Phase-field modelling for Ferroelectric Materials
Collaboration with IMF II, Forschungszentrum Karlsruhe

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Today's development and improvement of ferroelectric materials is mainly based on experimental approaches. To reduce development time and costs in the future, there is a demand for a virtual material development. This requires a knowledge-based multi-scale modelling chain which covers several orders of magnitude in length and time scale. The scope of the BMBF project COMFEM is the development of such a simulation chain for ferroelectric lead-zirconium-titanate-materials.

To close the gap between predictive ab initio methods and micromechanics within this multi-scale simulation chain, thermodynamically motivated phase-field simulations are applied to reproduce the self-organisation of the domain structure. The fundament of the phase-field theory is a free-energy-function ψ that represents the elastic, piezoelectric and dielectric properties of the ferroelectric material near its spontaneous polarized state:

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

$$+\frac{1}{2}\overline{a}_{ij}P_iP_j + \frac{1}{4}\overline{\overline{a}}_{ijkl}P_iP_jP_kP_l + \frac{1}{6}\overline{\overline{\overline{a}}}_{ijklmn}P_iP_jP_kP_lP_mP_n + \frac{1}{8}\overline{\overline{\overline{\overline{a}}}}_{ijklmnrs}P_iP_jP_kP_lP_mP_nP_rP_s \qquad \text{(II)}$$

$$+b_{ijkl}\varepsilon_{ij}P_kP_l + \frac{1}{2}c_{ijkl}\varepsilon_{ij}\varepsilon_{kl} + f_{ijklmn}\varepsilon_{ij}\varepsilon_{kl}P_mP_n + g_{ijklmn}\varepsilon_{ij}P_kP_lP_mP_n \qquad \text{(III)}$$

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

The free-energy ψ is a polynomial function of the polarisation P_i, the gradient of the polarisation $P_{i,j}$, the strains ε_{ij} and the dielectric displacement D_i. It consists of four main parts: (I) defines the thickness of domain walls by penalizing large polarisation gradients, (II) creates a non-convex energy landscape with minima located at spontaneous polarisation states, (III) fits the material's spontaneous strain along with the dielectric, elastic and piezoelectric properties about the spontaneous state and (IV) represents the energy stored within the free space occupied by the material

Temporal and spatial evolution of the polarisation order parameter is provided by the solution of the Ginzburg-Landau equation,

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

where β is an inverse mobility tensor. The state variables of the system can be obtained by derivation of the free-energy-function with respect to the natural variables.

Different forms of free energy functions that describe both tetragonal and rhombohedral polarised states have been taken from literature and examined. Here, higher-order polarisation terms were of special interest because of their profoundly sensitive impact. The influence of all inbound coefficients of the free energy was analysed to make further adaptation towards a more realistic material model based on results of ab initio calculations possible. A two-dimensional

free-energy landscape plot of a tetragonal polarised ferroelectric is shown in Fig. 1. The minima are located along the <100>-axes and correspond with the spontaneous polarised states.

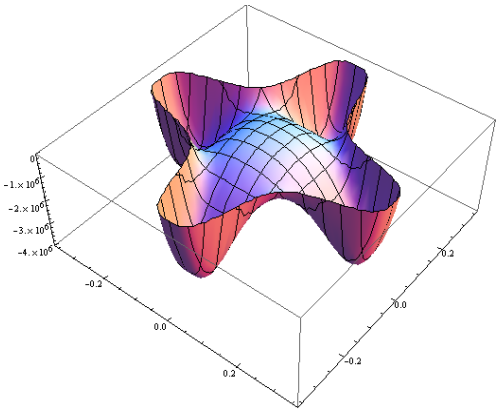

Fig. 1: Two-dimensional free energy landscape

Furthermore, the phase field theory was numerically implemented both in the finite-difference method and the finite element method. Stationary 180° and 90° domain walls could be investigated both in 1D and 2D, and for both configurations the domain wall energy was evaluated. As an example, Fig. 2 shows one-dimensional finite element calculations of domain walls in $BaTiO_3$, obtained by solving the Ginzburg-Landau equation. The width of the 180° domain wall is significantly smaller than the width of the 90° domain wall. This corresponds with the calculated domain wall energies, which are smaller in the 90° case and higher in the 180° case.

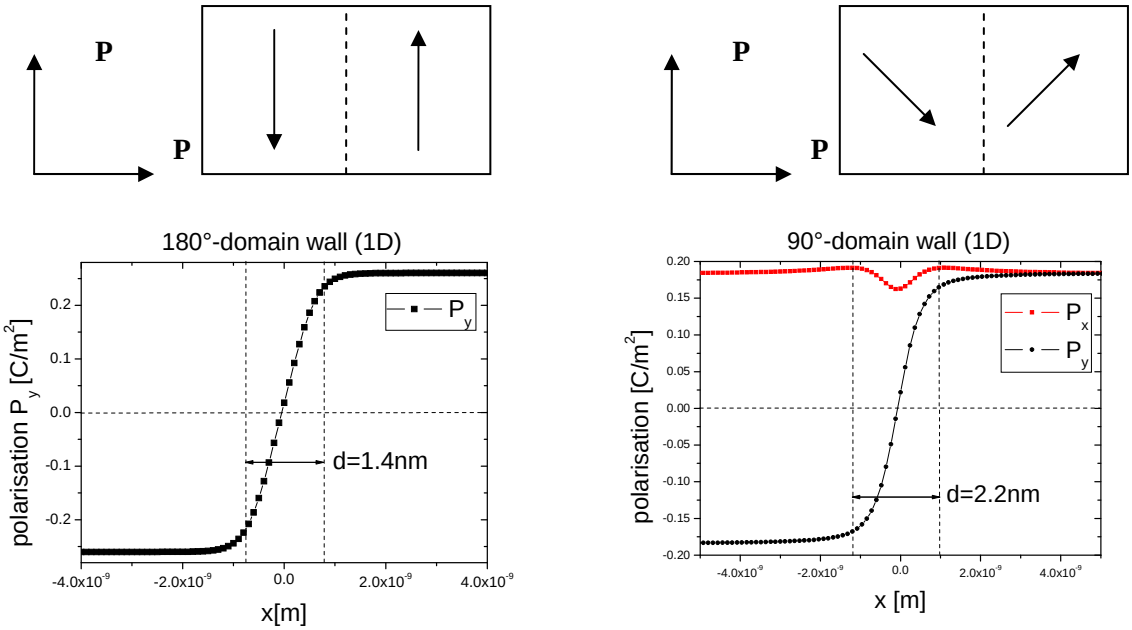

Fig. 2: Calculated width of domain walls in $BaTiO_3$