Finsler geometry simulation of PVDF deformation in external electric fields

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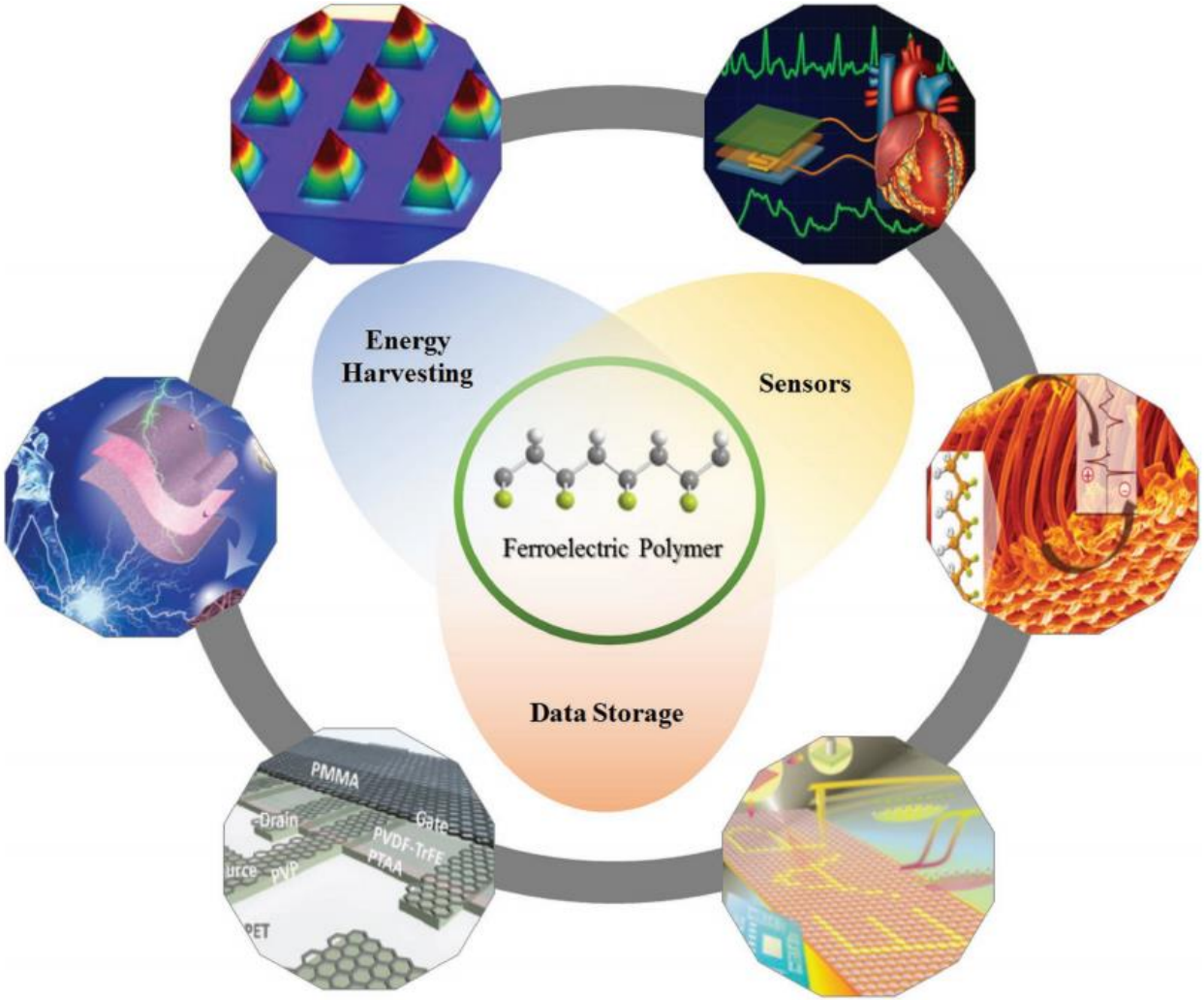
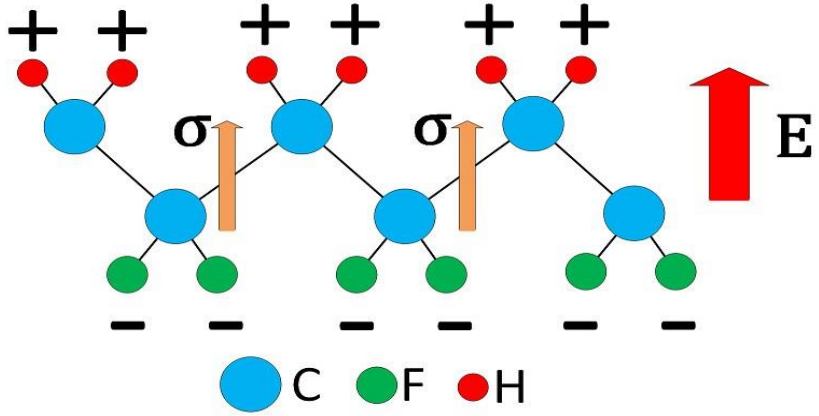
Applications of FEP



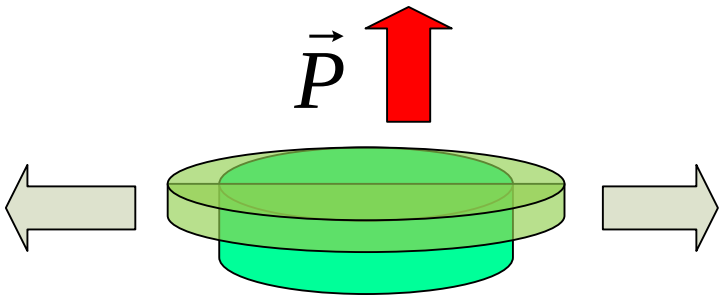
Chen, Xin, Xu Han, and Qun-Dong Shen. *Advanced Electronic Materials* 3.5 (2017): 1600460.

Polyvinylidene difluoride (β-conformation)

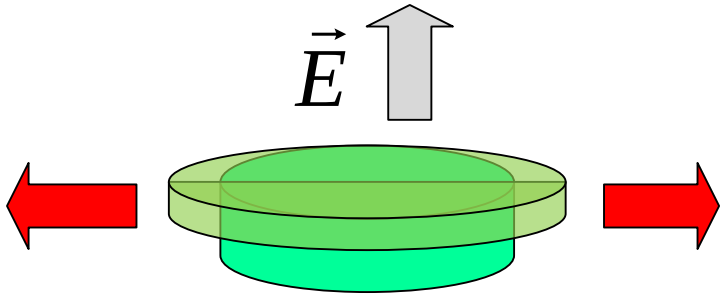


The structure of β-PVDF (σ is a dipole moment)

Direct piezoelectric effect



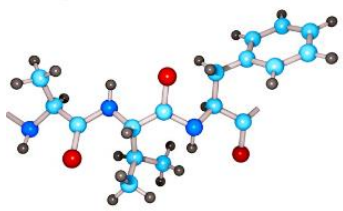
Reverse piezoelectric effect



Methods for simulations of polymers

Length scale

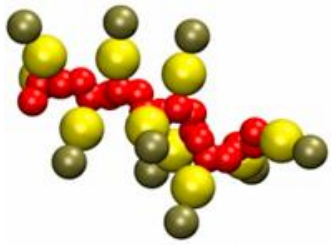
All-atom models



Computationally intensive

Very hard to calculate macroscopic quantities

Coarse-grained models



Continuum models with Euclidean metric

Local anisotropy isn't considered

Finsler geometry modeling can represent both orientational and translational freedom degrees in polymers on a macro scale

Finsler geometry model for ferroelectric polymers

Gaussian bond potential

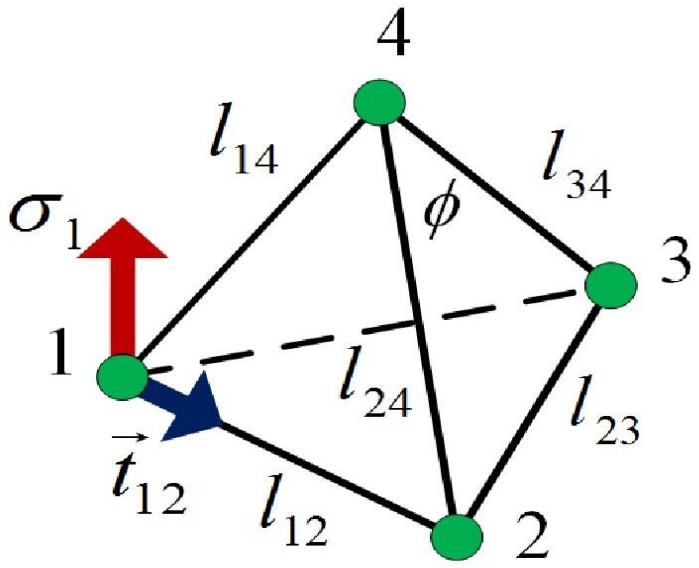
$$S_1 = \int \sqrt{g} g^{ab} \partial_a \vec{r} \cdot \partial_b \vec{r} d^3x$$

Finsler metric

$$g_{ab} = \begin{pmatrix} v_{12}^{-2} & 0 & 0 \\ 0 & v_{13}^{-2} & 0 \\ 0 & 0 & v_{14}^{-2} \end{pmatrix}$$

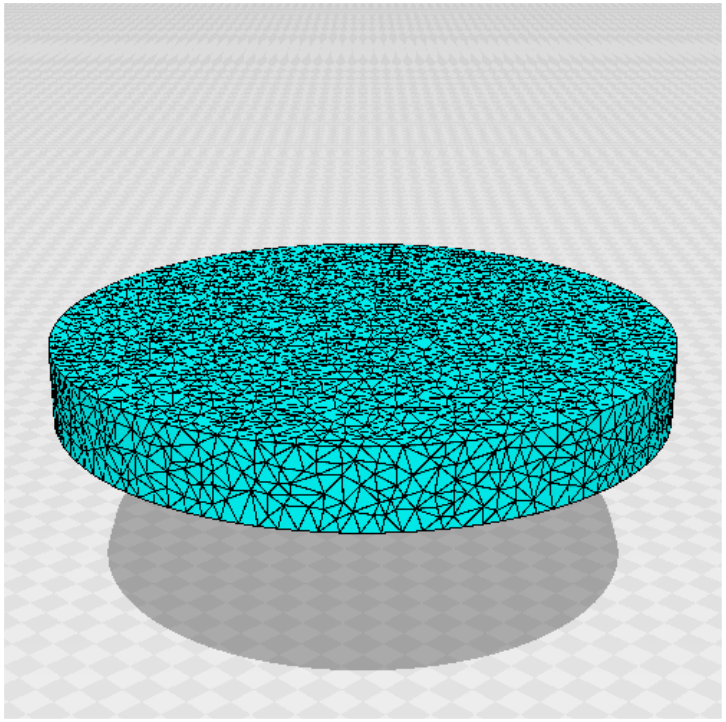
Finsler length

$$v_{ij} = \sqrt{1 - \left(\left|\vec{\sigma}_i \cdot \vec{t}_{ij}\right|\right)^2} + v_0$$



$\vec{\sigma}_i \in S^2$(unit sphere)

Discretization of Gaussian bond potential



$$S_1 = \sum_{ij} \Gamma_{ij} \ell_{ij}^2,\ \Gamma_{ij} = \frac{1}{\bar{N}} \sum_{\text{tet}} \gamma_{ij}(\text{tet})$$

$$\gamma_{12} = \frac{1}{4}\left(\frac{v_{12}}{v_{13}v_{14}} + \frac{v_{21}}{v_{23}v_{24}}\right)$$

$$\gamma_{13} = \frac{1}{4}\left(\frac{v_{13}}{v_{12}v_{14}} + \frac{v_{31}}{v_{32}v_{34}}\right)$$

$$\gamma_{14} = \frac{1}{4}\left(\frac{v_{14}}{v_{12}v_{13}} + \frac{v_{41}}{v_{42}v_{43}}\right)$$

$$\gamma_{23} = \frac{1}{4}\left(\frac{v_{23}}{v_{21}v_{24}} + \frac{v_{32}}{v_{31}v_{34}}\right)$$

$$\gamma_{24} = \frac{1}{4}\left(\frac{v_{24}}{v_{21}v_{23}} + \frac{v_{42}}{v_{41}v_{43}}\right)$$

$$\gamma_{34} = \frac{1}{4}\left(\frac{v_{34}}{v_{31}v_{32}} + \frac{v_{43}}{v_{41}v_{42}}\right)$$

Full Hamiltonian

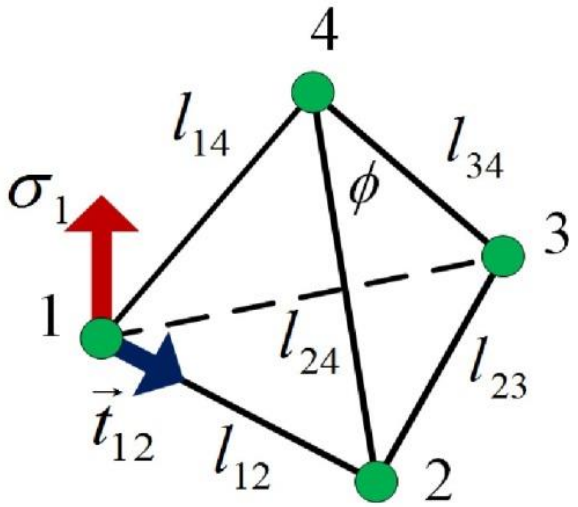
$$S = \lambda S_0 + S_1 + \kappa S_2 + S_3 + \alpha S_4$$

Heisenberg spin interaction

$$S_0 = -\sum_{\langle i,j \rangle} (\vec{\sigma_i} \cdot \vec{\sigma_j})$$

Bending energy

$$S_2 = \sum_i (1 - \cos(\phi_i - \pi/3))$$



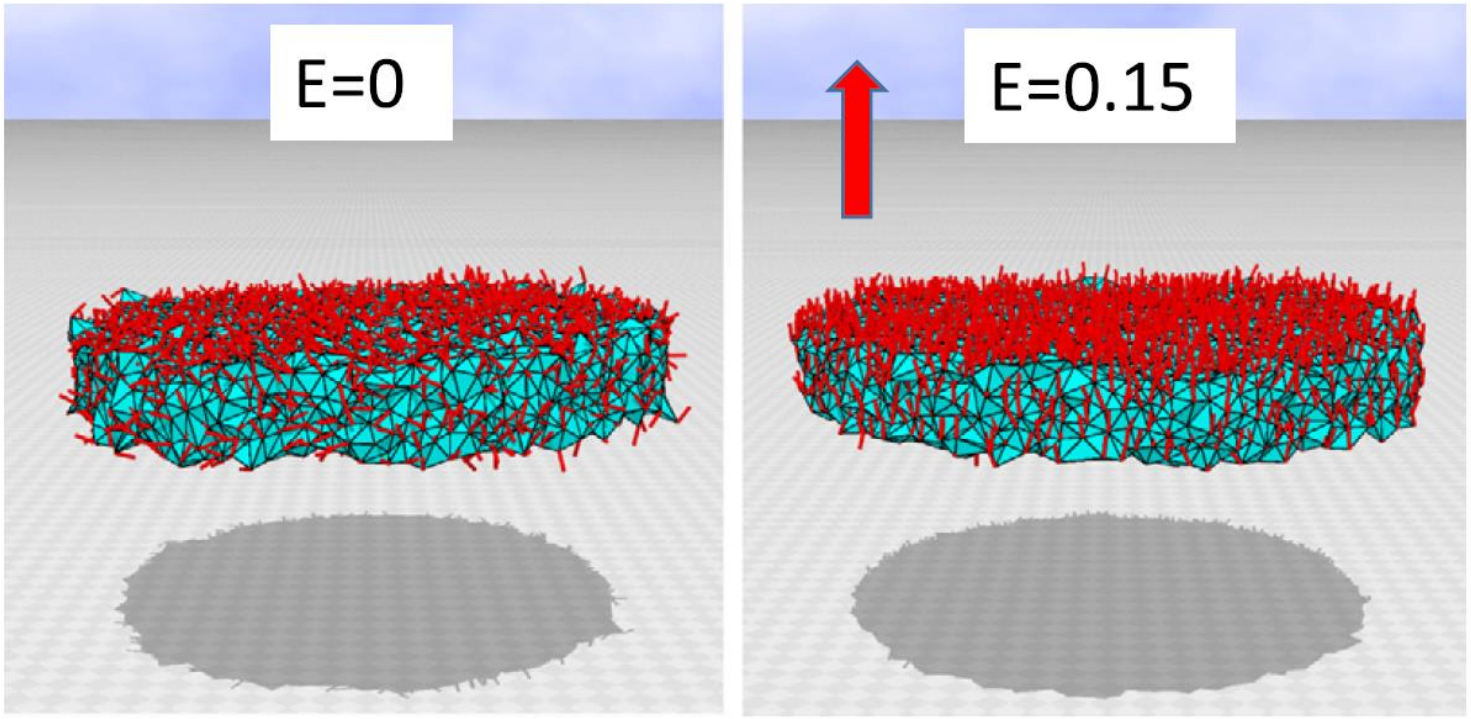
Dipole-field interaction

$$S_3 = -\sum_i (\vec{\sigma_i} \cdot \vec{E})$$

Electrostrictive term

$$S_4 = -\sum_i (\vec{\sigma_i} \cdot \vec{E})^2$$

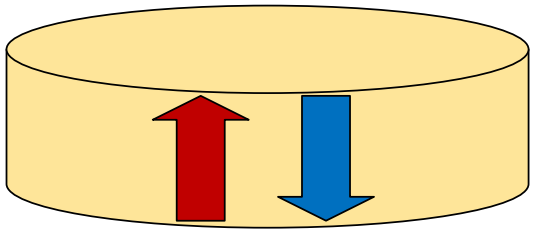
Deformation induced by the electric field



Polar interaction

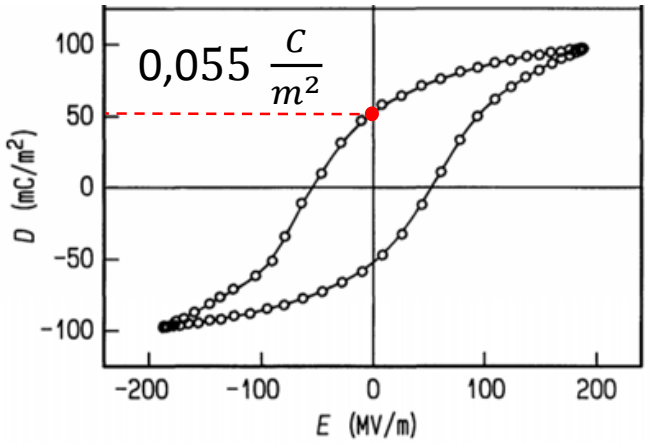
$$S = \lambda S_0 + S_1 + \kappa S_2 + S_3 + \alpha S_4$$

$$S_0 = -\sum_{\langle i,j \rangle} (\vec{\sigma_i} \cdot \vec{\sigma_j})$$

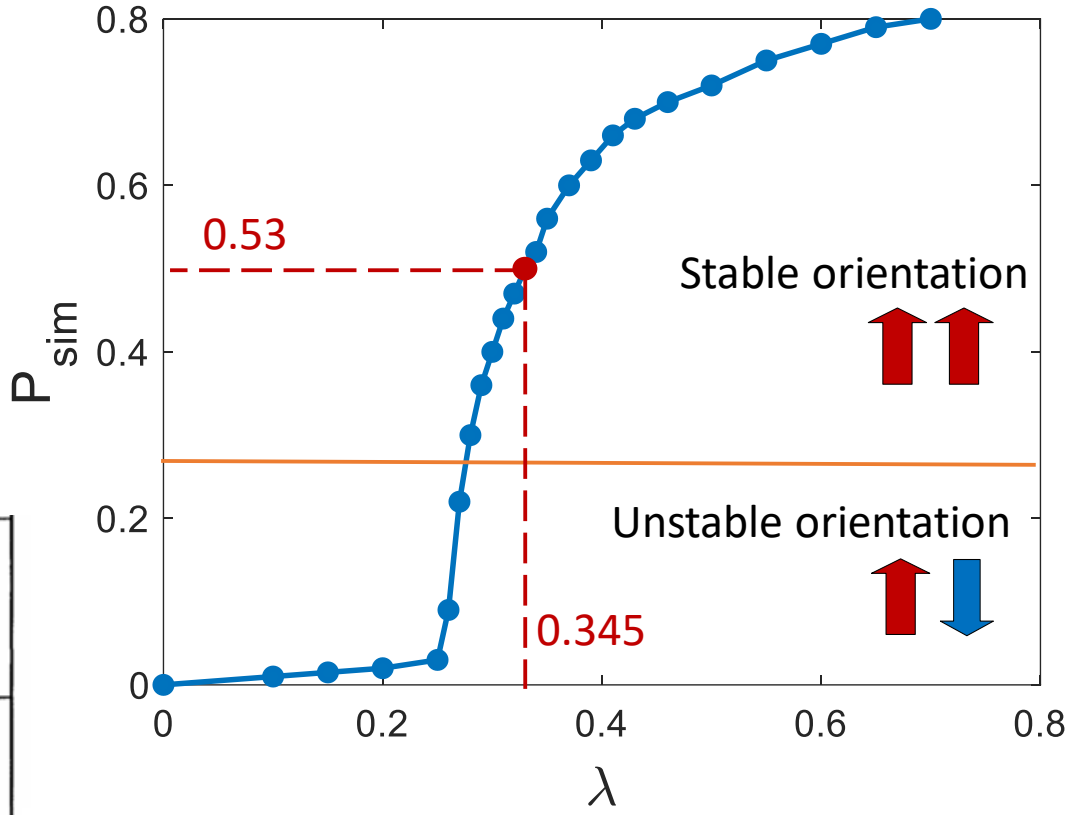


$$P_{max}^{exp} = 0{,}097 \frac{C}{m^2}$$

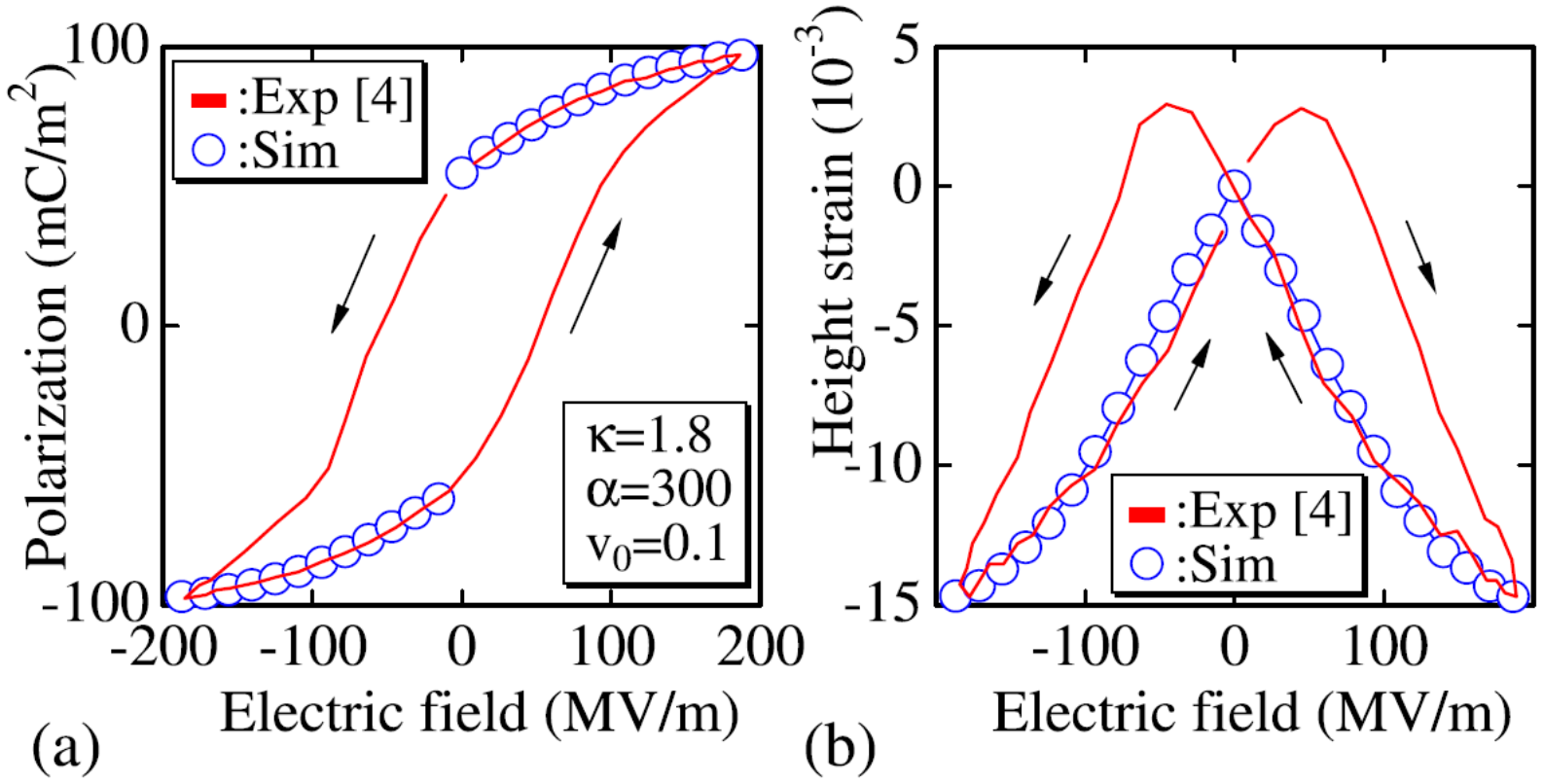
$$P_{rem}^{sim} = \frac{P_{max}^{sim}}{P_{max}^{exp}} P_{rem}^{exp} = 0{,}53$$



Spontaneous polarization



Simulation results ($\lambda = 0.345, \kappa = 1.8, \alpha = 300$)



T. Furukawa, N. Seo, Jpn. J. Appl. Phys. 29 (1990) 675.

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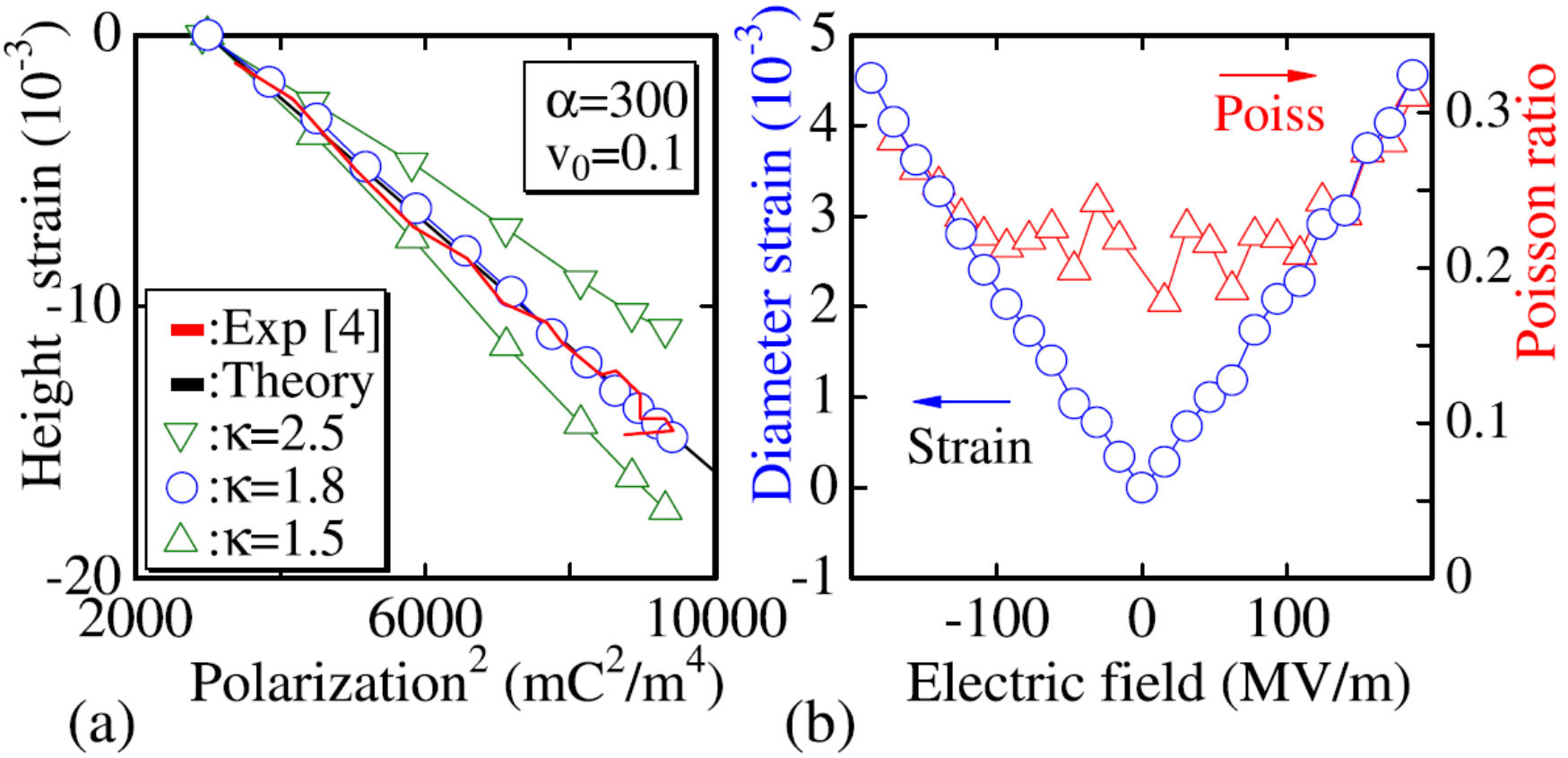

Scaling parameters

Electrostriction energy

$$\varepsilon_0 \Delta\varepsilon E_{exp}^2 = \alpha E^2 \frac{k_B T}{a^3}$$

$\Delta\varepsilon = 0.25$ (dielectric anisotropy[*])

a is a lattice spacing

$a = 7.01 * 10^{-9}$ m

$a > 10^{-10}$ van der Waals distance

Dipole-electric field energy

$$P_{exp} E_{exp} = \langle \sigma_Z \rangle E f \frac{N}{V} \frac{k_B T}{a^3}$$

f is the number of monomers associated with one vertex

$f = 900$

The estimated real monomer density $\frac{N_A \rho V a^3}{MN} \approx 570$

[*] S. Osaki, Polym. J. 28 (1996) 323.

Conclusive remarks

1. The Monte Carlo simulation results are in agreement with the experimental data of β-PVDF.
2. Both PE and SE field curves are reproduced using a single set of simulation parameters.
3. Calculated Poisson ratio is in the reasonable range
4. The FG technique is also applicable to ferroelectric ceramics and ferromagnetic materials

Egorov, V., et al. "Electromechanical properties of ferroelectric polymers: Finsler geometry modeling and a Monte Carlo study." *Physics Letters A* 396 (2021): 127230.