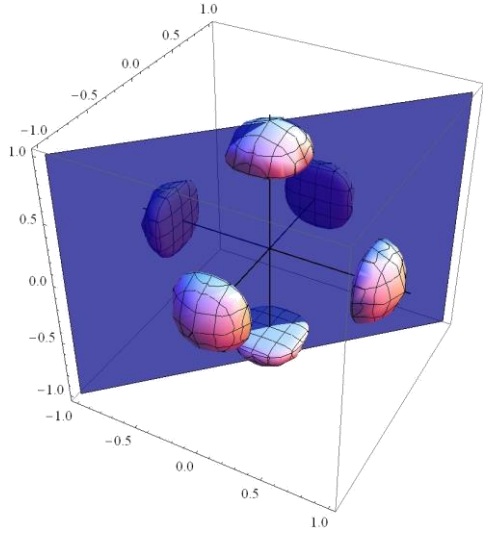
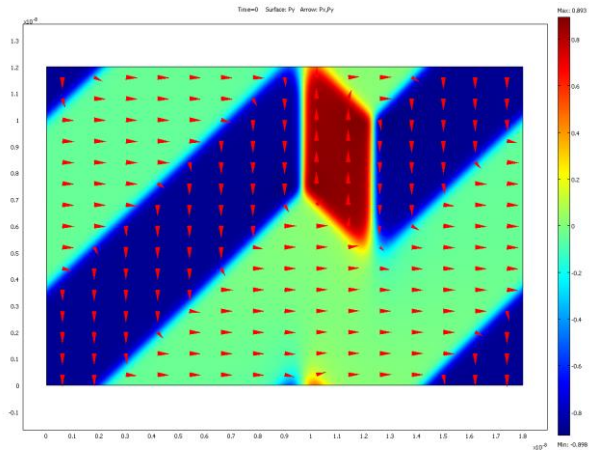
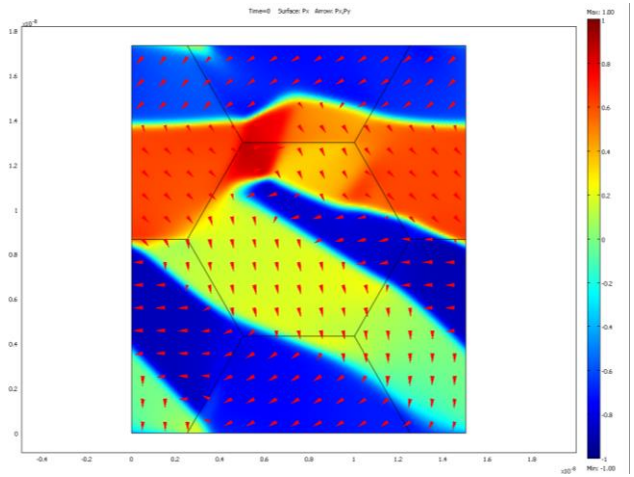
Philadelphia, PA

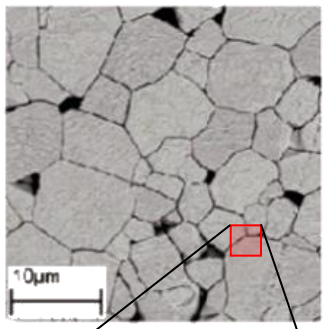
Institute for Materials Research (IMF II)





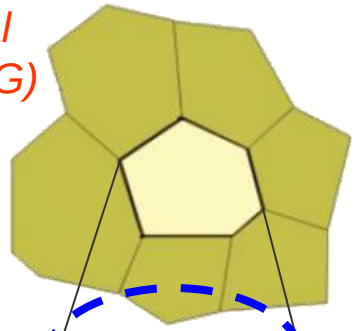


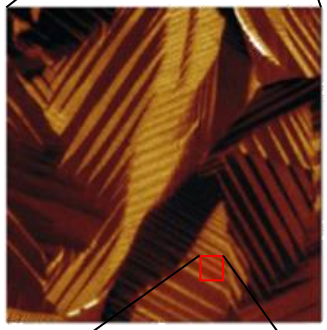
Motivation: virtual material development for ferroelectrics



Micromechanical modeling (RB/SAG)

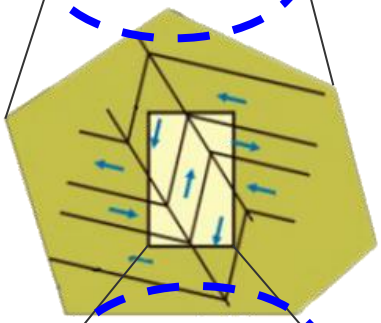
micro-scale:
grain structure

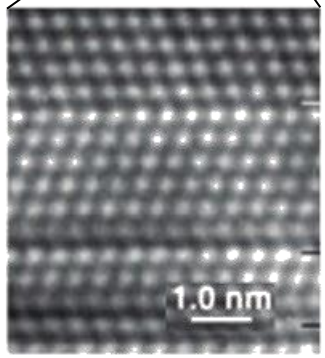




Phase field modeling (KIT)

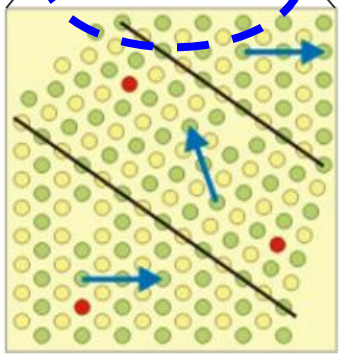
meso-scale:
ferroelectric
domain patterns





ab-initio / DFT / SMP (FhG-IWM)

nano-scale:
distorted unit cell



➔ need for multiscale-approach

➔ BMBF-Project COMFEM:
Computer based multiscale modeling for virtual development of polycrystalline ferroelectric materials (esp. PZT)

Project partners:

- Fraunhofer IWM Freiburg (FhG-IWM)
- Robert Bosch GmbH (RB)
- Siemens AG (SAG)
- PI Ceramic AG (PIC)
- CeramTec AG (CT)
- TU Hamburg-Harburg (TUHH)

Our aim:

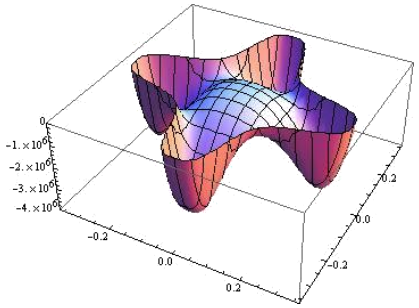
➔ development of two interfaces in simulation chain

Thermodynamically motivated phase-field theory

Aim: calculation of ferroelectric domain patterns on meso-scale

➔ Helmholtz free energy function contains all crystallographic and boundary information

$$\psi(P_i, P_{i,j}, \epsilon_{ij}, D_i)$$



➔ state variables: partial derivatives with respect to natural variables

$$\sigma_{ji} = \frac{\partial \psi}{\partial \epsilon_{ij}} \qquad E_i = \frac{\partial \psi}{\partial D_i}$$

➔ temporal and spatial evolution of polarization (order parameter):
time-dependent Ginzburg-Landau-equation

➔ domain switching caused by minimization of free energy

$$\left(\frac{\partial \psi}{\partial P_{i,j}} \right)_{,j} - \frac{\partial \psi}{\partial P_i} = \beta_{ij} \dot{P}_j$$

Formulation of the phase-field model's free energy

6th order free energy

$$\psi = \frac{1}{2} G_{ijkl} P_{i,j} P_{k,l}$$

$$+ \frac{1}{2}\alpha_{ij} P_i P_j + \frac{1}{2}\alpha_{ijkl} P_i P_j P_k P_l + \frac{1}{6}\alpha_{ijklmn} P_i P_j P_k P_l P_m P_n$$

$$+ q_{ijkl}\epsilon_{ij} P_k P_l + \frac{1}{2} c_{ijkl}\epsilon_{ij}\epsilon_{kl}$$

$$+ \frac{1}{2\kappa_0}(D_i - P_i)(D_i - P_i)$$

Main parts of energy function:

- gradient term
- Landau energy
- electromechanical coupling term
- elastic energy term
- electric field energy

Adjustment of 6th order free energy

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Interface ab-initio / phase field modeling: Adjustment of parameters

➔ ab-initio: (input)

- piezoelectric coefficients d_{ijk}
- dielectric permittivity κ_{ij}
- elastic stiffness C_{ijkl}
- spontaneous strain ε_S
- spontaneous polarization P^S
- domain wall energy (90°/180°) $\gamma_{90/180}$
- domain wall thickness (90°/180°) $\xi_{90/180}$

Ginzburg-Landau-theory:
15 parameters (6th order)

α_{ijklmn}
q_{ijkl}
c_{ijkl}
G_{ijklj}

$$\psi = \frac{1}{2}G_{ijkl}P_{i,j}P_{k,l}$$
$$+\frac{1}{2}\alpha_{ij}P_iP_j + \frac{1}{2}\alpha_{ijkl}P_iP_jP_kP_l + \frac{1}{6}\alpha_{ijklmn}P_iP_jP_kP_lP_mP_n$$
$$+q_{ijkl}\epsilon_{ij}P_kP_l + \frac{1}{2}c_{ijkl}\epsilon_{ij}\epsilon_{kl}$$
$$+\frac{1}{2\kappa_0}(D_i - P_i)(D_i - P_i)$$

- adjustment method has been developed
- applied to PTO and PZT

B. Völker, P. Marton, C. Elsässer, M. Kamlah: *"Multiscale Modeling of ferroelectric materials: a transition from the atomic level to phase-field modeling".* Continuum Mechanics and Thermodynamics, submitted on Sept. 3rd, 2010

Adjustment of 6th order free energy: Results for PTO and PZT

		unit	PTO first-principles data (input)	PTO phase-field model (adjusted)	PZT first-principles data (input)	PZT phase-field model (adjusted)
DFT	P_0	[C/m^2]	0.88	0.88	0.58	0.58
	$e_{\parallel}$		0.04209*	0.04209	0.012039*	0.012039
	$e_{\perp}$		−0.007388*	−0.007388	−0.0017946*	−0.0017946
	κ_{33}		$17\kappa_0$	$17\kappa_0$	$18\kappa_0$	$18\kappa_0$
	κ_{11}		$54\kappa_0$	$54\kappa_0$	$76\kappa_0$	$76\kappa_0$
	C_{11}	[Pa]	342×10^9	342×10^9	361×10^9	361×10^9
	C_{12}	[Pa]	131×10^9	131×10^9	115×10^9	115×10^9
	C_{44}	[Pa]	108×10^9	108×10^9	91×10^9	91×10^9
	d_{33}	[C/m]	2.46×10^{-11}	1.42×10^{-11}	1.57×10^{-11}	6.58×10^{-12}
	d_{31}	[C/m]	-8.04×10^{-12}	-2.52×10^{-12}	-4.32×10^{-12}	-9.87×10^{-13}
	d_{15}	[C/m]	1.72×10^{-11}	1.72×10^{-11}	1.53×10^{-12}	1.53×10^{-12}
	$\gamma_{\mathrm{DFT},180}$	[mJ/m^2]	112	173	96	96
	$\gamma_{\mathrm{DFT},90}$	[mJ/m^2]	24	71	-	-
	$\xi_{\mathrm{DFT},180}$	[m]	4.5×10^{-10}	4.5×10^{-10}	6.7×10^{-10}	6.7×10^{-10}
	$\xi_{\mathrm{DFT},90}$	[m]	5.4×10^{-10}	5.4×10^{-10}	-	-
SMP	$\gamma_{\mathrm{SMP},180}$	[mJ/m^2]	156	156	-	-
	$\gamma_{\mathrm{SMP},90}$	[mJ/m^2]	64	64	36	36
	$\xi_{\mathrm{SMP},180}$	[m]	3.9×10^{-10}	3.9×10^{-10}	-	-
	$\xi_{\mathrm{SMP},90}$	[m]	4.9×10^{-10}	4.9×10^{-10}	6.6×10^{-10}	6.6×10^{-10}

atomistic input:
DFT: density functional theory
SMP: shell-model potential
(P. Marton and C. Elsässer, IWM Freiburg)

generally good agreement, but:

- not enough degrees of freedom for piezoelectric coefficients
- only cubic elastic behavior taken into account

Formulation of the phase-field model's free energy

6th order free energy

$$\psi = \frac{1}{2} G_{ijkl} P_{i,j} P_{k,l}$$

$$+ \frac{1}{2}\alpha_{ij} P_i P_j + \frac{1}{2}\alpha_{ijkl} P_i P_j P_k P_l + \frac{1}{6}\alpha_{ijklmn} P_i P_j P_k P_l P_m P_n$$

$$+ q_{ijkl}\epsilon_{ij} P_k P_l + \frac{1}{2} c_{ijkl}\epsilon_{ij}\epsilon_{kl}$$

$$+ \frac{1}{2\kappa_0}(D_i - P_i)(D_i - P_i)$$

additional terms

$$+ f_{ijklmn}\epsilon_{ij}\epsilon_{kl} P_m P_n + g_{ijklmn}\epsilon_{ij} P_k P_l P_m P_n$$

[Su,Landis2007], for $BaTiO_3$

Main parts of energy function:

- gradient term
- Landau energy
- electromechanical coupling term
- elastic energy term
- electric field energy

benefit of additional terms:

more degrees of freedom
for adjustment process:

➔ f-term: tetragonal elastic behavior
➔ g-term: independent adjustment of d_{ijk}

Y. Su, C. M. Landis: *"Continuum thermodynamics of ferroelectric domain evolution: Theory, finite element implementation, and application to domain wall pinning".* Journal of the Mechanics and Physics of Solids, 55 (2007), 280–305

Improvement of adjustment process – additional energy terms

Additional elastic energy term

$$\psi_{\text{elast}}(\epsilon_{ij}, P_i) = c_{ijkl}\epsilon_{ij}\epsilon_{kl} + f_{ijklmn}\epsilon_{ij}\epsilon_{kl}P_mP_n$$

From [Su,Landis2007], for $BaTiO_3$

Idea: elastic stiffness depends on polarization $C_{ijkl} = \frac{\partial}{\partial\epsilon_{kl}}\sigma_{ij} = \frac{\partial^2}{\partial\epsilon_{ij}\partial\epsilon_{kl}}\psi(P_i, \epsilon_{ij})$

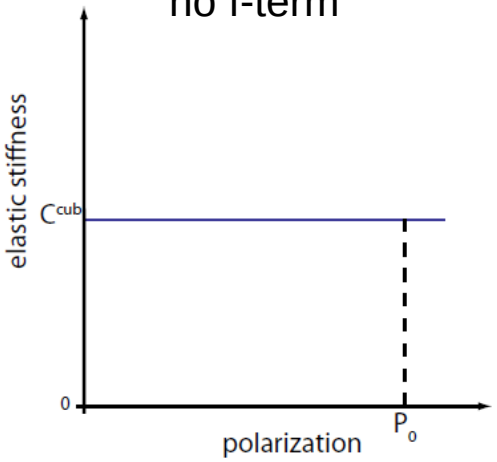
P=0: cubic elastic properties C^{cub}

$P=P_0$: tetragonal elastic properties C^{tetr}

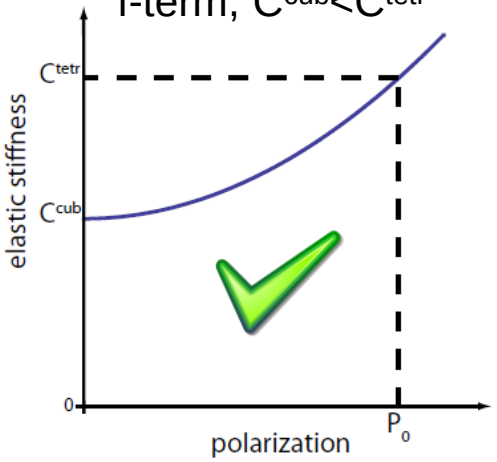
} can be adjusted independently

➔ works fine for $BaTiO_3$, but problematic for DFT predictions of $PbTiO_3$ and PZT

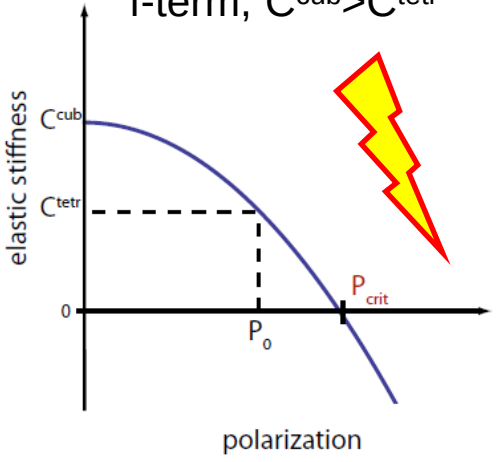
no f-term



f-term, $C^{cub}<C^{tetr}$



f-term, $C^{cub}>C^{tetr}$



Improvement of adjustment process – additional energy terms

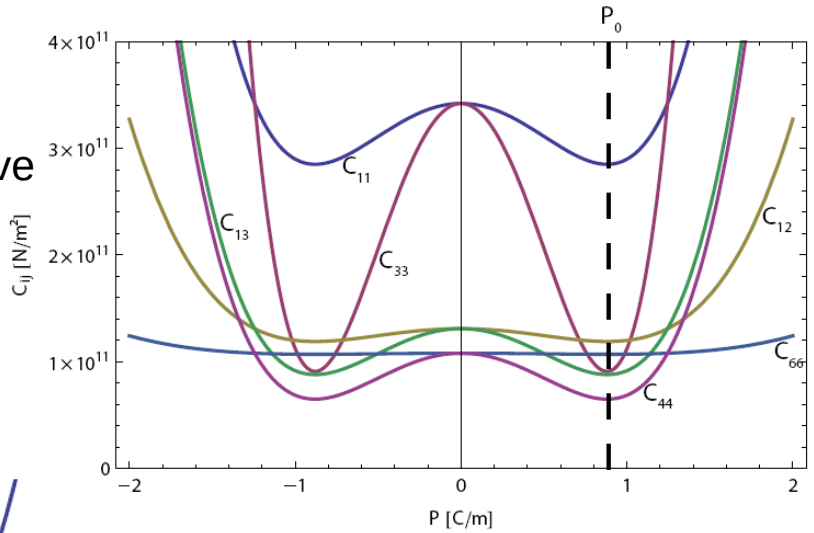
Suggestion: additional elastic energy term

$$\psi_{\text{elast}}(\epsilon_{ij}, P_i) = c_{ijkl}\epsilon_{ij}\epsilon_{kl} + f_{ijklmn}\epsilon_{ij}\epsilon_{kl}P_mP_n + h_{ijklmnrs}\epsilon_{ij}\epsilon_{kl}P_mP_nP_rP_s$$

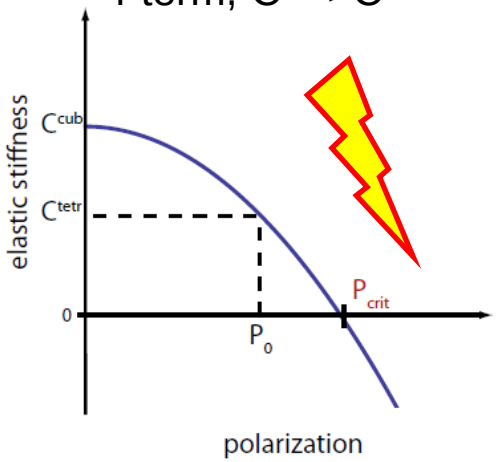
h-term necessary, when $C^{cub}>C^{tetr}$

➔ h-term: ensures elastic stiffness to remain positive

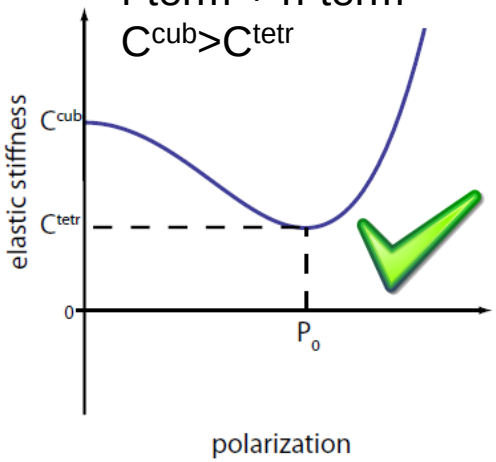
➔ one possibility: C(P) has minimum at $P=P_0$



f-term, $C^{cub}>C^{tetr}$



f-term + h-term
$C^{cub}>C^{tetr}$



Extended free energy

$$\psi = \frac{1}{2} G_{ijkl} P_{i,j} P_{k,l}$$

$$+\frac{1}{2}\alpha_{ij} P_i P_j + \frac{1}{2}\alpha_{ijkl} P_i P_j P_k P_l + \frac{1}{6}\alpha_{ijklmn} P_i P_j P_k P_l P_m P_n + \frac{1}{8}\alpha_{ijklmnrs} P_i P_j P_k P_l P_m P_n P_r P_s$$

$$+q_{ijkl}\epsilon_{ij} P_k P_l + \frac{1}{2} c_{ijkl}\epsilon_{ij}\epsilon_{kl} + f_{ijklmn}\epsilon_{ij}\epsilon_{kl} P_m P_n + g_{ijklmn}\epsilon_{ij} P_k P_l P_m P_n$$

[Su,Landis2007]

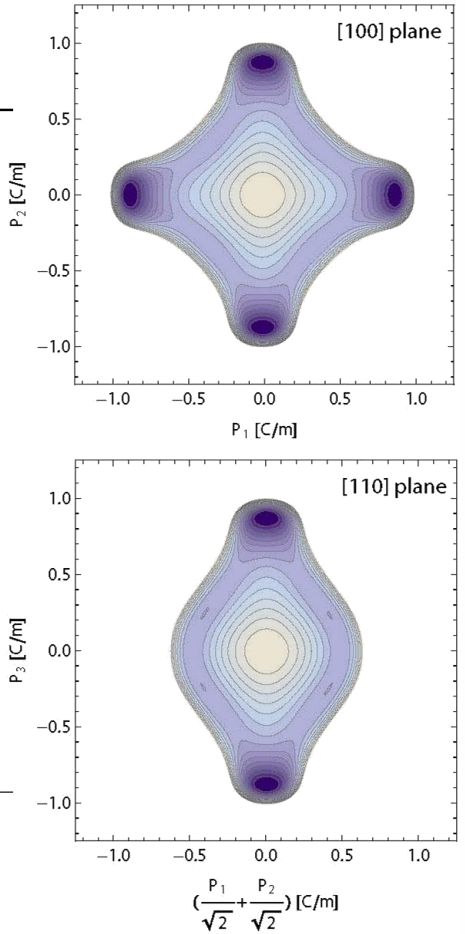
$$+\frac{1}{2\kappa_0}(D_i - P_i)(D_i - P_i) + h_{ijklmnrs}\epsilon_{ij}\epsilon_{kl} P_m P_n P_r P_s$$

Additional free energy terms:

Landau energy:	P^8-term	180° domain wall adjustment
	$P_i^4 P_j^4$-term	90° domain wall adjustment
Elastic energy:	f-term	tetragonal elastic behavior
	h-term	necessary if $C^{cub} > C^{tetr}$
coupling energy:	g-term	piezoelectric coefficients

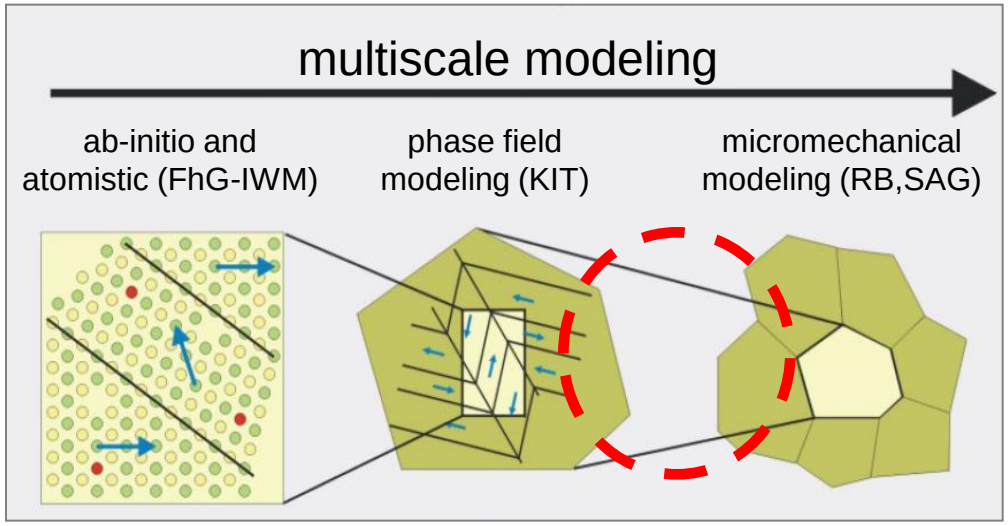
Results: Adjustment of 8th order free energy + additional terms

	unit	PTO first-principles data (input)	PTO phase-field model (adjusted)	PZT first-principles data (input)	PZT phase-field model (adjusted)
P_0	[C/m^2]	0.88	0.88	0.58	0.58
$e_\parallel$		0.04209	0.04209	0.012039	0.012039
$e_\perp$		−0.007388	−0.007388	−0.0017946	−0.0017946
κ_{33}		$17\kappa_0$	$17\kappa_0$	$18\kappa_0$	$18\kappa_0$
κ_{11}		$54\kappa_0$	$54\kappa_0$	$76\kappa_0$	$76\kappa_0$
C_{11}^{cub}	[Pa]	342×10^9	342×10^9	361×10^9	361×10^9
C_{12}^{cub}	[Pa]	131×10^9	131×10^9	115×10^9	115×10^9
C_{44}^{cub}	[Pa]	108×10^9	108×10^9	91×10^9	91×10^9
C_{11}^{tetr}	[Pa]	285×10^9	285×10^9	327×10^9	327×10^9
C_{33}^{tetr}	[Pa]	91×10^9	91×10^9	178×10^9	178×10^9
C_{12}^{tetr}	[Pa]	119×10^9	119×10^9	110×10^9	110×10^9
C_{13}^{tetr}	[Pa]	88×10^9	88×10^9	107×10^9	107×10^9
C_{44}^{tetr}	[Pa]	65×10^9	65×10^9	73×10^9	73×10^9
C_{66}^{tetr}	[Pa]	108×10^9	108×10^9	92×10^9	92×10^9
d_{33}	[C/m]	2.46×10^{-11}	2.46×10^{-11}	1.57×10^{-11}	1.57×10^{-11}
d_{31}	[C/m]	-8.04×10^{-12}	-8.04×10^{-12}	-4.32×10^{-12}	-4.32×10^{-12}
d_{15}	[C/m]	1.72×10^{-11}	1.72×10^{-11}	1.53×10^{-12}	1.53×10^{-12}
γ_{180}	[mJ/m^2]	112	208	96	96
γ_{90}	[mJ/m^2]	24	24	$(36)^\dagger$	36
ξ_{180}	[m]	4.5×10^{-10}	4.5×10^{-10}	6.7×10^{-10}	6.7×10^{-10}
ξ_{90}	[m]	5.4×10^{-10}	5.4×10^{-10}	$(4.9 \times 10^{-10})^\dagger$	4.9×10^{-10}



PZT: complete agreement between atomistic input and adjusted phase-field model
PTO: only 180° domain wall energy too high, otherwise complete agreement

Second interface: phase-field - micromechanics



Input for micromechanical model:

- domain effective material parameters:

$$d_{ijk}^{eff} \qquad C_{ijkl}^{eff} \qquad \kappa_{ij}^{eff}$$

- irreversible switching behavior

FE-Implementation: [Su,Landis2007]

degrees of freedom per node: u_i, P_i, ϕ ➔ independent variables $\epsilon_{ij}, P_i, P_{i,j}, E_i$

Weak form: $$\int_V \left(\sigma_{ji}\delta\epsilon_{ij} - D_i\delta E_i + \eta_i\delta P_i + \xi_{ji}\delta P_{i,j}\right) dV = \int_S \left(t_i\delta u_i - \omega\delta\phi\right) dS$$

subdomain (volume) terms

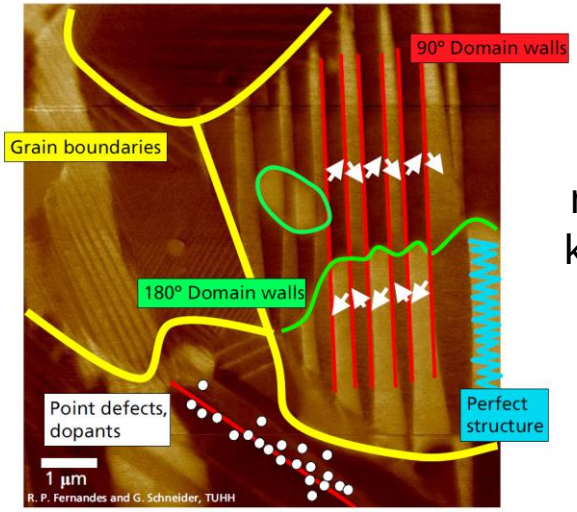
boundary terms

➔ direct implementation of weak form in COMSOL Multiphysics

Aim: investigation of typical bulk domain structures

How to obtain typical domain configurations?

Simulation of a whole grain (Ø~µm): not possible!



real domain structure: no knowledge about pinning, boundaries, …

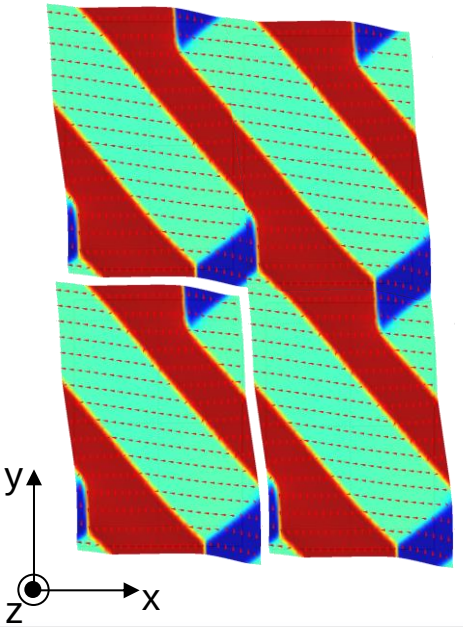
FE-model:

- 2D
- DOF: P_x, P_y, P_z, u_x, u_y, u_z, Φ
- x/y: periodic boundary conditions (P_i, u_i, Φ)
- z-direction: plain strain
- reasonable mesh density: 5-6 nodes / nm

1) bulk behavior: periodic boundary conditions required
2) stabilize configuration: apply global strain

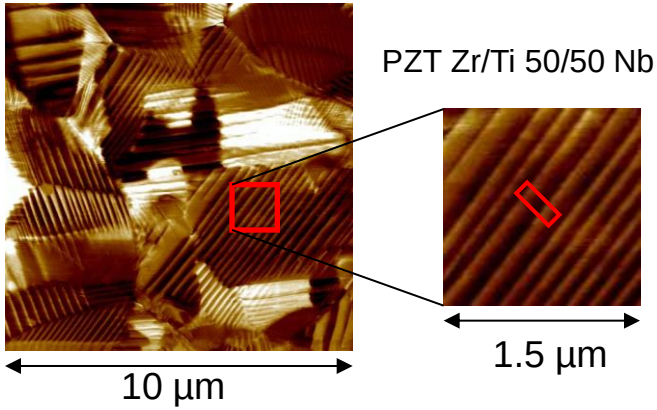
➔ investigate “typical” domain structures:

- monodomain
- ideal 90° domain stack
- defect-free bulk domain structures
- influence of charge defects and grain boundaries



Example 1: Investigation of 90° domain stacks

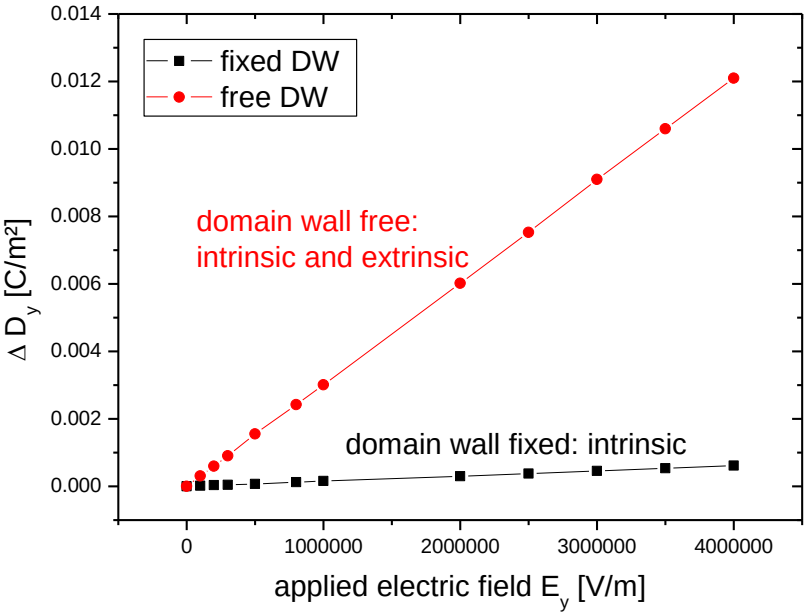
From PFM-experiments: typical domain width ~100-200 nm [Fernandéz/Schneider,TUHH]



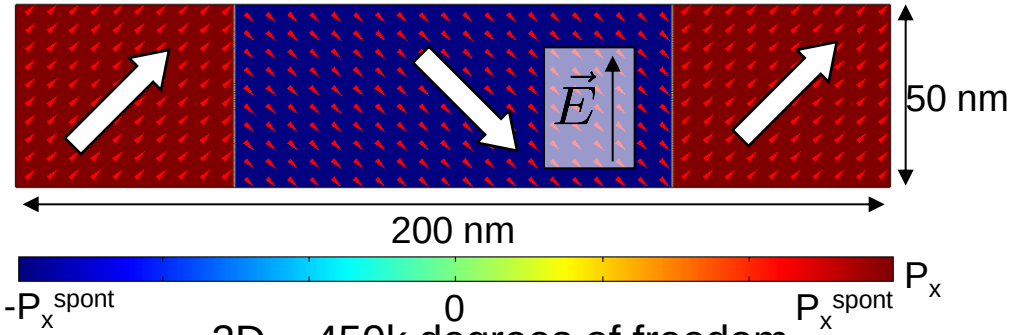
Example: 90°- stack, electrical loading (Y-direction)

Domain wall (DW):
1) artificially completely fixed
2) free

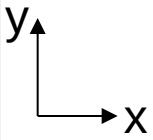
slope: domain effective dielectric permittivity



Phase field model: 90° domain stack



- 2D, ~450k degrees of freedom
- periodic boundary conditions
- electrical / mechanical loading

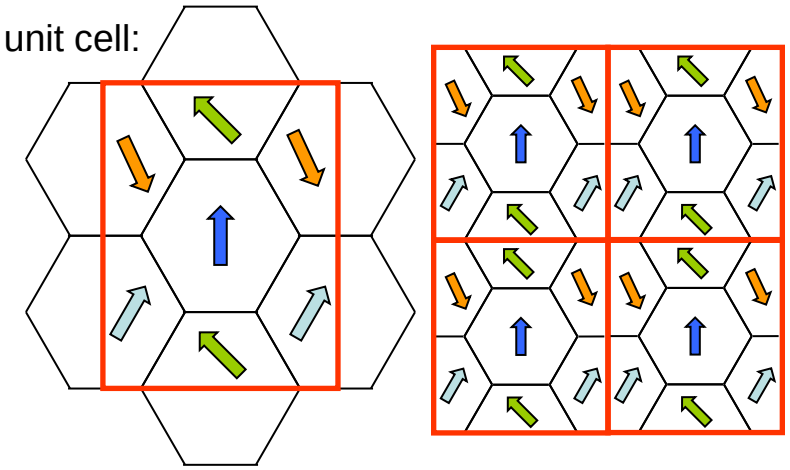


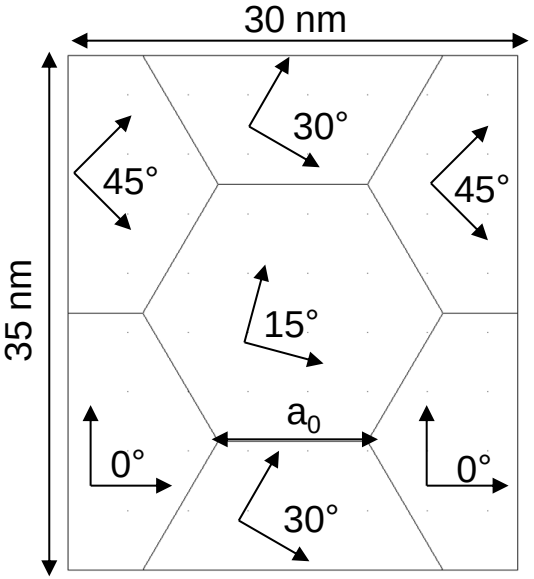
➔intrinsic/ extrinsic piezoelectric effect
➔(reversible) DW motion

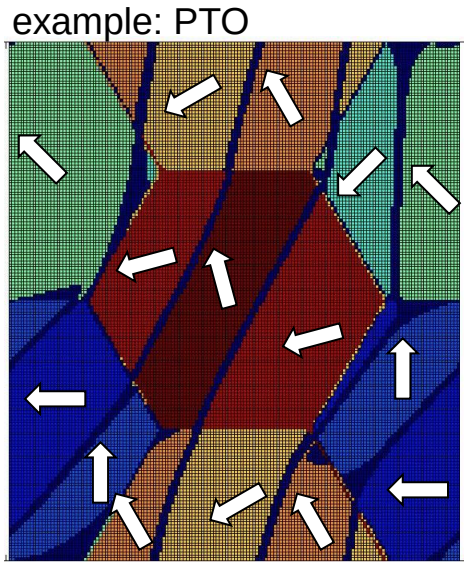
small signal behavior: reversible domain wall motion identified as governing process

Example 2: Influence of grain boundaries

Motivation: Influence of polarization orientation mismatch at grain boundaries on domain structure







➔ simple model:

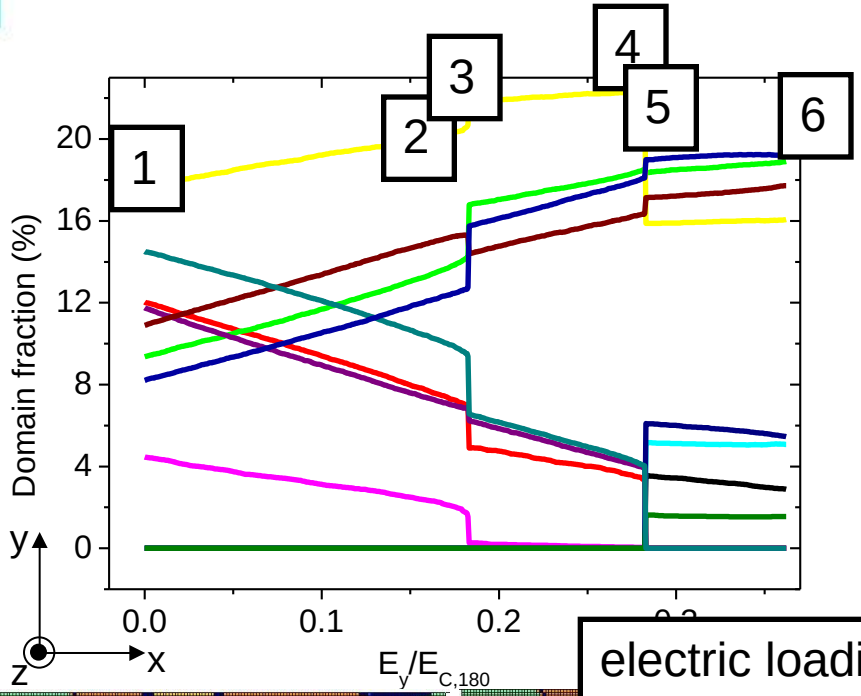
- allows for different polarization directions
- can be continued periodically

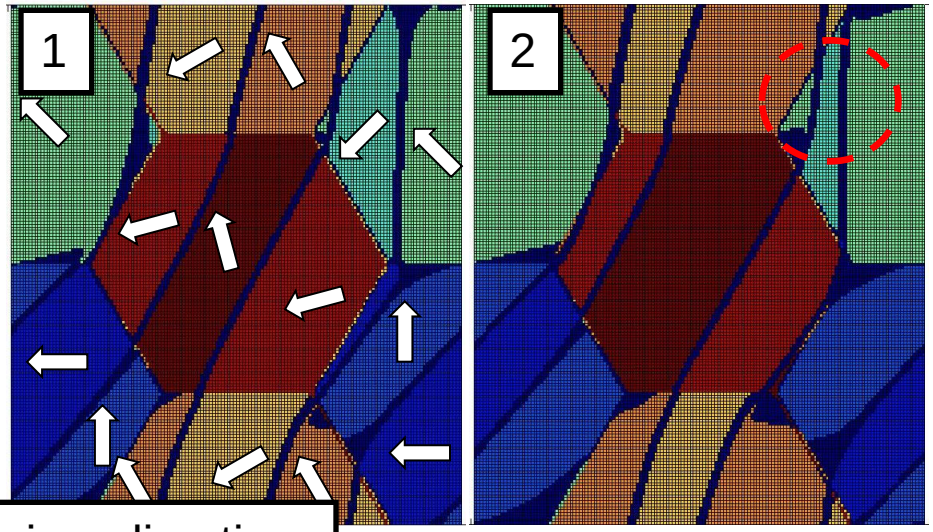
example:

→ 4 “grains” rotated between 0° and 45°around (001)-axis

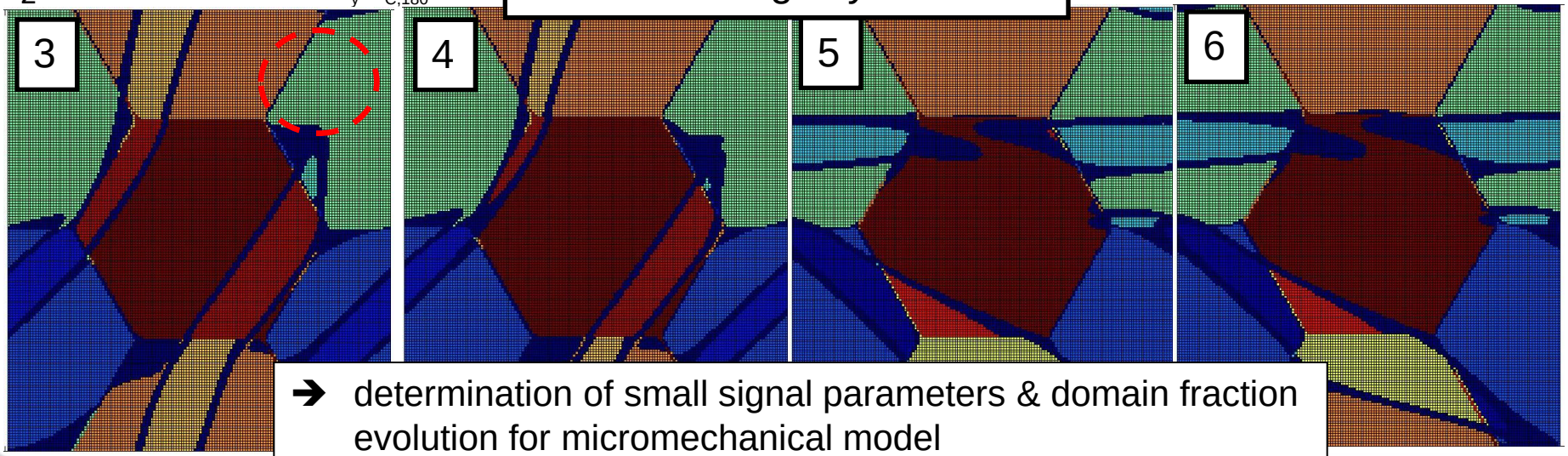
→ a_0 = 10nm

Reversible DW motion and irreversible switching



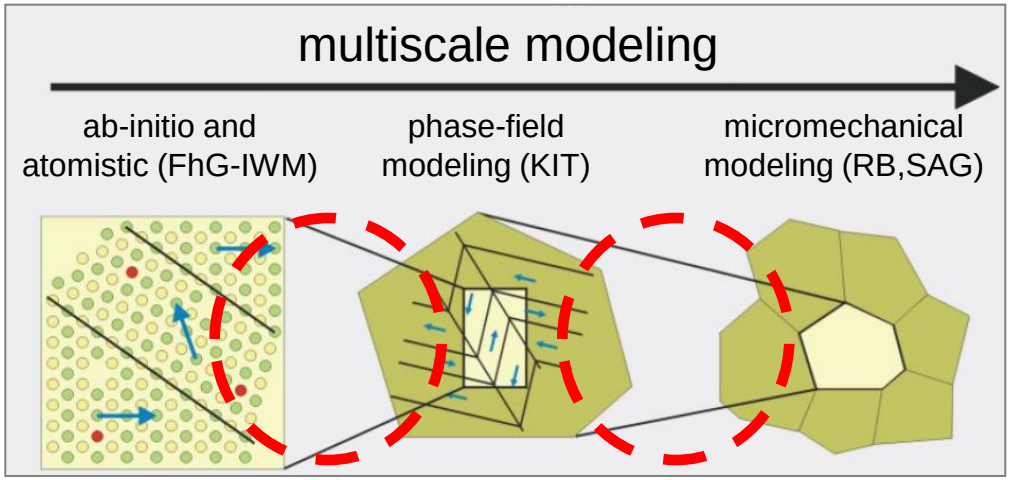


electric loading in y-direction:



➔ determination of small signal parameters & domain fraction evolution for micromechanical model

Summary & Outlook

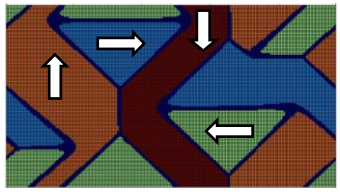


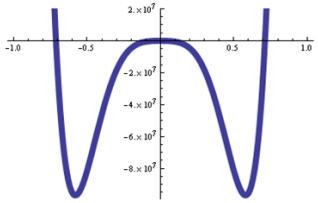
Interface ab-initio / phase-field

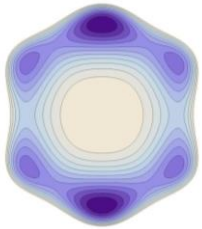
- ➔ new approach for adjustment of energy function parameters *solely* based on results of atomistic calculations
- ➔ additional energy term introduced enabling tetragonal elastic behavior in PTO and PZT
- ➔ successfully applied to PTO and PZT

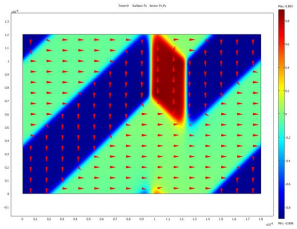
Interface phase-field / micromechanics

- ➔ FE-implementation in COMSOL Multiphysics, including periodic boundary conditions
- ➔ intensive investigation of typical bulk domain structures
- ➔ computation of small signal parameters, can be transferred to micromechanical model

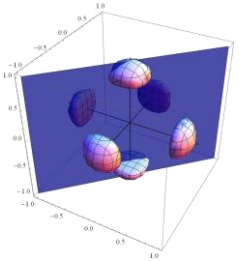


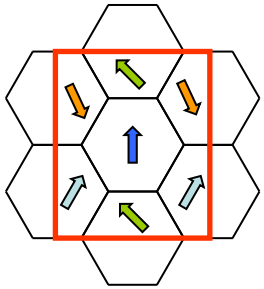


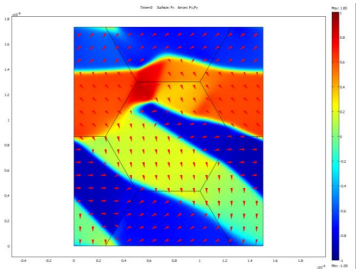




Thanks for your attention!







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