UNIVERSITY OF OXFORD

Phase field methods for simulating ferroelectrics and other materials

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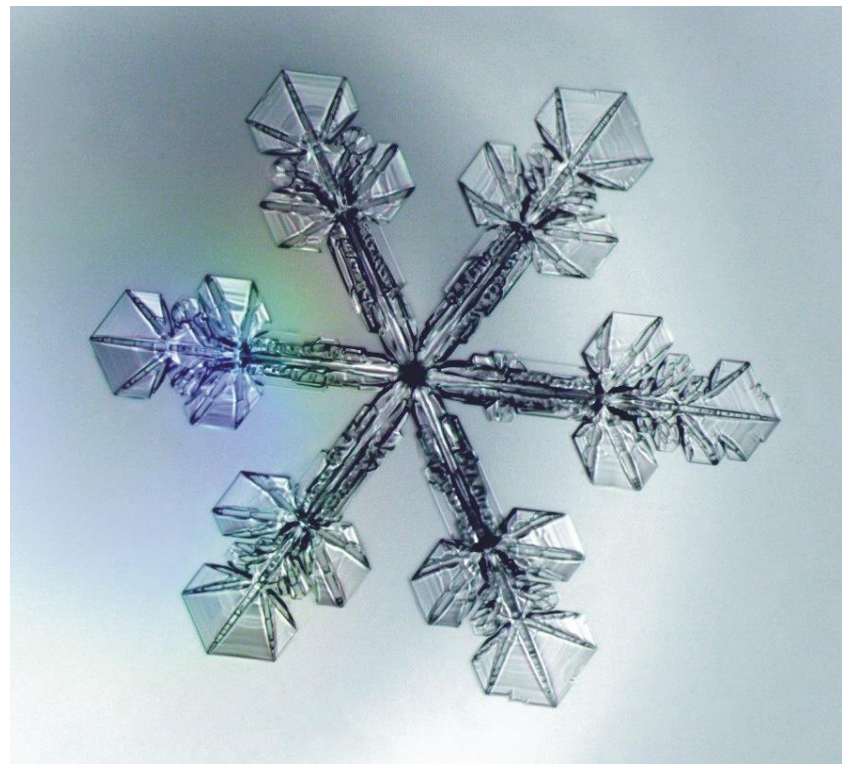
Acknowledgements: Craig Carter, MIT, Yet-Ming Chiang, MIT, Ingo Muench KIT, Chad Landis, UT Austin, Richard D James, University of Minnesota

Idea of Phase field models



To model the interface between “phases” by a continuous variation of an order parameter

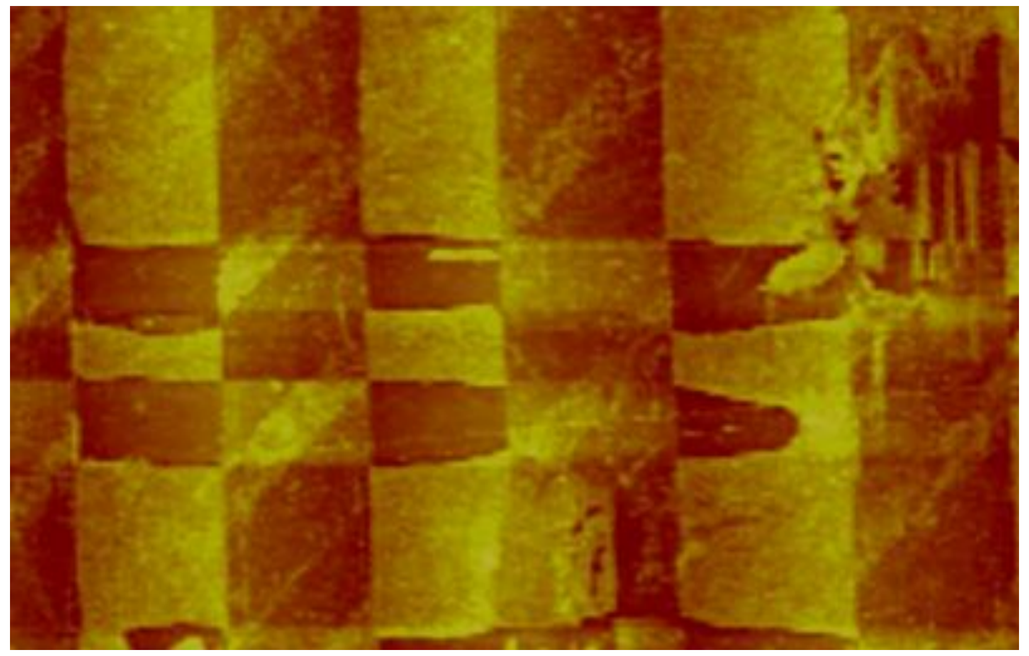
To model the variations of composition etc. within an interface

To track a moving interface

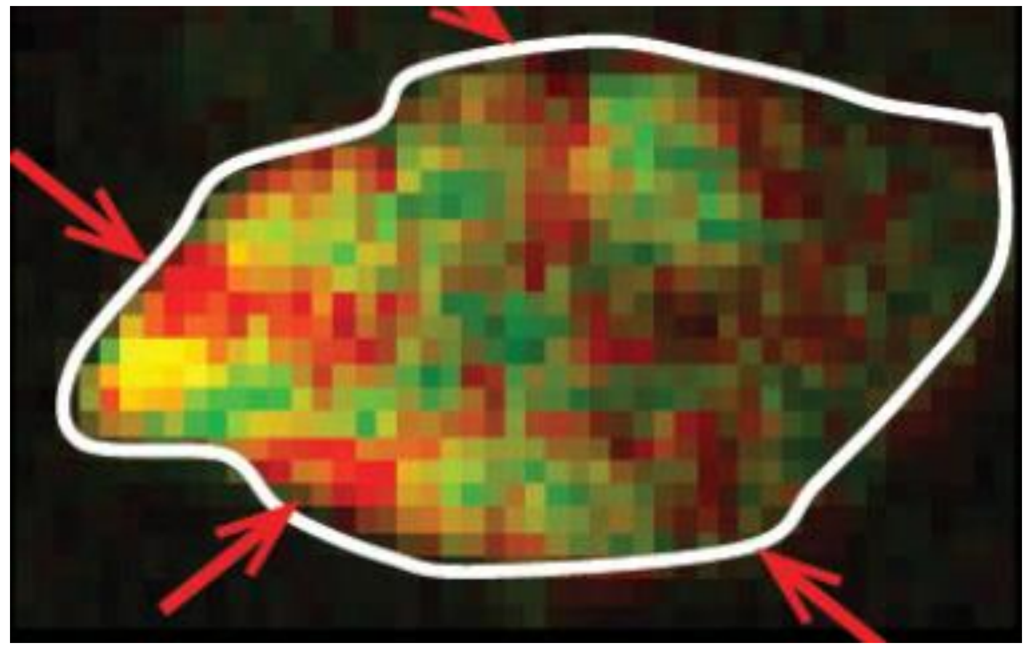
Applications

- Solidification of pure substances and alloys
- Solid-state phase transformations
- Coarsening of precipitates
- Grain growth
- Twinning and domains in multiferroics
- Crack growth (as continuum damage)
- Dislocation dynamics

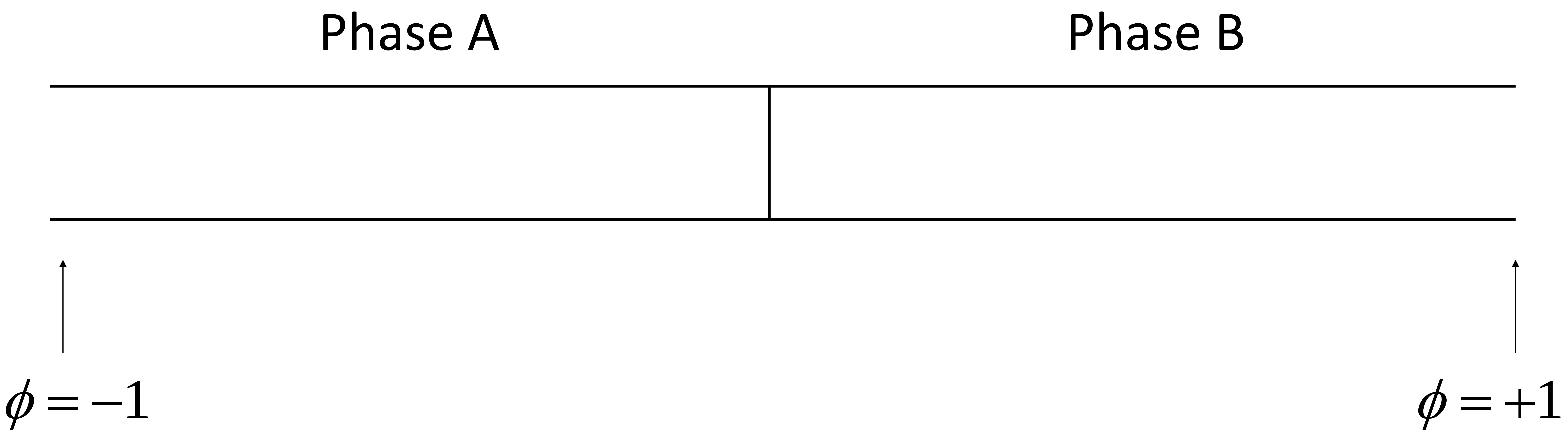
Ferroelectric materials



Battery materials



Simple Example



Assume a free energy of the form:

$$\psi = \psi(\phi, \nabla\phi, \nabla\phi \otimes \nabla\phi, \cdots)$$

The $\nabla\phi$ dependence should be even for symmetry.

The simplest case is: $\psi = f(\phi) + \dfrac{\alpha}{2}\left|\nabla\phi\right|^2$

$$\Psi = A\int_{-\infty}^{\infty} f(\phi) + \frac{\alpha}{2}\left|\frac{\mathrm{d}\phi}{\mathrm{d}x}\right|^2 \,\mathrm{d}x$$

Ginzburg-Landau equation

To minimise Ψ consider variation of Ψ

$$\delta\Psi = A\int_{-\infty}^{\infty}\left(\frac{\mathrm{d}f}{\mathrm{d}\phi} - \alpha\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2}\right)\delta\phi\,\mathrm{d}x$$

Minimise Ψ by relaxation (or assume linear kinetics)

$$\dot{\phi} = -\frac{1}{\beta}\frac{\delta\Psi}{\delta\phi}$$

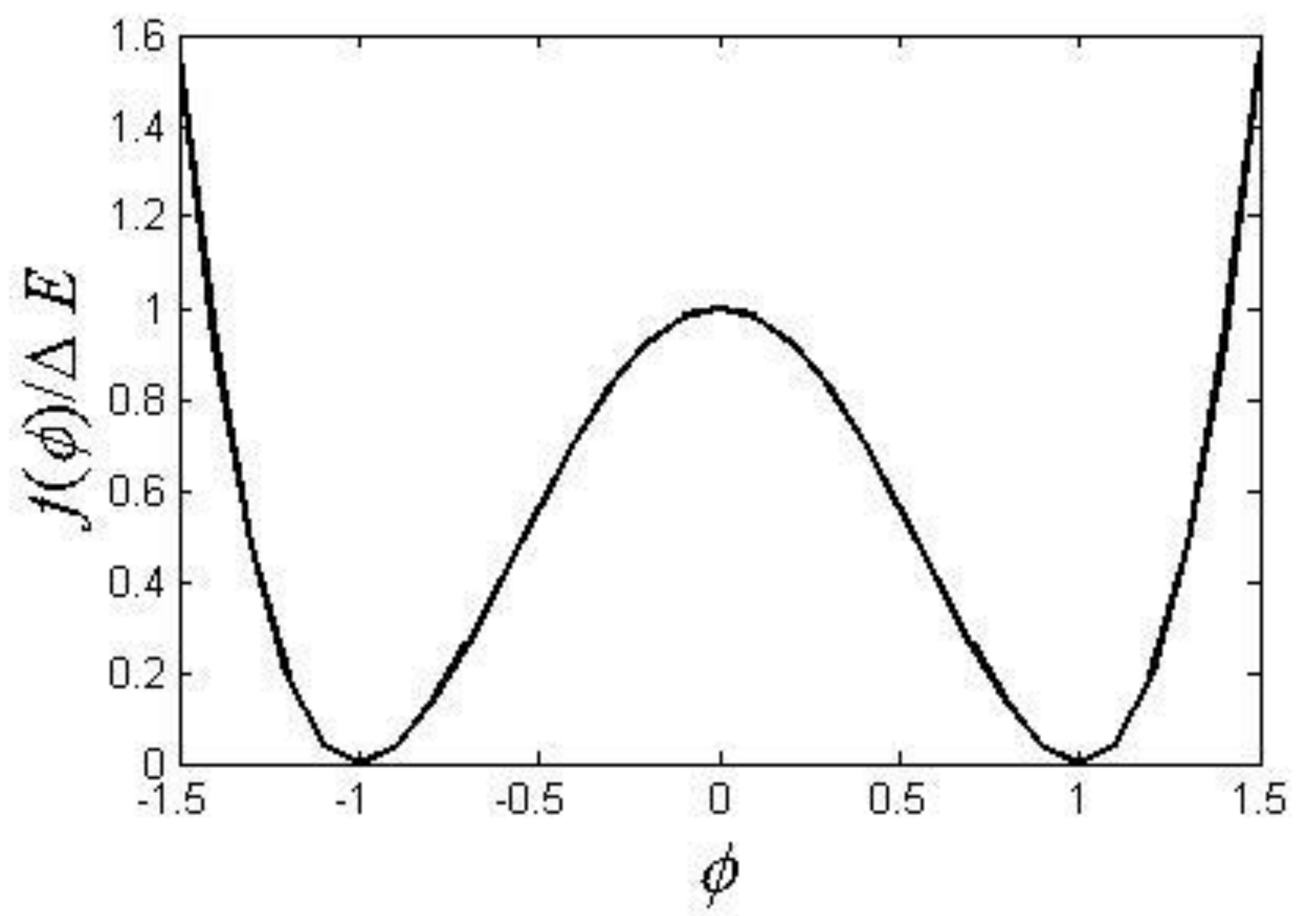
Giving:

$$\underbrace{\beta\dot{\phi} = \alpha\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} - \frac{\mathrm{d}f}{\mathrm{d}\phi}}_{\text{The celebrated Ginzburg-Landau equation}}$$

Simple Example

We still need to specify the free energy, $f(\phi)$

For example:

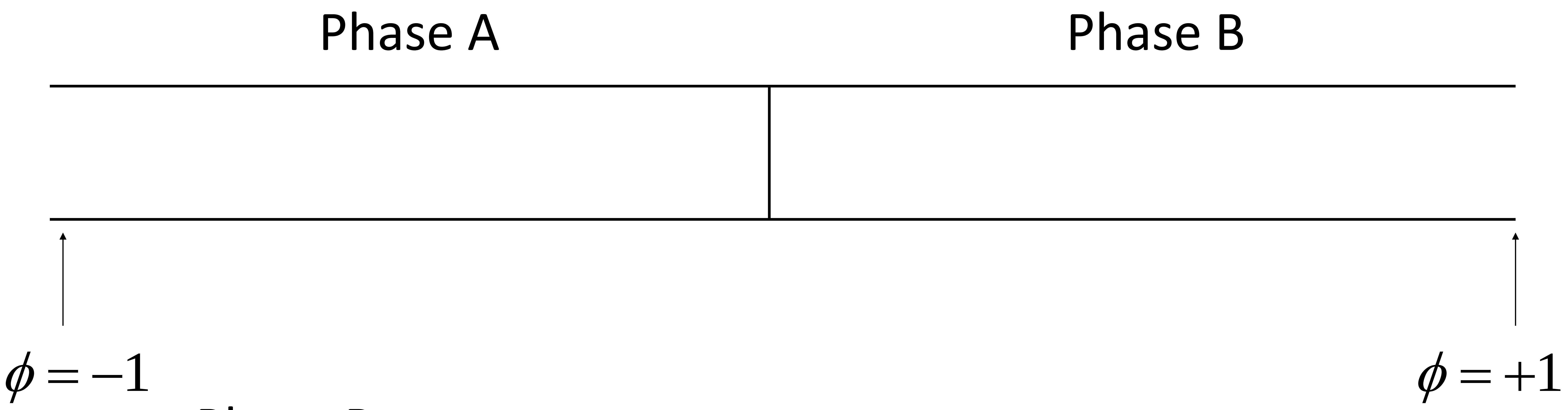


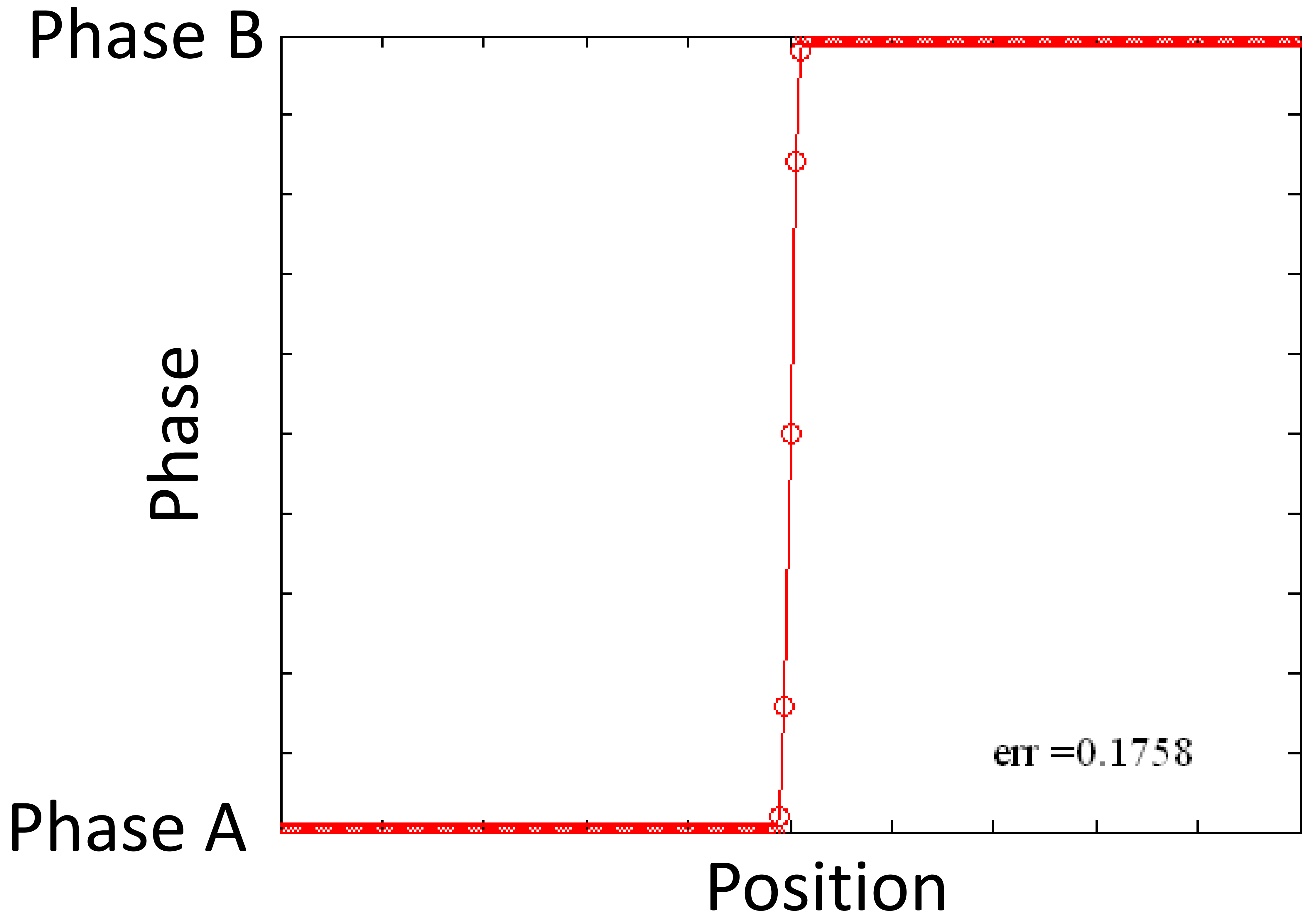
$$f(\phi) = \Delta E\left(\phi - 1\right)^2\left(\phi + 1\right)^2$$

Then our evolution law becomes:

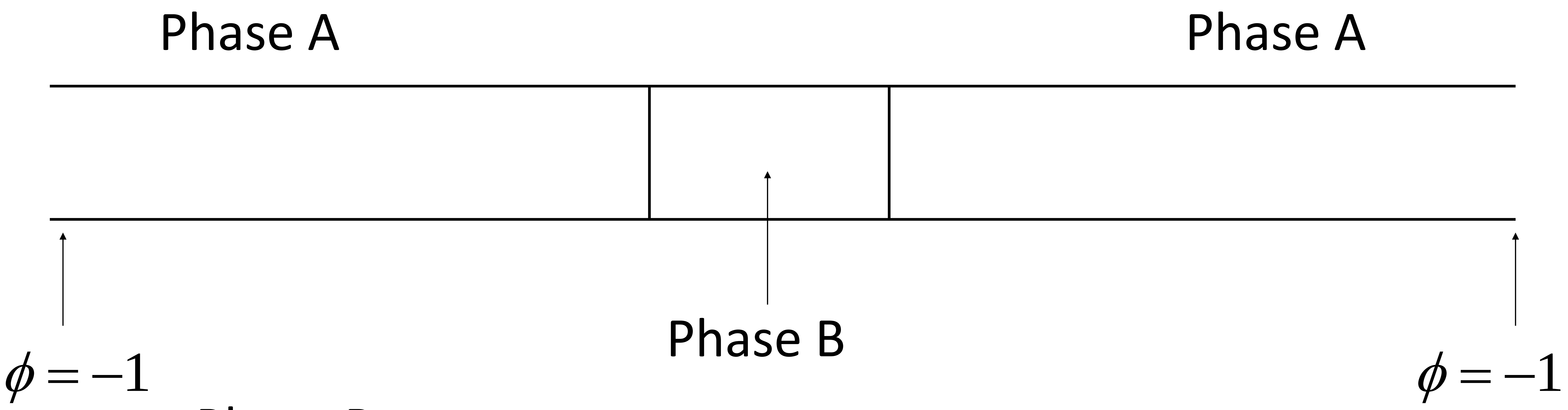
$$\beta\dot{\phi} = \alpha\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} - 4\Delta E\left(\phi^3 - \phi\right)$$

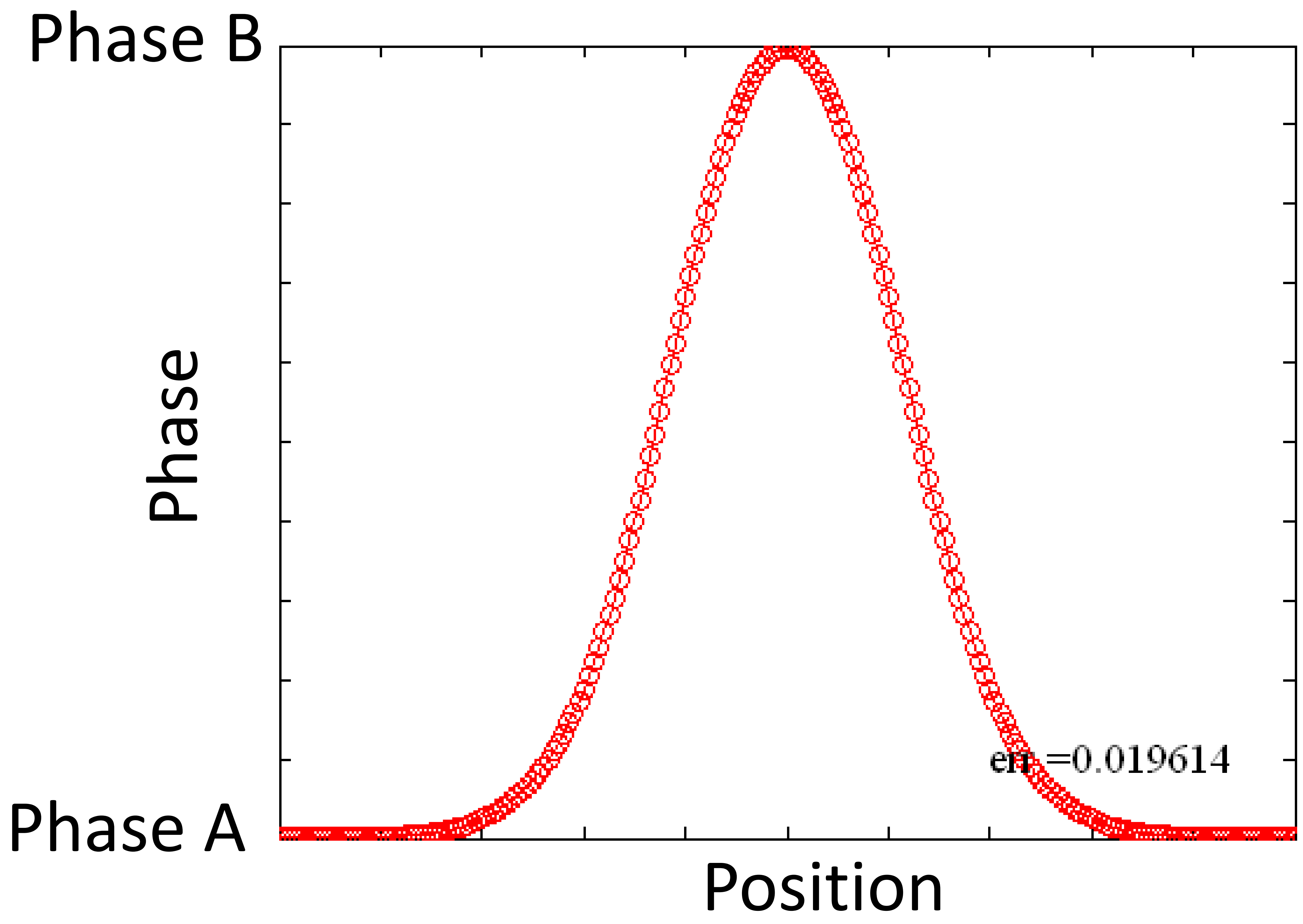
Phase boundary



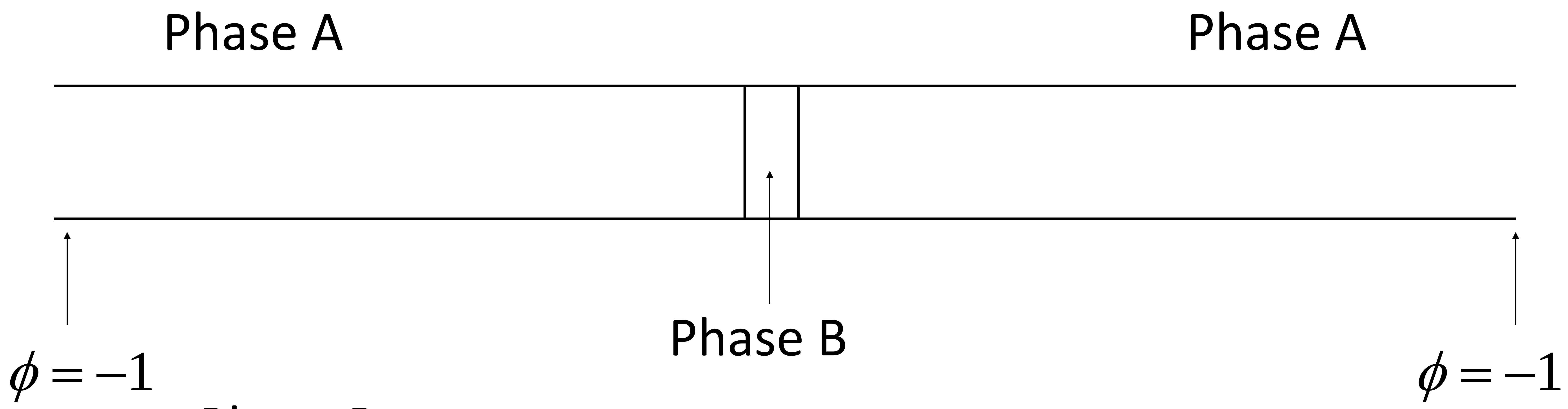


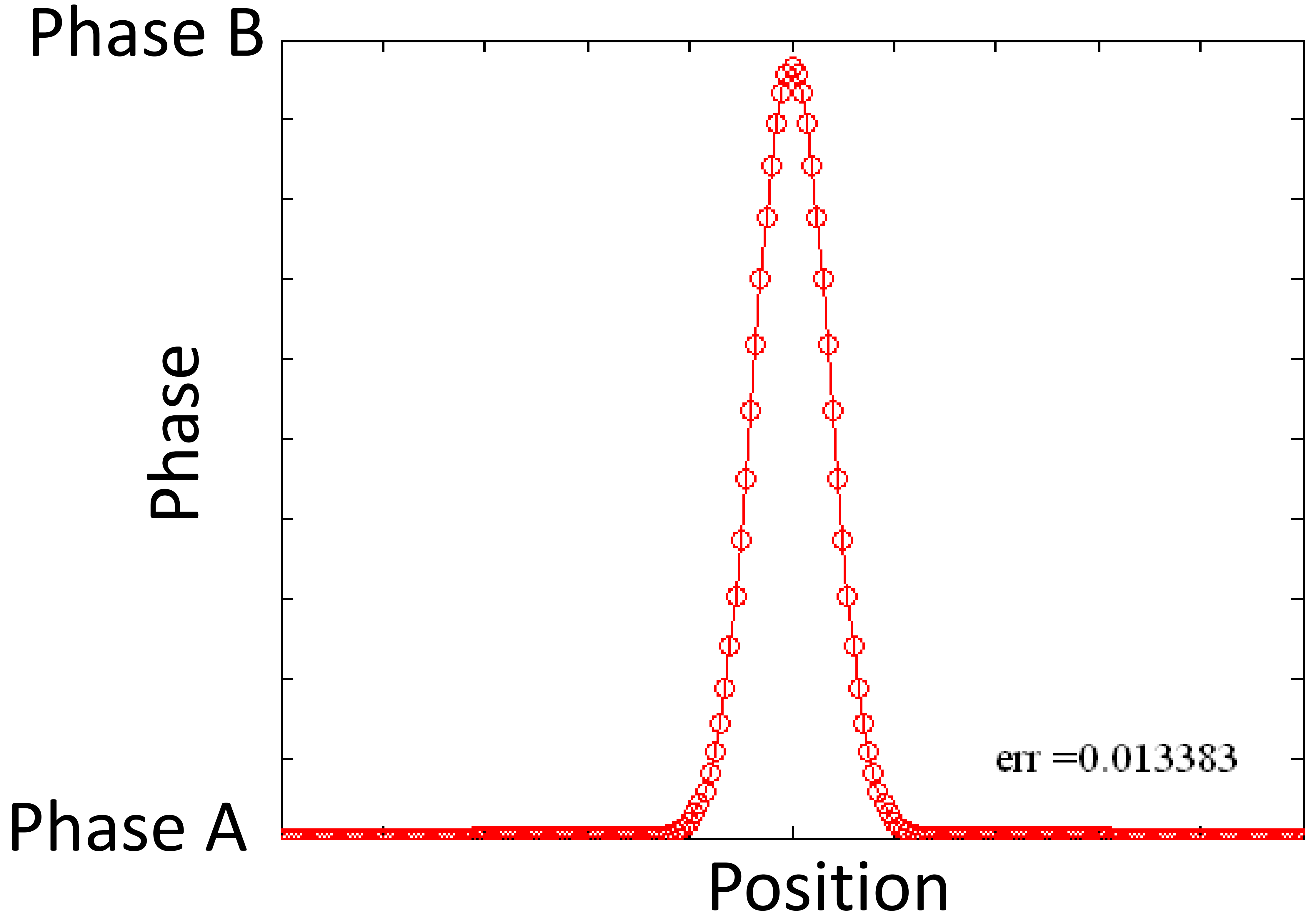
Stable nucleus





Unstable nucleus





Balance of configurational forces

Fried & Gurtin (1993,1994), Gurtin (1996):
If the free energy depends on an independent order parameter there is need for a system of configurational forces that are work conjugate to the order parameter

$\langle \boldsymbol{\gamma}, \phi \rangle$ ... power density expended due to external sources
$\langle \boldsymbol{\xi} \cdot \mathbf{n}, \phi \rangle$ ... power density expended across body surface
$\langle \boldsymbol{\pi}, \phi \rangle$ ... power density expended by internal re-ordering of atoms (dissipation)

$$\int_{\partial V} \boldsymbol{\xi} \cdot \mathbf{n} \; \mathrm{ds} + \int_{V} \boldsymbol{\pi} + \boldsymbol{\gamma} \; \mathrm{dv} = 0$$

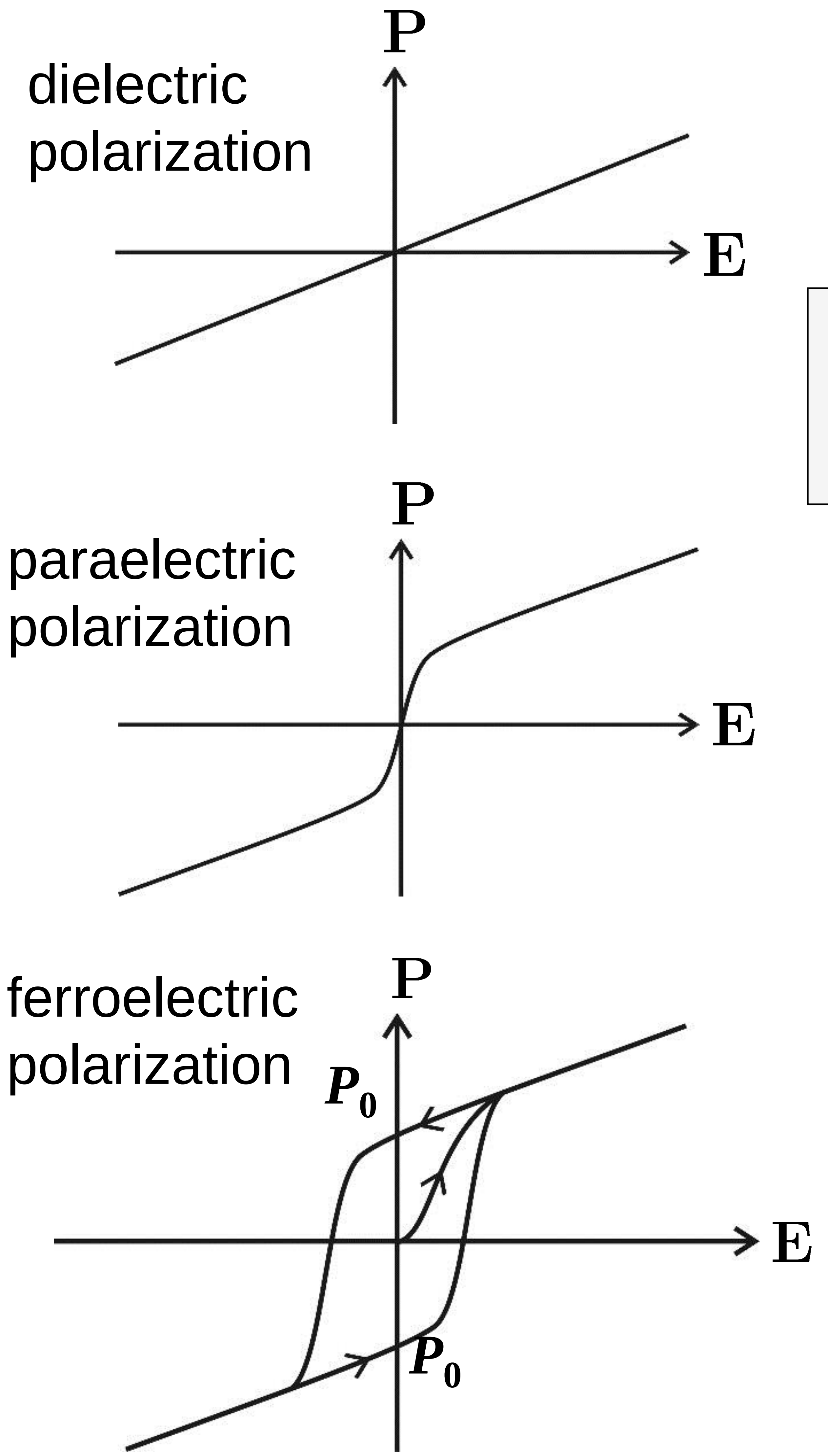
balance of configurational forces in weak form

$$\mathrm{Div}[\xi] + \pi + \gamma = 0$$

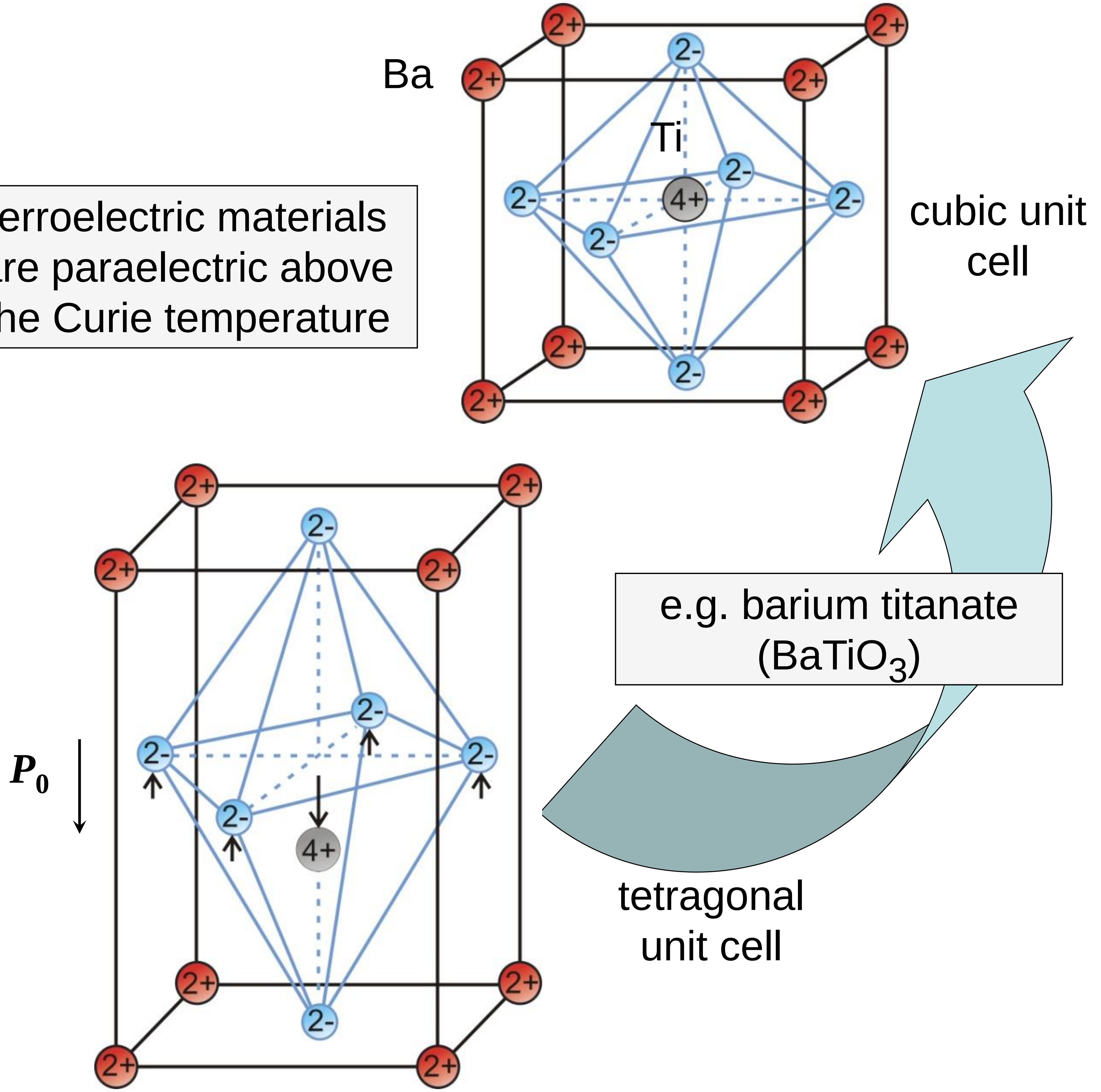
balance of configurational forces in strong form

E. Fried & M. E. Gurtin: Physica D (**68**) 326-343, 1993. ; M. E. Gurtin: Physica D (**92**) 178-192, 1996.

Application: nanoscale ferroelectric crystal

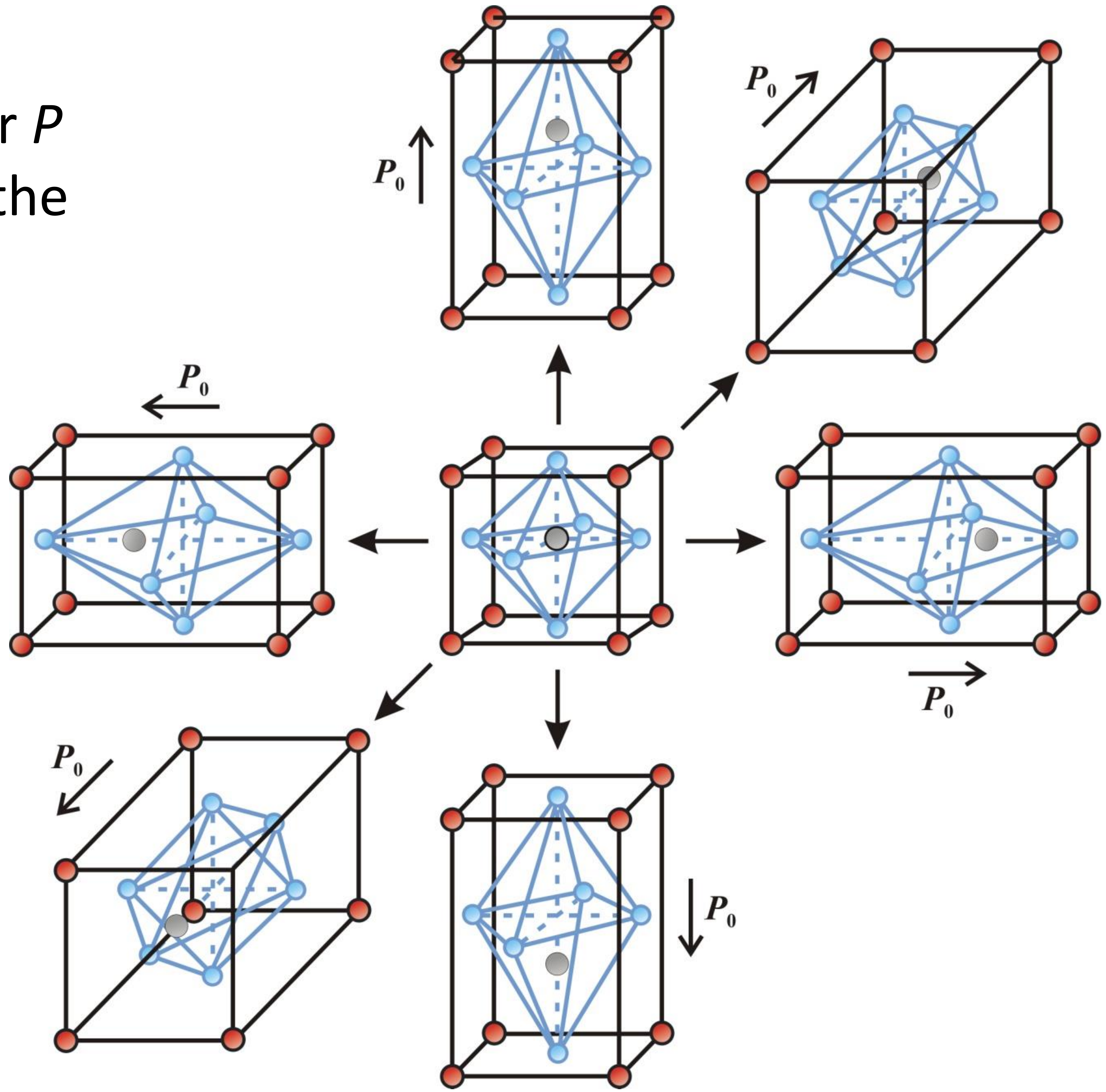


ferroelectric materials are paraelectric above the Curie temperature



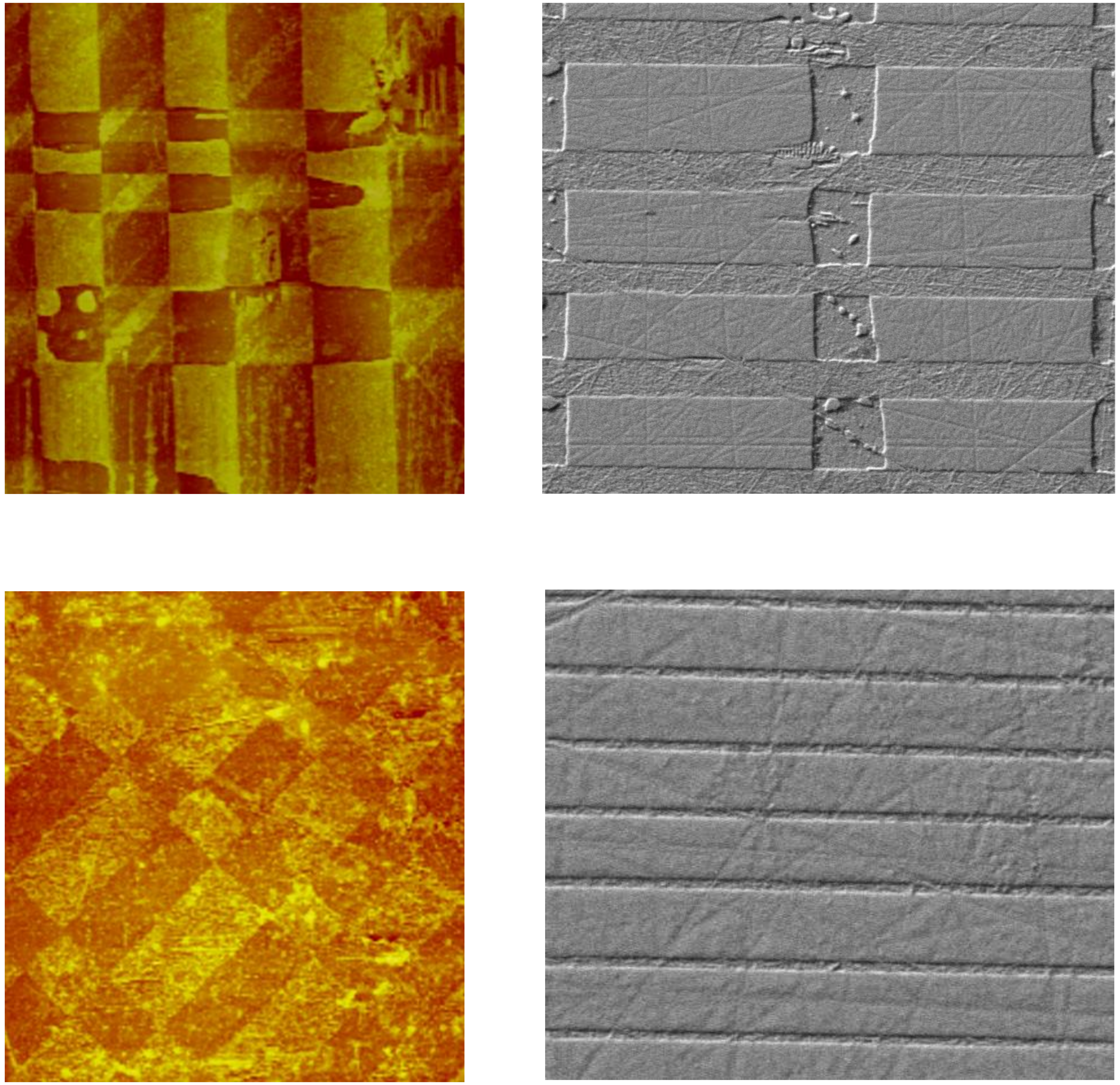
Multiple stable states in BT

The Polarization vector *P* is a natural choice for the order parameter



Typical microstructures in $BaTiO_3$

(~ 10μm)



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balance of configurational forces in strong form

E. Fried & M. E. Gurtin: Physica D (**68**) 326-343, 1993. ; M. E. Gurtin: Physica D (**92**) 178-192, 1996.

Equations to be solved

Mechanical equilibrium $\quad \mathrm{Div}[\boldsymbol{\sigma}] + \mathbf{b} = \rho\, \ddot{\mathbf{u}}\,, \qquad \boldsymbol{\sigma} \cdot \mathbf{n} = \mathbf{t}\,,$

Electrical equilibrium $\quad \mathrm{Div}[\mathbf{D}] - q = 0\,, \qquad \mathbf{D} \cdot \mathbf{n} = -\omega\,,$

Equilibrium of configurational forces $\quad \mathrm{Div}[\boldsymbol{\xi}] + \boldsymbol{\pi} + \boldsymbol{\gamma} = 0$

Definitions

$$\mathbf{D} = \mathbf{P} + \kappa_0\, \mathbf{E}$$

$$\mathbf{E} = -\mathrm{Grad}[\varphi]$$

$$\boldsymbol{\varepsilon} = \mathrm{Sym}[\mathrm{Grad}[\mathbf{u}]]$$

Second Law

$$\int_{\mathcal{B}} \dot{\Psi}\ \mathrm{d}V \leq \int_{\mathcal{B}} (\langle \mathbf{b}, \dot{\mathbf{u}} \rangle + \varphi\, \dot{q} + \langle \boldsymbol{\gamma}, \dot{\mathbf{P}} \rangle)\, \mathrm{d}V + \int_{\partial\mathcal{B}} (\langle \mathbf{t}, \dot{\mathbf{u}} \rangle + \varphi\, \dot{\omega} + \langle \boldsymbol{\xi} \cdot \mathbf{n}, \dot{\mathbf{P}} \rangle)\, \mathrm{d}A - \frac{\mathrm{d}}{\mathrm{dt}} \int_{\mathcal{B}} \frac{1}{2} \rho\, \langle \dot{\mathbf{u}}, \dot{\mathbf{u}} \rangle\ \mathrm{d}V$$

Formulation for finite element solution

$$\int_{\mathcal{B}} \langle \boldsymbol{\xi}, \mathrm{Grad}[\delta \mathbf{P}] \rangle + \langle \boldsymbol{\eta}, \delta \mathbf{P} \rangle - \langle \boldsymbol{\gamma}, \delta \mathbf{P} \rangle + \langle \boldsymbol{\beta} \cdot \dot{\mathbf{P}}, \delta \mathbf{P} \rangle \, \mathrm{d}V - \int_{\partial \mathcal{B}} \langle \boldsymbol{\xi} \cdot \mathbf{n}, \delta \mathbf{P} \rangle \, \mathrm{d}A$$

$$+ \int_{\mathcal{B}} \langle \boldsymbol{\sigma}, \delta \varepsilon \rangle - \langle \mathbf{b}, \delta \mathbf{u} \rangle + \langle \rho \, \ddot{\mathbf{u}}, \delta \mathbf{u} \rangle \, \mathrm{d}V - \int_{\partial \mathcal{B}} \langle \mathbf{t}, \delta \mathbf{u} \rangle \, \mathrm{d}A$$

$$- \int_{\mathcal{B}} \langle \mathbf{D}, \delta \mathbf{E} \rangle + q \, \delta \varphi \, \mathrm{d}V + \int_{\partial \mathcal{B}} \omega \, \delta \varphi \, \mathrm{d}A \stackrel{!}{=} 0$$

with

$$\boldsymbol{\sigma} := \frac{\partial \bar{\Psi}}{\partial \varepsilon}, \; \mathbf{D} := -\frac{\partial \bar{\Psi}}{\partial \mathbf{E}} \qquad \boldsymbol{\xi} := \frac{\partial \bar{\Psi}}{\partial \mathrm{Grad}[\mathbf{P}]}, \; \boldsymbol{\eta} := \frac{\partial \bar{\Psi}}{\partial \mathbf{P}}$$

and $\bar{\Psi} = \Psi - \langle \mathbf{E}, \mathbf{D} \rangle$

and we are assuming kinetics of the following form for the evolution of the order parameter

$$\mathrm{Div}[\boldsymbol{\xi}] - \boldsymbol{\eta} + \boldsymbol{\gamma} = \boldsymbol{\beta} \cdot \dot{\mathbf{P}}$$ with scalar constant $\boldsymbol{\beta}$

It remains to specify the constitutive relationship. i.e. $\bar{\Psi}$

Free Energy expression

following Su & Landis (2007) a suitable form of electric enthalpy is

$$\bar{\Psi} = \bar{\Psi}(\varepsilon,\, \mathbf{E},\, \mathbf{P},\, \mathrm{Grad}[\mathbf{P}])$$

$$= \frac{1}{2} C_{ijkl}\, \varepsilon_{ij}\, \varepsilon_{kl} + b_{ijkl}\, \varepsilon_{ij}\, P_k\, P_l + f_{ijklmn}\, \varepsilon_{ij}\, \varepsilon_{kl}\, P_m\, P_n + g_{ijklmn}\, \varepsilon_{ij}\, P_k\, P_l\, P_m\, P_n$$

elastic properties, piezoelectric coefficients

$$+ \frac{1}{2} \bar{a}_{ij}\, P_i\, P_j + \frac{1}{4} \bar{\bar{a}}_{ijkl}\, P_i\, P_j\, P_k\, P_l + \frac{1}{6} \bar{\bar{\bar{a}}}_{ijklmn}\, P_i\, P_j\, P_k\, P_l\, P_m\, P_n + \frac{1}{8} \bar{\bar{\bar{\bar{a}}}}_{ijklmnrs}\, P_i\, P_j\, P_k\, P_l\, P_m\, P_n\, P_r\, P_s$$

spontaneous polarization

$$+ \frac{1}{2} a_{ijkl}\, P_{i,j}\, P_{k,l}$$

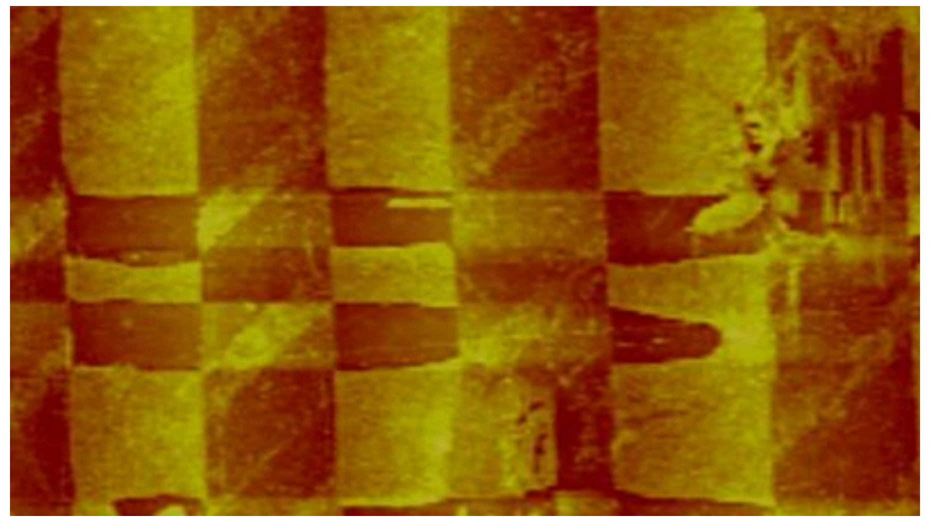
domain wall thickness

$$- \frac{1}{2} \kappa_0\, E_i\, E_i - E_i\, P_i$$

dielectric permittivity

Y. Su & C. M. Landis: J. Mech. Phys. Solids (**55**) 280-305, 2007.

Outline of the talk



Ferroelectrics

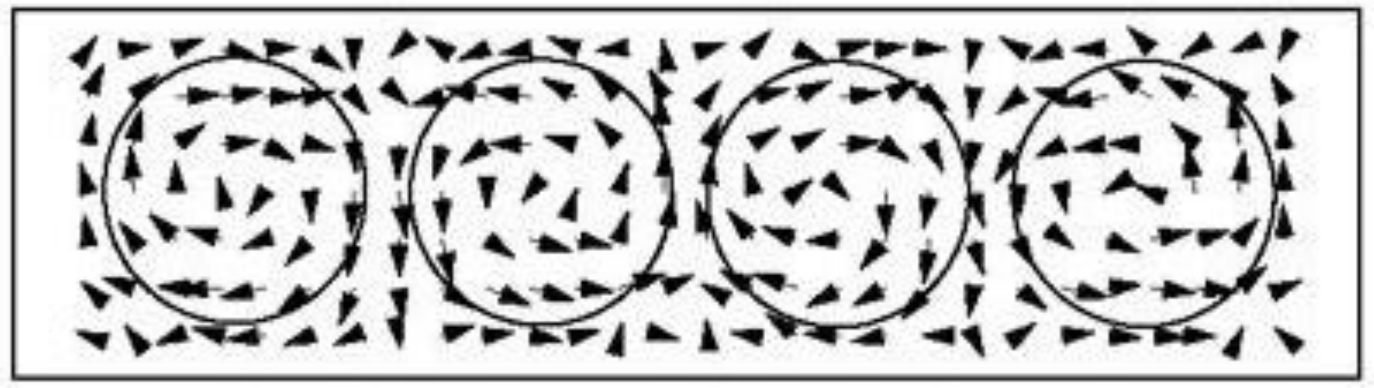
Battery materials

Light-interactive materials

John E. Huber

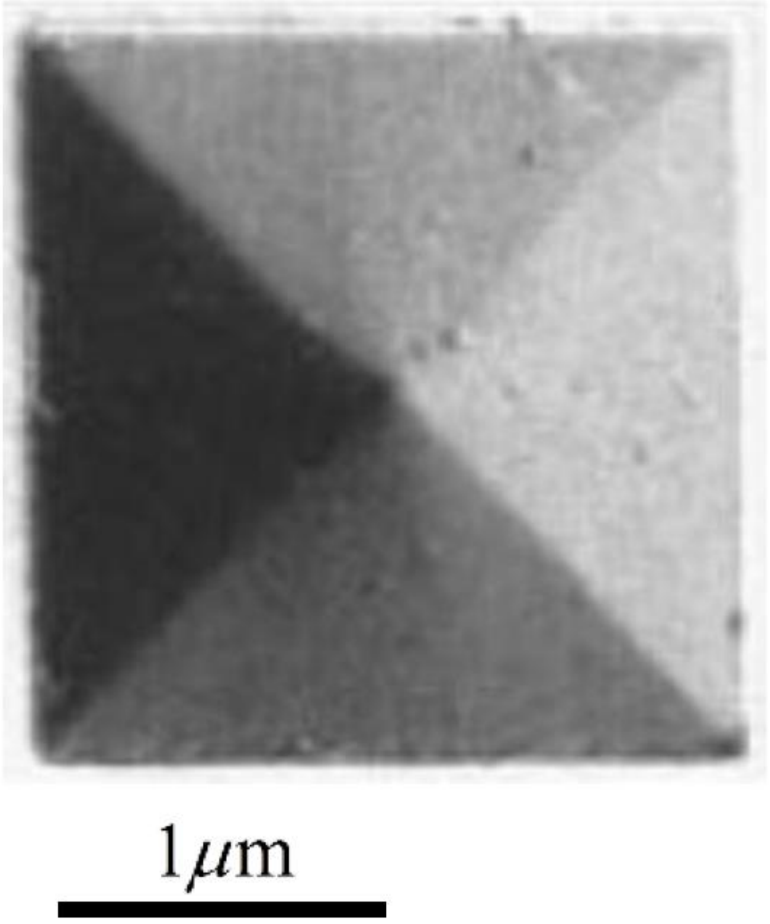
Vortex patterns greatly enhance memory storage density

Hayward et al., Ferroelectrics, 255, 2001

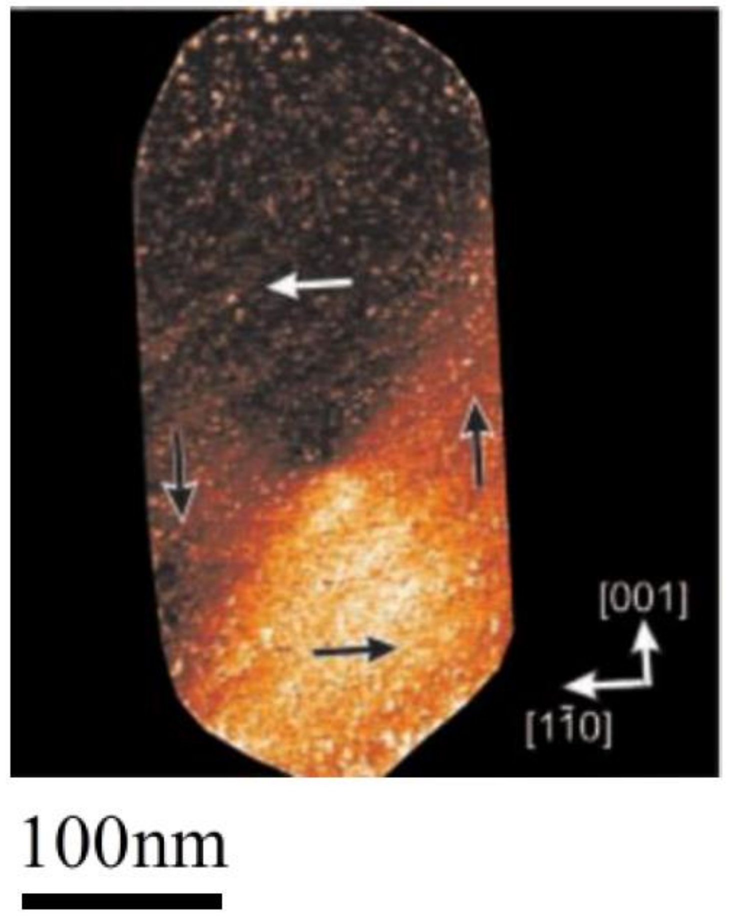


Naumov et al., Nature, 432, 2004

Ferromagnets

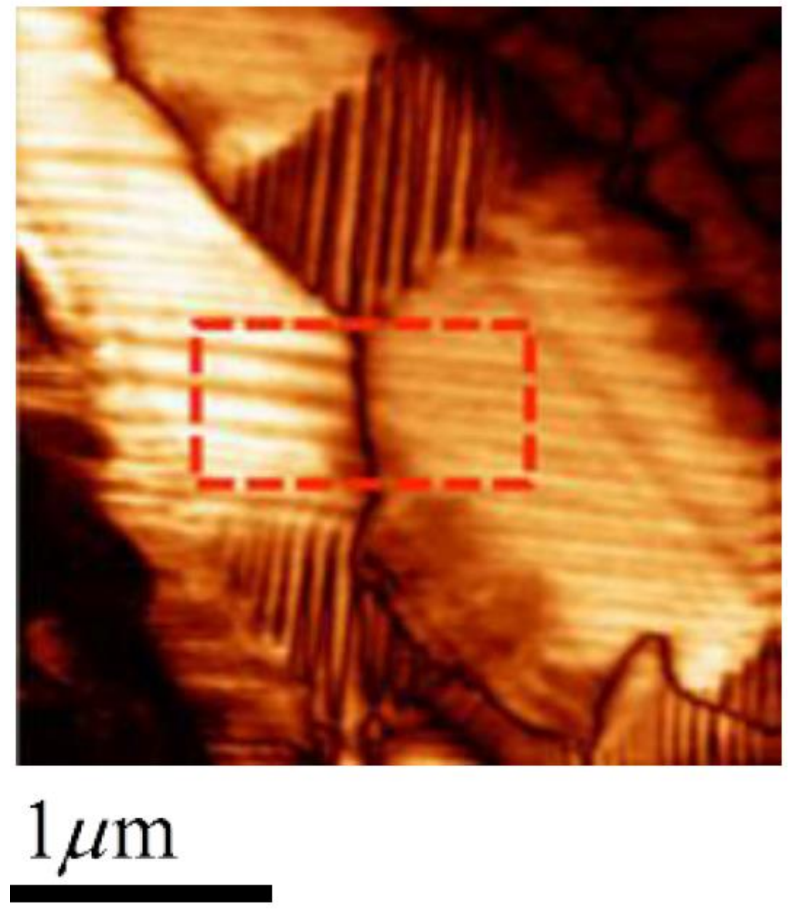


Gomez, Chapman et al., J. Appl. Phys., 85, 1999



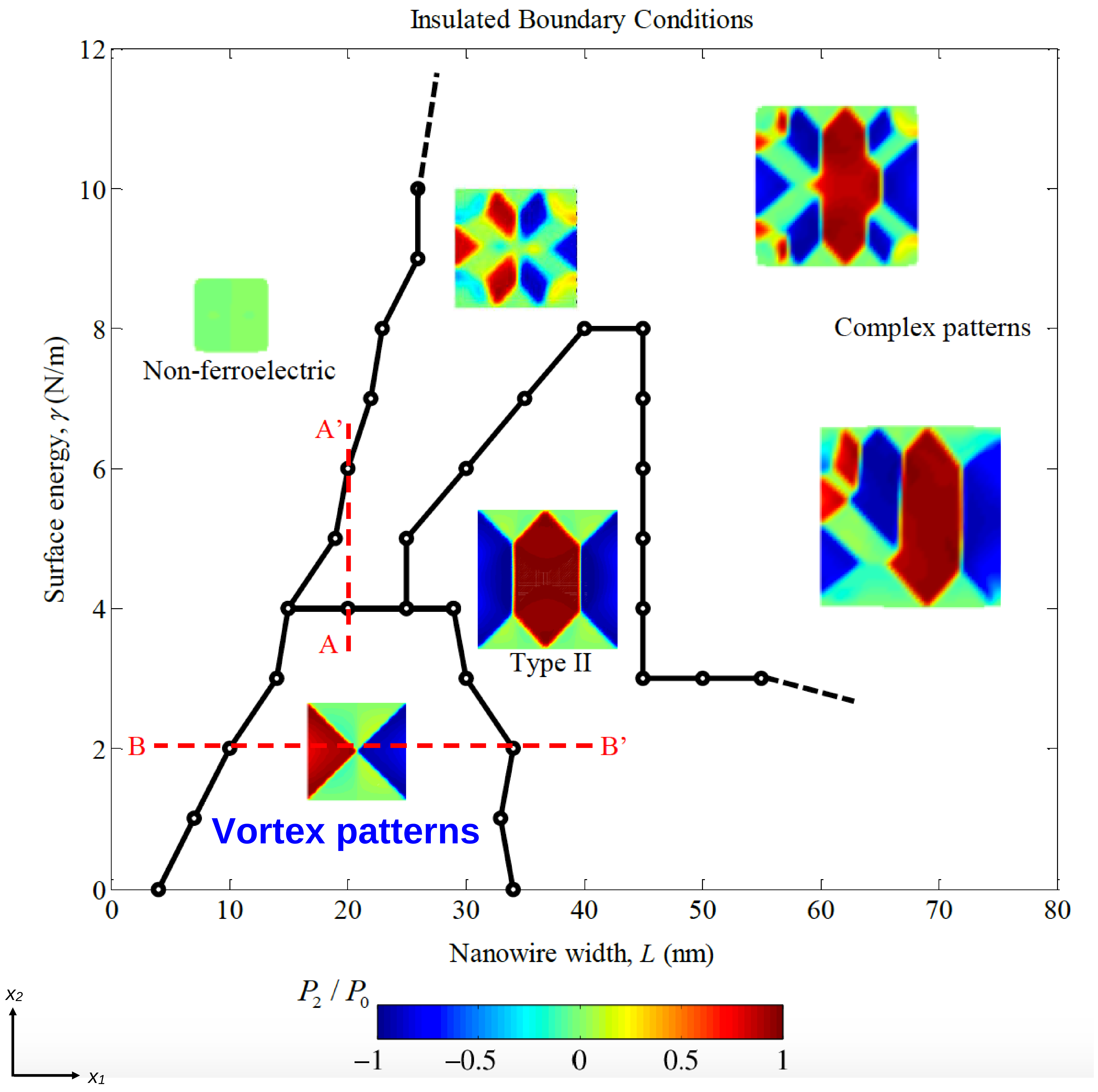
Wachowiak et al., Science, 298, 2002

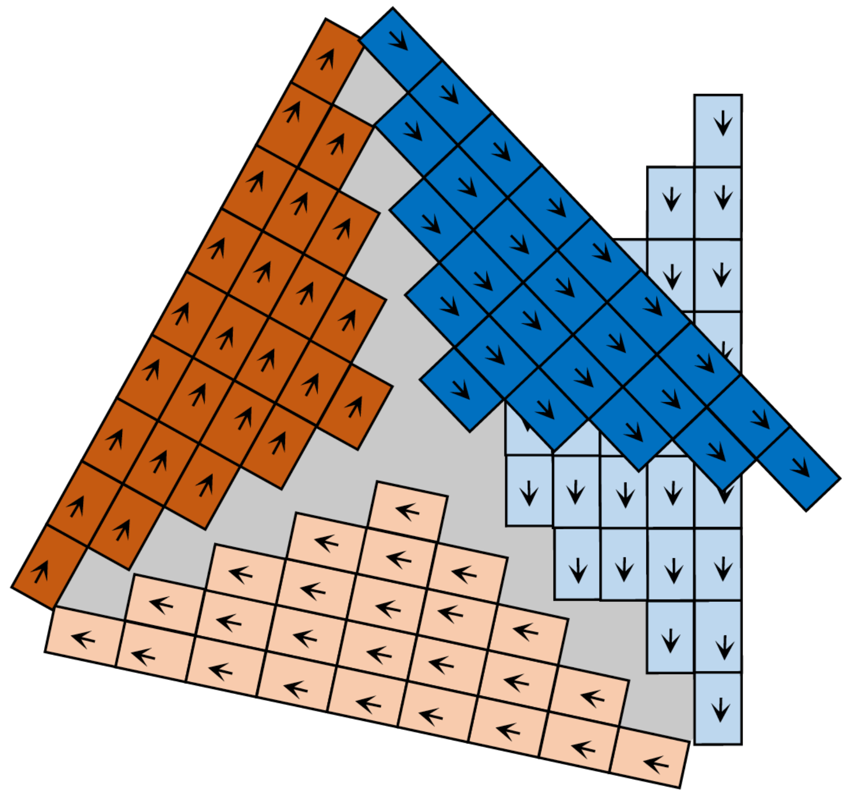
Ferroelectrics

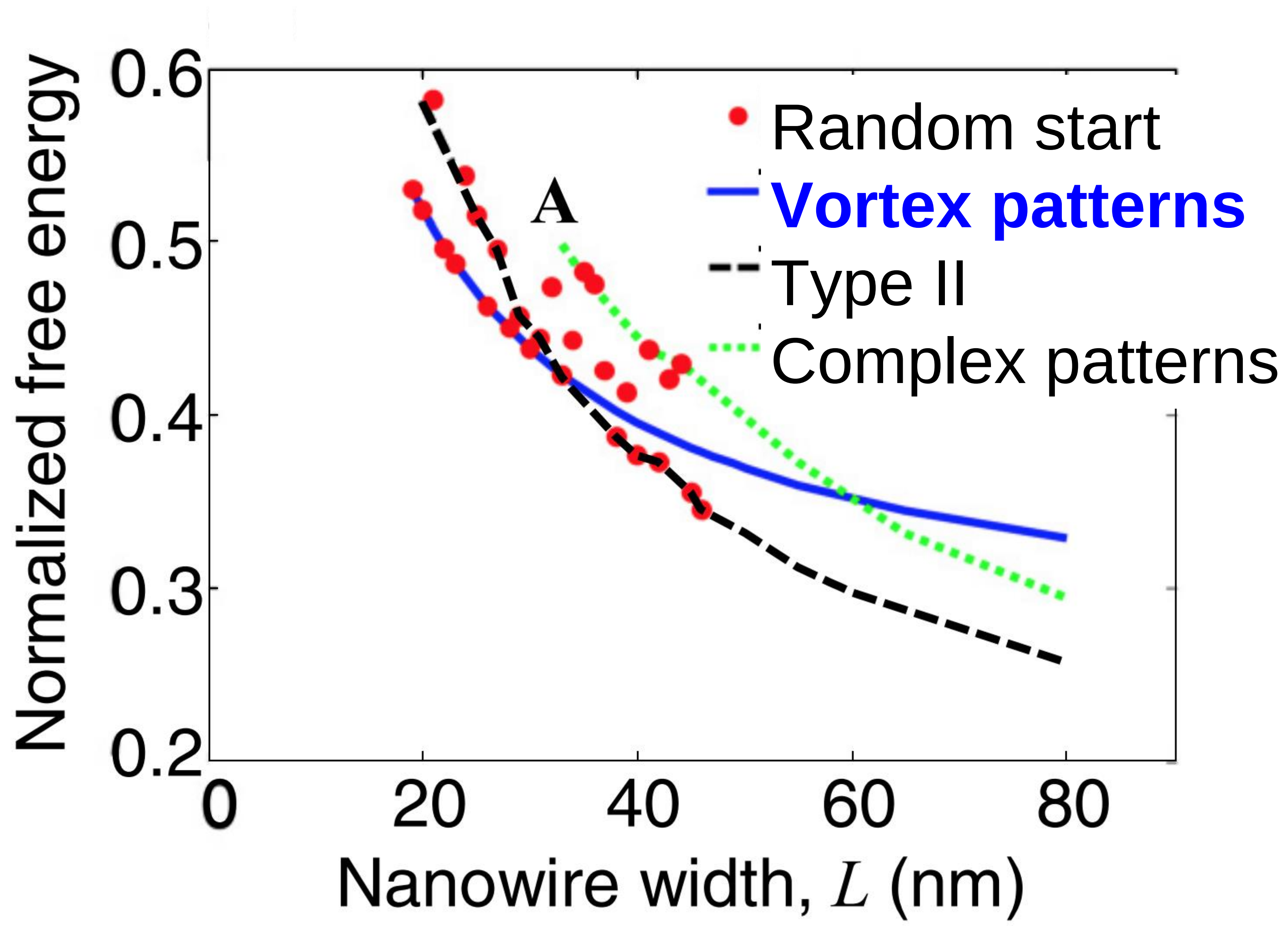


Chang, Gregg et al., Nano Lett., 13, 2013

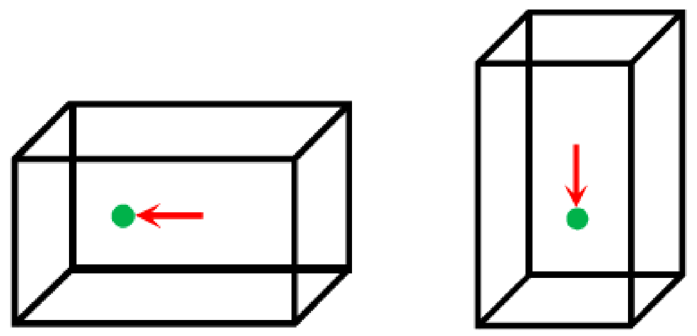
Vortex patterns are favorable at small length scales





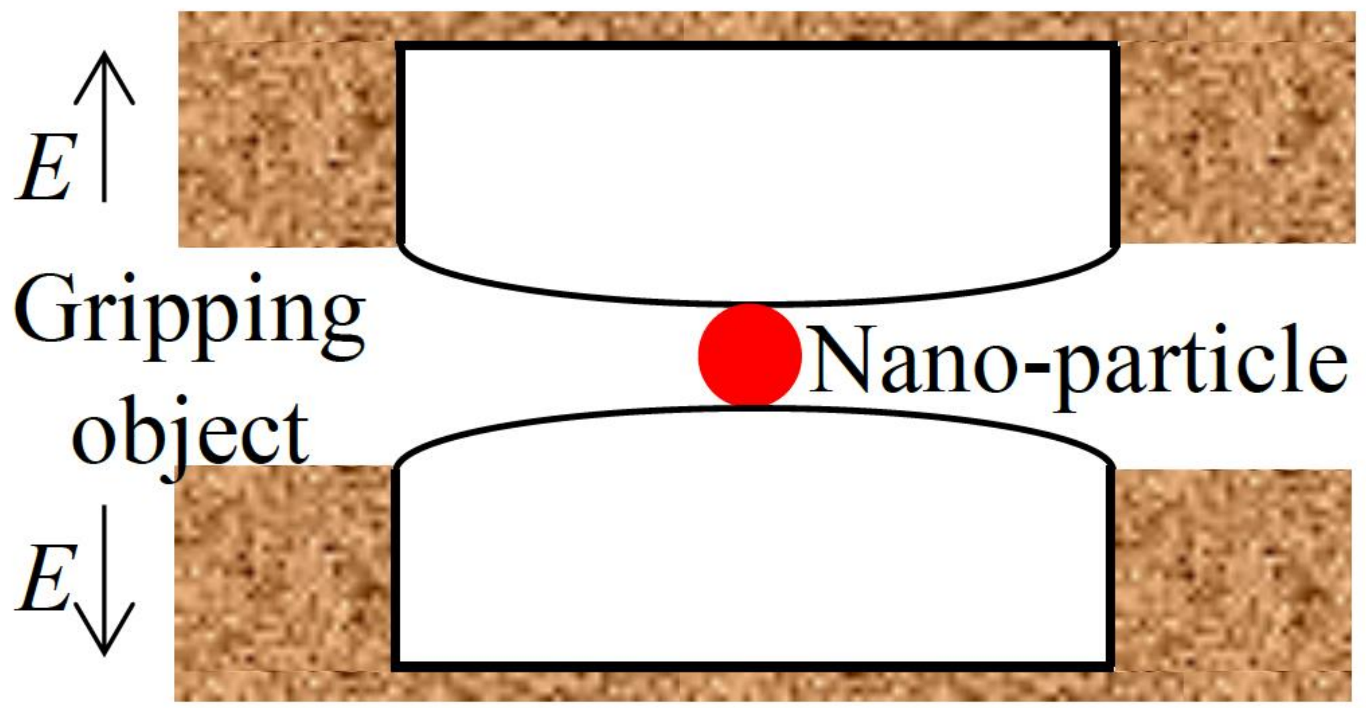


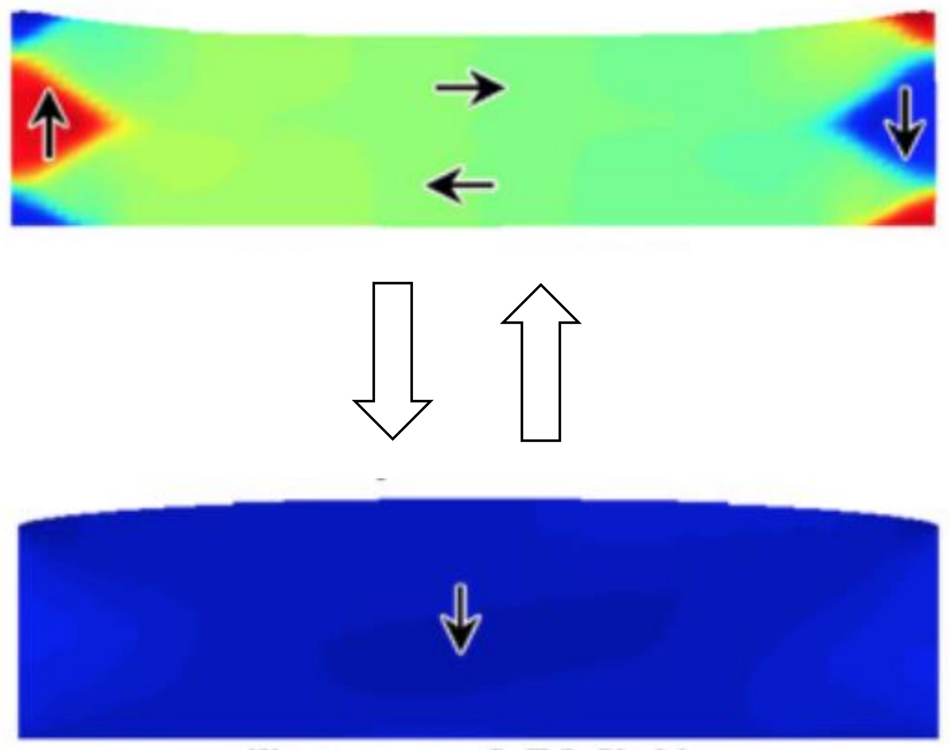
Balakrishna and Huber, Appl. Phys. Lett., 106, 2015



Phase-field model as a design-tool

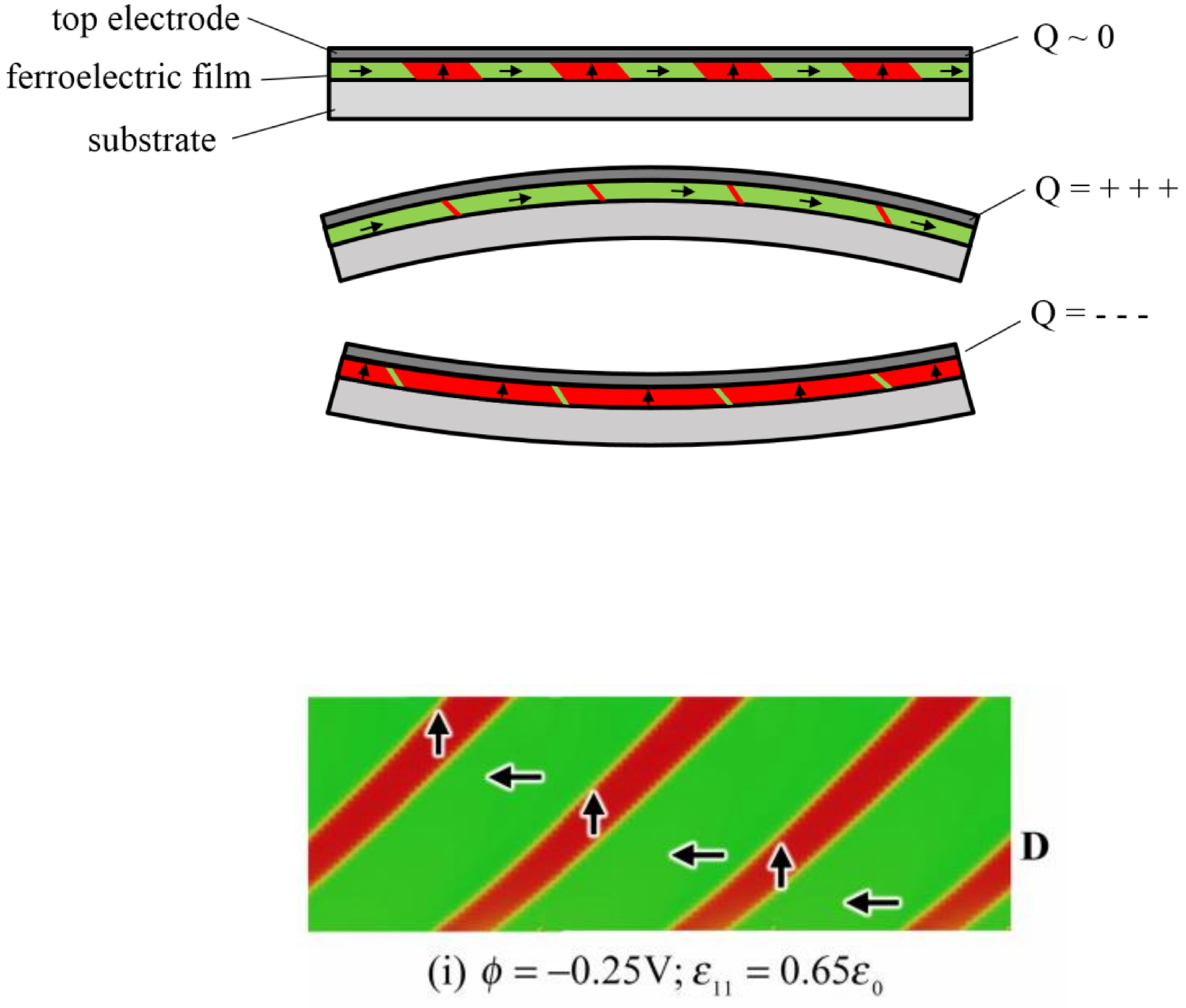
Nano-actuators





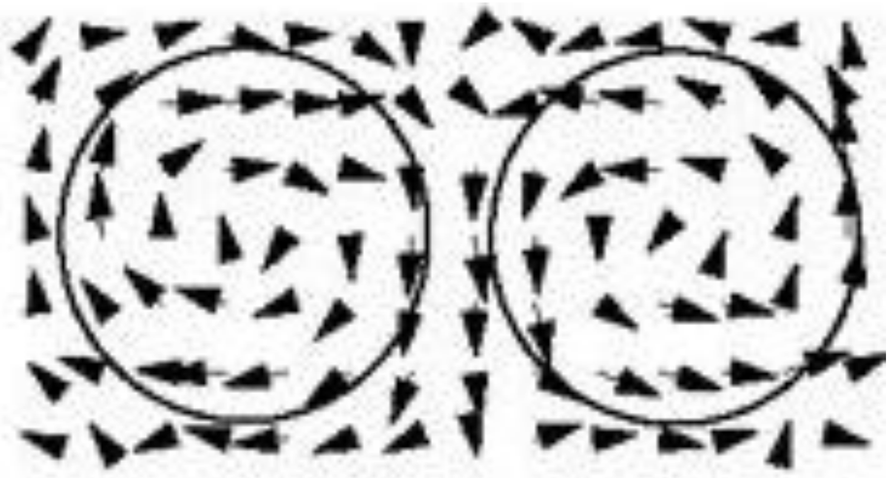
Balakrishna, Huber and Landis,
Smart Mat. Struc., 23, 2014

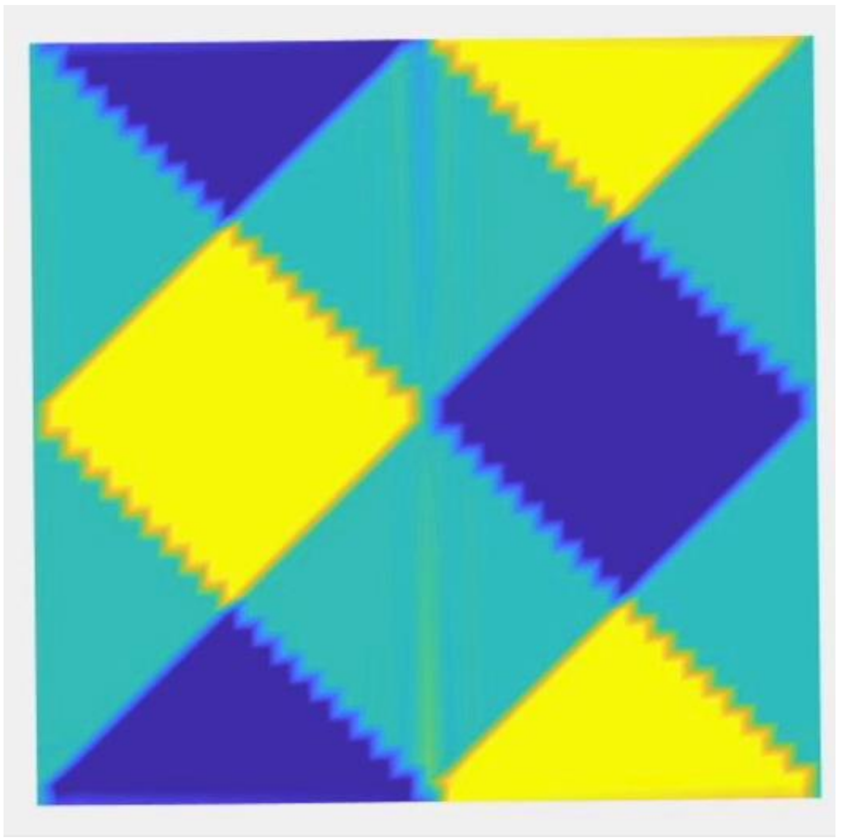
Energy Harvesters



Balakrishna and Huber,
Smart Mat. Struc., 25, 2016

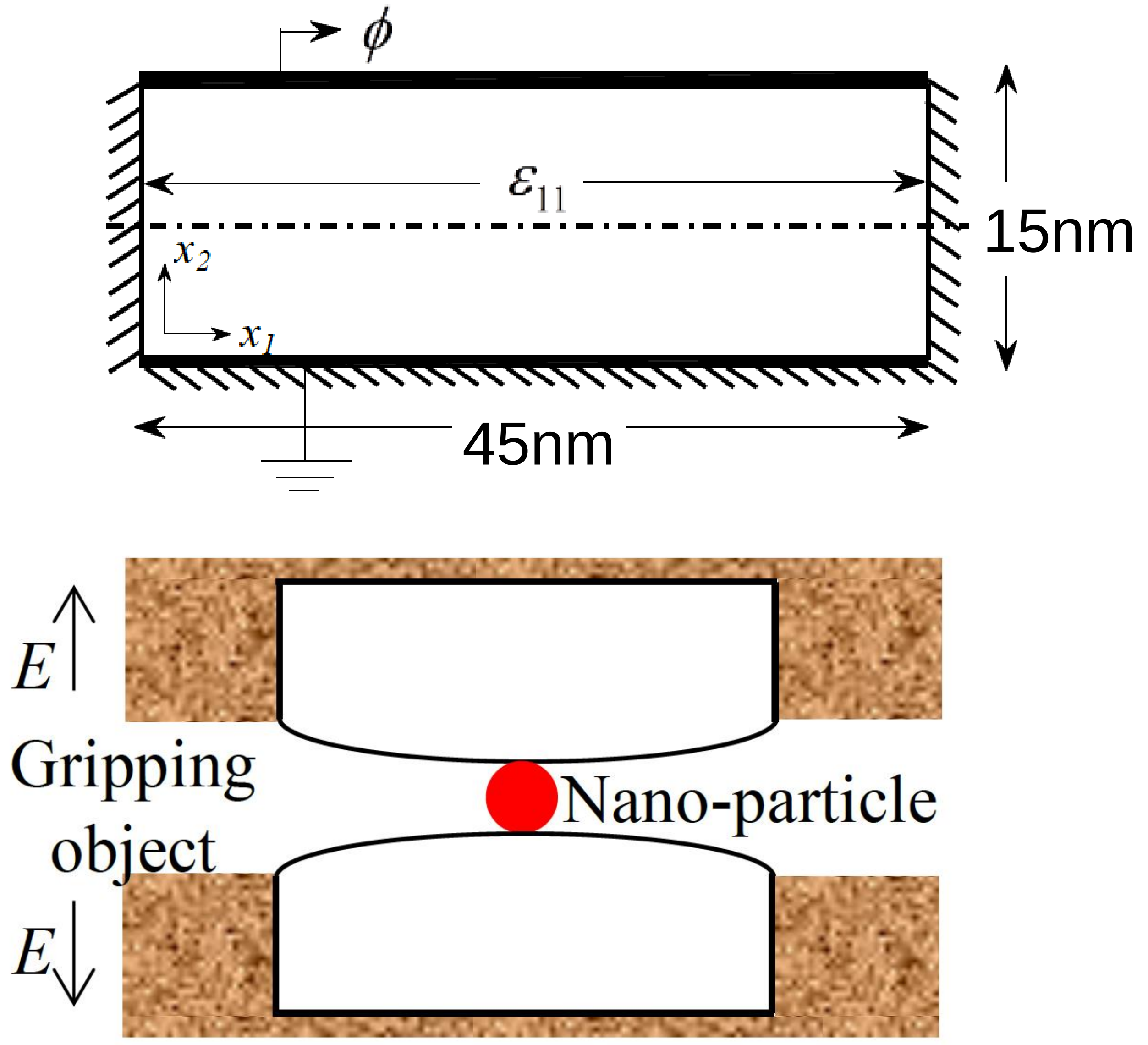
Memory elements

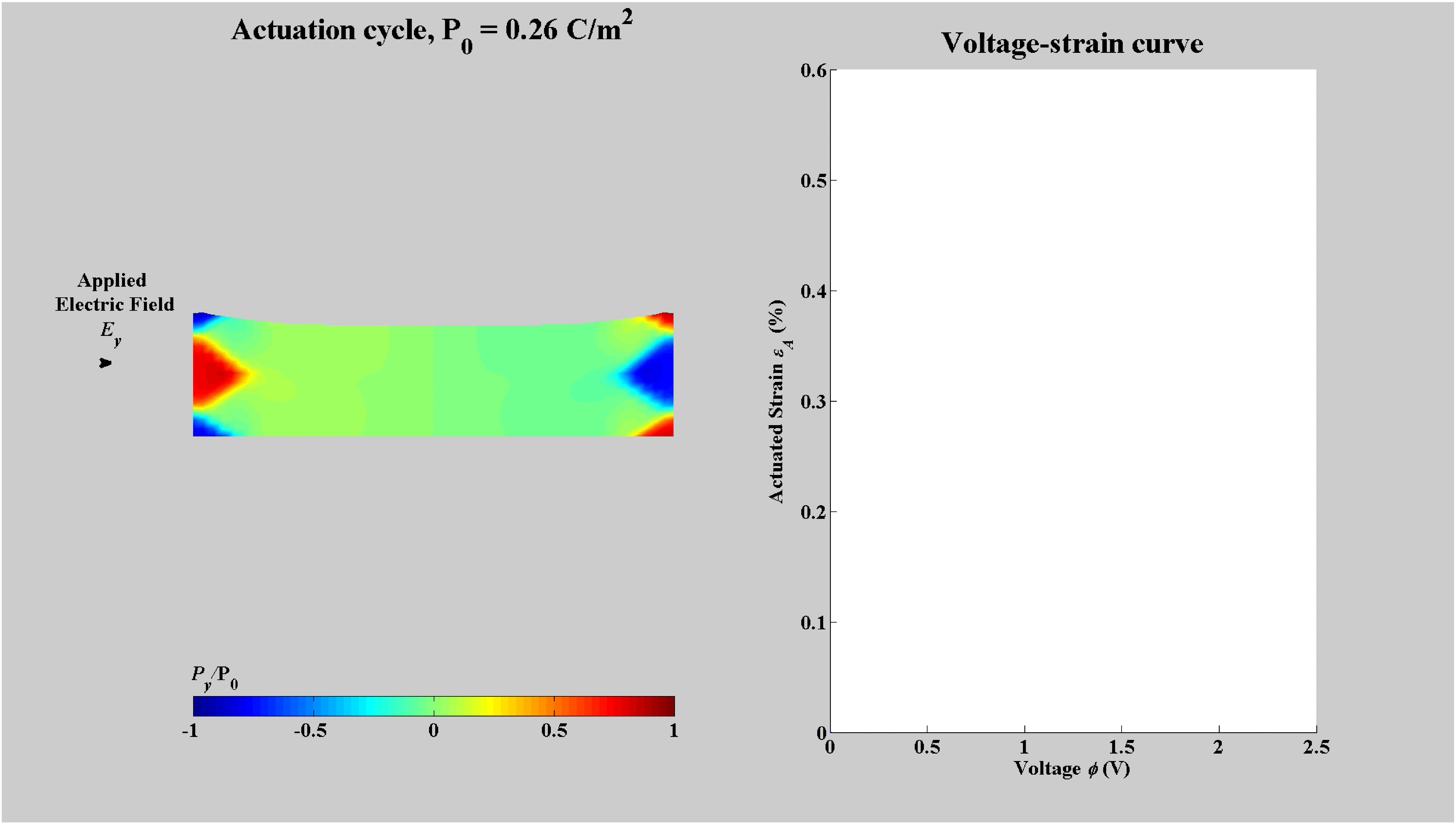




Balakrishna, Muench, Huber,
Phys. Rev B, 93, 2016

Ferroelectric actuators generate strains larger than piezoceramics





Balakrishna, Huber and Landis, Smart Mat. Struc., 23, 2014

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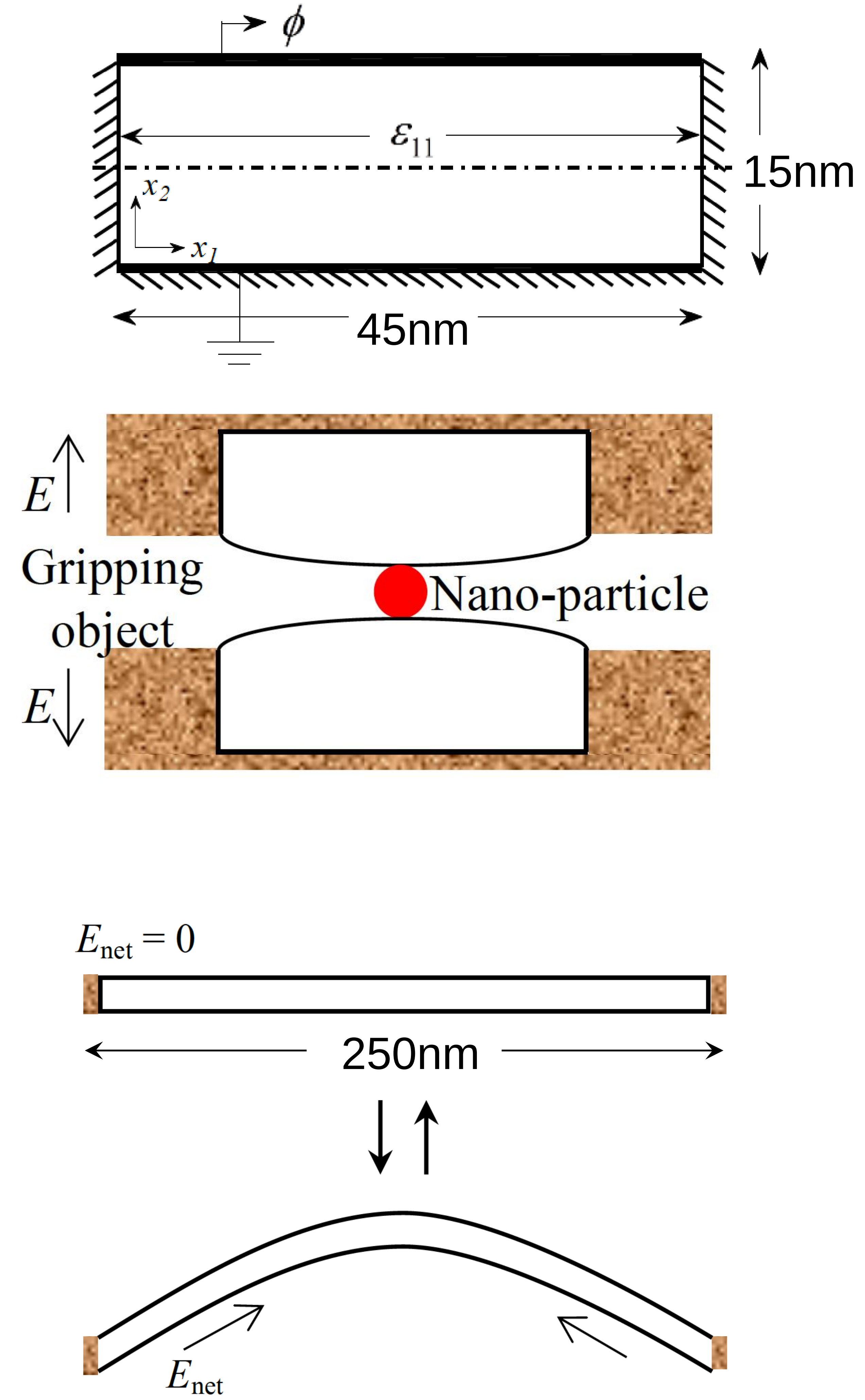
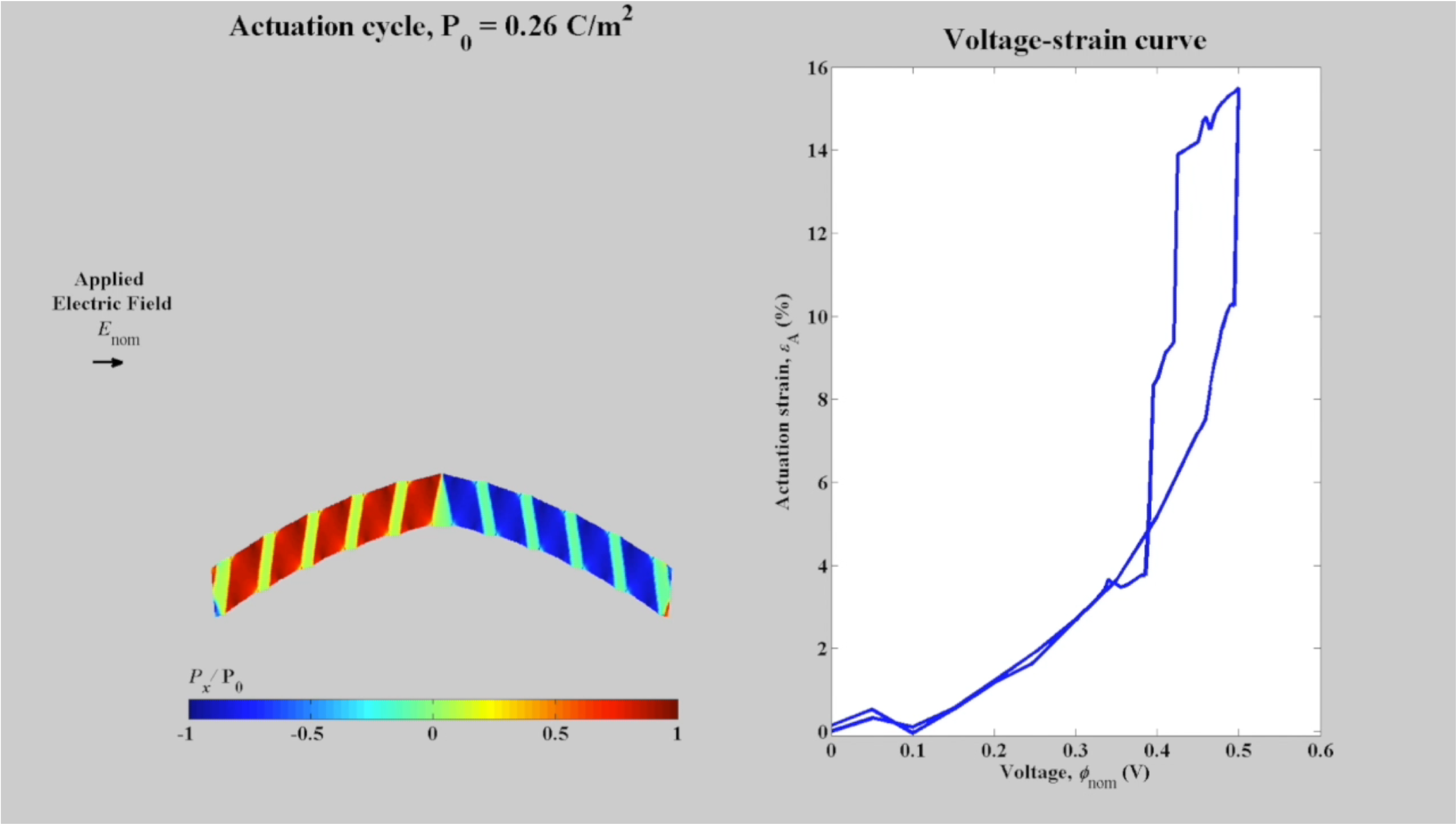
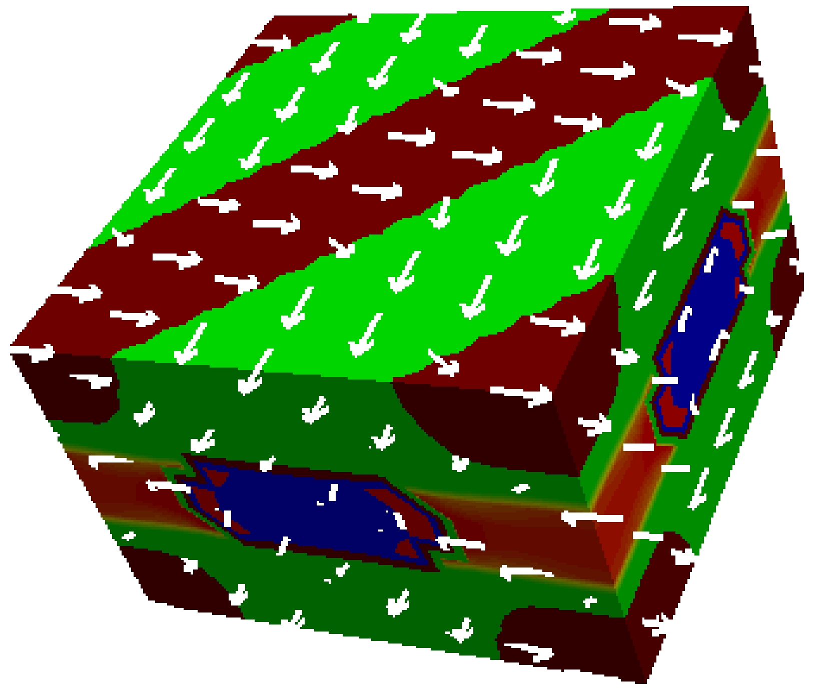


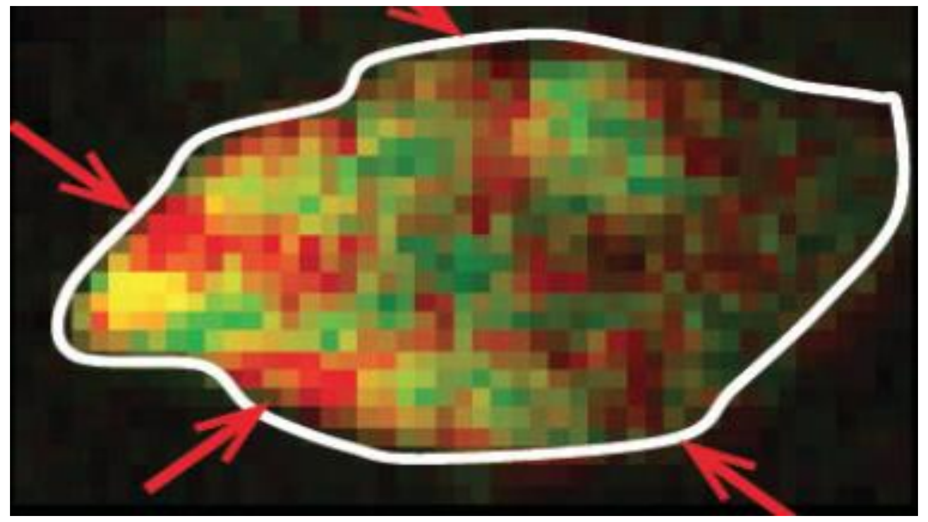


Balakrishna, Huber and Landis, Smart Mat. Struc., 23, 2014

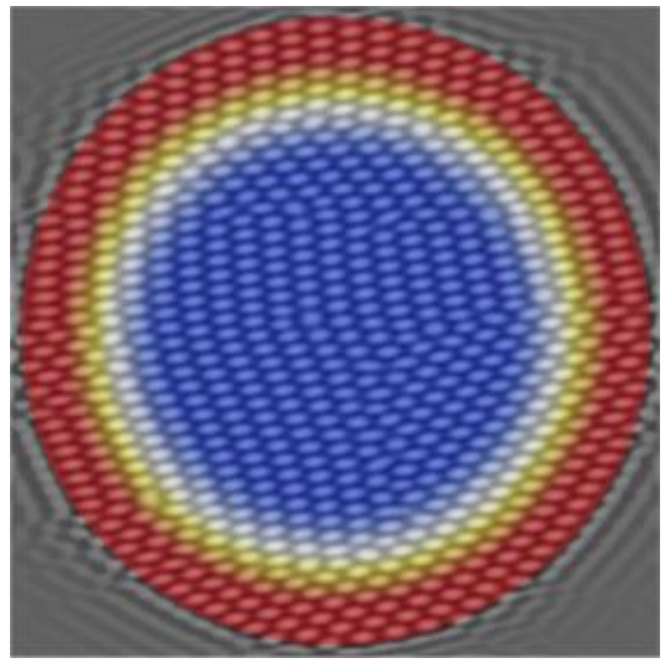
Outline of the talk

Ferroelectrics





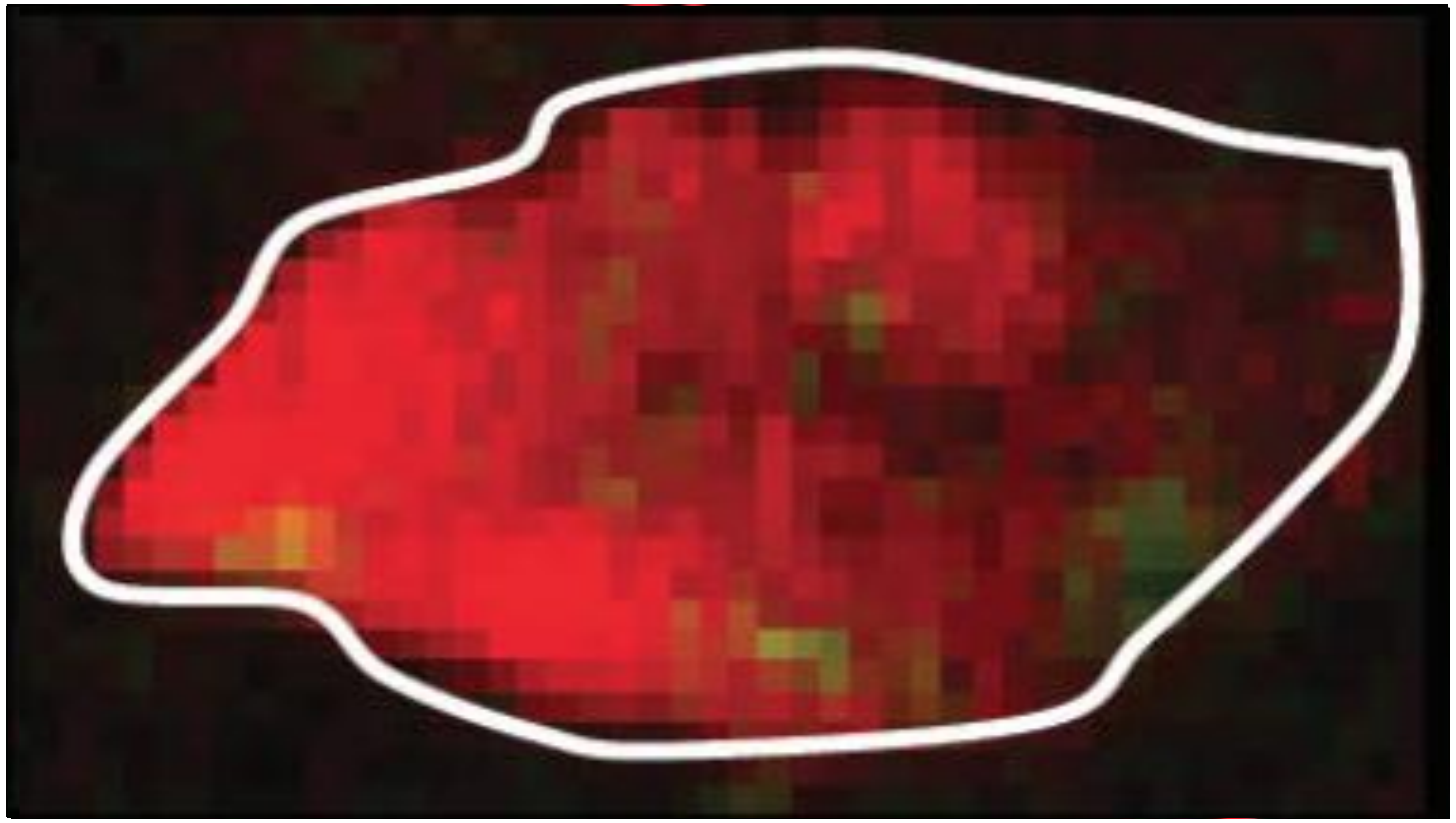
Battery materials



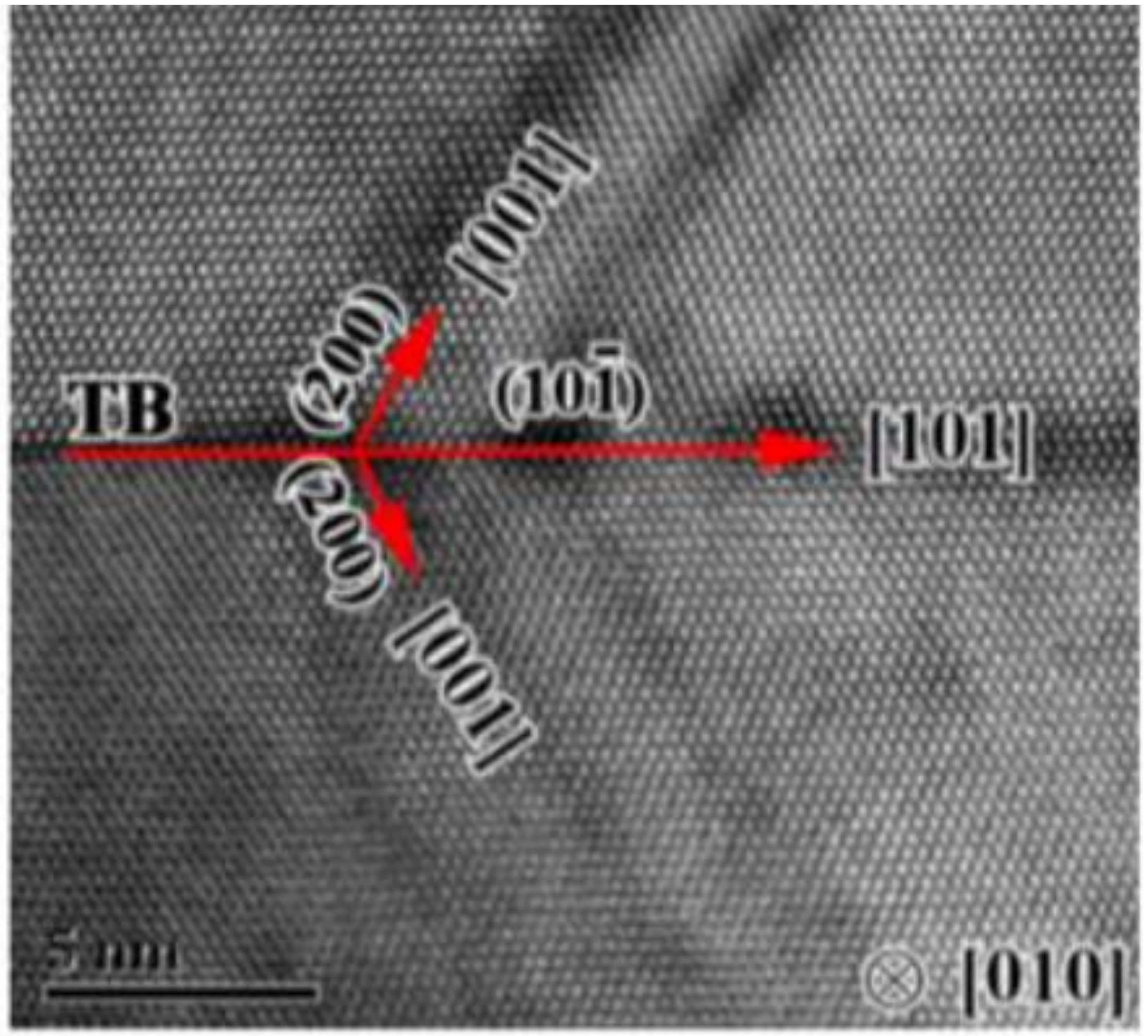
Light-interactive materials

W. Craig Carter
Yet-Ming Chiang

Crystallographic texture of battery materials can significantly affect its properties

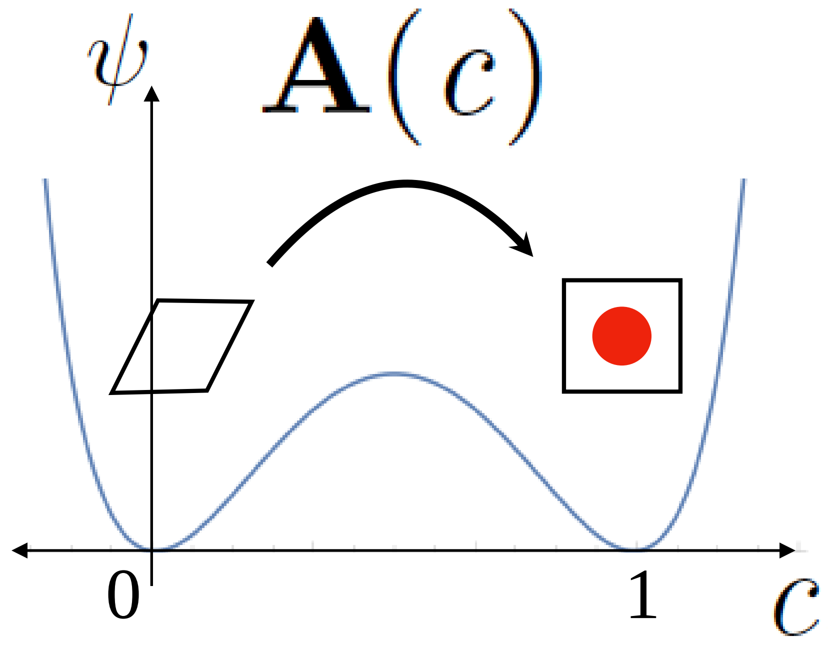


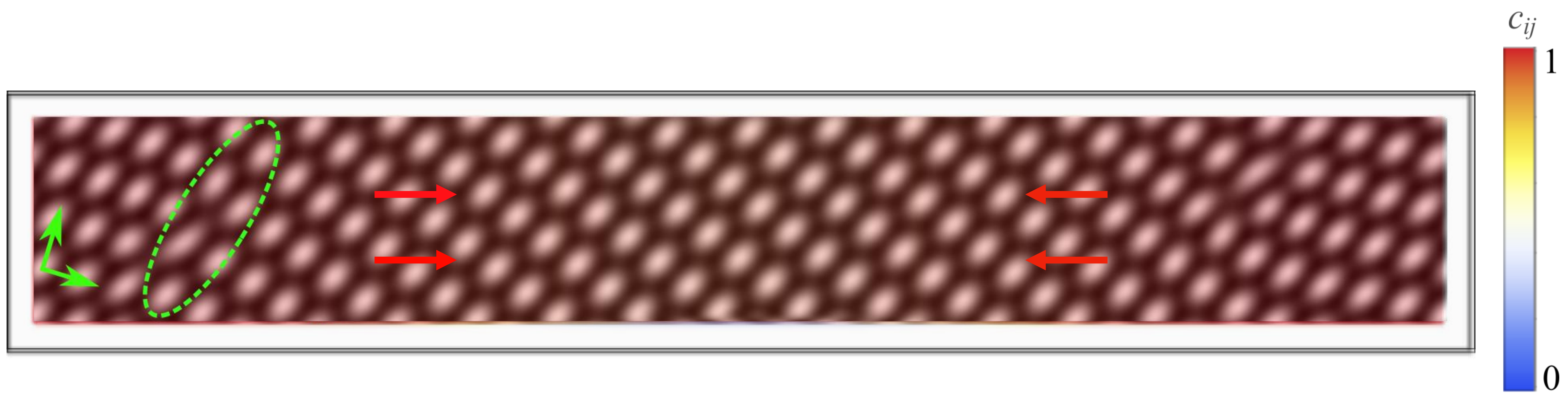
Li, Chueh et al., Adv. Func. Mat., 25, 2015



Nie, Yassar et al., Nano Lett., 15, 2015

Computing evolution of microstructure *and* crystallographic texture





$$\psi = \int [\nabla c . \kappa \nabla c + f(c,T)$$

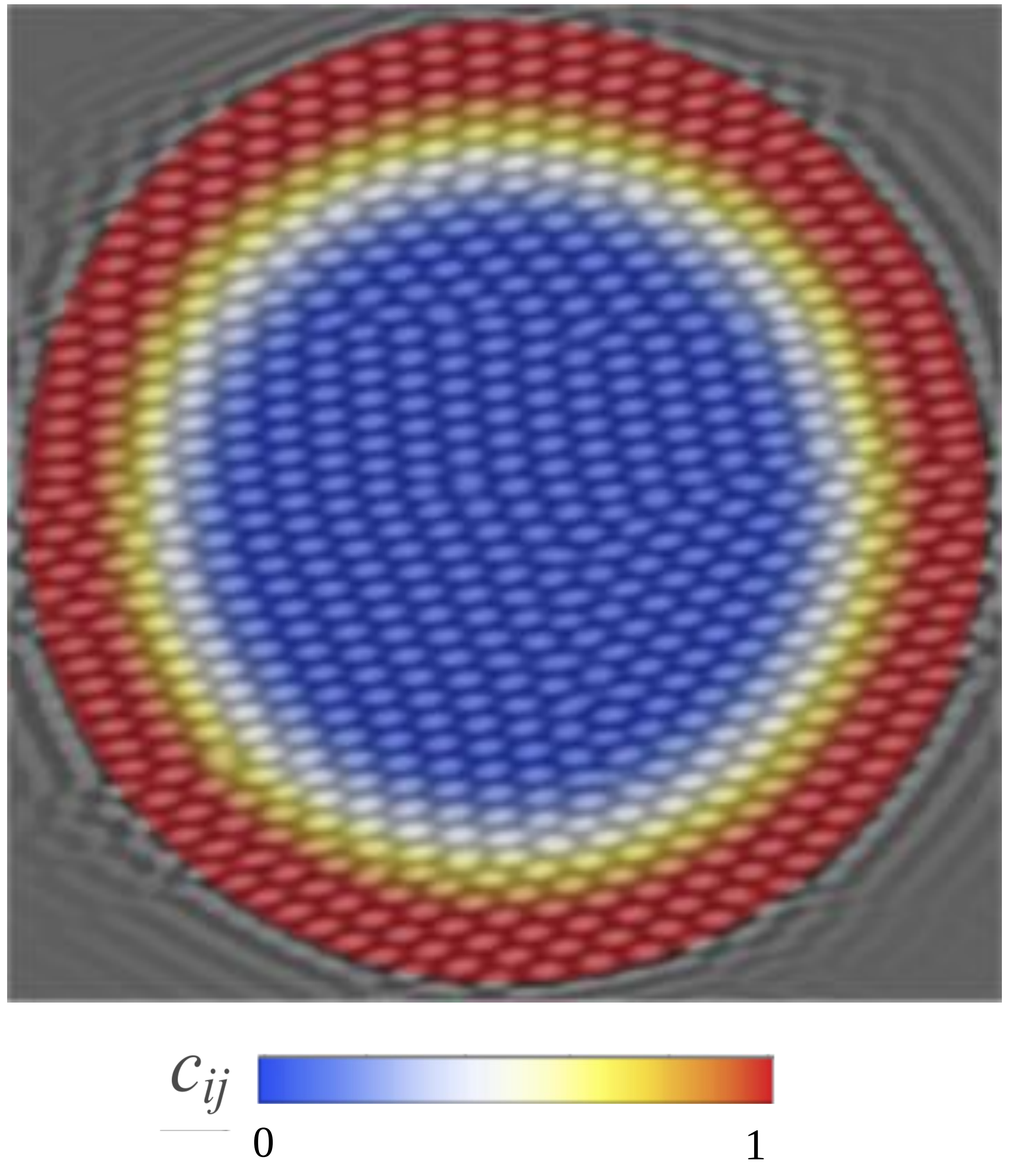
$$+ \gamma(g(\phi, r) + \frac{\phi}{2}(1 + \nabla_c^2)^2 \phi)] \mathrm{d}\mathbf{x}$$

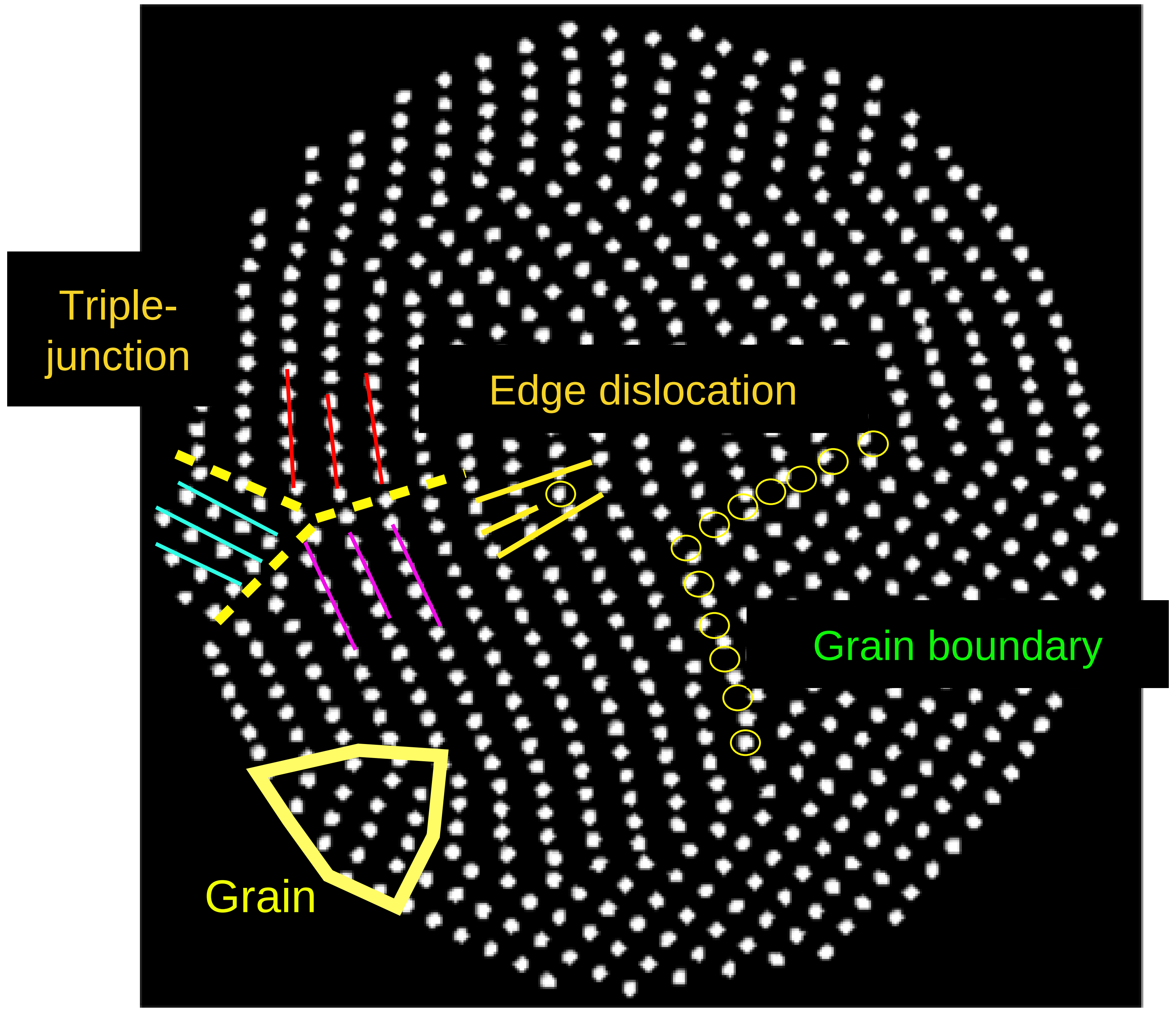
$$\frac{\partial c}{\partial \tau} = \nabla^2 \frac{\delta \psi}{\delta c}$$

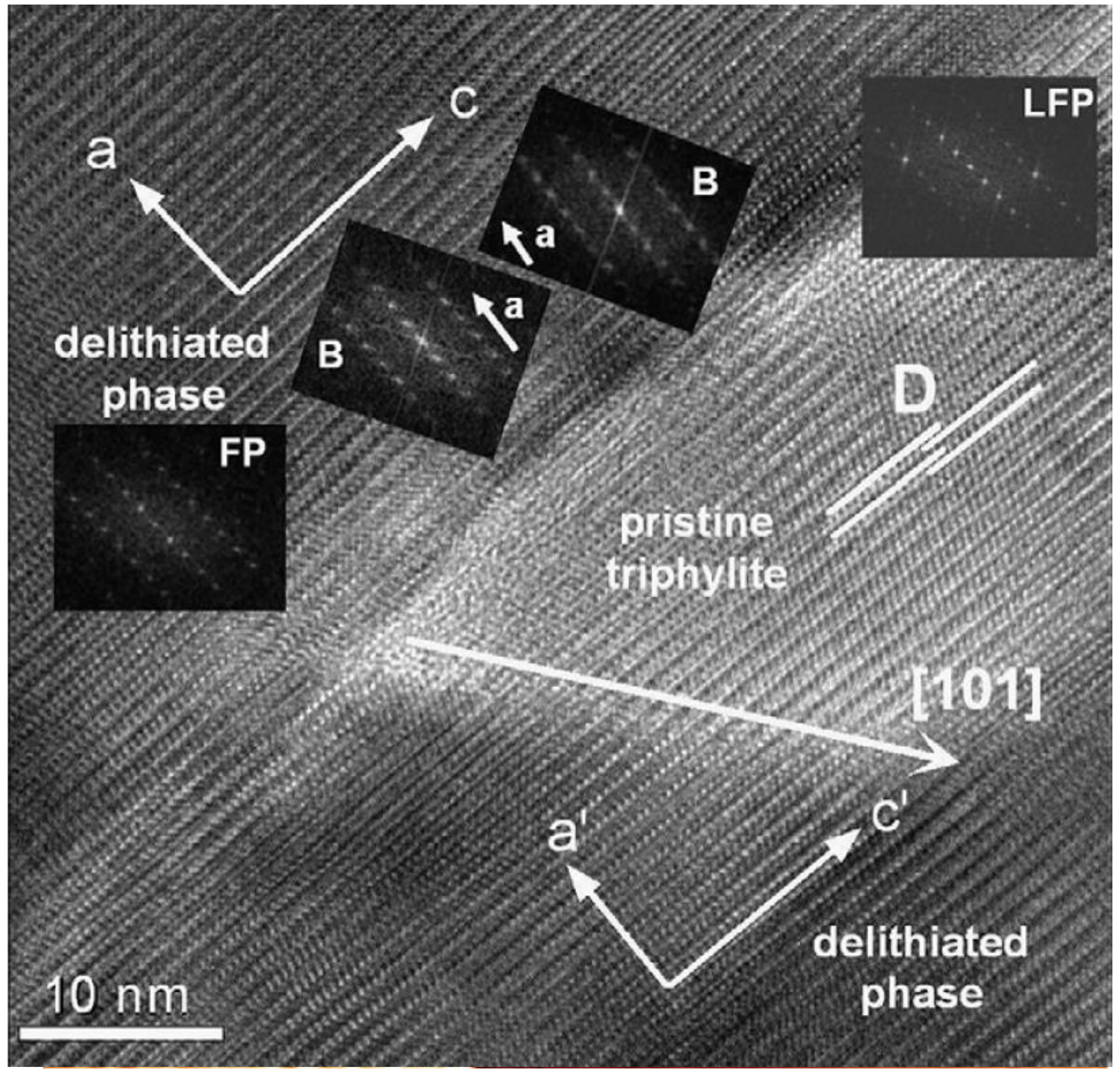
$$\frac{\partial \phi}{\partial n} = \nabla^2 \frac{\delta \psi}{\delta \phi}$$

Balakrishna and Carter, Phys. Rev. E, 97, 2018

Crystalline electrodes contain grain boundaries and edge-dislocation defects



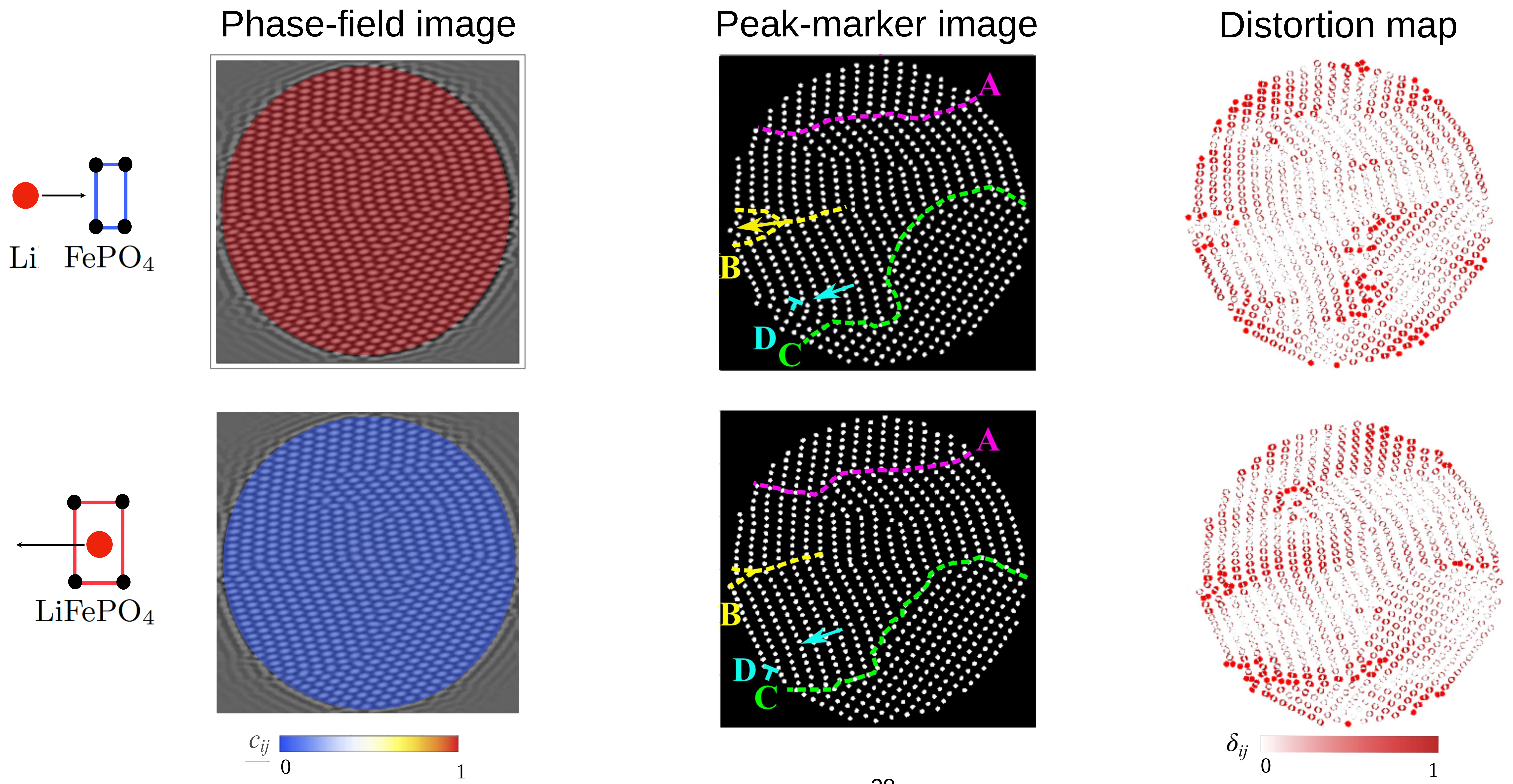




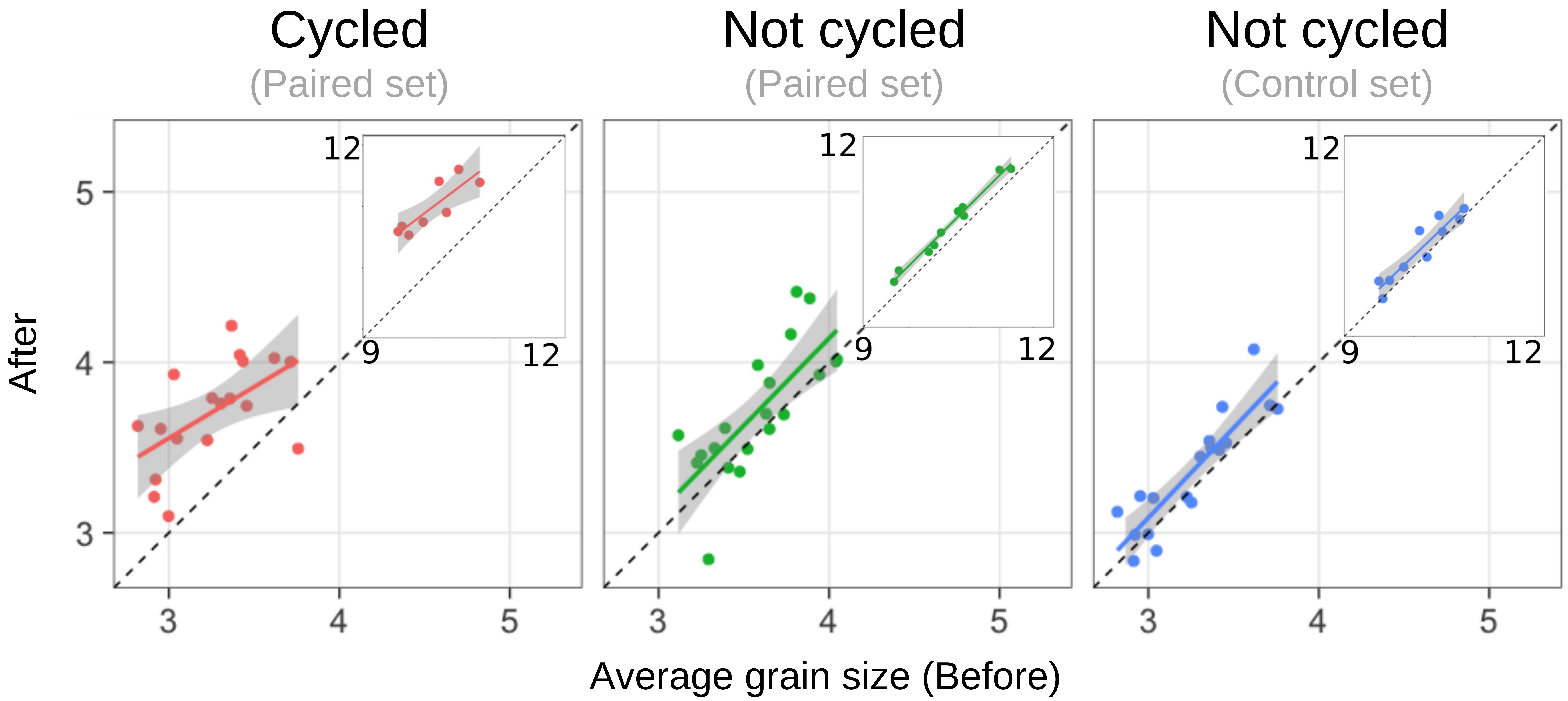
Ramana et al., J. of Power Sources 187, 2009

Balakrishna, Chiang and Carter, Under review, arXiv:1806.06890

Li-intercalation induces grain boundary migration

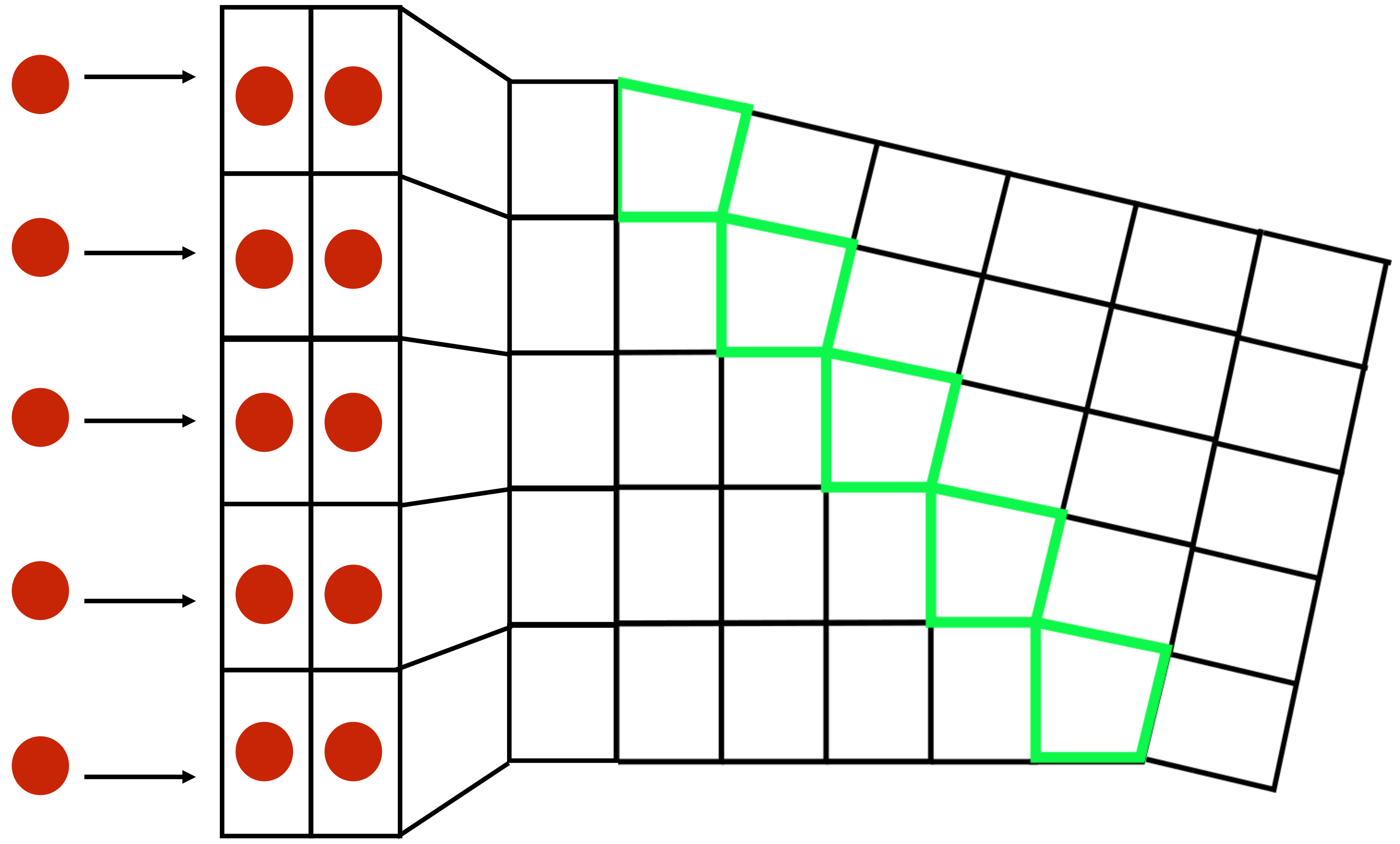


Electrochemical cycling accelerates grain growth in electrodes



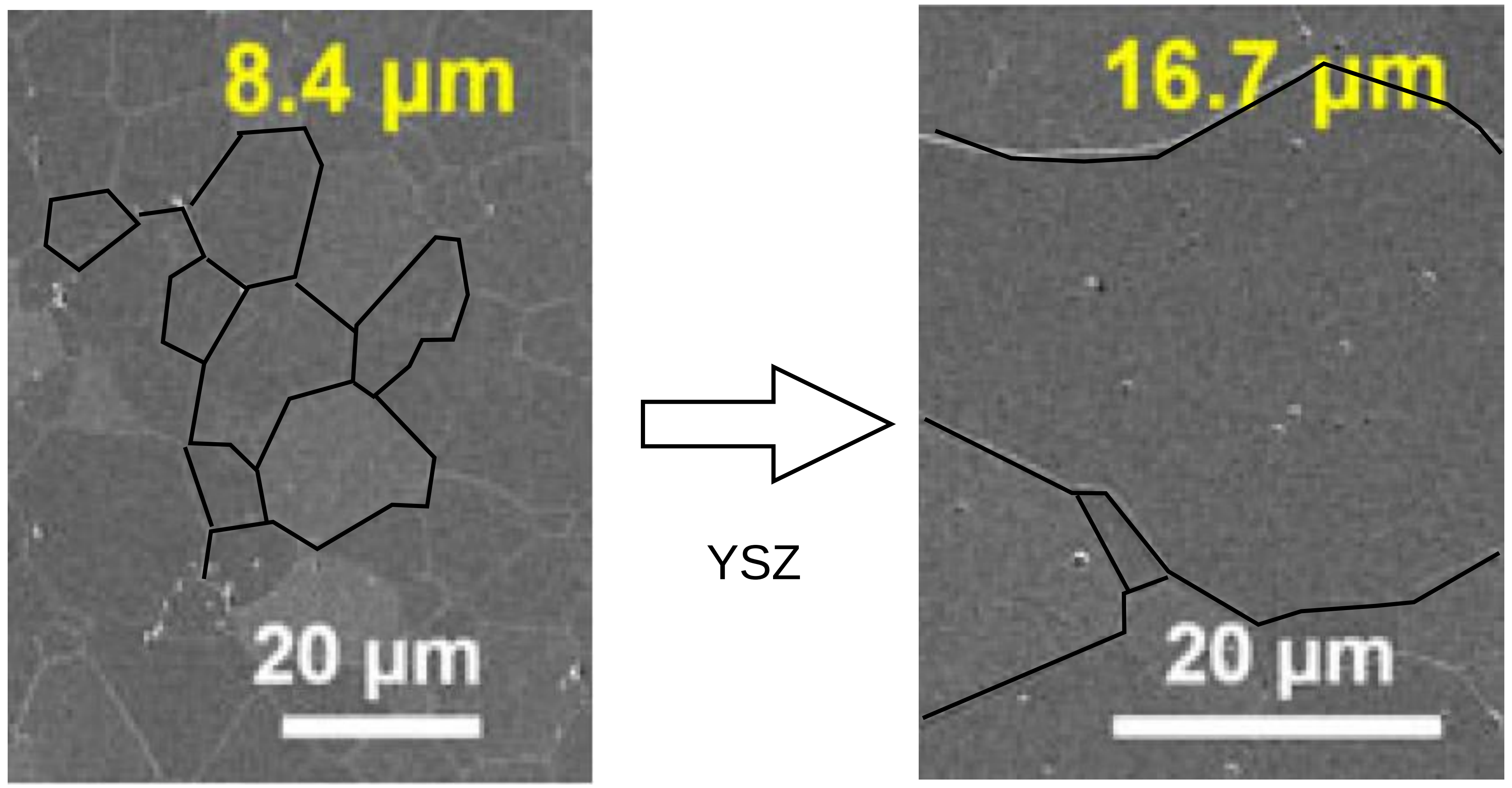
Balakrishna, Chiang and Carter, Under review, arXiv:1806.06890

Electrochemical cycling makes electrodes brittle



Handwerker and Cahn,
MRS Proc. Archive, 106, 1987.

Grain-size enhancement



S.-W.Kim et al. J. Am. Ceram. Soc., 94, 2011

Outline of the talk

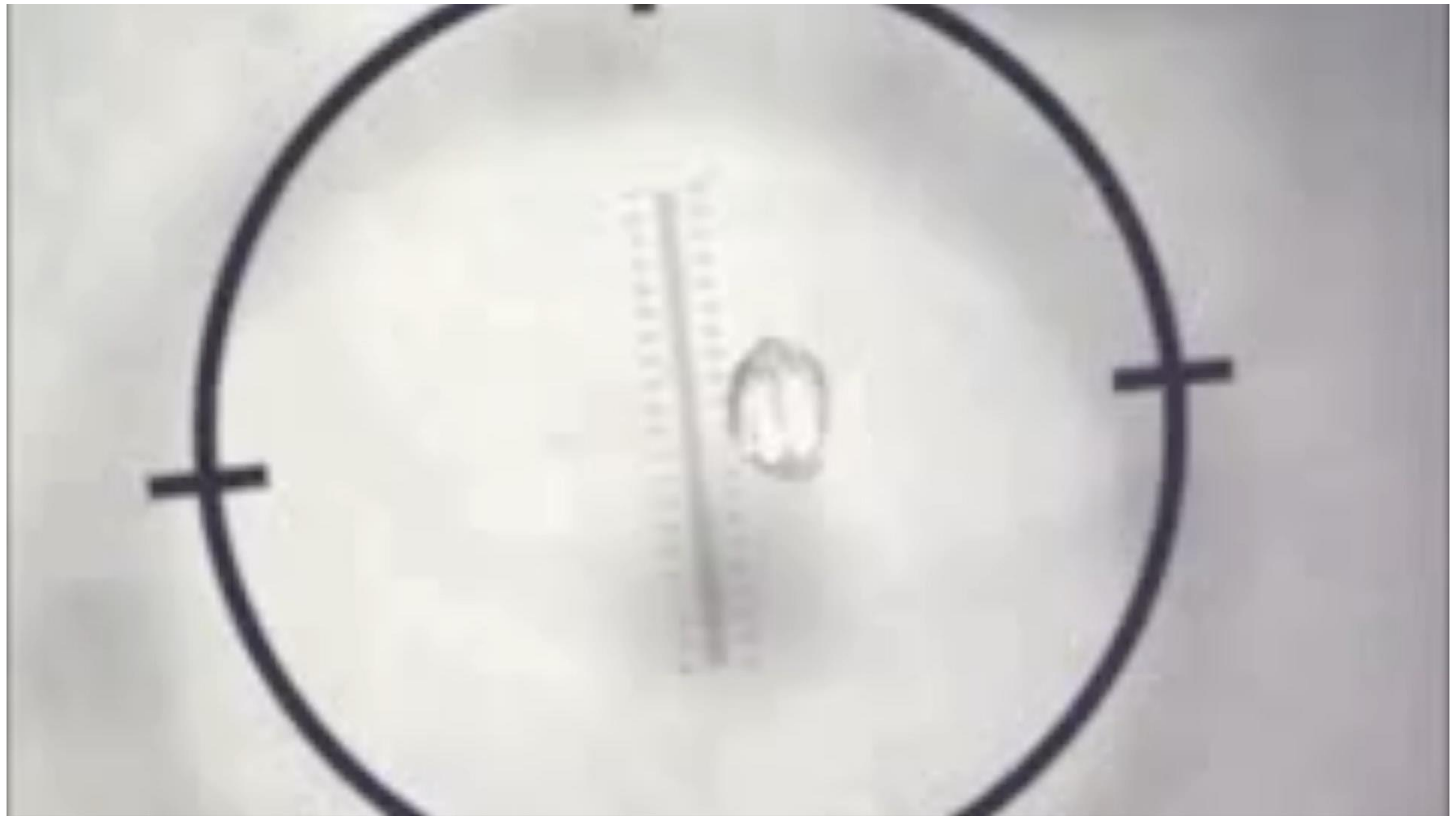
Ferroelectrics

Battery materials

Light-interactive materials

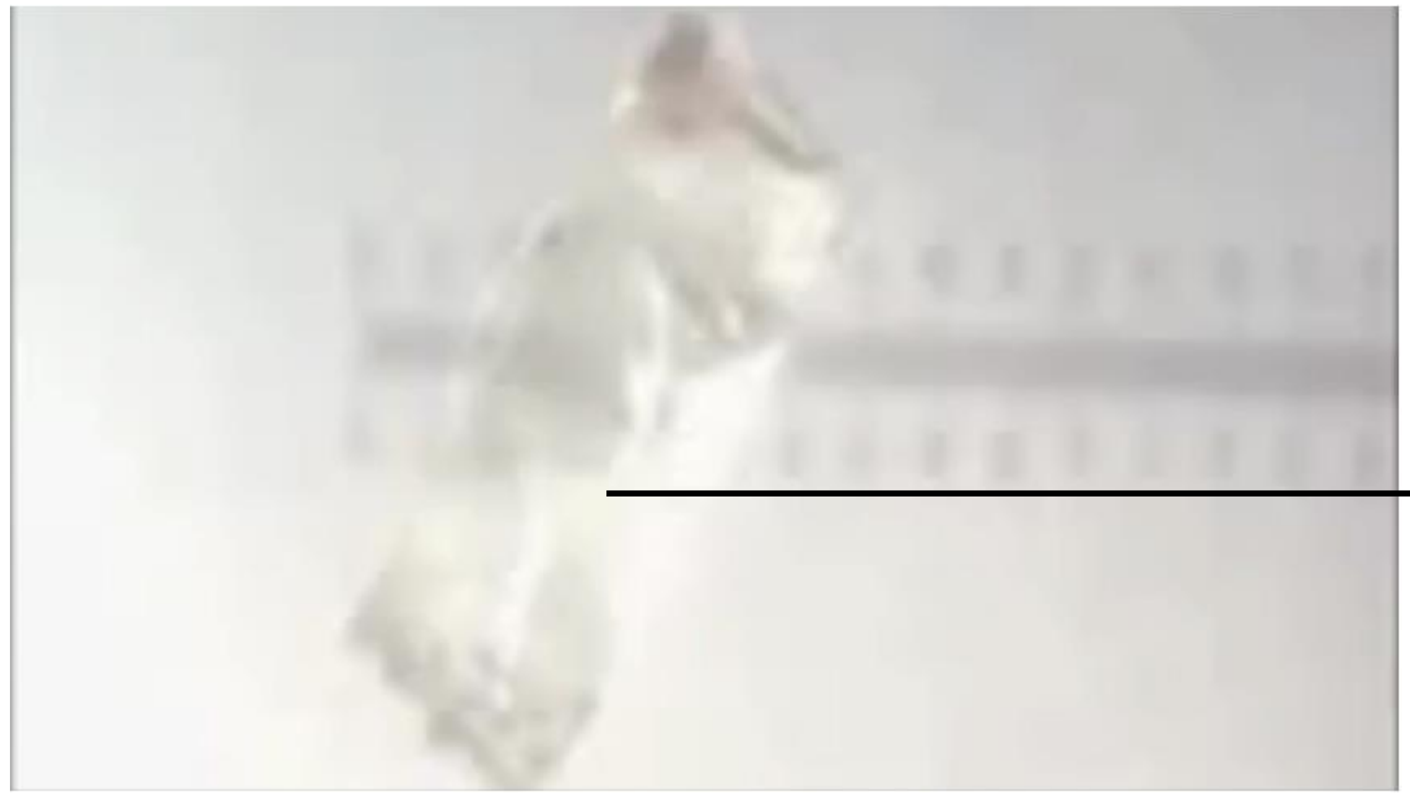
Richard D. James

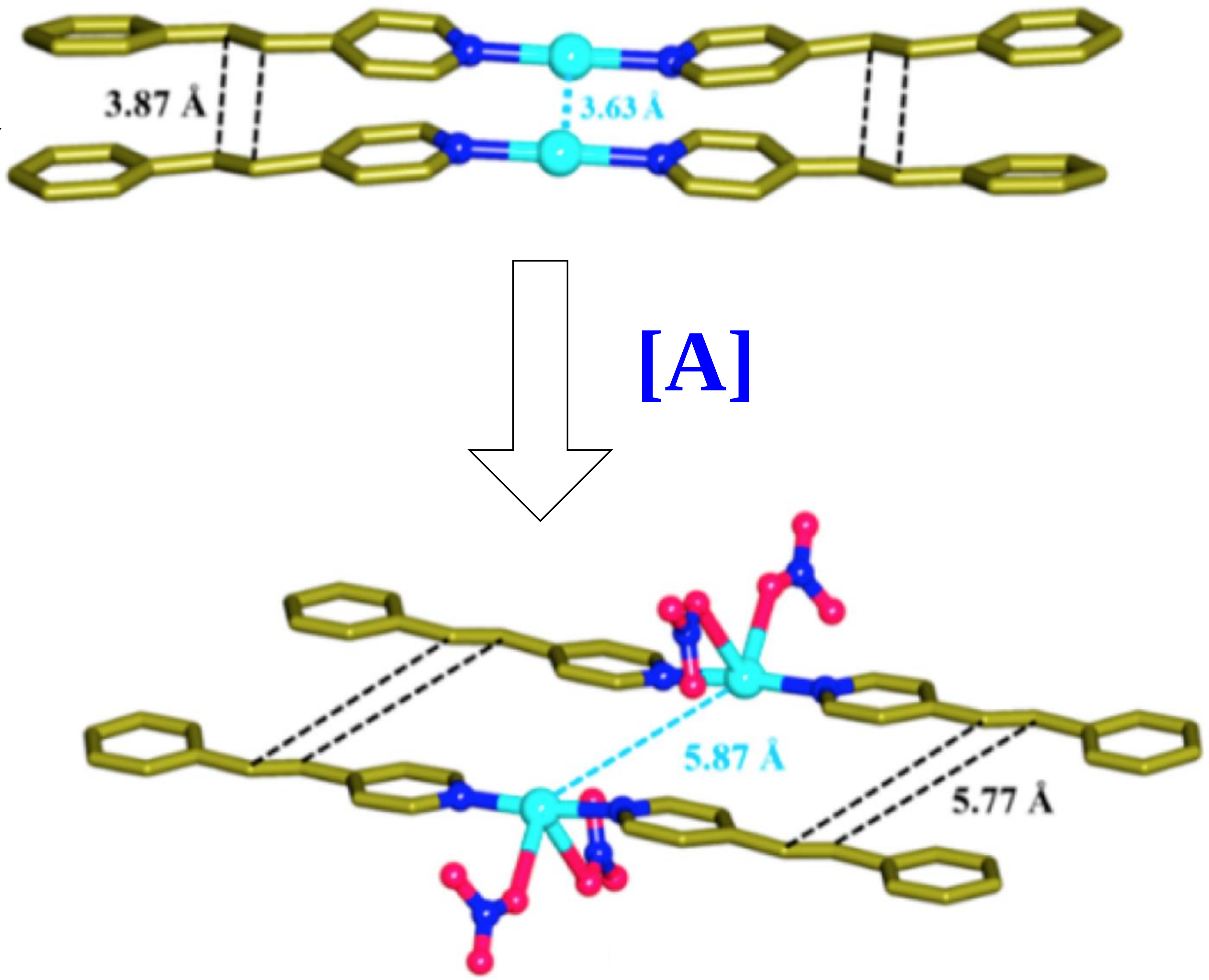
Light induces actuation mechanisms in molecular materials

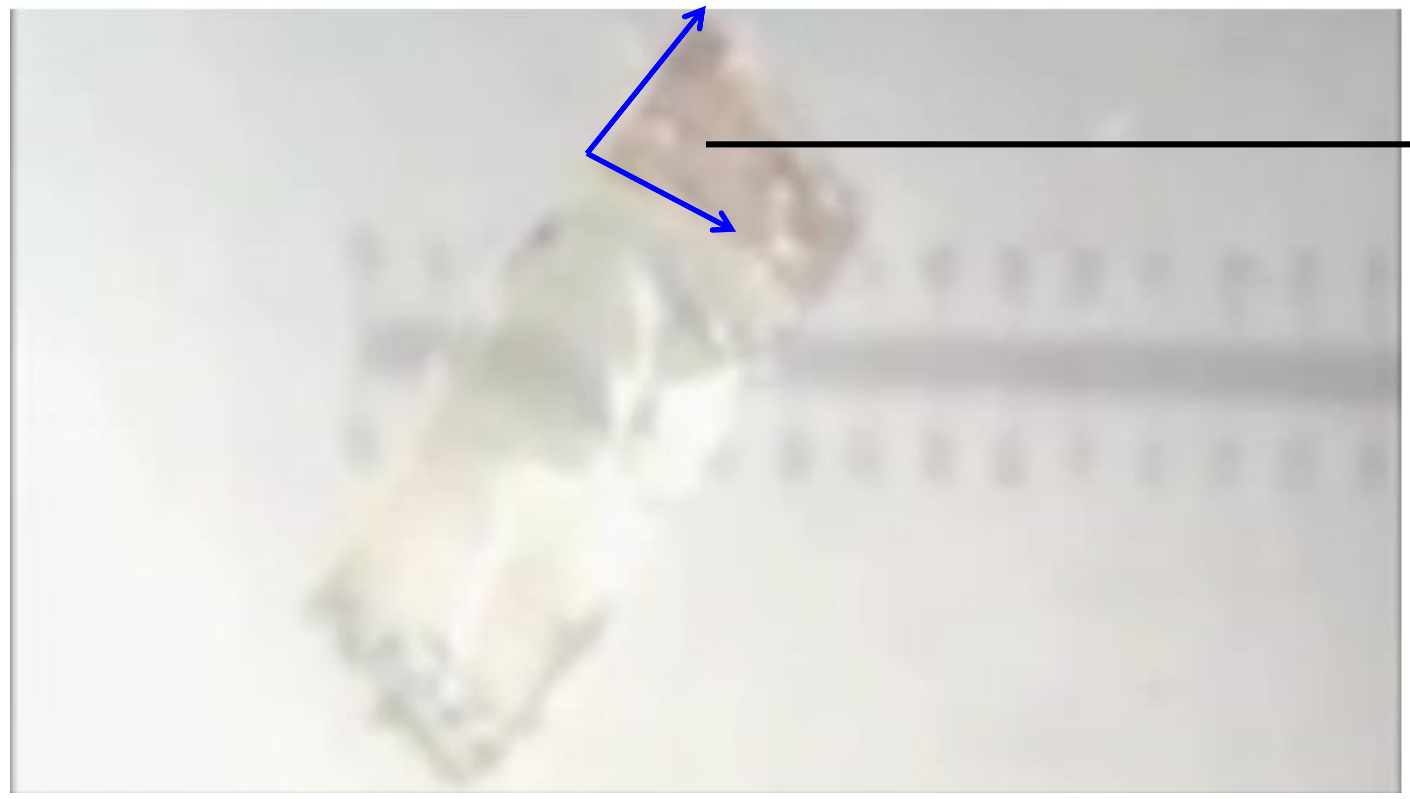


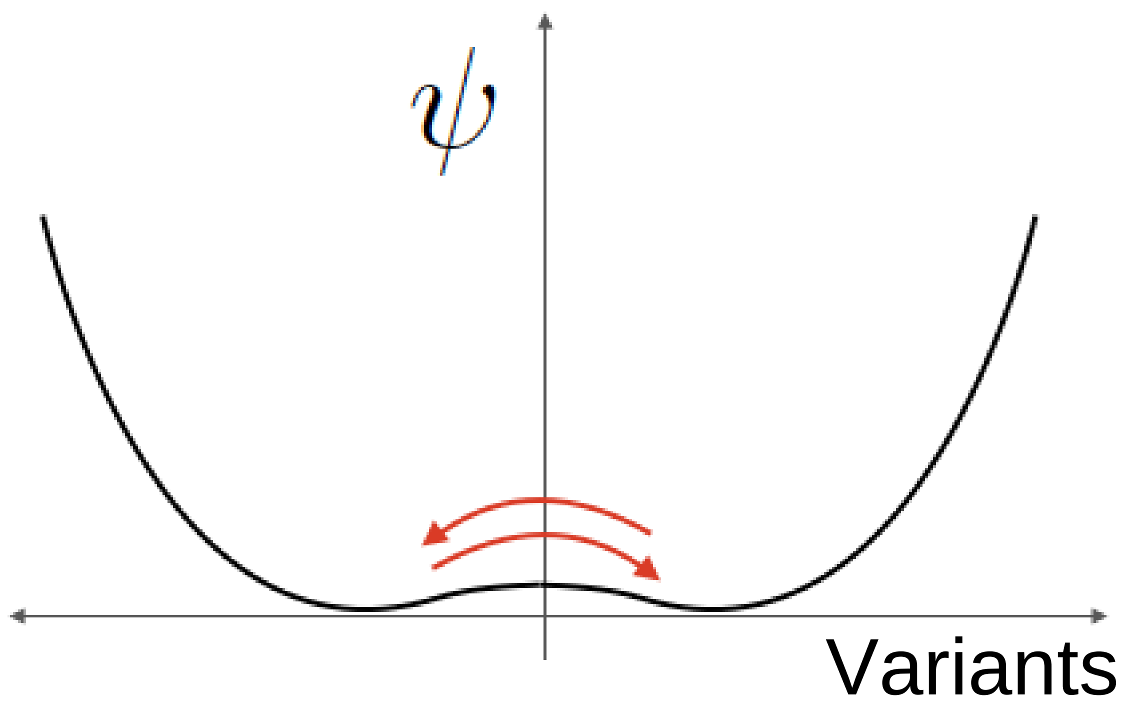
Medishetty, Naumov, Vittal et al., Chem Mater., 27, 2015

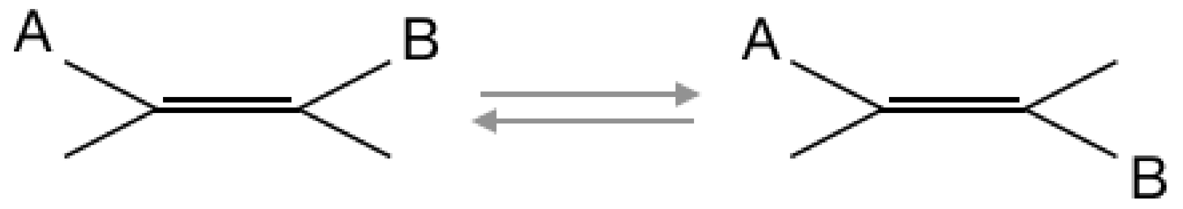
Molecular arrangement is transformed in the presence of light

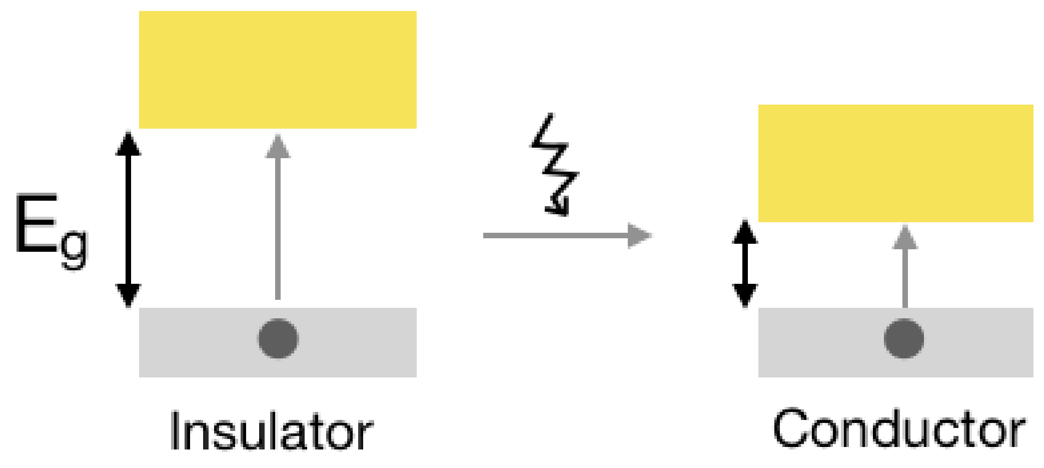








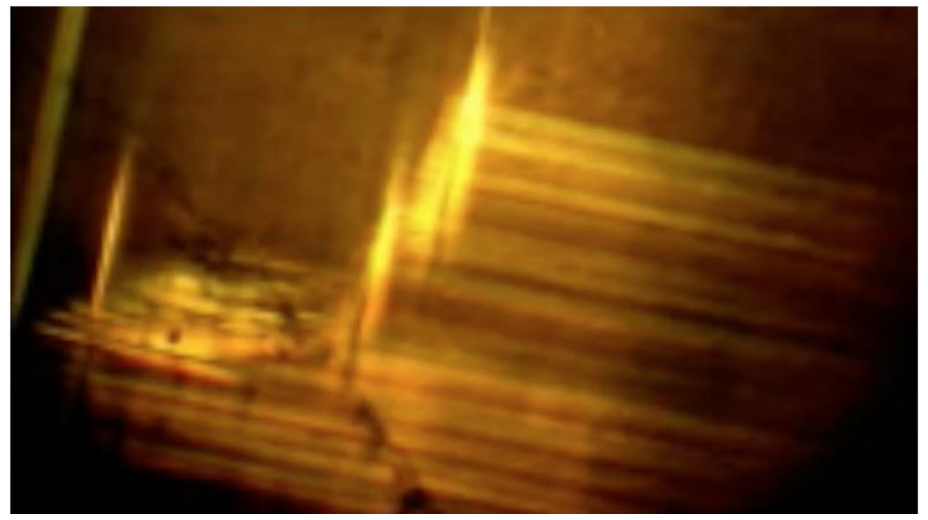




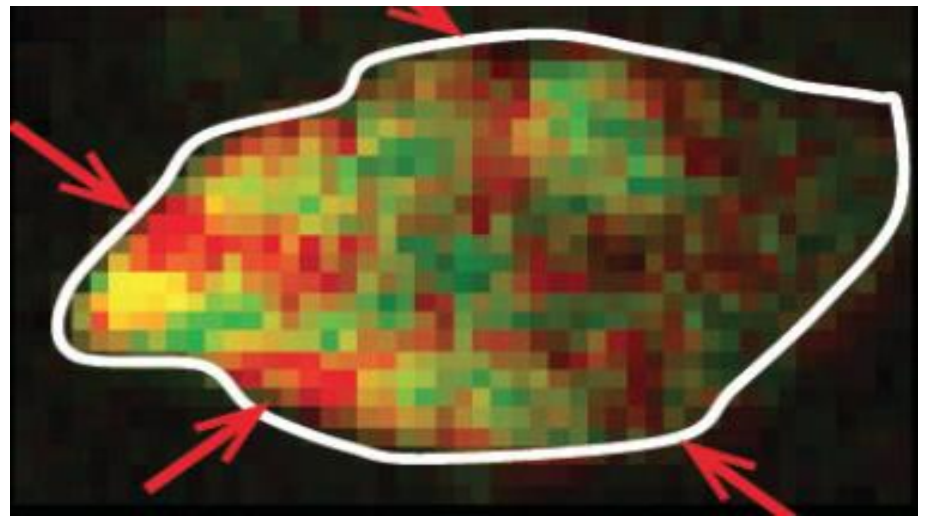
Medishetty, Naumov, Vittal et al., Chem Mater., 27, 2015

Balakrishna and James, ongoing research

Outline of the talk



Ferroelectrics



Battery materials

Light-interactive materials