Karlsruhe Institute of Technology

Phase-field Modeling of Ferroelectric Materials

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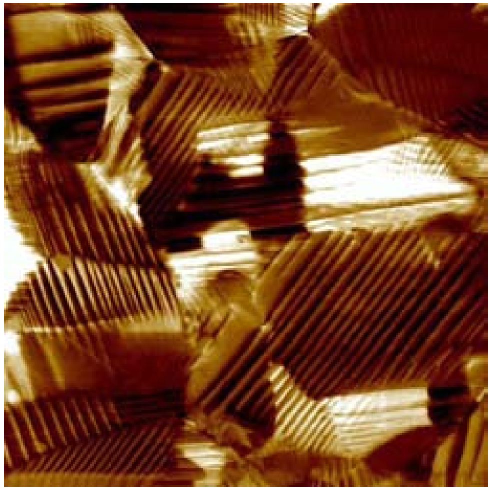
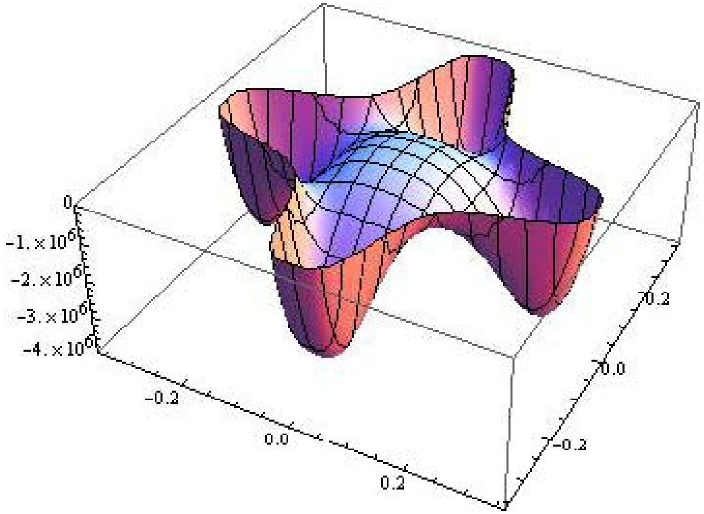
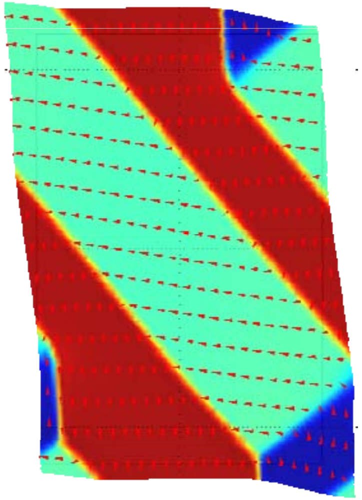
INSTITUTE FOR MATERIALS RESEARCH II





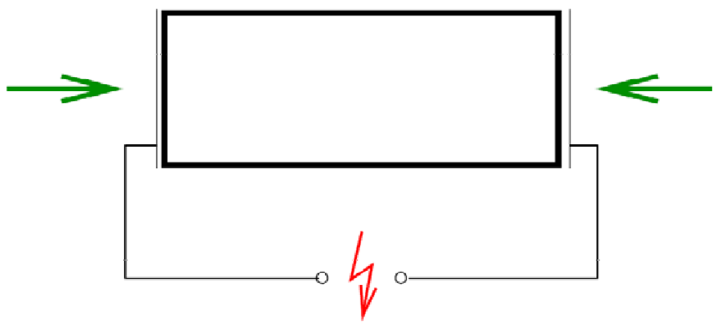


Contents

Technical applications

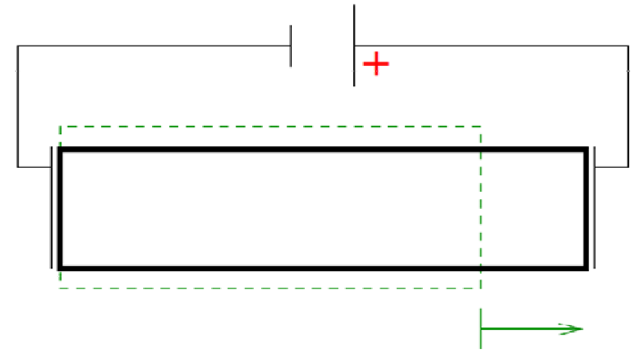
piezoelectricity (Pierre and Jaques Curie, 1880)

- direct piezoelectric effect



→ sensors

- inverse piezoelectric effect

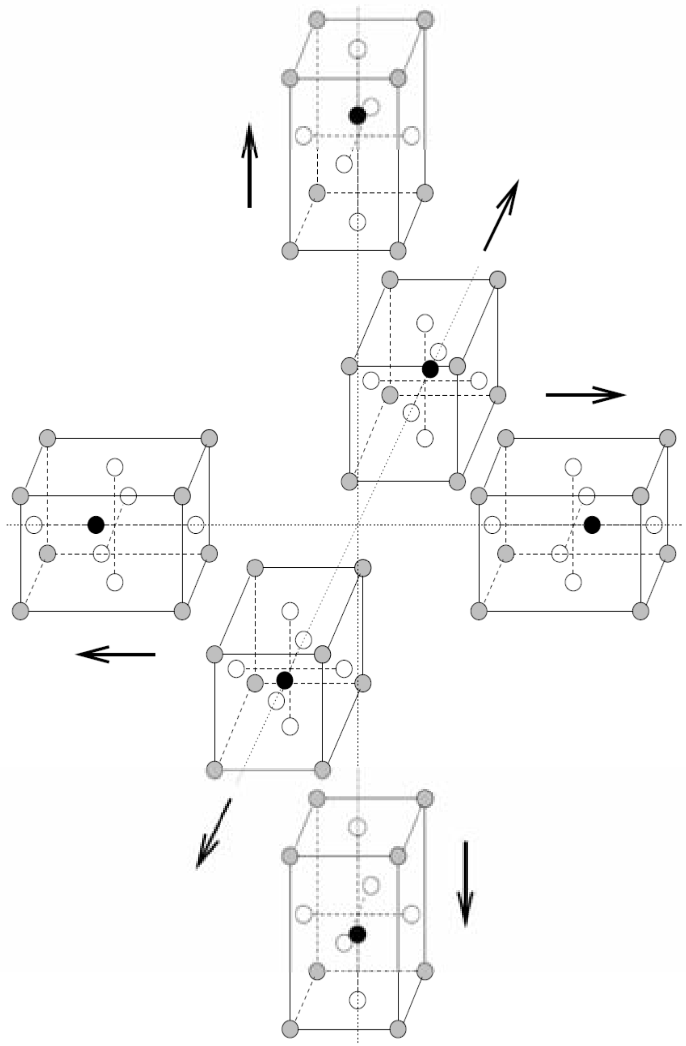


→ actuators

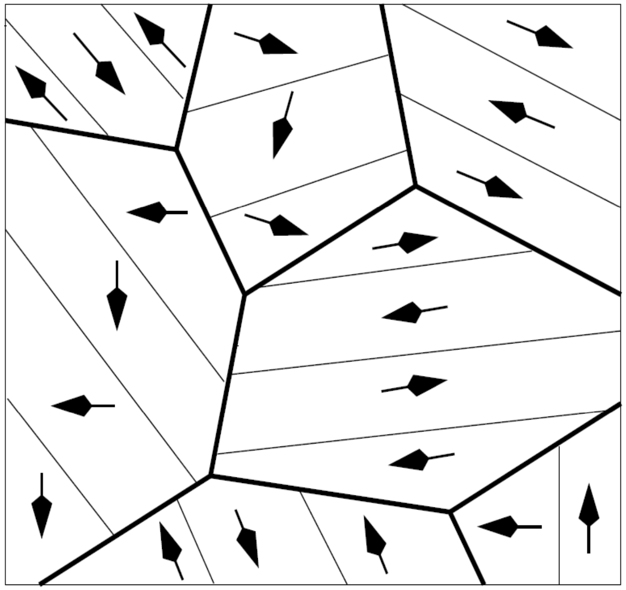
- applications
  - actuators and sensors in microsystems
  - ultra sonic motors
  - adaptive structures
  - stack actuators (Deutscher Zukunftspreis 2005)
  - NEMS
  - Memories

Ferroelectric materials

- 6 variants at phase transition

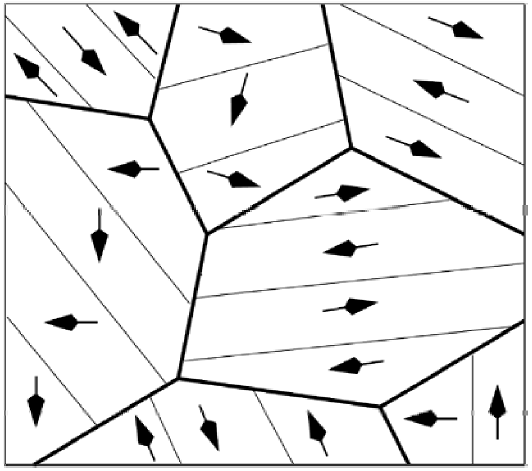


- occurence of domains
  as substructure in each grain



⟶ macroscopic isotropy
after sintering

Phase-field modeling

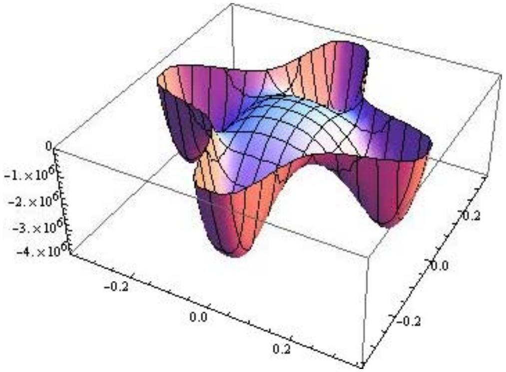


- polarization as continuous order parameter fluctuating at the scale of domain dimensions
- Total Helmholtz Free Energy density

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

$$G_{ijkl} P_{i,j} P_{k,l} + \hat{\psi}(\varepsilon_{ij}, P_i) + \frac{1}{2\kappa_0}(D_i - P_i)(D_i - P_i) =$$

$$G_{ijkl} P_{i,j} P_{k,l} + \hat{\psi}^{Lan}(P_i) + \hat{\psi}^{em}(\varepsilon_{ij}, P_i) + \frac{1}{2\kappa_0}(D_i - P_i)(D_i - P_i)$$



- System Free Energy $\Psi[P_i] = \int_V \psi(P_i(x_k), P_{i,j}(x_k))dV$
- equilibrium condition for order parameter

$$\Psi[P_i] \rightarrow Min \quad \Rightarrow \quad \frac{\delta\Psi}{\delta P_i} := \frac{\partial\hat{\psi}}{\partial P_i} - \left(\frac{\partial\psi}{\partial P_{i,j}}\right)_{,j} = 0$$

- temporal and spatial evolution: relaxation towards equilibrium:

$$\dot{P}_i(x_k, t) \sim -\frac{\delta\Psi}{\delta P_i}$$

Boundary value problem

- field equations

$\sigma_{ij,j} + b_i = \rho \ddot{u}_i$ balance of momentum

$D_{i,i} = q$ Gaussian law

$\left(G_{ijkl} P_{k,l}\right)_{,j} - \dfrac{\partial \psi}{\partial P_i} = \beta_{ij} \dot{P}_j$ time dependent Ginzburg-Landau eqn.

- boundary conditions

mechanical: $\sigma_{ij} n_j = t_i$ or u_i

electrical: $D_i n_i = -\omega$ or ϕ

polarization: $P_{i,j} n_j = 0$ or P_i

- potential relations

$\sigma_{ij} = \dfrac{\partial \psi}{\partial \varepsilon_{ij}}$ and $E_i = \dfrac{\partial \psi}{\partial D_i}$

- kinematics

$\varepsilon_{ij} = \dfrac{1}{2}\left(u_{i,j} + u_{j,i}\right)$ and $E_i = -\phi_{,j}$

Structure of Helmholtz Free Energy density

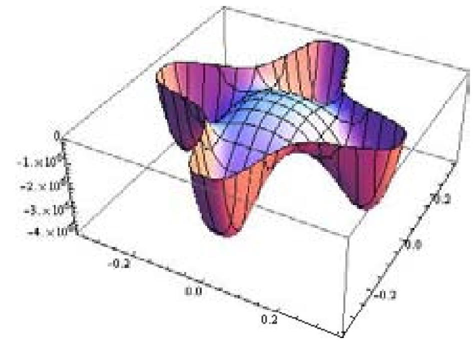
free energy contains crystallographic and boundary information: $\psi(P_i, P_{i,j}, \epsilon_{ij}, D_i)$

$$\psi = \frac{1}{2}G_{ijkl}P_{i,j}P_{k,l} \quad \text{(I)}$$

$$+\frac{1}{2}\alpha_{ij}P_iP_j + \frac{1}{2}\alpha_{ijkl}P_iP_jP_kP_l + \frac{1}{6}\alpha_{ijklmn}P_iP_jP_kP_lP_mP_n \quad \text{(II)}$$

$$+q_{ijkl}\epsilon_{ij}P_kP_l + \frac{1}{2}c_{ijkl}\epsilon_{ij}\epsilon_{kl} \quad \text{(III)}$$

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



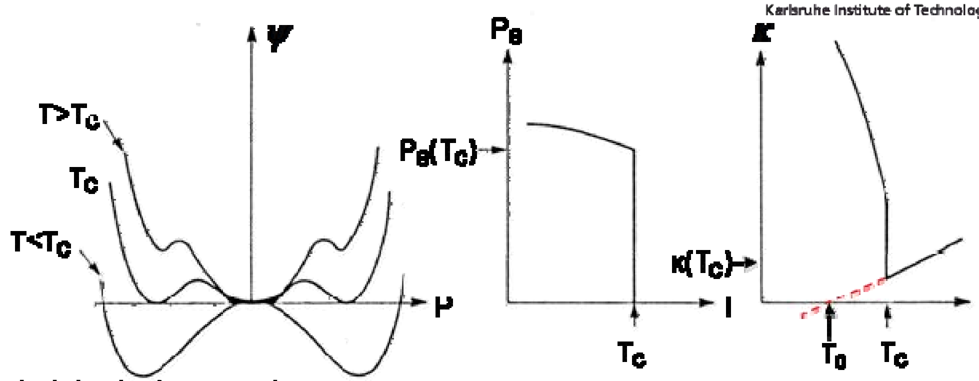
ε: mechanical strain
D: dielectric displacement
P: polarization (order parameter, continuous on domain walls)

- (I) exchange energy: allows formation of domain walls with finite thickness
- (II) non-convex energy surface, minima at spontaneous polarization states (Landau energy)
- (III) adjustment of material properties (electromechanical coupling, elastic properties of spontaneous polarized states)
- (IV) energy stored within free space occupied by material

Adjustment of free energy density

Phenomenological approach:

- fit to first order phase transition
- based on experimental observations
- requires $\kappa(T_C)$, $P^S(T_C)$, T_C, T_0



however: ab-initio calculations can‘t yield this information

[Devonshire1954]

this project: virtual material development (BMBF WING, COMFEM)

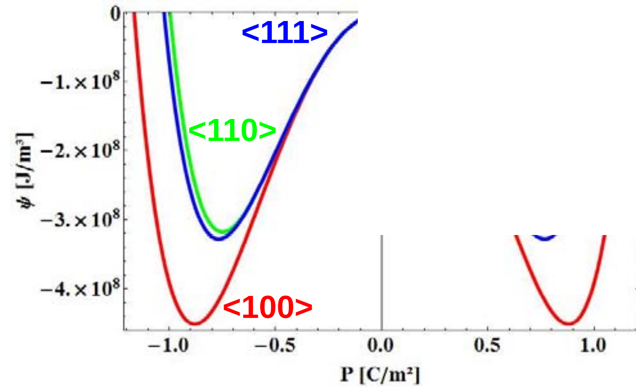
➔new approach needed for multiscale simulation chain

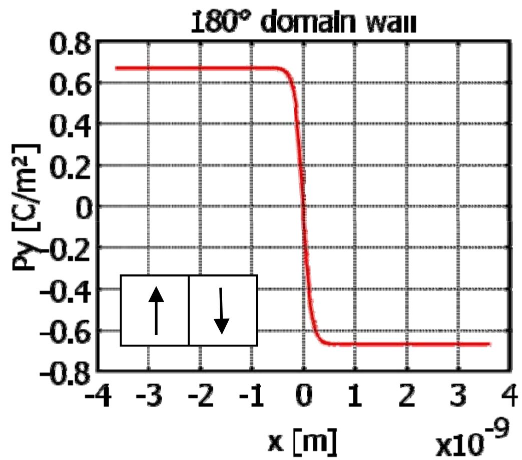
ab-initio / atomistic			Ginzburg-Landau-theory
piezoelectric coefficients	d_{ijk}	**Aim:**	
dielectric permittivity	κ_{ij}	**development**	free energy parameters
mechanical stiffness	C_{ijkl}	**of a new**	α_{ijklmn}
spontaneous strain	ε_S	➔	q_{ijkl}
spontaneous polarization	P^S		c_{ijkl}
domain wall energy (90°/180°)	$\gamma_{90/180}$	**adjustment**	G_{ijkl}
domain wall thickness (90°/180°)	$\xi_{90/180}$	**method**	

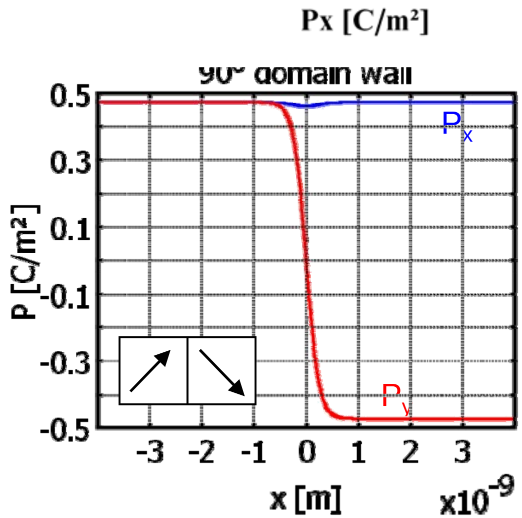
Adjustment of free energy

adjustment for $PbTiO_3$:

	ab-initio/ atomistic (input)	phase-field (adjusted)
P^S [C/m²]	0,880	0,880
ε_{11}^S	-7,388E-03	-7,388E-03
ε_{33}^S	4,209E-02	4,209E-02
K_{11}	53,7	53,7
K_{33}	16,91	16,9
C_{11} [N/m²]	2,86E+11	2,86E+11
C_{12} [N/m²]	1,17E+11	1,17E+11
C_{44} [N/m²]	6,70E+10	6,70E+10
ξ_{90} [nm]	0,478	0,478
γ_{90} [mJ/m²]	64	63.8
ξ_{180} [nm]	0,390	0,390
γ_{180} [mJ/m²]	156	156







➔ adjustment completely with ab-initio/atomistic results

➔ method works fine for $PbTiO_3$

Finite element implementation

- electric enthalpy: Legendre transformation

$$h(\varepsilon_{ij}, E_i, P_i, P_{i,j}) = \psi(\varepsilon_{ij}, D_i, P_i, P_{i,j}) - D_i E_i$$

potential relations

$$\sigma_{ij} = \frac{\partial h}{\partial \varepsilon_{ij}} = \frac{\partial \psi}{\partial \varepsilon_{ij}} \quad , \quad D_i = -\frac{\partial h}{\partial E_i} \quad , \quad \frac{\partial h}{\partial P_i} = \frac{\partial \psi}{\partial P_i} \quad , \quad \frac{\partial h}{\partial P_{i,j}} = \frac{\partial \psi}{\partial P_{i,j}}$$

- mechanical strain-displacement relations and electric potential

$$h(\varepsilon_{ij}, E_i, P_i, P_{i,j}) = h(u_{i,j}, \phi_{,j}, P_i, P_{i,j})$$

- primary nodal variables for finite element formulation

$$u_i, \phi, P_i$$

- physical principle:

minimize System *Free Energy* WRT $P_i(x_k)$ for given $\varepsilon_{ij}(x_k), D_i(x_k)$

Implementation in COMSOL (1)

- general PDE form in COMSOL $e_a u_{,tt} + d_a u_{,t} + \Gamma_{j,j} = F$, $\Gamma_i = \Gamma_i(u, u_{,t}, u_{,j}, u_{,jk}, \ldots)$

$$\rho u_{i,tt} - \left(\frac{\partial h}{\partial \varepsilon_{ij}}\right)_{,j} = b_i$$

$$\left(\frac{\partial h}{\partial E_i}\right)_{,i} = -q$$

$$\beta_{ij} P_{j,t} - \left(\frac{\partial h}{\partial P_{i,j}}\right)_{,j} = \gamma_i - \frac{\partial h}{\partial P_i}$$

- boundary conditions in COMSOL $-n_i \Gamma_i = G$ or $0 = R$

mechanical: $\frac{\partial h}{\partial \varepsilon_{ij}} n_j = t_i$ or u_i

electrical: $\frac{\partial h}{\partial E_i} n_i = \omega$ or ϕ

polarization: $\frac{\partial h}{\partial P_{i,j}} n_j = 0$ or P_i

Implementation in COMSOL (2)

- weak form in COMSOL $\int_{\Omega}\left(\Gamma_i \nu_{,i} + F\nu\right)\, dV = \int_{\partial\Omega}\left(\Gamma_i n_i \nu\right)\, dA$
- principle of virtual work for phase-field theory, equilibrium states $\partial P_i / \partial t = 0$

$$\int_V \left\{ \sigma_{ij}\delta\varepsilon_{ij} - D_i\delta E_i + \left[\frac{\partial h}{\partial P_i} + \frac{\partial}{x_j}\left(\frac{\partial h}{\partial P_{i,j}}\right)\right]\delta P_i \right\} dV = \int_S \left\{ t_i\delta u_i - \omega\delta\phi + \left(G_{ijkl}P_{k,l}\right)n_j\delta P_i \right\} dA$$

- expressing by means of electric enthalpy

$$\int_V \left\{ \frac{\partial h}{\partial\varepsilon_{ij}}\delta\varepsilon_{ij} + \frac{\partial h}{\partial E_i}\delta E_i + \frac{\partial h}{\partial P_i}\delta P_i + \frac{\partial h}{\partial P_{i,j}}\delta P_{i,j} \right\} dV =$$

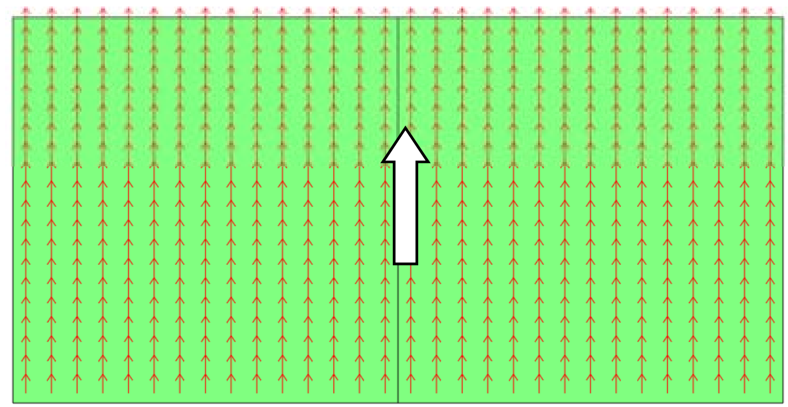
$$\int_S \left\{ \frac{\partial h}{\partial\varepsilon_{ij}} n_j\delta u_i - \frac{\partial h}{\partial E_j} n_j\delta\phi + \frac{\partial h}{\partial P_{i,j}} n_j\delta P_i \right\} dA$$

- formulation of complex analytical expression to be entered in COMSOL by symbolic algebra software

Importance of boundary conditions

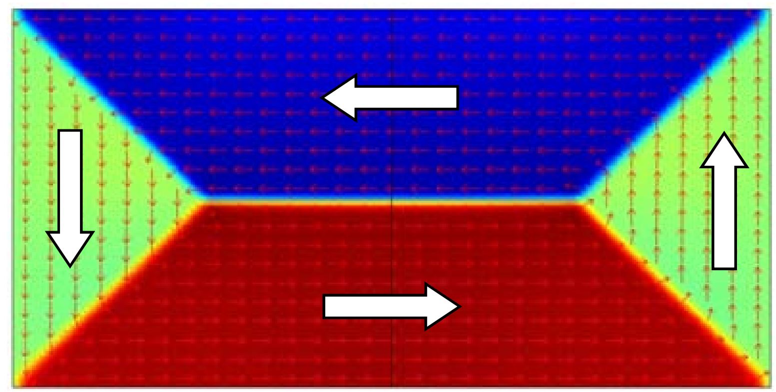
- short circuited boundary: $\phi = 0$

  ➔ monodomain is lowest energy state



- open circuited boundary conditions: $D_i n_i = 0$

  ➔ flux closure, vortex



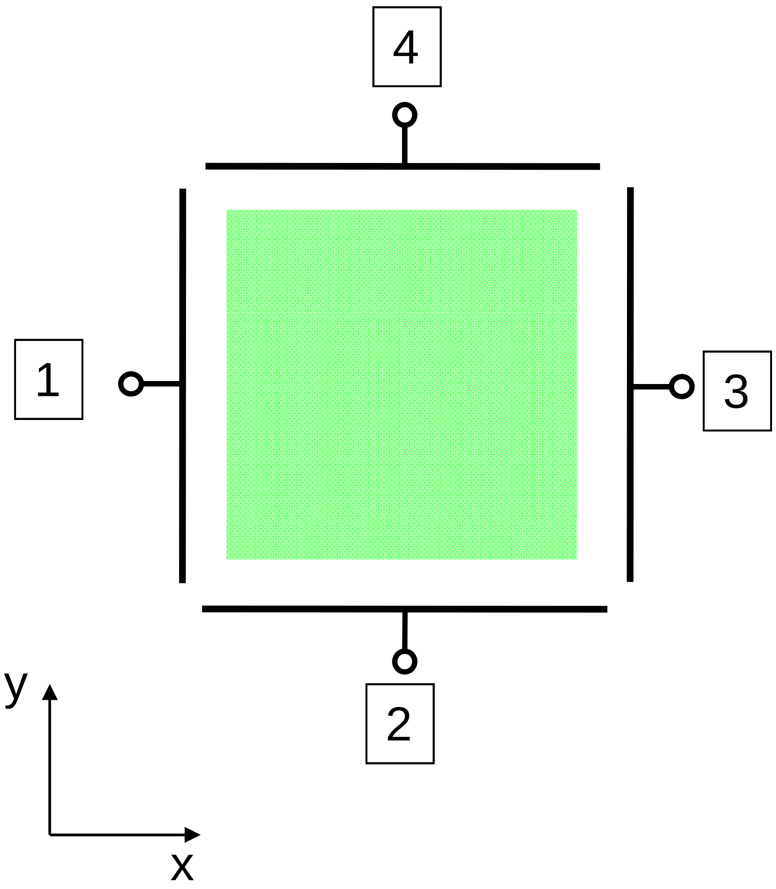
- in this activity: bulk material behavior, far from free surface

  ➔ periodic boundary conditions, “elimination“ of the boundary

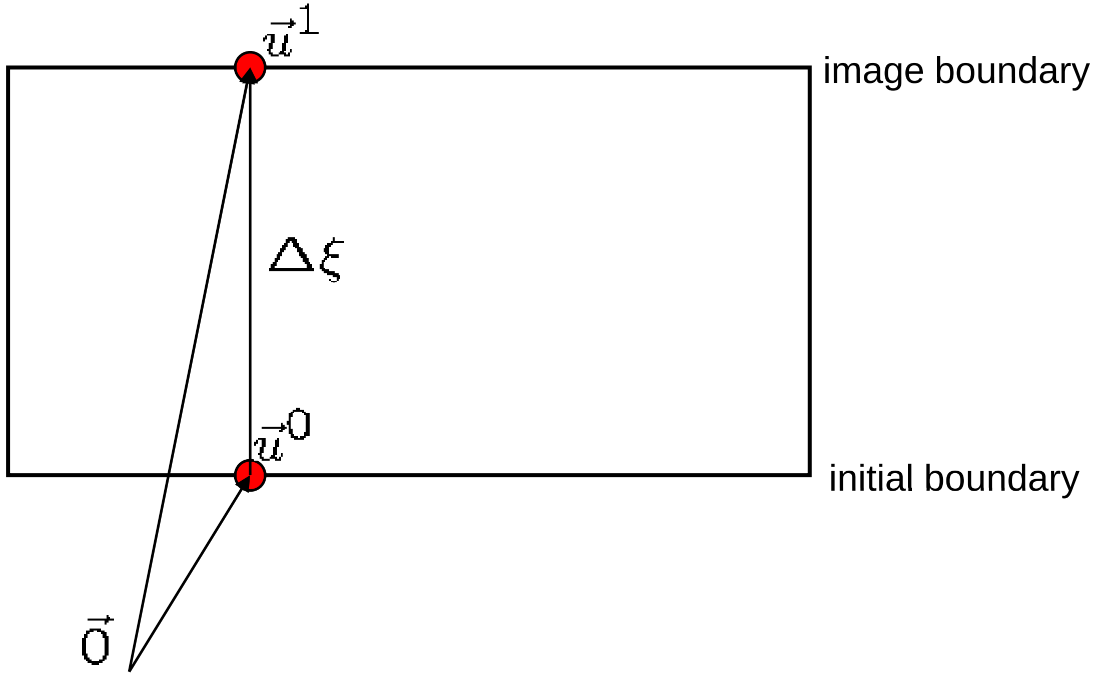
Periodic boundary conditions (1)

Periodic boundary conditions (part 1):
polarization, electric potential

1 = 3	2 = 4
P_x	P_x
P_y	P_y
$\Phi + V_x$	$\Phi + V_y$



Periodic boundary conditions (2)

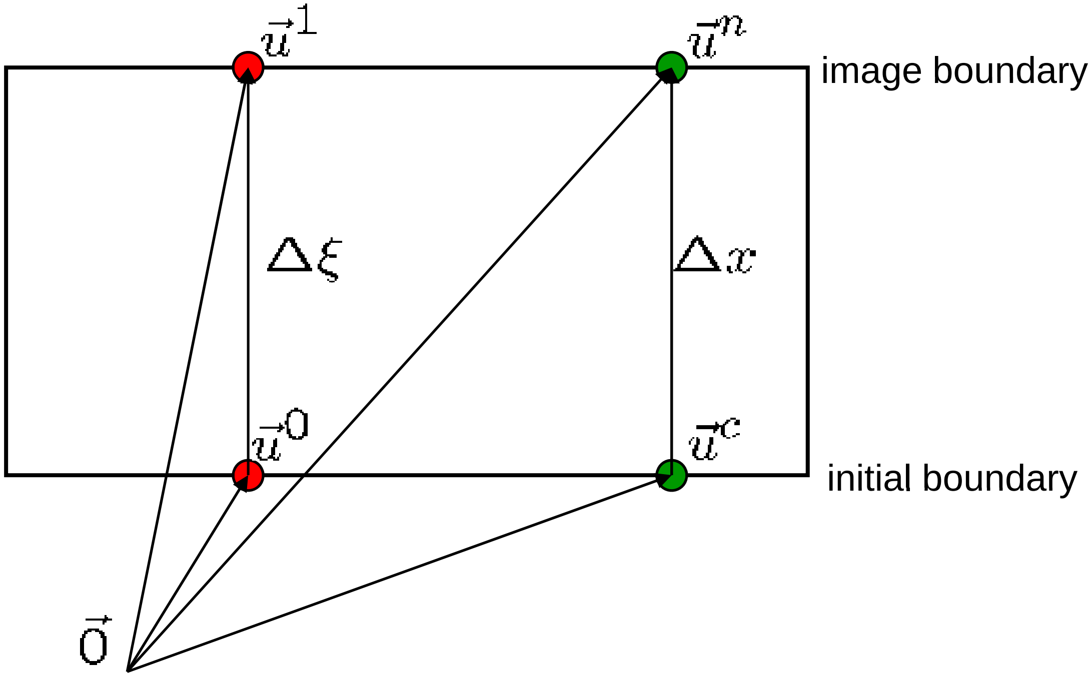


Approach:

1) define reference nodes $\vec{u}^1 \vec{u}^0$
2) define S_{ij}

$$S_{ij} = \frac{u_i^1 - u_i^0}{\Delta\xi_j}$$

Periodic boundary conditions (2)



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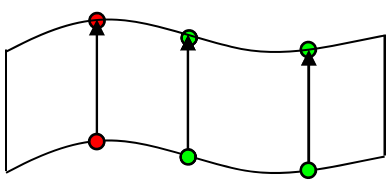
2) define S_{ij}

$$S_{ij} = \frac{u_i^1 - u_i^0}{\Delta\xi_j}$$

3) apply S_{ij} to all other nodes:
   - "new" node on image boundary: $\vec{u}^n$
   - corresponding node on initial boundary: $\vec{u}^c$

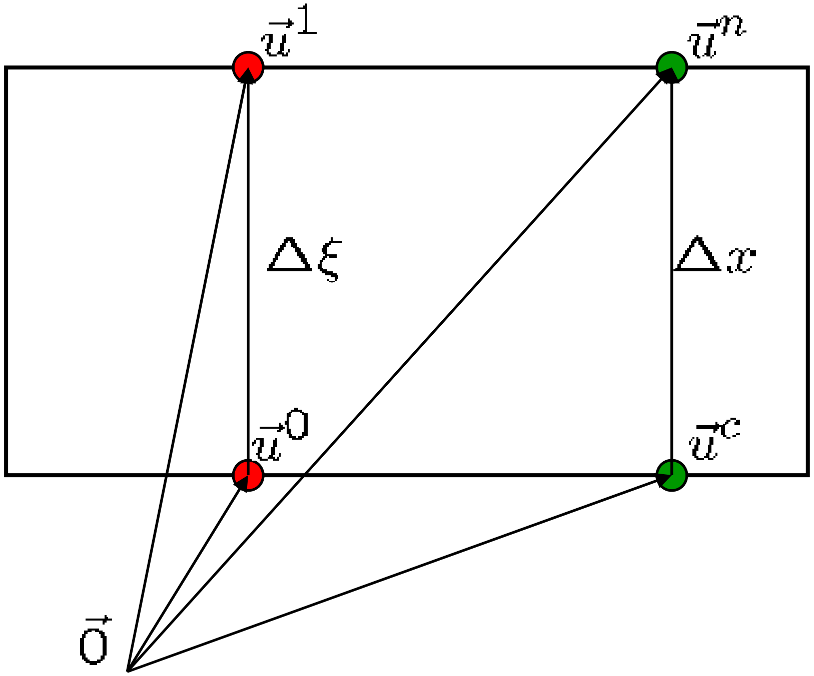
<u>periodic BC:</u> for all nodes on image boundary:

$$u_i^n = u_i^c + S_{ij}\Delta x_j$$



➔ only one DOF left

Periodic boundary conditions (2)



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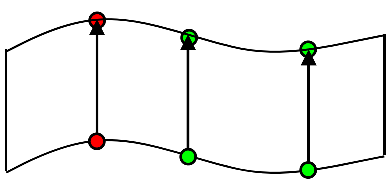


➔ only one DOF left

Problem:

- only one reference node
- may coincide with domain wall

➔ improvement: averaging over boundary
➔ **integration** of displacement over boundary

$$\bar{S}_{ij} = \frac{\bar{u_i^1} - \bar{u_i^0}}{\Delta\xi_j}$$

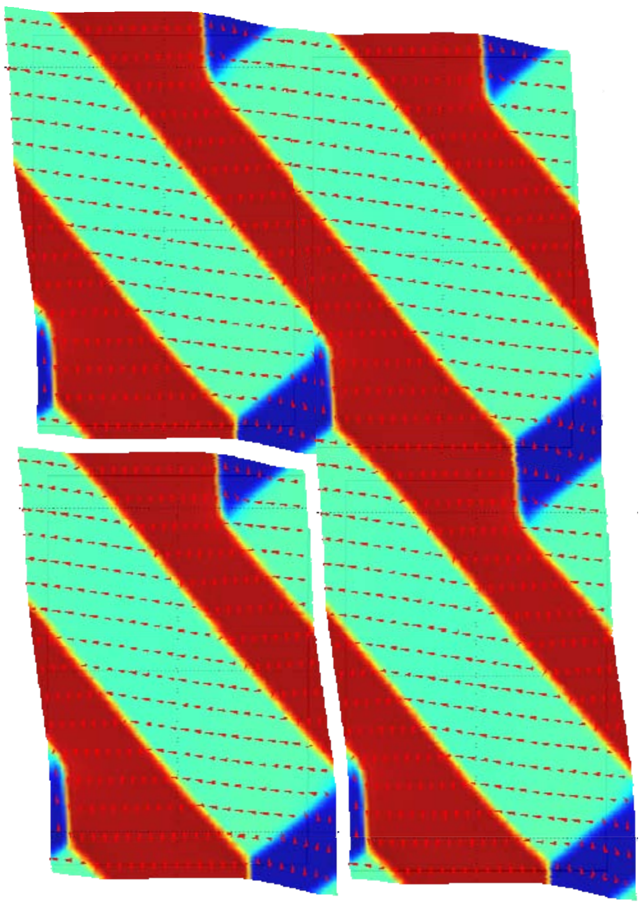
➔ integration coupling variables

Periodic boundary conditions (2)

Illustration of periodic boundaries:

➔deformation plot (u_x,u_y) of domain structure

➔color coding / arrows: polarization P_y



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➔ improvement: averaging over boundary

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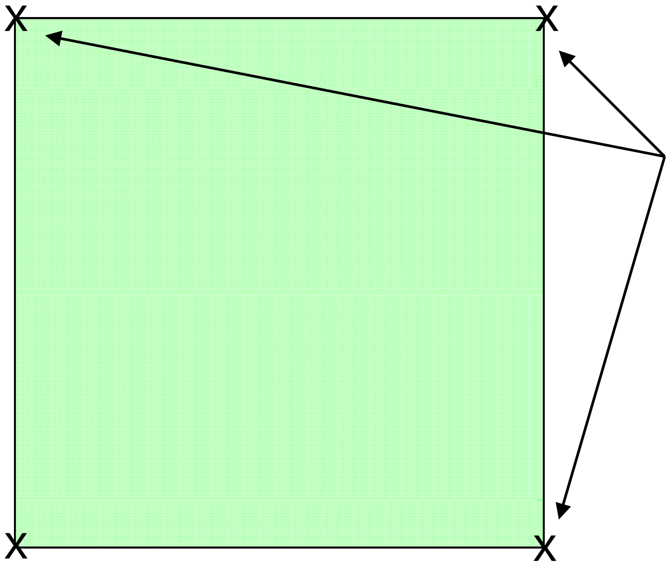
$$\bar{S}_{ij} = \frac{\overline{u_i^1} - \overline{u_i^0}}{\Delta \xi_j}$$

➔ integration coupling variables

Mechanically predefined configurations

<u>stable (90°) configuration:</u> ➔ pinning mechanical displacement u_i on corners of geometry

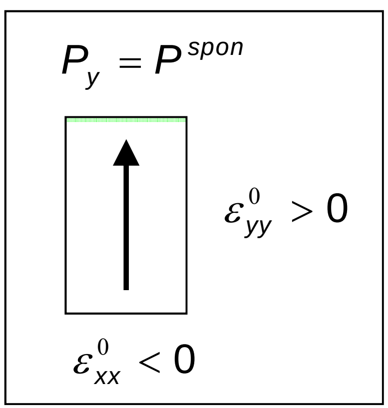


example: equal domain fractions

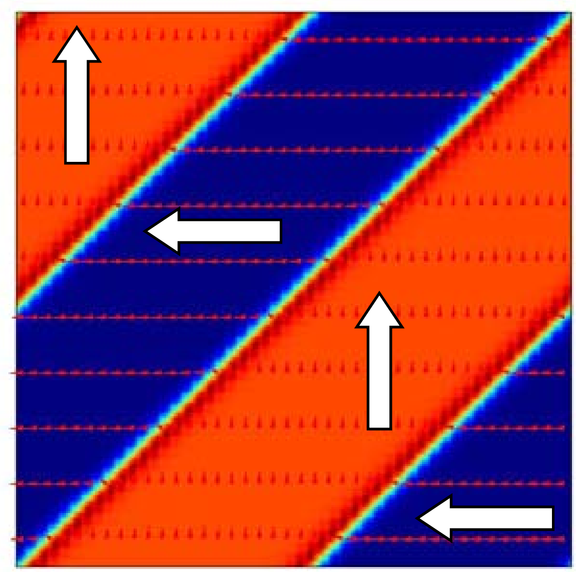
$$u_x = \frac{\varepsilon_{xx}^0 + \varepsilon_{yy}^0}{2} \Delta x$$

$$u_y = \frac{\varepsilon_{xx}^0 + \varepsilon_{yy}^0}{2} \Delta y$$

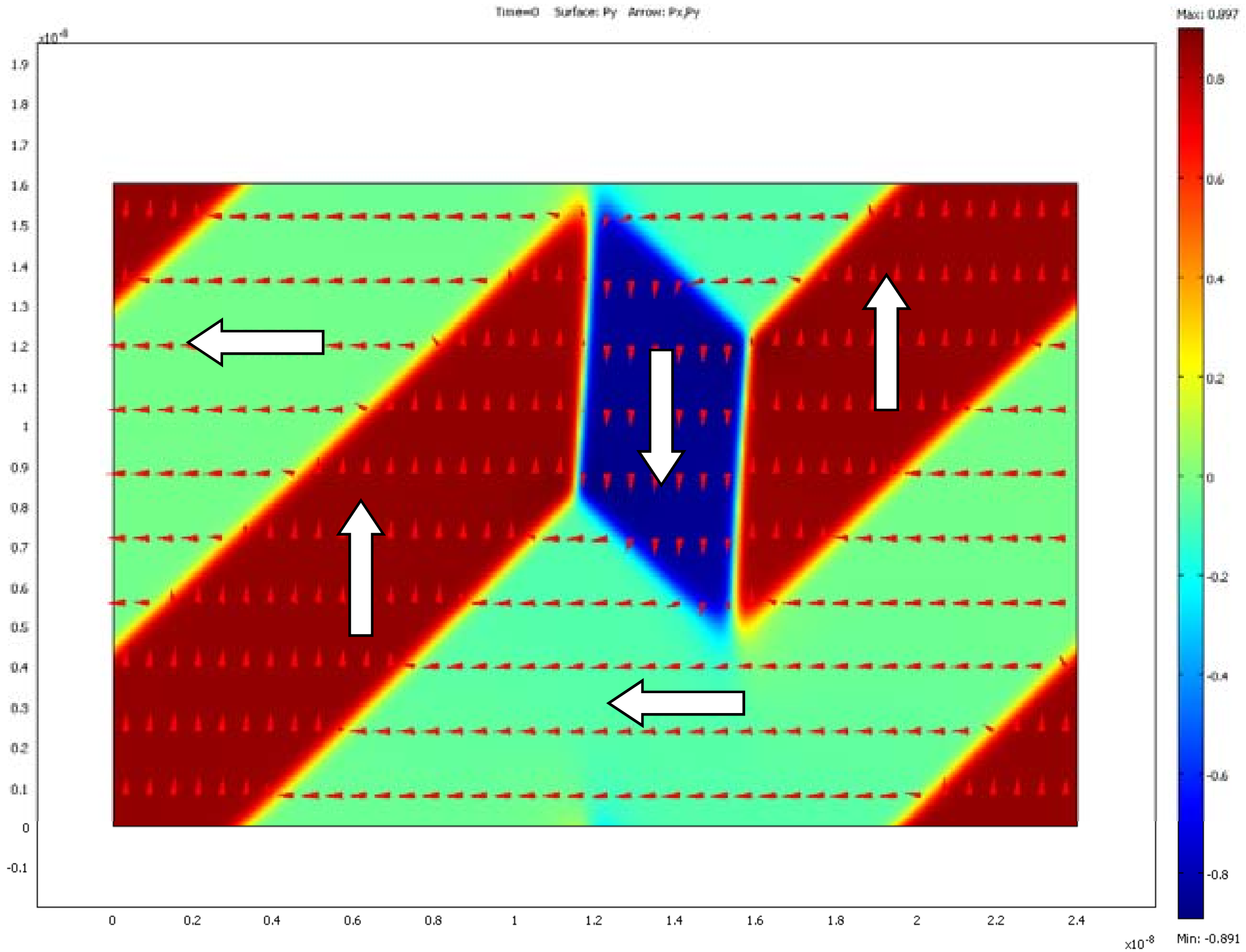
$$u_x = 0$$
$$u_y = 0$$



- periodic boundary conditions
- minimum energy: 90°-domains

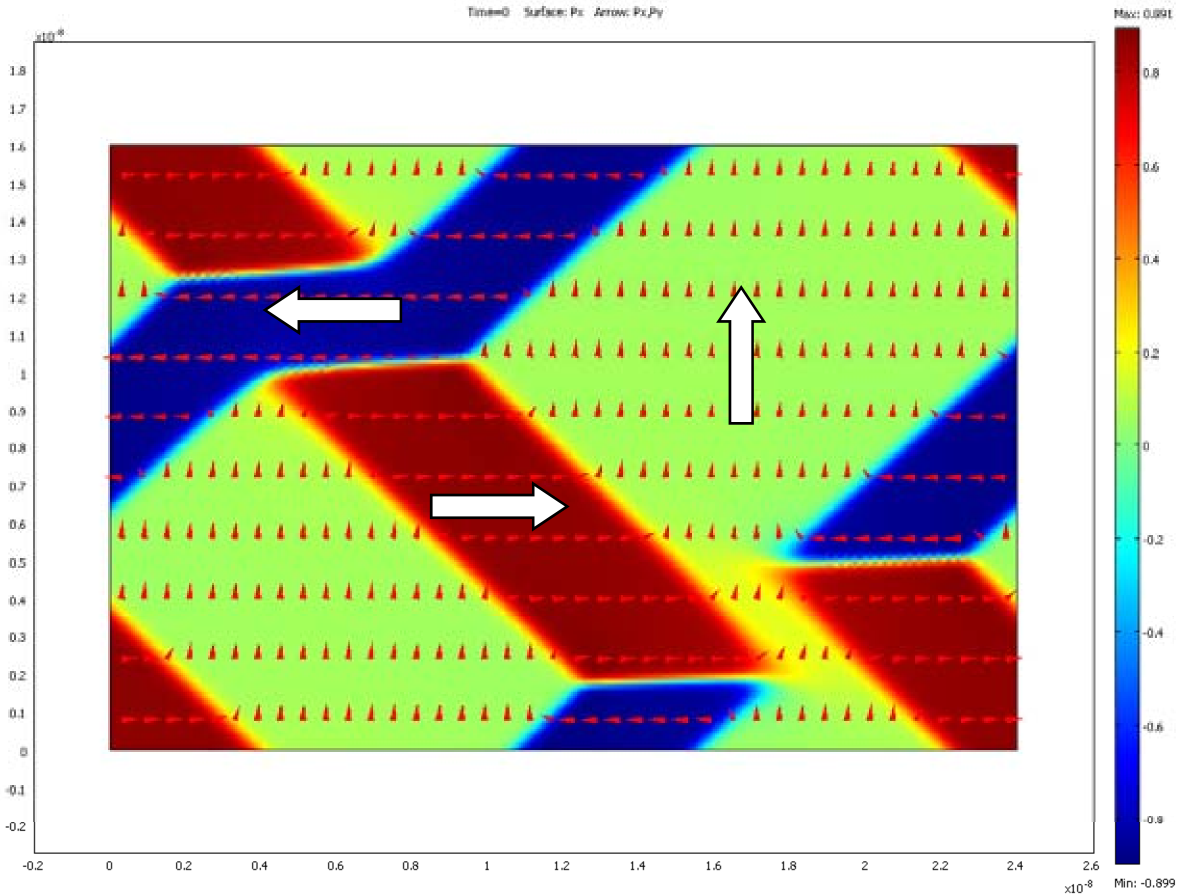


Mechanically predefined configurations



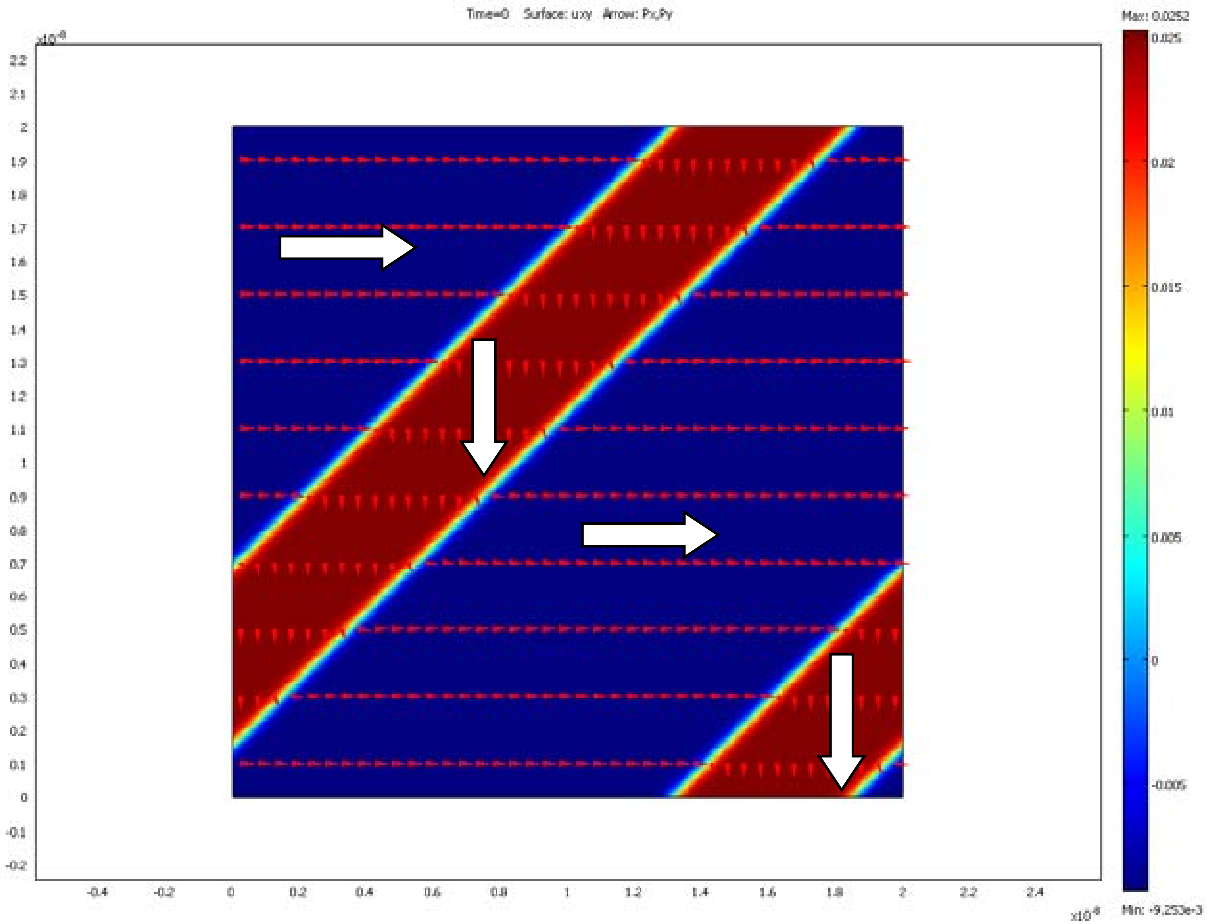
- model size: 16 nm x 24 nm
- stable configuration with 3 domains

Mechanically predefined configurations



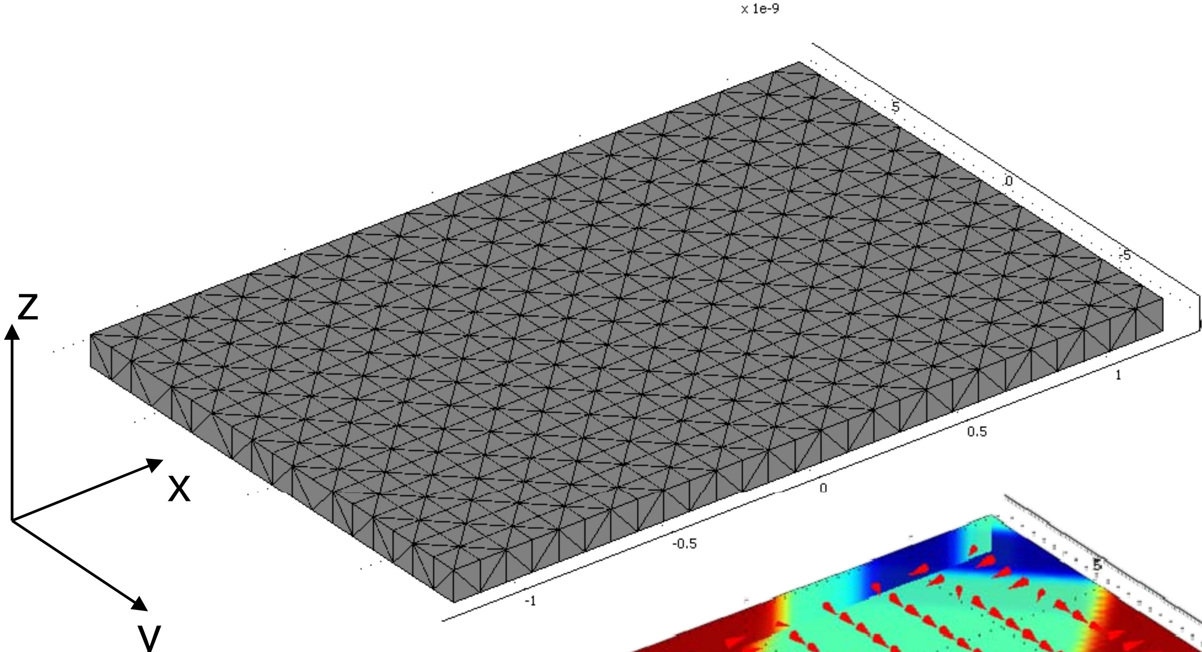
- model size: 16 nm x 24 nm
- stable configuration with 3 domains
- different initial condition

Mechanically predefined configurations



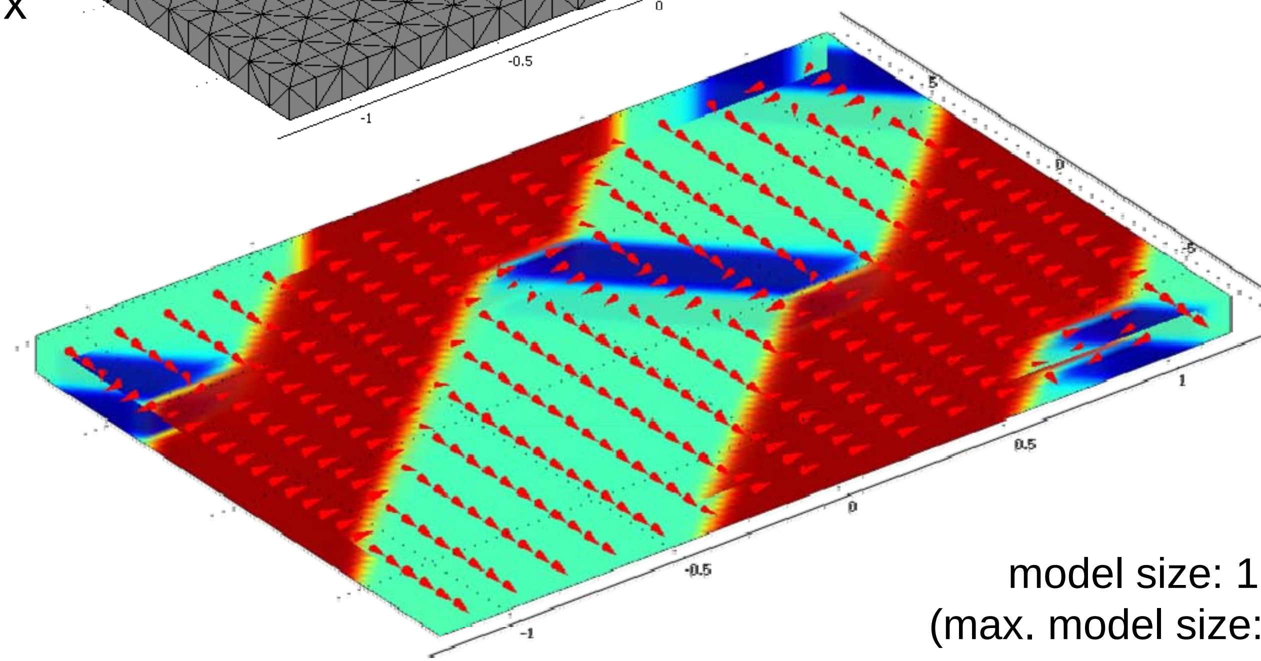
- model size: 20 nm x 20 nm
- different domain ratio

3D layer model (plain stress conditions)



<u>x/y – direction</u>
as 2D-model:
- periodic for P_i, u_i, Φ

<u>z – direction</u>
- strain u_{zz} free! (can move..)
- $P_z=0$

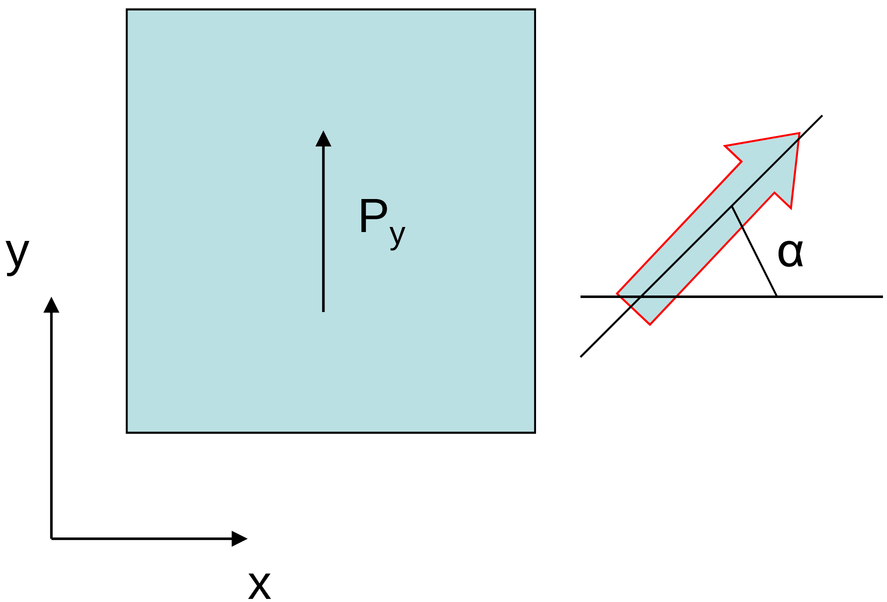


model size: 16 nm x 24 nm
(max. model size: ~20 nm x 30 nm)

Applied external loads

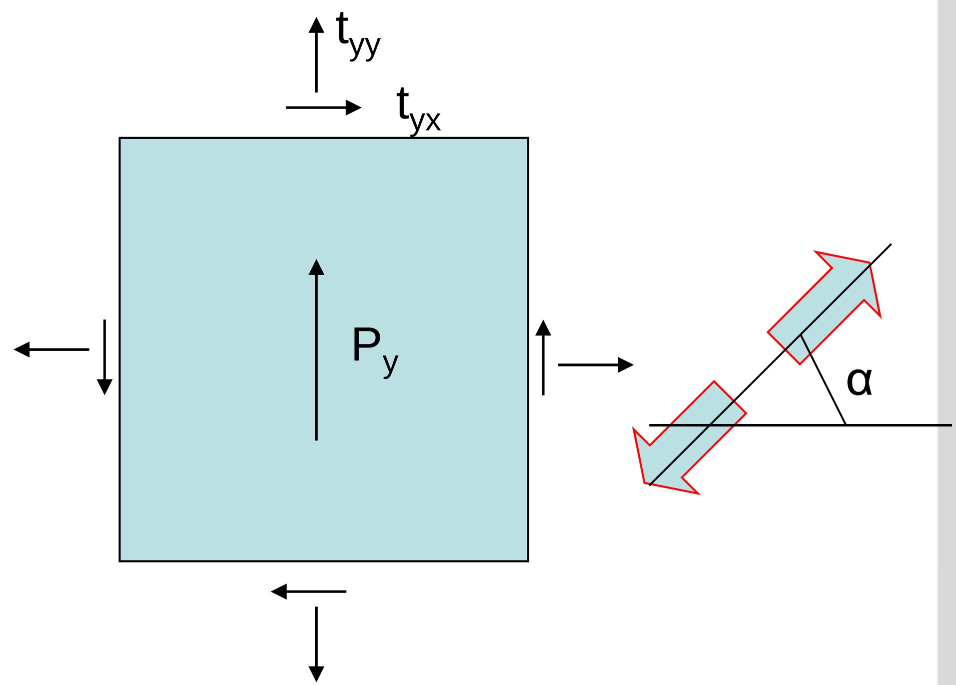
applied electric field

➔ user defined angle α



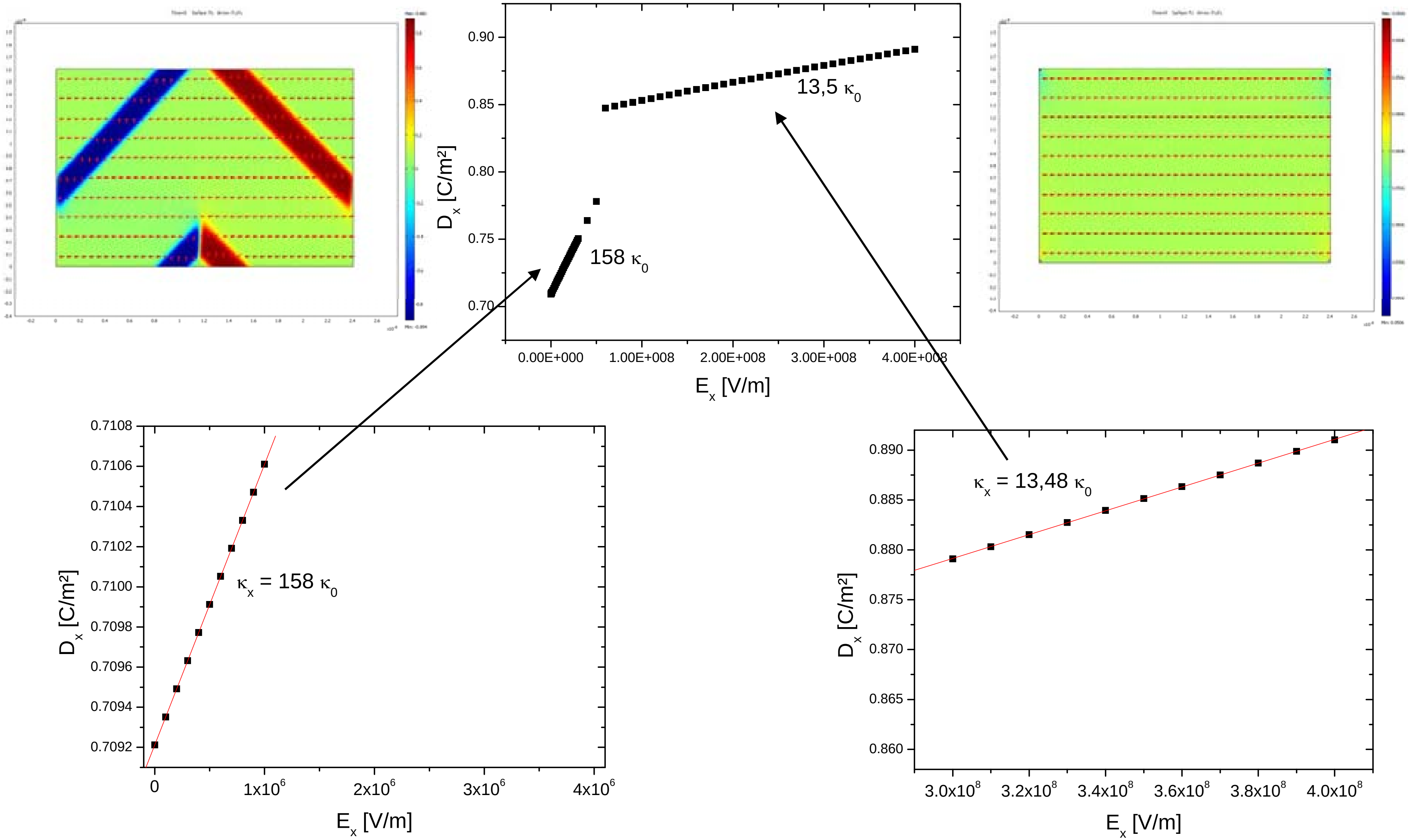
applied stress

➔ user defined angle α



$\underline{R}(\alpha) * \underline{t} * \underline{R}(\alpha)^T$

Contribution of reversible domain wall motion



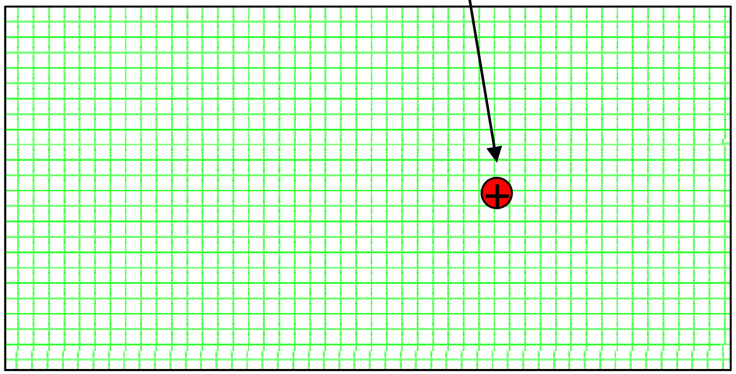
Modeling defects in the phase-field model

1. Charged defect

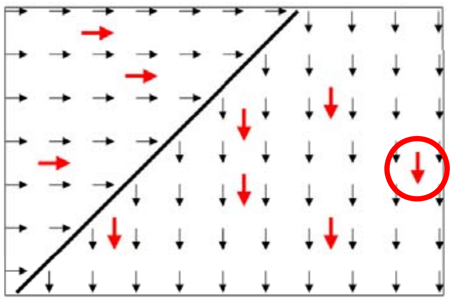
$$\int_V \left(\sigma_{ji}\delta\epsilon_{ij} - D_i\delta E_i + \eta_i\delta P_i + \xi_{ji}\delta P_{i,j}\right) dV = \int_S \left(t_i\delta u_i - \omega\delta\phi\right) dS$$

subdomain (volume) terms

boundary terms



2. “Fixed” polarization



e.g.:
$P_y = -P^{defect}$

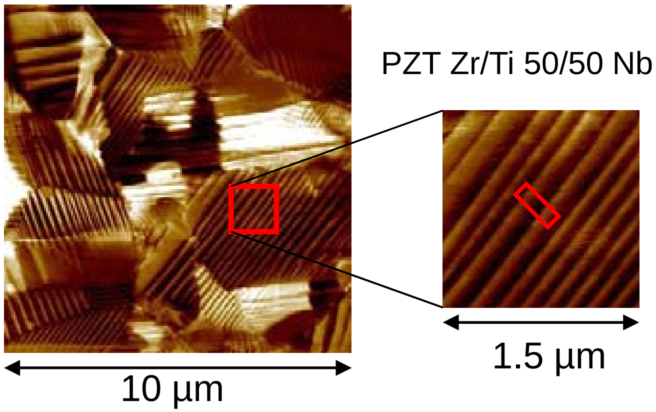
➔ *approach for defects:*
- create geometric “point”
- define defect via boundary conditions
- mesh geometry
- solve

Throughout simulation:
defect properties: constant

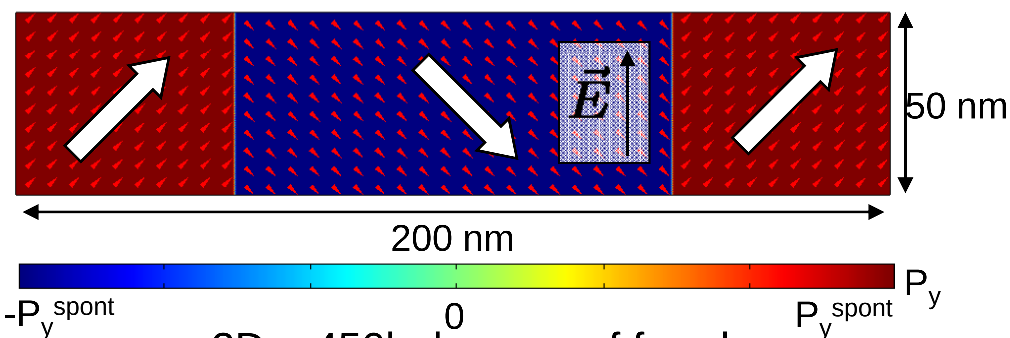
➔defects cannot switch
➔defects cannot move

Investigation of 90° domain stacks

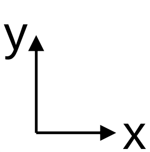
From PFM-experiments: typical domain width ~100-200 nm [Fernandéz/Schneider,TUHH]



Phase field model: 90° domain stack

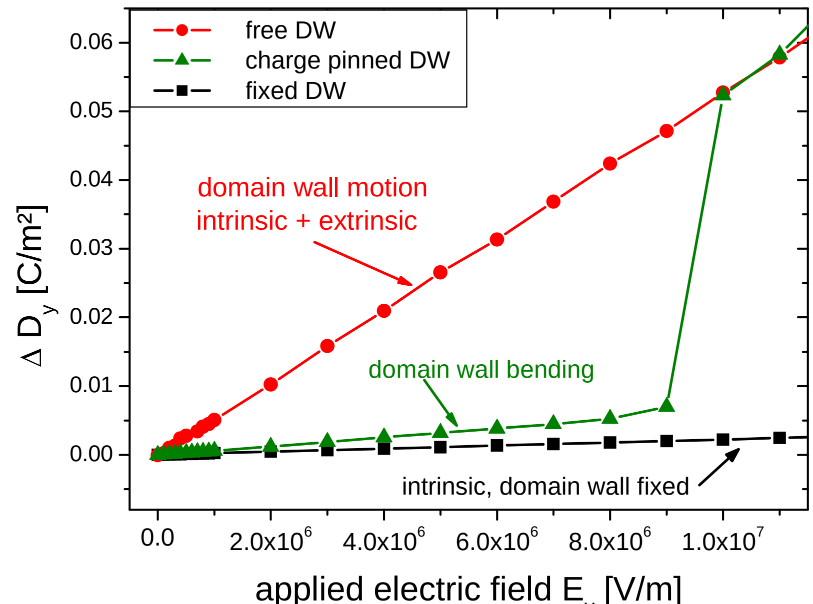


- 2D, ~450k degrees of freedom
- periodic boundary conditions
- electrical / mechanical loading



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

Domain wall (DW):
1) artificially completely fixed
2) free
3) pinned by charged (line) defect



➔intrinsic/ extrinsic piezoelectric effect
➔(reversible) DW moving / bending

Conclusions

- theory of phase-field modeling of ferroelectric materials
- parameter identification in free energy density
- finite element implementation
- periodic boundary conditions
- domain configurations
- intrinsic and extrinsic contributions to small signal properties

➔ COMSOL: a powerful tool for nowadays mathematical physics

Acknowledgements

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