MONTE CARLO SIMULATIONS OF LIQUID CRYSTAL ELASTOMER UNDER ELECTRIC FIELDS

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Abstract

In this paper, the elongation phenomenon of liquid crystal elastomer (LCE) under electric field is studied by Finsler geometry (FG) modeling technique and Monte Carlo (MC) simulations. In this FG technique, the geometry inside the LCE is modified by replacing the ordinary Euclidean metric by a Finsler metric. As a consequence of this replacement, the polymer position is included in the Hamiltonian as a dynamical variable, and an interaction of LC molecules and polymers is effectively or implicitly introduced. The MC results for the elongation of LCE are compared with existing experimental data. We find that the MC results are in good agreement with the experimental data. This implies that the FG modeling correctly describes the interaction of LC molecules and polymers in spite of the fact that the interaction is implicitly introduced by the modification of the geometry inside the material.

Key words: *J-shaped Stress-strain Diagram, Collagen Fibers, Finsler Geometry Model, Monte Carlo*

1. INTRODUCTION

Liquid crystal molecules (LC) are combined with polymers and form a meta-material, the so-called liquid crystal elastomer (LCE) (Warner and Terentjev 2007). LCE elongates into a direction along which the LC molecules align due to the activation forces such as external electric fields (Urayama et.al. 2005; Urayama Honda and Takigawa 2005; Urayama Honda and Takigawa 2006) The temperature change also makes LCE oblong and anisotropic (Shahinpoor Kim and Mojarrad 2007; Tajbakhsh and Terentjev 2001). This LCE elongation has been studied for its engineering application to sensors or actuators such as artificial muscle (Shahinpoor Kim and Mojarrad 2007; Chamacho-Lopez et.al. 2004).

The reason for the elongation is qualitatively well understood, and its statistical mechanical study have been extensively conducted on the basis of the theory of LC molecules combined with the theory of elasticity using the strain variables of polymers (Warner and Terentjev 2007). The major parts of the elongation phenomena including soft elasticity and other related properties are well described by those models. However, the interaction between the LC molecules and polymers is not yet fully understood in the studies so far, because the polymer position is not directly included in the interaction Hamiltonian. For this reason, the quantitative understanding of the LCE elongation is still insufficient from the microscopic perspective.

Recently, we applied Finsler geometry (FG) modeling technique for the soft elasticity and elongation of LCE, and we obtained the results which are consistent with the reported experimental data (Osari and Koibuchi 2017). The so-called J-shaped diagram of soft biological tissues such as animal skin and muscles can also be reproduced by the FG model (Takano and Koibuchi 2017). This FG technique introduces an interaction of LCE directional degree of freedom and the polymer position via the Finsler metric. We should emphasize that the interaction is defined by modifying the underlying geometry inside the materials, and therefore, this technique is in sharp contrast to the standard modeling technique, in which an interaction is defined by introducing an energy term as the interaction Hamiltonian. For this reason, the FG technique should be checked in more detail in specific phenomena in the field of material science or nanotechnology, though it has a lot of applications in cosmology and quantization theories (Bogoslovsky 2012; Ootsuka and Tanaka 2010).

In this paper, we apply the FG model technique to analyze LCE elongations caused by external electric fields. Monte Carlo (MC) results for the strain vs. electric filed will be compared with the reported experimental data (Urayama et.al. 2005; Urayama Honda and Takigawa 2005; Urayama Honda and Takigawa 2006). The detailed information of the topic in this manuscript will be reported in (Proutorov, E. Matsuyama, N. and Koibuchi, H.).

2. MODEL

The FG model for LCE is a statistical mechanical model, which is defined by a partition function and Hamiltonian, in which an interaction is described using dynamical variables. The model for LCE is defined by extending a 2-dimensional model for membranes to a 3-dimenional model, and the 2-dimensional model for membranes is well known as an extension of the one-dimensional model for linear polymers of Doi and Edwards (Doi and Edwards 1986). This extended Hamiltonian of the 3-dimensional version is given by

$$S_1 = \int \sqrt{g} d^3x g^{ab} \frac{\partial \vec{r}}{\partial x_a} \cdot \frac{\partial \vec{r}}{\partial x_b}, \tag{1}$$

where $\vec{r}$ is the three dimensional position vector of the LC molecule or polymer, $x_a (a = 1,2,3)$ denote a local coordinate inside the material, and g^{ab} is the inverse of the Finsler metric g_{ab}, which is a 3×3 matrix

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

defined on a tetrahedron in Fig. 1. In this g_{ab}, the symbol v_{ij} is given by

$$v_{ij} = |\vec{t}_{ij} \cdot \sigma_i| + v_0, \tag{3}$$

where v_0 is a cutoff parameter and also plays a role of the parameter that controls the interaction strength.

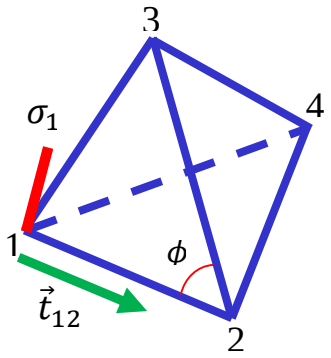
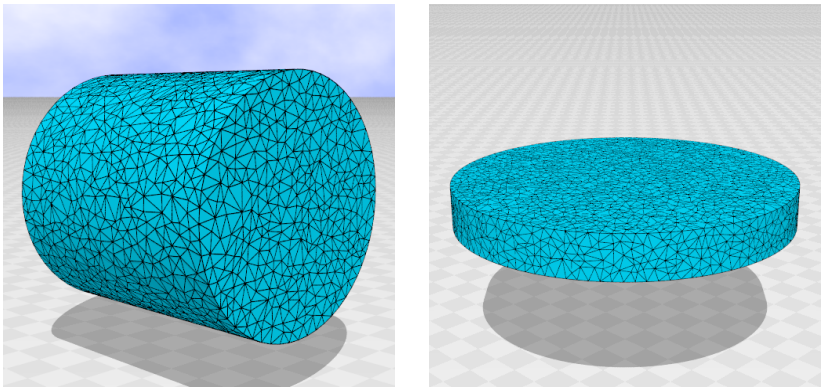


Fig. 1. A tetrahedron of the vertices 1,2,3,4. The Finsler length v_{12} along the direction from the vertices 1 to 2 is defined by the director σ_1 at the vertex 1 and the unit tangential vector $\vec{t}_{12}$.

This continuous Hamiltonian is discretized on tetrahedrons, which form the 3D lattices for the numerical simulations (Figs. 2(a) and 2(b)).



(a) **(b)**

Fig. 2. Cylinders constructed with tetrahedrons using Voronoi discretization. The ratio of the length(height)/diameter is (a) $L/D = 1$, and (b) $H/D = 1/8$.

The dynamical variables of the model are $\vec{r}$ and σ, where σ is a 3-dimenional unit vector and denotes the direction of LC molecule. We should note that σ is identified with $-\sigma$ because of its nonpolar interaction.

The discrete S_1 is given by

$$S_1 = \sum_{ij} \Gamma_{ij} \ell_{ij}^2, \quad \Gamma_{ij} = \frac{1}{4\bar{N}} \sum_{tet} \gamma_{ij}(tet), \quad \ell_{ij}^2 = \left(\vec{r}_i - \vec{r}_j\right)^2, \quad \bar{N} = (1/N_B) \sum_{ij} n_{ij}, \tag{4}$$

where N_B is the total number of the bonds, n_{ij} is the total number of the tetrahedrons sharing the ij bond, and $\sum_{tet}$ in Γ_{ij} denotes the sum over tetrahedrons that share the bond ij. The coefficients γ_{ij} in Γ_{ij} are defined by

$$\begin{aligned} \gamma_{12} &= \frac{v_{12}}{v_{13}v_{14}} + \frac{v_{21}}{v_{23}v_{24}} \quad \gamma_{13} = \frac{v_{13}}{v_{12}v_{14}} + \frac{v_{31}}{v_{32}v_{34}}, \\ \gamma_{14} &= \frac{v_{14}}{v_{12}v_{13}} + \frac{v_{41}}{v_{43}v_{42}} \quad \gamma_{23} = \frac{v_{23}}{v_{21}v_{24}} + \frac{v_{32}}{v_{31}v_{34}}, \\ \gamma_{24} &= \frac{v_{24}}{v_{23}v_{21}} + \frac{v_{42}}{v_{41}v_{43}} \quad \gamma_{34} = \frac{v_{34}}{v_{31}v_{32}} + \frac{v_{43}}{v_{41}v_{42}}. \end{aligned} \tag{5}$$

The total Hamiltonian $S(\vec{r}, \sigma)$ of the FG model is defined by a linear combination of S_1 and other 4 terms such as

$$\begin{aligned} &S(\bar{r}, \bar{\sigma}) = \lambda S_0 + S_1 + \kappa S_2 + \alpha S_3 + U_{3D}, \\ &S_0(\bar{\sigma}) = \tfrac{1}{2} \sum_{ij} \left[1 - 3\left(\vec{\sigma}_i \cdot \vec{\sigma}_j\right)^2\right], \quad S_2(\vec{r}) = \sum_i [1 - \cos(\phi_i - \pi/3)], \\ &S_3(\vec{\sigma}) = -\alpha \sum_i \left(\vec{\sigma}_i \cdot \vec{E}\right)^2, \quad \vec{E} = (E, 0, 0), \\ &U_{3D} = \sum_{\text{tet}} U_{3D}(\text{tet}), \qquad U_{3D}(\text{tet}) = \begin{cases} 0 & (\text{Vol}(\text{tet}) > 0) \\ \infty & (\text{otherwise}) \end{cases}. \end{aligned} \tag{6}$$

The first term $S_0(\bar{\sigma})$ is called Lebwohl-Lasher potential, which is assumed for the interaction between LCs (Lebwohl and Lasher 1972). The second term $S_2(\vec{r})$ plays a role in maintaining the shape of tetrahedron, where ϕ_i is an internal angle of the triangle. The αS_3 is the interaction energy between $\vec{\sigma}$ and the external electric field $\vec{E}$, where α corresponds to the dielectric anisotropy $\Delta\varepsilon$. The potential U_{3D} protects the tetrahedron volume from being negative.

The partition function is defined by:

$$Z = \sum_{\vec{\sigma}} \int \prod_{i=1}^{N} d\vec{r}_i \exp[-S(\vec{r}, \vec{\sigma})], \tag{7}$$

where $\Sigma_{\vec{\sigma}}$ denotes the sum of all possible values of $\vec{\sigma}$.

Here, we discuss the difference between the FG modeling and the conventional modeling techniques and how the FG modeling is new. Indeed, the FG modeling is completely new in the sense that a "complex interaction energy" between LC molecules and polymers is not "explicitly" introduced but it is "implicitly" introduced in the total Hamiltonian S. Instead of introducing a complex interaction between LCs and polymers "explicitly ", we deform the intrinsic geometry of the LCE by modifying the metric tensor from Euclidean metric to Finsler metric. This Finsler metric is itself very simple. In this FG modeling, the position $\vec{r}\,(\in \mathbb{R}^3)$ of polymer is directly treated, and as a consequence the mechanical response can be calculated independent of how the orientation of the director σ changes.

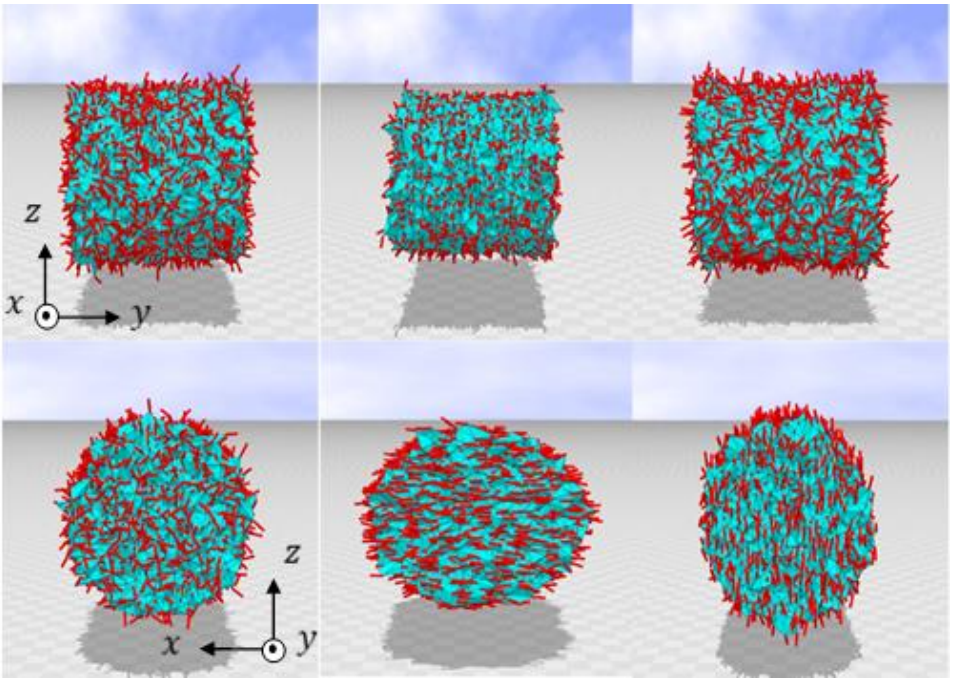
We should note that the material is placed in the Euclidean space $\mathbb{R}^3$, and therefore the experimental measurements are not influenced at all by this Finsler metric. The Finsler metric is used only for modifying the definition of "derivative interaction" in S_1 of Eq. (1). The discrete "derivative interaction" is simply obtained by the discretization of the continuous S_1 by replacing the differentials $\partial_1\vec{r}$ and $\partial_2\vec{r}$ with the corresponding differences. As a result of this modification of the metric, the interaction of LCs and polymers is "implicitly" introduced using the variables σ and $\vec{r}$. Indeed, S_1 is modified from $S_1 = \sum_{ij} \ell_{ij}^2$ to $S_1 = \sum_{ij} \Gamma_{ij} \ell_{ij}^2$, where ℓ_{ij} is the length of bond ij; a part of polymer, and Γ_{ij} represents the modified interaction, which is automatically determined from the Finsler metric. In this sense, the interaction is determined in a more basic level and constructive manner from the geometries inside the material and of the space $\mathbb{R}^3$.

In the case of the conventional statistical mechanical modeling for LCE, the variable σ for LC molecule is also introduced, however, the interaction between LCs and polymer-positions is not directly assumed. The interaction assumed in the conventional model is the one between σ and the strain variable, which is defined by a displacement field $\vec{u}$. The displacement field is defined by the displacement from its original position $\vec{r}_0$ such that $\vec{r} = \vec{r}_0 + \vec{u}$, however, this $\vec{r}_0$ is unknown in general.

In contrast, the FG model for LCE is a combination of "statistical mechanical model of LCs" and "3-dim extension of the statistical mechanical model for 2D membranes", where the dynamical variable of the former model is σ and that of the latter is $\vec{r}$. The interaction between these σ and $\vec{r}$ is introduced not by "interaction energy" but by Finsler metric as described above. Therefore, the variable $\vec{r}$ is directly treated statistical mechanically in the FG model. More than that, as mentioned above, this latter part of the model is considered as a natural extension of the model of Doi-Edwards, because the 2D membrane model is simply considered as an extension of Doi-Edwards model for linear polymer (Doi and Edwards 1986).

Thus, the coupling of the directional degrees of freedom σ of LCs and the bulk shape is the one that is implemented in a very simple and constructive way in the FG modeling. Even though this coupling is successfully implemented, the bulk shape of LCE does not respond to σ when σ is isotropic. However, once σ aligns into a direction spontaneously (by an internal phase transition) or artificially (by an external stimulus such as electric filed), then the bulk shape responds to σ. This is the most interesting side of the FG modeling.

3. NUMERICAL RESULTS



(a) **(b)** **(c)**

Fig. 3. Snapshots of cylindrical lattices. The small lines on the surfaces represent the variable σ. The electric field E is applied to the direction of x axis, and (a) $E = 0$, (b) $E = 0.68$ with positive dielectric constant α, and (c) $E = 0.63$ with negative α. $N = 19784$.

First, we show the results of MC simulations for the experimental data reported in (Urayama et.al. 2005). The external electric field E is included in the Hamiltonian as the energy term $-\alpha\sum_i(\sigma_i \cdot \vec{E})^2$, where α is the dielectric anisotropy. Snapshots of the cylindrical lattices are shown in Fig. 2, where (a) $E = 0$, (b) $E = 0.68$ with positive α, and (c) $E = 0.63$ with negative α. We find that LCE elongates along the direction of $\vec{E}$ for positive α, while it shrinks in the direction of $\vec{E}$ for negative α.

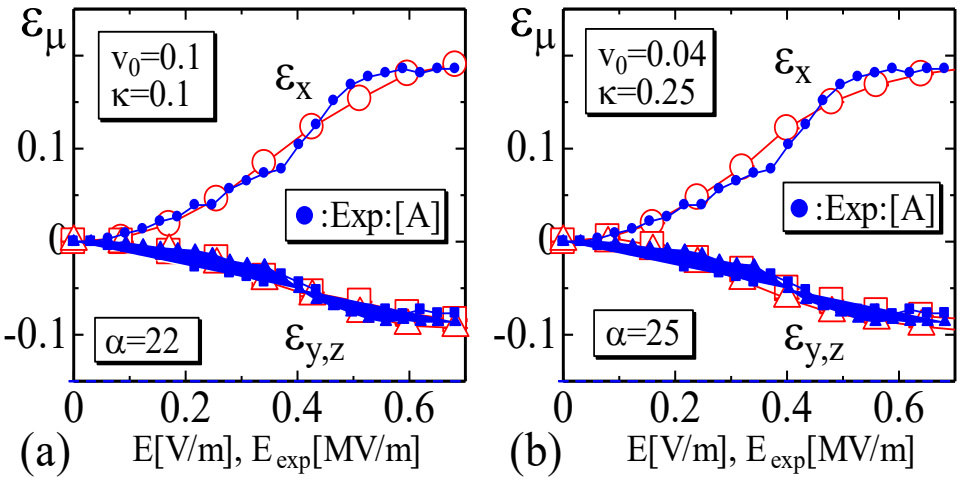
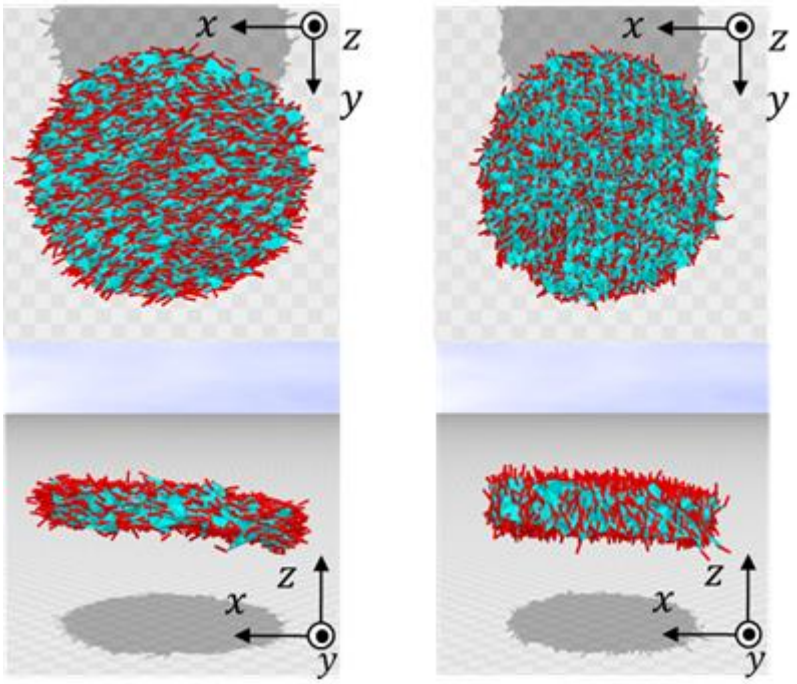


Fig. 4. The strain ε_μ vs. electric field E for (a) positive α, and (b) negative α. The solid symbols Exp:[A] denote the experimental data in (Urayama et.al. 2005), and the open symbols denote the simulation data.

Figures 4(a) and 4(b) show the strains ε_μ vs. E. The strains $\varepsilon_\mu(\mu = x, y, z)$ are defined by

$$\varepsilon_\mu = \frac{D_\mu}{D_\mu^0} - 1, \quad (\mu = x, y, z), \tag{2}$$

where D_x and D_z are the diameters and D_y is the length L of the cylinder, and D_μ^0 $(\mu = x, y, z)$ are those for $E = 0$. The simulation results (open symbols) are almost in good agreement with the experimental data (solid symbols) which were reported in (Urayama et.al. 2005). The parameters v_0 and κ are fixed to suitable values in the simulations, and the meaning of these parameters is written in more detail in (Proutorov, E. Matsuyama, N. and Koibuchi, H.).



(a) **(b)**

Fig. 5. Snapshots of thin-cylinders for the simulations corresponding to the experimental data in (Urayama Honda and Takigawa 2005; Urayama Honda and Takigawa 2006). In the simulations, a small electric field E_0 is applied to the x axis to make the variable σ aligns, because LC molecules align parallel to surface direction in the nematic LCE disk in the experiment. The electric field E, which is different from E_0, is applied to the z axis such that (a) $E = 0$ and (b3.

Next, we show the results corresponding to the experimental data reported in (Urayama Honda and Takigawa 2005; Urayama Honda and Takigawa 2006), where LCE in the nematic phase is used. The LC molecules in the plate used in (Urayama Honda and Takigawa 2005; Urayama Honda and Takigawa 2006) align in a direction parallel to the plate. For this reason, a small electric field E_0 in the direction of x axis is assumed in the model (Fig.5(a)). This constant field E_0 is always assumed even when E is applied along the z axis (Fig.5(b)). Thus, the LC direction simply changes from $\sigma = (1,0,0)$ to $\sigma = (0,0,1)$, and therefore D_y remains unchanged while the external filed strength E increases from zero to sufficiently large, because $\sigma_y(= 0)$ remains unchanged.

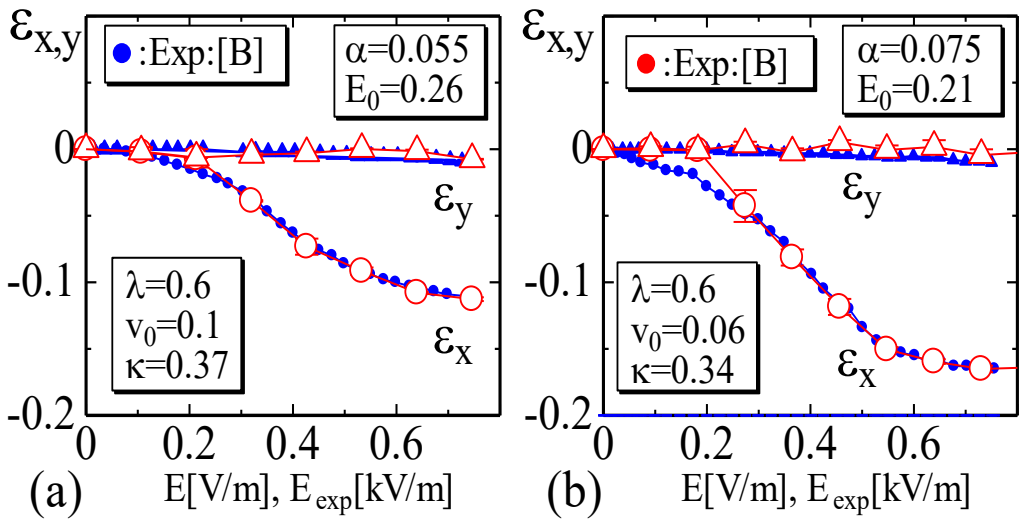


Fig. 6. The strain ε_μ vs. Electric field E for positive dielectric constants α with the crosslinker densities (a) $C = 7[\text{mol}\%]$ and (b) $C = 3[\text{mol}\%]$. The solid symbols Exp:[B] denote the experimental data in (Urayama Honda and Takigawa 2005; Urayama Honda and Takigawa 2006) and the open symbols denote the simulation data.

In Figs. 6(a) and 6(b), we show the strains $\varepsilon_\mu(\mu = x, y)$ vs. E. The open (solid) symbol denotes the simulation (experimental) data (Urayama Honda and Takigawa 2005; Urayama Honda and Takigawa 2006). We confirm that the strain ε_y remains almost zero when E is increased as mentioned above.

4. CONCLUSION

We studied the experimental diagrams of strain vs. electric field of LCE, reported in (Urayama et.al. 2005; Urayama Honda and Takigawa 2005; Urayama Honda and Takigawa 2006), by Finsler geometry modeling technique. The results obtained by MC simulations are almost in good agreement with the reported experimental data. We confirm that the FG modeling technique is successful for describing the elongation of LCE caused by electric field. This work is supported in part by JSPS KAKENHI Grant No. 17K05149.

REFERENCES

Bogoslovsky, B. (2012). Dynamic Rearrangement of Vacuum and the Phase Transitions in the Geometric Structure of Space-time. *Int. J. Geom. Methods Mod. Phys.* 9, 1250007(1-20).

Chamacho-Lopez, M. Finkelmann, H. Palffy-Muhoray, P. and Shelley, M. (2004). Fast liquid-crystal elastomer swims into the dark. *Nature Mat*. 3, pp.307-310.

Doi, M. and Edwards, S.F. (1986). *The Theory of Polymer Dynamics*, Oxford University Press.

Lebwohl, P. A. and Lasher, G. (1972). Nematic-Liquid-Crystal Order—A Monte Carlo Calculation. *Phys. Rev. A* 6, pp.426-429.

Ootsuka, T. and Tanaka, E. (2010). Finsler geometrical path integral. *Phys. Lett. A* 374, pp.1917-1921.

Osari, K. and Koibuchi, H. (2017). Finsler geometry modeling and Monte Carlo study of 3D liquid crystal elastomer. *Polymer* 114, pp.355-369.

Proutorov, E. Matsuyama, N. and Koibuchi, H. (submitted).

Selinger, J.V., Jeon, H.G., and Ratna, B.R. (2002). Isotropic-Nematic Transition in Liquid-Crystalline Elastomers. *Phys. Rev. Lett.* 89, 225701.

Shahinpoor, M. Kim, K.J. and Mojarrad, M. (2007) *Artificial Muscles: Applications of Advanced Polymeric Nanocomposites*, NewYork: Taylor and Francis.

Tajbakhsh, A.R. and Terentjev, E.M. (2001). Spontaneous thermal expansion of nematic elastomers. *Euro. Phys. J. E* 6, pp.181-188.

Takano Y. and Koibuchi H. (2017). J-shaped stress-strain diagram of collagen fibers: Frame tension of triangulated surfaces with fixed boundaries. *Phys. Rev. E* 95, 042411.

Urayama, K., Kondo, H., Arai, Y. and Takigawa, T. (2005). Electrically driven deformations of nematic gels. *Physical Review E*, 71, 051713(1-8).

Urayama, K. Honda S. and Takigawa T. (2005). Electrooptical Effects with Anisotropic Deformation in Nematic Gels. *Macromol*. 38, pp.3574-3576.

Urayama, K. Honda S. and Takigawa T. (2006). Deformation Coupled to Director Rotation in Swollen Nematic Elastomers under Electric Fields. *Macromol*. 39, pp.1943-1949.

Warner, M. and Terentjev, E.M. (2007). *Liquid crystal elastomers*. 1st ed. Oxford: Oxford University Press.