Modeling shape and volume transitions in liquid crystal elastomers

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Abstract. Shape and volume phase transitions of liquid crystal elastomers (LCEs) immersed in a solvent are studied within the framework of the Finsler geometry (FG). In the FG model of an LCE, an internal variable is introduced to describe the directional degrees of freedom of liquid crystals. We also introduce an Ising-like variable to effectively describe the swelling behavior of the LCE. From the results of Monte Carlo simulations, we find that the model successfully reproduces changes in the swelling degree as well as the smooth change in the shape anisotropy with increasing temperature. Moreover, the maximal value of the shape anisotropy is close to the experimentally observed value.

1. Introduction
Liquid crystal elastomers (LCEs) are composite materials of liquid crystals and polymers that exhibit novel properties that are not inherent in liquid crystals or polymers individually. LCEs exhibit shape and volume changes induced by thermal, chemical and light stimuli. This leads to potential applications of LCEs as soft actuators and in robotics [1, 2]. The thermally induced shape changes of LCEs immersed in a solvent have been studied extensively [3]. With temperature variations, the volume of LCEs also changes by absorbing and expelling the solvent. This swelling behavior is coupled with nematic order, and as a consequence, the shape becomes anisotropic in the nematic phase. When the nematic-isotropic transition in a monodomain LCE occurs at temperature \( T_{NI}^G \), the volume continuously decreases during the cooling process [4] (Fig. 1). At temperatures higher than \( T_{NI}^G \), the shape of the LCE is isotropic, while the solvent exhibits a transition at lower temperature \( T_{NI}^S \) due to a dilution effect of the nonnematogenic solvent on the network nematicity.

Swelling behavior has been studied by means of mean-field theory, with which Matsuyama et al. calculated temperature-swelling phase diagrams [5]. This theory qualitatively well describes the experimental data and demonstrates that the observed volume and shape changes are governed by the nematic order in the LCE and the solvent. However, the theoretical results overestimate the value of the shape anisotropy and predict its discontinuous change at the temperature \( T_{NI}^G \). Additionally, the theoretical phase diagrams reflect a discontinuous change
in the swelling degree at the same temperature. This change was observed to be smooth in polydomain LCEs [6]. However, the reason for the smooth transition of the swelling degree in monodomain LCEs remains unclear.

In this work, we present a novel method for studying the volume and shape transitions in LCEs. The method is based on the Finsler geometry (FG) model, which was introduced in [7], where the behavior of LCEs under external electric fields was studied. Here, we further extend this FG model by including an Ising-like variable to incorporate swollen and nonswollen states of LCEs. This method allows us to effectively implement the volume changes observed in LCEs.

Figure 1. (a) Temperature dependence of the equilibrium swelling degree and (b) the degree of shape anisotropy \( \alpha \) for MONO-LCN in 7CPB. The data are taken from [4]. (c) Schematic picture of the temperature dependence of \( \alpha \) and that of the volume in a monodomain LCE

2. The Finsler geometry model of an LCE

A more detailed description of the FG model for an LCE is reported in [7]. Here, we briefly outline the model and concentrate on the details of modifications for implementing the swelling and reswelling processes. The FG modeling comes from the Hamiltonian

\[
S_1 = \int \sqrt{g} d^3x \, g^{ab} \frac{\partial \vec{r}}{\partial x^a} \cdot \frac{\partial \vec{r}}{\partial x^b},
\]

where \( \vec{r}(\in \mathbb{R}^3) \) is a position vector of a three-dimensional body with local coordinates \( x^a (a = 1, 2, 3) \). The symbol \( g^{ab} \) is the inverse of the Finsler metric \( g_{ab} \), and \( g \) is its determinant.

To define the metric tensor and the discrete Hamiltonian, the three-dimensional body is discretized by tetrahedrons. At vertex \( i \) of a tetrahedron, two variables \( \vec{\sigma}_i (\in S^2; \text{unit sphere}) \) and \( \tau_i (\in \{-1, 1\}) \) are introduced. \( \vec{\sigma}_i \) represents the shape anisotropy of the LCE, and the novel Ising-like variable \( \tau_i \) indicates swollen and nonswollen states of the LCE. The Finsler metric is defined by these two variables at vertex 1 of tetrahedron 1234 (Fig. 2(a)) as follows:

\[
g_{ij} = \begin{pmatrix}
\rho_{ij}^2 v_{ij}^{-2} & 0 & 0 \\
0 & \rho_{ij}^2 v_{ij}^{-2} & 0 \\
0 & 0 & \rho_{ij}^2 v_{ij}^{-2}
\end{pmatrix}, \quad v_{ij} = |\vec{\sigma}_i \cdot \vec{t}_{ij}| + v_0, \quad \rho_i = \begin{cases} 1 & (\tau_i = 1) \\
c & (\tau_i = -1)
\end{cases},
\]

where \( \vec{t}_{ij} \) is a unit tangential vector of bond \( ij \), \( v_0 = 0.0001 \) is a cutoff, and \( c \) is a parameter that determines the magnitude of the volume change. Replacing the integration in Eq. (1) with...
a sum over tetrahedrons and including the symmetric terms obtained by index replacements and with a factor of 1/4, we have a discrete version of $S_1$. With some extra terms, the discrete Hamiltonian for the FG model of an LCE is given by

$$S = \epsilon S_\tau + \lambda S_0 + \gamma(T) S_1 + \kappa S_2 - S_B, \quad (\gamma(T) = T), \quad S_\tau = \sum_{ij} (1 - \tau_i \cdot \tau_j),$$

$$S_0 = \frac{1}{2} \sum_{ij} (1 - 3[\vec{\sigma}_i \cdot \vec{\sigma}_j]^2), \quad S_1 = \sum_{ij} \Gamma_{ij} \ell_{ij}^2, \quad \Gamma_{ij} = (1/N) \sum_{\text{tet}} \gamma_{ij}(\text{tet}),$$

$$S_2 = \sum_i (1 - \cos(\phi_i - \pi/3)), \quad S_B = \sum_i \tau_i \cdot B,$$

and the partition function is given by

$$Z = \sum_\tau \sum_\sigma \int \prod_i d\vec{r}_i \exp \left( -\frac{S}{T} \right).$$

The simulation unit is defined by $k_B = 1$ and $a = 1$, which are the Boltzmann constant and the unit of length, respectively. The symbol $T$ denotes the temperature, and the tension coefficient $\gamma(T)$ is assumed to be identical to $T$. $\ell_{ij}$ in $S_1$ denotes the length of bond $ij$. The coefficients $\Gamma_{ij}(\Gamma_{ij} = \Gamma_{ji})$ are given by the sum of tetrahedrons sharing bond $ij$, where $N$ is the number of these tetrahedrons. The $\gamma_{ij}(\text{tet})$ for the tetrahedron of vertices 1234 are determined via components of the metric tensor as follows:

$$\gamma_{12} = \frac{1}{4} \left( \frac{\rho_{11} v_{12} + \rho_{12} v_{13}}{v_{12} v_{13}} + \frac{\rho_{13} v_{14}}{v_{13} v_{14}} \right), \quad \gamma_{13} = \frac{1}{4} \left( \frac{\rho_{11} v_{13} + \rho_{12} v_{14}}{v_{12} v_{13}} + \frac{\rho_{13} v_{11}}{v_{13} v_{11}} \right), \quad \gamma_{14} = \frac{1}{4} \left( \frac{\rho_{11} v_{14} + \rho_{12} v_{11}}{v_{12} v_{14}} + \frac{\rho_{14} v_{13}}{v_{14} v_{13}} \right),$$

$$\gamma_{23} = \frac{1}{4} \left( \frac{\rho_{21} v_{23} + \rho_{22} v_{24}}{v_{21} v_{23}} + \frac{\rho_{23} v_{22}}{v_{23} v_{22}} \right), \quad \gamma_{24} = \frac{1}{4} \left( \frac{\rho_{21} v_{24} + \rho_{22} v_{21}}{v_{21} v_{24}} + \frac{\rho_{24} v_{22}}{v_{24} v_{22}} \right), \quad \gamma_{34} = \frac{1}{4} \left( \frac{\rho_{31} v_{34} + \rho_{32} v_{31}}{v_{31} v_{34}} + \frac{\rho_{34} v_{32}}{v_{34} v_{32}} \right).$$

The interaction between the variables $\sigma_i$ is defined in the same way as in the Ising model by the term $c S_\sigma$. In addition, we introduce an "external field" $B$ that makes $\tau$ take the value of 1, corresponding to the nonswollen state. The term $\lambda S_0$ is the Lebwohl-Lasher potential for LC molecules with the interaction coefficient $\lambda$ [8]. $\kappa S_2$ in Eq. (3) plays a role in the deformation strength against bending and shear deformation, where $\phi_i$ is the internal angle of the triangle.

3. Simulation results
Monte Carlo simulations are carried out on a spherical lattice (Fig. 2(b)), where the total number of vertices is $N = 4601$. The variables $\tau$ and $\sigma$ and positions of vertices are updated by the Metropolis algorithm. The snapshots in Figs. 2(c) and (d) are qualitatively consistent with the experimentally observed snapshot.

The parameters are fixed to $c = 0.7, \epsilon = 0.09, \lambda = 0.27, \kappa = 0.2$, and $B = 0.28$. The temperature $T$ is varied around $T = 1.0$. The degree of shape anisotropy $\alpha$ is calculated by
\[ \alpha = 2D_{\text{max}}/(D_{\perp 1} + D_{\perp 2}) \]

where \( D_{\text{max}} \) is the mean value of the maximal diameter and \( D_{\perp 1} \) and \( D_{\perp 2} \) are the mean values of diameters along axes perpendicular to the maximal diameter axis. The volume \( V \) vs. \( T \) (Fig. 3(a)) is discontinuous at \( T \simeq 1 \), which is not typical of monodomain LCEs. The order parameter \( M = (1/2)(1 - \sum_i \tau_i / N) \) of \( \tau \) and the maximum (minimum) eigenvalue \( \Sigma_1 \) (\( \Sigma_3 \)) of the tensor order parameter \( Q_{\mu\nu} = (3/2)(\sigma_{\mu\nu} - \delta_{\mu\nu}/3) \) are plotted in Fig. 3(b)). These plots of order parameters indicate that the model undergoes volume and shape transitions at the same temperature \( T \simeq 1 \). The degree of shape anisotropy \( \alpha \) (Fig. 3(c)) exhibits a smooth change at \( T \simeq 1 \). The minimal value of \( \alpha \) differs from 1 because the lattice cannot be completely isotropic due to its fluctuations. However, the maximal shape anisotropy is considerably closer to the experimental value than that predicted in [5]. As one can see from Fig. 3(c), the smooth changes in the shape and the volume are coupled with the variable \( \sigma \). Meanwhile, the discontinuous change in the volume was caused by a rapid change in \( \tau \).

4. Conclusion

The volume and shape transitions of an LCE are studied by the FG model and Monte Carlo technique and are observed at the same transition temperature. The temperature dependence of the simulation results for the volume and shape is qualitatively in good agreement with the experimental data. Moreover, the numerically obtained maximal value of the shape anisotropy is close to the experimentally observed value. Our model exhibits a discontinuous volume change, which is predicted by many theories, but experimentally, it is not observed in monodomain LCEs. Nevertheless, it is interesting to study the possible hypotheses for explaining the smooth change mentioned in [3] from the Finsler geometric principle, which will be studied in the future.

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