Finsler geometry modeling of reverse piezoelectric effect in PVDF

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Abstract. We apply the Finsler geometry (FG) modeling technique to study the electric field-induced strain in ferroelectric polymers. Polyvinylidene difluoride (PVDF) has a negative longitudinal piezoelectric coefficient, which is unusual in ferroelectrics, and therefore the shape changes in this material are hard to predict. We find that the results of Monte Carlo simulations for the FG model are in good agreement with experimental strain-electric field curves of PVDF-based polymers in both longitudinal and transverse directions. This implies that FG modeling is suitable for reproducing the reverse piezoelectric effect in PVDF.

1. Introduction
The reverse piezoelectric effect in ferroelectrics is widely used for creating actuators to convert the electrical energy into the mechanical energy, or vise versa. One of the most important goals in material science is to develop flexible elastic materials with piezoelectric properties. For this purpose, polyvinylidene difluoride (PVDF)-based polymers need to have increased mechanical strength, shock resistance, and flexibility compared with low-weight molecular ferroelectrics. However, PVDF has an unusual shrinking behavior along the direction of the external field, of which the mechanism is not yet completely understood [1]. Furthermore, the shape-change of the material caused by the electric field is typically very complex and difficult to simulate.

Finsler geometry (FG) technique has been successfully applied for modeling the deformation of materials with an anisotropy of mechanical properties like rubbers and soft biological materials [2, 3]. Also, the shape transformation of liquid crystal elastomers under external electric fields has been studied by this technique [4]. In the present work, we further extend the FG model for describing the reverse piezoelectric effect in ferroelectric polymers. In the FG model, Finsler metric is used instead of Euclidean metric, which is always used in simulations of surface...
models for membranes. The Finsler metric is defined by using an internal degree of freedom $\sigma$, which represents the dipole moment in the case of PVDF. This approach precisely or effectively implements the role of the positional and directional degrees of freedom in polymers.

2. The model

More detailed description of 3D FG model is reported in [5]. For the simulation of a field-induced deformation, we modify the Hamiltonian in [5] by taking into account an additional dipole interaction with the external electric field. In this section, the 3D FG approach is briefly outlined. The continuous Hamiltonian $S_1$ corresponding to the Gaussian bond potential is given by:

$$ S_1 = \int \sqrt{g} g^{ab} \frac{\partial \vec{r}}{\partial x_a} \frac{\partial \vec{r}}{\partial x_b} d^3 x, $$

where $\vec{r}$ is a position vector of a three-dimensional body with coordinates $x_a (a = 1, 2, 3)$. The symbol $g^{ab}$ is the inverse of metric tensor $g^{ab}$ and $g$ is its determinant.

To define the discrete Hamiltonian, we use a thin cylindrical body (Fig.1(a)). This body is discretized by tetrahedrons using the Voronoi tessellation. We introduce a variable $\sigma_i$, which corresponds to the direction of the dipole moment at the vertex $i$. The discrete metric tensor has the form: $g_{ab} = \begin{pmatrix} v_{i1}^{-2} & 0 & 0 \\ 0 & v_{i3}^{-2} & 0 \\ 0 & 0 & v_{i4}^{-2} \end{pmatrix}$. This form is obtained from Euclidean metric by replacing its diagonal elements with $v_{ij}^{-2}$, where $v_{ij}$ is the Finsler length given by the projection $\sigma_i \cdot \hat{t}_{ij}$ of $\sigma_i$ on link $\hat{t}_{ij}$ of the tetrahedron such that

$$ v_{ij} = \sqrt{1 - |\sigma_i \cdot \hat{t}_{ij}|^2 + v_0}, $$

where $\hat{t}_{ij}$ is an unit tangential vector of the bond $ij$ (Fig.1(b)), and $v_0 = 0.001$ is a cutoff. Almost all ferroelectric polymers have a dipole moment, which is oriented perpendicular to the carbon skeleton (the structure of $\beta$-PVDF is illustrated in Fig.1(c)).

Replacing the integration in Eq.(1) with a sum over tetrahedrons and including the symmetric terms obtained by index replacement with the factor $1/4$, we have a discrete version of $S_1$ [5]. With some extra terms, the discrete Hamiltonian for the FG model of the ferroelectric polymer is given by:
\[ S = \gamma S_1 + \kappa S_2 - bs_3 - cS_4 + U_{3D} + U_{\text{vol}}, \quad S_1 = \sum_{ij} \Gamma_{ij} \gamma_{ij}^{(\text{tet})}, \quad \Gamma_{ij} = (1/N) \sum_{\text{tet}} \gamma_{ij}^{(\text{tet})}, \]

\[ S_2 = \sum_{ij} (1 - \cos(\phi_i - \pi/3)), \quad S_3 = \sum_{i} \sigma_i \cdot \vec{E}, \quad S_4 = \sum_{i} (\sigma_i \cdot \vec{E})^2, \]

\[ U_{3D} = \begin{cases} \infty & (V_{\text{tet}} \leq 0), \\ 0 & (V_{\text{tet}} > 0) \end{cases}, \quad U_{\text{vol}} = \begin{cases} \infty & (|V - V_0| \leq \Delta V), \\ \max & (\text{otherwise}) \end{cases}, \tag{3} \]

where \( l_{ij} \) denotes a length of the bond \( ij \). The coefficients \( \Gamma_{ij} \) are given by the sum of tetrahedrons sharing the bond \( ij \), and \( \gamma_{ij}^{(\text{tet})} \) for the tetrahedron of vertices 1234 are determined via components of the metric tensor such that [5]:

\[ \gamma_{12} = \frac{1}{4} \left( \frac{\nu_{12} \nu_{14} + \nu_{21} \nu_{24}}{\nu_{12} \nu_{21} \nu_{14} \nu_{24}} \right), \quad \gamma_{13} = \frac{1}{4} \left( \frac{\nu_{13} \nu_{14} + \nu_{31} \nu_{34}}{\nu_{13} \nu_{31} \nu_{14} \nu_{34}} \right), \quad \gamma_{14} = \frac{1}{4} \left( \frac{\nu_{14} \nu_{12} + \nu_{41} \nu_{42}}{\nu_{14} \nu_{12} \nu_{41} \nu_{42}} \right), \]

\[ \gamma_{23} = \frac{1}{4} \left( \frac{\nu_{23} \nu_{24} + \nu_{32} \nu_{34}}{\nu_{23} \nu_{32} \nu_{24} \nu_{34}} \right), \quad \gamma_{24} = \frac{1}{4} \left( \frac{\nu_{24} \nu_{23} + \nu_{42} \nu_{43}}{\nu_{24} \nu_{23} \nu_{42} \nu_{43}} \right), \quad \gamma_{34} = \frac{1}{4} \left( \frac{\nu_{34} \nu_{32} + \nu_{43} \nu_{42}}{\nu_{34} \nu_{32} \nu_{43} \nu_{42}} \right). \tag{4} \]

The second term \( \kappa S_2 \) in Eq.(3) plays a role of deformation strength against bending and shear deformation, both of which have an influence on the material shape. \( \phi_i \) is an internal angle of the triangle. The third term \( bS_3 \) is an energy of the dipole interaction with the external electric field, which causes the piezoelectric effect. \( cS_4 \) is the potential describing the quadratic electrostrictive effect. \( U_{3D} \) is a constraint for the volume of the tetrahedron for not being negative. To prevent the volume from changing, the last term \( U_{\text{vol}} \) is introduced, where \( \Delta V \) is a mean value of the volume of one tetrahedron and \( V_0 \) is an initial volume of the whole cylinder which is determined by the simulation without \( U_{\text{vol}} \) in the absence of external electric field.

3. The simulation results

In this work, we use a cylinder of size \((N, N_B, N_T, N_{\text{tet}}) = (10346, 69964, 116041, 56422)\), where \( N, N_B, N_T, N_{\text{tet}} \) denote the total number of vertices, bonds, triangles, and tetrahedrons, respectively. The ratio of the cylinder height and its diameter is equal to 0.125. For this cylinder, the simulation of electric field-induced deformation is carried out by Monte Carlo method. The Monte Carlo (MC) updates of locations of vertices and \( \sigma \) are performed using the standard Metropolis algorithm. The uniform external electric field is applied along the axis of the cylinder i.e. along the \( z \) axis. The snapshots in Figs. 2(a)-(d) show how the shape of the cylinder is changed. We can see that the height shrinks and the diameter expands with increasing electric field.

The absolute value of thickness strain \( |\varepsilon_z| \) and diameter strain \( \varepsilon_d \) vs. the external electric field \( E \) for different values of the bending stiffness are presented in Figs.2(e),(f). The values of \( c \) and \( b = \sqrt{\bar{c}} \) were chosen by data analysis for the best correspondence of the experimental and the simulation data. We compare our simulation results for longitudinal shrinking with experimental data of highly electrostrictive networks of \( \beta \)-PVDF [6]. For the transverse stretching comparison, the strain-field diagram of P(VDF-TrFE-CFE) films is used [7]. To summarize, the simulation results are in good agreement with experimental data in both longitudinal and transverse directions.

From the comparison of the energy \( cS_4 \) and the physical dielectric energy, we obtain \( cE^2k_B T/a^3 = \varepsilon_0 \Delta\varepsilon E_{\text{exp}}^2 \) [4], where \( \varepsilon_0 = 8.85 \times 10^{-12}[\text{F/m}] \), \( \Delta\varepsilon \) is the dielectric anisotropy, \( a \) is the lattice spacing, \( k_B T \) is given by \( k_B T = 4 \times 10^{-21}[\text{J}] \) at room temperature. If the experimental data \( \varepsilon_z \) or \( \varepsilon_d \) at \( E_{\text{exp}} \) in units of \([10^9 \text{V/m}]\) are comparable with those simulation data at \( E \), then we conclude that \( E = 10^{-6}E_{\text{exp}} \) [4]. In this case, we have \( a = (ck_B T \varepsilon_0 \Delta\varepsilon E_{\text{exp}})^{1/3} \approx (7.7 \times 10^{-8})(c/\Delta\varepsilon)^{1/3} \text{[m]}. \) Using the value of \( \Delta\varepsilon = 0.25 \) [8] and the input \( c = 0.024[\text{MV}^{-2}] \), we find that \( a \simeq 3.5 \times 10^{-8}[\text{m}] \) in \( \beta \)-PVDF model, which is clearly larger than the van der Waals
Figure 2. Snapshots of the cylinder with the external field: (a),(b) \( E_{\text{exp}} = 0 \), and (c),(d) \( E_{\text{exp}} = 20 \) with the bending stiffness value \( \kappa = 0.4 \). (e) The thickness-strain \( |\varepsilon_z| \) v.s. \( E_{\text{exp}} \) and (f) the diameter-strain \( \varepsilon_d \) vs. \( E_{\text{exp}} \) with several different \( \kappa \) values.

distance \( D_{\text{VWD}} \simeq 10^{-10}[\text{m}] \). In P(VDF-TrFE-CFE) model with \( c = 0.0003[\text{MV}^{-2}] \), we have less value of the lattice spacing \( a \simeq 8.1 \times 10^{-9}[\text{m}] \), which is reasonable because the experimental samples of P(VDF-TrFE-CFE) were thinner than ones of \( \beta \)-PVDF.

4. Conclusion

We propose a simulation model on the basis of Finsler geometry for describing the reverse piezoelectric effect in PVDF. The simulation results of deformation, induced by the electric field, are in good agreement with reported experimental data for both longitudinal shrinking and transverse stretching. Hence, we conclude that this model is suitable to predict the shape transformation of PVDF-based actuators.

Acknowledgments

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