

Numerical study of light-induced phase behavior of smectic solids

Hayoung Chung, Jaesung Park, and Maenghyo Cho

Division of Multiscale Mechanical Design, School of Mechanical and Aerospace Engineering, Seoul National University, San 56-1, Shillim-Dong, Kwanak-Ku, Seoul 151-744, South Korea

(Received 6 August 2016; published 26 October 2016)

By the chemical cross-linking of rigid molecules, liquid crystal polymer (LCP) has been envisaged as a novel heterogeneous material due to the fact that various optical and geometric states of the liquid crystalline (LC) phases are projected onto the polymeric constituents. The phase behavior, which refers to the macroscopic shape change of LCP under thermotropic phase change, is a compelling example of such optical-mechanical coupling. In this study, the photomechanical behavior, which broadly refers to the thermal- or light-induced actuation of smectic solids, is investigated using three-dimensional nonlinear finite element analysis (FEA). First, the various phases of LC are considered as well as their relation to polymeric conformation defined by the strain energy of the smectic polymer; a comprehensive constitutive equation that bridges the strong, optomechanical coupling is then derived. Such photomechanical coupling is incorporated in the FEA considering geometric nonlinearity, which is vital to understanding the large-scale light-induced bending behavior of the smectic solid. To demonstrate the simulation capability of the present model, numerous examples of photomechanical deformations are investigated parametrically, either by changing the operating conditions such as stimuli (postsynthesis) or the intrinsic properties (presynthesis). When compared to nematic solids, distinguished behaviors due to smectic substances are found herein and discussed through experiments. The quasisoftness that bidirectionally couples microscopic variables to mechanical behavior is also explained, while considering the effect of nonlinearity. In addition to providing a comprehensive measure that could deepen the knowledge of photomechanical coupling, the use of the proposed finite element framework offers an insight into the design of light-responsive actuating systems made of smectic solids.

DOI: [10.1103/PhysRevE.94.042707](https://doi.org/10.1103/PhysRevE.94.042707)

I. INTRODUCTION

During the past few decades, liquid crystal polymer (LCP) has been vigorously investigated as a novel material with anomalous phase behaviors [1–3] that stem from the combination of polymeric elasticity and the self-organizing traits of the liquid crystal (LC). In other words, the polymeric conformation shows the mechanical and optical anisotropies whenever the LC molecules possess certain types of symmetries. Recently, the phase behavior that broadly refers to the change of such anisotropy that entails the mechanical behavior is envisaged as a promising candidate for applications requiring novel smart actuation, such as artificial muscles, self-propulsion units, and microscaled actuators [4–7]. Predominantly, such coupled behavior has two distinguished traits. (1) The actuation is basically integrated within the structure itself, by which some hurdles for the future actuation system can be circumvented. (2) Various exotic deformations are possibly generated out of seemingly equivalent models; when LC textures are tuned either via rubbing, photoalignment, or doping functionalized inhomogeneity [1–3,8–10], they show unevenly distributed principal directions of local deformation.

Some recent studies have further explored the possibility of the photoactuator, which is a light-driven variant of the coupled behavior. Provided that incorporated mesogens exhibit photochromism, such as the azobenzene chromophore that reversely changes its form to *cis* (boat shape) out of an initially *trans* (chair shape) state upon exposure to photons with adequate frequency, the polymeric conformation similarly changes with light. Given that actinic light is bombarded onto the surface of photoresponsive LCP, the energy of the photon is continuously absorbed into the matrix while it

travels through the materials and isomerizes the photochromic molecules. An increased number of kinked molecules reduce the phase-transition temperatures as these molecules lose their rigidity and cannot contribute to the order, thereby rendering the state of the LC inhomogeneous in the depthwise direction. As a result, differential photoinduced strain is generated in out-of-plane directions; this strain simultaneously bends and elongates the specimen. Moreover, reversibility of such mechanism has been proven to generate no plastic deformation, thereby rendering the photobending mechanism an attractive means for the remotely controlled smart actuation [11–14], of which the behaviors are possibly alternated whenever we change the backbone, domain, and even the type of liquid crystallinity.

Most of these works, however, are limited to nematic-isotropic transition, which is characterized by one transition temperature T_{NI} and an orientational order parameter S , as the nematic phase only has rotational symmetry and is stable in a wide temperature range [15] that eases the fabrication. The nematic solids are also favored as they often yield large strain up to a few hundred percent [1] of their initial length. Meanwhile, the use of smectic solids has received far less interest than the use of nematic solids, not only due to their lower thermal stability than nematic solids upon cross-linking, but also because they involve additional parameters for the symmetry—smectic-nematic transition temperature $T_{NA} \leq T_{NI}$ and complex order parameters $\psi = \rho_o \exp(i\vec{q} \cdot \vec{x})$. Recent works have demonstrated that the addition of such symmetry yields unprecedented elasticity, as the layer undulation becomes another mode of soft, unstable mechanical responses: The opacity of the material changes when uniaxial loading exceeds the threshold value [16–18]. Concerning

phase behaviors, the projection of the translational symmetry on the onset of nematic-to-smectic transition significantly influences the conformation of the polymer; it flattens the overall shape in the longitudinal direction and hence induces a pretransitional effect [2,19,20]; thus the phase behavior becomes nonmonotonic. To date, works on the smectic solids and their characterizations are largely indebted to experimental studies such as small-angle x-ray scattering (SAXS) based observation, and supplemented only by a few physical and numerical simulation results. For example, the mechanical instability upon mechanical loading is investigated with respect to mechanical property [17], and implemented to the numerical model via quasiconvexation [18]. Nevertheless, studies on phase behaviors and especially on light-driven behaviors are largely unfound, thereby rendering both the understanding and design of smectic-solid based systems imperative. We therefore employ a finite-element-based approach for the phase behavior of the smectic solids with the following considerations: (i) As in the studies on nematic solids [21,22], a direct relation between stimuli and mechanical responses must be established by multiphysical stimuli-order constitutive coupling; (ii) bending is a dominant deformation model upon irradiation; the method should be capable of simulating large deformation along with rigid-body motion to consider bending, twisting, etc.; and (iii) in addition to stimuli responsiveness, the method should provide users with sufficient space to design the material, both macroscopically and microscopically (e.g., spatially distributed mesogen).

This paper is organized into two sections: (1) Background and (2) Results and Discussions. In the first section, we present a formulation of the finite-element-based framework, which incorporates the multiphysical coupled constitutive equations into the geometrically nonlinear finite element method. In the first part, the Landau model of smectic-nematic-isotropic phase transition based on the order parameter description of the LC phases is briefly introduced, followed by the formulation of the tensorial constitutive equation via the variational principle, where the free energy of the smectic solids and material incompressibility are considered. Next, the constitutive equation is combined with the faceted shell finite element, of which nonlinearity is reflected by corotational formulation. In the Results and Discussions section, we first describe a parametric study on the phase-induced mechanical changes of the smectic solids by changing the presynthesis and postsynthesis conditions. The quasisoftness provoked in photomechanical behavior and director-dependent behavior is also presented, demonstrating the need for the comprehensive framework of the material. Lastly, the geometric nonlinearity of the light-induced deflection is discussed by comparing with the linear solution.

II. BACKGROUND

In this chapter, we describe the theoretical background of the present work. Firstly, the order parameters that characterize each LC state are briefly introduced. Their thermotropic phase change is considered by means of the polynomial Landau model, which is simple yet efficient for simulating phase transitions. Being pivotal to understanding the mechanical coupling between the LC state and the structure, the shape

parameter r that parametrizes polymeric conformation is also described in terms of order parameters and experimental findings [22,23] on smectic solids. Lastly, the constitutive relationship that incorporates the shape parameter into the stress strain is derived by the variational principle with the strain energy of smectic- A solids. The combination of the constitutive equation and nonlinear finite element formulation is described hereafter, where a short review of the corotational formulation is given with a description of the flat, faceted shell element regarding photomechanics.

For smectic- A liquid crystals, their mesogenic order is commonly described by two types of symmetries: rotational and translational. A scalar orientational order s parametrizes the degree of alignment of the chromophores with respect to their average direction, provided that biaxiality is not provoked; the tensorial format of orientational order $\underline{Q} = \text{diag}(-s/2, -s/2, s)$ is also frequently used. On the other hand, the translational symmetries, which require a periodic function that accounts for the spacing between each layer and the layer normal, are commonly described by the complex scalar order parameter [24–26] in Eq. (1).

$$\psi = \rho_o \exp(i\vec{q} \cdot \vec{x}). \quad (1)$$

An order parameter ψ of position $\vec{x}$ is defined by an amplitude of density modulation ρ_o , and a real density wave phase $\vec{q}$. In smectic- A liquid crystal, there is no tilting between layer normal and mesogenic alignment; we therefore reduce $\vec{q} \cdot \vec{x}$ into $q_o \vec{n} \cdot \vec{x}$, in terms of the scalar layer spacing q_o and the director $\vec{n}$. Equation (2) describes the values of order parameters for each given phase.

$$\begin{aligned} s = 0, \quad \rho_o = 0, \quad q_o = 0 &: \text{isotropic}(I), \\ s \neq 0, \quad \rho_o = 0, \quad q_o = 0 &: \text{nematic}(N), \\ s \neq 0, \quad \rho_o \neq 0, \quad q_o > 0 &: \text{smectic}(\text{Sm-}A). \end{aligned} \quad (2)$$

In order to comprehend the first order phase transition between each state, various models have been proposed since the work of McMillan *et al.* [24], which utilizes the modified Maier-Saupe nematic model (see Ref. [26] for a comprehensive review on a theoretical model for the multiphase model). In the present work, we employ the simple polynomial Landau model; it is not only theoretically practical due to the energetic convexity given that the parameters abide by the numerical constraints, but it can also be extended to reflect the variants of the LC composition such as molecular flexibility and external field. An adapted form of the recent work on unified phase transition [25] is presented in Eq. (3) as a Landau model; it models the comprehensive transitions between smectic (Sm), nematic (N), and isotropic (I), and even their tricritical points.

$$\begin{aligned} F[\underline{Q}, \psi] &= \int_{\Omega} \sigma_{\text{LdG}}(\underline{Q}) + \sigma_{\text{el,sm}}(\nabla \psi) + \sigma_{\text{sm}}(|\psi|) \\ &\quad + \sigma_{n,\text{sm}}^{(1)}(\underline{Q}, |\psi|) + \sigma_{n,\text{sm}}^{(2)}(\underline{Q}, \nabla \psi) d\mathbf{v} \\ &= \frac{2}{9} \{3as^2 - bs^3 + cs^4\} + \{b_1 \rho_o^2 q_o^2 + b_2 \rho_o^4 q_o^4\} \\ &\quad + \{\tilde{a} \rho_o^2 + \tilde{c} \rho_o^4\} + \frac{2}{3} \{-\tilde{b} \rho_o^2 s^2 + e \rho_o^2 q_o^2 s\}, \end{aligned} \quad (3)$$

where σ_{LdG} , $\sigma_{\text{el,sm}}$, σ_{sm} , and $\sigma_{n,\text{sm}}$ refer to the Landau-de Gennes energy in the nematic state, elastic-smectic coupling, smectic, and nematic-smectic coupling energy. These penalize a nematic phase transition, a layer dilatation, an onset of smectic phase, and a nematic-smectic transition, respectively. Note that liquid crystal distortion energy (i.e., Frank elasticity) is not considered and ρ_o , q_o , and s are presented as the variables of functional F in polynomial form because the phase behavior, in which directional distortions of LC are assumed to be negligible, is the primary consideration of the present work; hence the director distortion within the layer [16,17] and the self-organizing effect of the directors are not an objective of the present work. However, it is worth noting that such LC elasticity must be taken into account whenever the alignment is distorted significantly, such as the inner coupling between mechanical load and mesogen distribution [27–29] or schlieren texture [2], because the present assumptions are violated due to the nonzero $\nabla \vec{n}$ that affects $\nabla \psi$. Moreover, by ruling out the Sm-C consideration, the numerical nonconvexity (e.g., chevron distribution) that stems from energy invariance regardless of the tilting direction is not considered herein. Considering the aforementioned assumptions and schematics, the present phase transition free energy is easily computed with either numerical optimization or analytic approaches. Following Ref. [25], the constitutive parameters are assumed to consider (1) the existence of solutions and (2) thermotropic Sm-A-N-I transition upon critical temperatures, T_{NA} (N-Sm-A transition) and T_{NI} (N-I transition).

$$\begin{aligned} b > 0, \quad c > 0, \quad b_2 > 0, \quad \tilde{c} > 0, \quad \tilde{b} > 0, \quad c > 0, \quad e \leq 0, \\ \tilde{a} = \hat{a}(T - T_{NA}) + \frac{2}{3}\tilde{b}s_+^2, \quad b_1 = \hat{b}(T - T_{NA}) - \frac{2}{3}es_+, \\ a = a_o(T - T_{NI})\hat{a} > 0, \quad \hat{b} > 0, \quad a_o > 0. \end{aligned} \quad (4)$$

Figure 1 exemplifies the evolution of the order parameters during temperature change; a detailed description of the parameters is given in Table I.

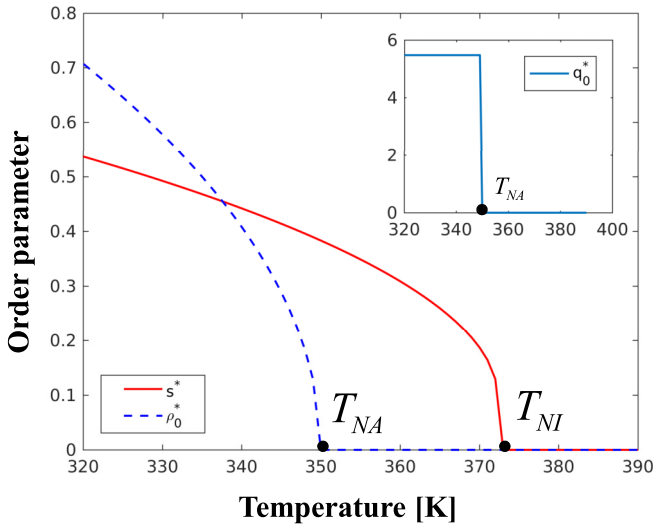


FIG. 1. Order parameter s^* , ρ_o^* , q_o^* with increasing temperature; first order phase transition is observed due to assumed Landau form of free energy.

TABLE I. Constitutive parameters for Landau-formulation for phase transition.

Parameter	Value	Parameter	Value
a_o	1	b_2	100
b	100	$\tilde{c}$	3000
c	400	T^*	370
$\hat{a} = \hat{b}$	400	T_{NA}	350

However, two aspects of the evaluation of the order parameter need to be improved. Firstly, even though the constitutive parameters presented in Table I are carefully selected in order to retain the order parameters within the acceptable range found in the experiment [24], the parameters still need to be evaluated by either fitting from the experiment or low-scale *in silico* simulation in order to improve their physical accuracy. Additionally, the transitions between Sm-A-N and N-I are both first order, marked by the C^0 continuity in the graphs, which differ from the experimental results on polymerized mesogens [30], where the formation of the symmetries is attenuated by the presence of the vicinal polymeric chains.

Concerning the light-induced effect, we employ a classical dilution model [Eq. (5)], by which the characteristic temperatures for phase transition (T_{NI} and T_{NA}) are assumed to decrease in linear proportionality by the ratio of *cis* molecules based on the reduction of the rigidity of the chromophores due to *trans*-to-*cis* isomerization [2,23].

$$T_{NI}(I) = T_{NI}^0 - \beta n_{\text{cis}}(I), \quad T_{NA}(I) = T_{NA}^0 - \beta n_{\text{cis}}(I). \quad (5)$$

In addition, the evolution of the *cis* molecules for the given light intensity and heat is modeled in population dynamics shown in Eq. (6), wherein light-induced *trans*-to-*cis* isomerization determined by the absorption rate Γ and light intensity I competes with the constant-rate recovery explained by *cis* lifetime τ^{-1} . In this work, the steady-state value of the *cis* population ratio is also obtained in terms of effective light intensity I_{eff} .

$$\dot{n}_{\text{cis}} = (\Gamma I)n_{\text{trans}} + \tau^{-1}n_{\text{cis}}, \quad (6a)$$

$$n_{\text{cis}}^\infty = \frac{\tau \Gamma I}{1 + \Gamma \tau I} \triangleq \frac{I_{\text{eff}}}{1 + I_{\text{eff}}}. \quad (6b)$$

It is worth noting that the present light-temperature-order model is largely indebted to various fields such as polymer physics (the freely jointed model), phase-transition theory, light decay, etc. The basic formula, therefore, offers much room for improvement because it is a field that undergoes rapid improvement due to the advance of low-scale *in silico* experiments [31] and multiscale description [32,33] as demonstrated in the case of nematic solids.

In the present work, the normal layer of the liquid crystal's lamellar form and nematic director remains coaxial since the smectic-A solid is considered; a uniaxial shape conformation (i.e., shape parameter r) that is defined by the square of the ratio between the principal radii of gyration is therefore similarly used. Following the nematic description, the conformation matrices are described by r [22] and nematic description $\vec{n}$. However, determining the shape parameter found in the

smectic solid is nontrivial. The statistically based shape parameter, as in the nematic case, is not obtained due to the translational symmetry; in the nematic case, mesogenic distribution is parametrized by a unit sphere, whereas the smectic case requires an additional two variables for amplitude and wavelength. Therefore, in the present work, the shape parameter of the nematic case, $r_n = 1 + 3s$, is modified by considering additional constraints found in the experiment [20] and by definition of order parameters [25]. First, the sign invariance of ρ_o is required, as a sign of the ρ_o is trivial as shown in Eq. (1). Also, the pretransitional effect between Sm-A and N, which flattens the uniaxial anisotropy, must be reflected, although it should increase as the temperature decreases in either the deep-smectic-A or the nematic regime. Lastly, the right-handed limit of the orientational order parameter of $s^+ \equiv \lim_{T \rightarrow T_{NI}} s$ must be included in the model, in order to build a shape parameter that comprehensively explains both the Sm-A-N-I transition and the Sm-A-I transition. The resulting shape parameter is described in Eq. (7),

$$r(s^*, \rho_o^*, q_o^*; \alpha, \beta, \gamma) = 1 + 3\alpha s^* - \beta s^+ \left[\frac{1}{\{1 + \exp(-\gamma |\rho_o^*| q_o^*)\}} - 0.5 \right]. \quad (7)$$

Here, the asterisk indicates the minimizers of smectic phase free energy, and the parameters with greek letters (α, β, γ) are tunable variables where α is 1 when a freely jointed chain is assumed. It is worth noting that shape parameters can be obtained either by experiment or full-atomistic multiscale simulation. For the sake of brief simulation, we assume $\alpha = \beta = \gamma = 1$. Note that the pretransitional flattening effect is considered to be caused by the shifting of the sigmoid function by -0.5 , which is zero in either the nematic or isotropic case (i.e., $\rho_o^* = q_o^* = 0$) and rapidly settles to βs^+ . In contrast to the Heaviside step function, the present term retains C^1 continuity for all real domains. This is not only beneficial to the continuity of the shape function, but it also mitigates the abruptness of the first order phase transition, thereby removing unphysical “jumps” during the photomechanical analysis. It is also worth noting that such a trait is also favored in analytic differentiation in gradient based analysis such as optimization [34].

Concerning the constitutive equation, the elastic energy of the smectic-A solid f_{el} [17] is considered as well as the incompressibility condition. The total potential energy

functional is constructed as in Eq. (8).

$$\Pi = f_{el}(\underline{\lambda}, \vec{n}_o, r_o, r) - p[\det(\underline{\lambda}) - 1]. \quad (8)$$

$\underline{\lambda}$ is a deformation gradient and p is a Lagrange multiplier for constraint $\det(\underline{\lambda}) \equiv J = 1$. By statistical modeling of the cross-linking points of polymer strands lying on the LC lamellar layer, a neoclassical form of the smectic-A free energy is presented in Eq. (9).

$$f_{el} = \frac{\mu}{2} \text{tr}(\underline{\lambda}^{-1} \underline{\lambda} \underline{\lambda}_o^T) + \frac{B}{2} (|\underline{\lambda}^{-T} \cdot \vec{n}_o|^{-1} - 1)^2, \quad (9)$$

where μ and B are the shear and layer modulus, respectively; $|\cdot|$ indicates an L^2 norm. The first term corresponds to a trace formula found in Verwey-Terentjev-Warner (VTW) energy, whereby anisotropic neo-Hookean material is analyzed. Without biaxiality, the shape tensors $\underline{\lambda}$ and $\underline{\lambda}_o$ are uniaxial and serve as metric tensors [21] and thus are positive definite. Equation (8) describes such a metric, comprised of a shape parameter r and a layer normal $\vec{n}$, where subscript o indicates that they are reference properties.

$$\underline{\lambda}_o = \underline{g}_o = r_o^{-1/3} [\underline{I} + (r_o - 1) \vec{n}_o \otimes \vec{n}_o], \quad (10a)$$

$$\begin{aligned} \underline{\lambda}^{-1} &= \underline{g}^{-1} = r^{1/3} [\underline{I} + (r^{-1} - 1) \vec{n} \otimes \vec{n}] \\ &= r^{1/3} [\underline{I} + (r^{-1} - 1) |\underline{\lambda}^{-T} \cdot \vec{n}_o|^{-2} \underline{\lambda}^{-T} (\vec{n}_o \otimes \vec{n}_o) \underline{\lambda}^{-1}]. \end{aligned} \quad (10b)$$

Note that an affine transformation from the reference to the deformed coordinate is assumed in the layer normal vector; the rotated layer normal is $\vec{n} = \underline{\lambda}^{-T} \vec{n}_o / |\underline{\lambda}^{-T} \vec{n}_o|$, while $1/|\underline{\lambda}^{-T} \vec{n}_o|$ is the layer-to-layer distance dilatation. It is worth to remark that the present hypothesis is valid as long as the phase behavior of the material is the regime of interest, where the nonconvexity of the energy is not evoked due to mechanical loading; otherwise, the layer rotation must be penalized by LC distortion energy (i.e., Frank-Oseen elasticity), such as the inner coupling that induces free soft modes of LC rotation.

A governing equation of mechanical equilibrium is derived as in Eq. (11), where $\underline{P}$ and $\underline{\sigma}$ are the first Piola-Kirchhoff (P-K) and Cauchy stresses, respectively (see Appendix A for detailed derivation).

$$\begin{aligned} \frac{\partial \Pi}{\partial \underline{\lambda}} &= \underline{P} = \left\{ \begin{aligned} &\mu \underline{g}^{-1} \underline{\lambda} \underline{g}_o + \mu r^{1/3} (r^{-1} - 1) [(\vec{n} \cdot \underline{\lambda} \underline{g}_o^T \cdot \vec{n}) (\vec{n} \otimes \vec{n}) \underline{\lambda}^{-T} - (\vec{n} \otimes \vec{n}) (\underline{\lambda} \underline{g}_o)] \\ &+ B (|\underline{\lambda}^{-T} \vec{n}_o|^{-2} - |\underline{\lambda}^{-T} \vec{n}_o|^{-1}) (\vec{n} \otimes \vec{n}) \underline{\lambda}^{-T} \end{aligned} \right\} - p J \underline{\lambda}^{-T} \\ &= \left(\mu \left(\frac{r}{r_o} \right)^{1/3} \left\{ [\underline{\lambda} + (r_o - 1) \underline{\lambda} \vec{n}_o \otimes \vec{n}_o] + \frac{r_o(r^{-1}-1)}{|\underline{\lambda}^{-T} \vec{n}_o|^4} (\underline{\lambda}^{-T} \vec{n}_o \otimes \vec{n}_o \underline{\lambda}^{-1} \underline{\lambda}^{-T}) \right\} \right. \\ &\quad \left. + B (|\underline{\lambda}^{-T} \vec{n}_o|^{-4} - |\underline{\lambda}^{-T} \vec{n}_o|^{-3}) (\underline{\lambda}^{-T} (\vec{n}_o \otimes \vec{n}_o) \underline{\lambda}^{-1} \underline{\lambda}^{-T}) \right) - p J \underline{\lambda}^{-T}, \\ \underline{\sigma} &= J^{-1} \underline{P} \underline{\lambda}^T = J^{-1} \left(\mu \left(\frac{r}{r_o} \right)^{1/3} \left\{ [\underline{\lambda} \underline{\lambda}^T + (r_o - 1) \underline{\lambda} \vec{n}_o \otimes \vec{n}_o \underline{\lambda}^T] + \frac{r_o(r^{-1}-1)}{|\underline{\lambda}^{-T} \vec{n}_o|^4} (\underline{\lambda}^{-T} \vec{n}_o \otimes \vec{n}_o \underline{\lambda}^{-1}) \right\} \right. \\ &\quad \left. + B (|\underline{\lambda}^{-T} \vec{n}_o|^{-4} - |\underline{\lambda}^{-T} \vec{n}_o|^{-3}) [\underline{\lambda}^{-T} (\vec{n}_o \otimes \vec{n}_o) \underline{\lambda}^{-1}] \right) - p. \end{aligned} \quad (11)$$

As can be seen, the derived constitutive equations incorporate initial and current shape parameters, an initial director,

and a deformation gradient, demonstrating the optomechanical coupling considering that the shape parameter is a derivative

of the optical order parameters. Note that symmetries are found in the Cauchy-stress tensor, which is analogous to the nematic case wherein a coaxiality between $\underline{\underline{g}}$ and $\underline{\underline{\lambda}} \underline{\underline{g}} \underline{\underline{\lambda}}^T$ is given by a rotational equilibrium. In the present case, the strong constraints on the affine deformation of the layer normal generate such inexistence of inner coupling, thereby concluding that the material is non-Cosserat. Objectivity is then satisfied in both stress measures. It is worth noting that the present findings on the inner coupling do not necessarily indicate the uniqueness of the solution; the nonlinear model of the stretching-induced buckling instability [16,17] that avoids the layer undulation is equivalent to the zero-shear stress condition of the first P-K stress in Eq. (11), although it is not shown herein (see Appendix B for a comparison between the equation in Ref. [17] and the present equation).

In recent works, the aforementioned nonuniqueness of the solution was investigated in view of the evolution of the microstructure. Such complexity stems from the nonquasiconvex

governing potential; several methods have been proposed to circumvent the issue, such as quasiconvexation [27,28] and numerical relaxation [29]. The linearization scheme [22,32], although ruling out the unconstrained microstructure evolution (e.g., stress-free rotation of the mesogen), is proven to be sufficient whenever phase behavior is of interest. In contrast to the soft modes, for example, which consider mechanically induced mesogenic rotation, light-induced bending or heat-induced shrinkage does not provoke large-scale microscopic changes [2], possibly because they are similar to stress-free configuration for given eigenstress.

In this work, we therefore linearize the present nonlinear constitutive equation by the given assumptions: (1) Due to a substantially higher layer modulus than the shear one, the layer dilatation remains near 1; (2) the elongation tensor $\underline{\underline{\lambda}} - \underline{\underline{I}} = \underline{\underline{H}}$ is infinitesimal. The first and second assumptions are reflected by the assumed equalities presented in Eqs. (12a) and (12b), respectively.

$$\begin{aligned} \underline{\underline{\lambda}} \underline{\underline{\lambda}}^T &\cong \underline{\underline{I}} + \underline{\underline{H}} + \underline{\underline{H}}^T \cong 1 + 2\underline{\underline{\varepsilon}}, \quad \underline{\underline{\lambda}}^{-1} \cong \underline{\underline{I}} - \underline{\underline{H}}, \\ \underline{\underline{\lambda}}(\vec{n}_o \otimes \vec{n}_o) \underline{\underline{\lambda}}^T &\equiv (\vec{n}_o \otimes \vec{n}_o) + \underline{\underline{H}}(\vec{n}_o \otimes \vec{n}_o) + (\vec{n}_o \otimes \vec{n}_o) \underline{\underline{H}}^T, \\ &\cong (\vec{n}_o \otimes \vec{n}_o) + (\underline{\underline{\varepsilon}} + \underline{\underline{\omega}})(\vec{n}_o \otimes \vec{n}_o) + (\vec{n}_o \otimes \vec{n}_o)(\underline{\underline{\varepsilon}} - \underline{\underline{\omega}}), \end{aligned} \quad (12a)$$

$$\begin{aligned} \underline{\underline{C}} &\equiv \underline{\underline{\lambda}}^T \underline{\underline{\lambda}}, \quad |\underline{\underline{\lambda}}^{-T} \vec{n}_o| = \sqrt{\vec{n}_o \cdot \underline{\underline{\lambda}}^{-1} \underline{\underline{\lambda}}^{-T} \vec{n}_o}, \\ 1/\sqrt{\vec{n}_o \cdot \underline{\underline{C}}^{-1} \vec{n}_o}^4 &= 1 + 4(\vec{n}_o \cdot \underline{\underline{\varepsilon}} \cdot \vec{n}_o), \quad \sqrt{\vec{n}_o \cdot \underline{\underline{C}}^{-1} \vec{n}_o}^{-4} - \sqrt{\vec{n}_o \cdot \underline{\underline{C}}^{-1} \vec{n}_o}^{-3} = (\vec{n}_o \cdot \underline{\underline{\varepsilon}} \cdot \vec{n}_o). \end{aligned} \quad (12b)$$

By introducing scaled layer modulus $\hat{b} \triangleq B/\mu(r_o/r)^{1/3}$, the linearized constitutive equation is obtained as in Eq. (13).

$$\sigma = \mu \left(\frac{r}{r_o} \right)^{1/3} \left[\begin{aligned} &\underline{\underline{I}} + 2\underline{\underline{\varepsilon}} + (\vec{n}_o \cdot \underline{\underline{\varepsilon}} \cdot \vec{n}_o)(\vec{n}_o \otimes \vec{n}_o) \{ 4(\frac{r_o}{r} - r_o) + \hat{b} \} \\ &+ \{ \underline{\underline{\varepsilon}}(\vec{n}_o \otimes \vec{n}_o) + (\vec{n}_o \otimes \vec{n}_o) \underline{\underline{\varepsilon}} \} (2r_o - \frac{r_o}{r} - 1) \\ &+ \{ \underline{\underline{\omega}}(\vec{n}_o \otimes \vec{n}_o) - (\vec{n}_o \otimes \vec{n}_o) \underline{\underline{\omega}} \} (\frac{r_o}{r} - 1) \\ &+ (\vec{n}_o \otimes \vec{n}_o) (\frac{r_o}{r} - 1) \end{aligned} \right] - p \underline{\underline{I}}. \quad (13)$$

In contrast to the conventional stress-strain equation, the present constitutive equation contains both infinitesimal strain $\underline{\underline{\varepsilon}}$ and rotation $\underline{\underline{\omega}}$. A fourth term indicates an eigenstress induced by phase behavior, which is a function of the initial or current shape parameters and initial director.

In order to maintain flexibility with comprehensive smart actuation, LCP is frequently fabricated in the form of a thin strip [1,19,20]; a flat faceted shell is therefore formulated herein. We assume that the plane stress condition is applied in the z direction by assuming that both the nematic director and the layer normal found in the smectic LC are located within the x - y plane. The present assumed directions correspond to the alignment methods, by which the director remains in plane, as well as the principal modes of actuation such as uniaxial elongation and bending, driven by a gradient generated in the transverse (z) direction. Equation (14) shows the plane stress condition, whereby the Lagrange multiplier p is determined on the basis of incompressibility [i.e., $\text{tr}(\underline{\underline{\varepsilon}}) = 0$].

$$\begin{aligned} \sigma_{33} &= \mu \left(\frac{r}{r_o} \right)^{1/3} [1 + 2\varepsilon_{33}] - p \\ &= \mu \left(\frac{r}{r_o} \right)^{1/3} [1 - 2\varepsilon_{11} - 2\varepsilon_{22}] - p = 0, \\ \sigma_{3\alpha} &= 0. \end{aligned} \quad (14)$$

In conclusion, the constitutive equation of plane stress is derived as Eq. (15). The elastic term ($\sigma_{\alpha\beta}^e$) and eigenstress term ($\sigma_{\alpha\beta}^{\text{ph}}$) are found, where the greek indices range between integer 1 and integer 2.

$$\begin{aligned}\sigma_{\alpha\beta} &= \sigma_{\alpha\beta}^e(\xi, \omega, r, r_o, \vec{n}_o) + \sigma_{\alpha\beta}^{\text{ph}}(r, r_o, \vec{n}_o), \\ \sigma_{\alpha\beta}^e &= \mu \left(\frac{r}{r_o} \right)^{1/3} \left[2(\varepsilon_{11} + \varepsilon_{22})\delta_{\alpha\beta} + 2\varepsilon_{\alpha\beta} + (n_\gamma^o \varepsilon_{\gamma\eta} n_\eta^o) n_\alpha^o n_\beta^o \{ 4(\frac{r_o}{r} - r_o) + \hat{b} \} \right. \\ &\quad \left. + \{ \varepsilon_{\alpha\gamma} n_\gamma^o n_\beta^o + n_\alpha^o n_\eta^o \varepsilon_{\eta\beta} \} (2r_o - \frac{r_o}{r} - 1) + \{ \omega_{\alpha\gamma} n_\gamma^o n_\beta^o - n_\gamma^o n_\alpha^o \omega_{\gamma\beta} \} (\frac{r_o}{r} - 1) \right], \\ \sigma_{\alpha\beta}^{\text{ph}} &= \mu \left(\frac{r}{r_o} \right)^{1/3} (n_\alpha^o n_\beta^o) \left(\frac{r_o}{r} - 1 \right).\end{aligned}\tag{15}$$

In contrast to the nematic cases, shear modulus does not converge to 0 regardless of the ratio of the shape parameters. Such effect arises due to the rigid constraint on the layer normal, and indicates that shear-induced softness is significantly alleviated in the smectic case.

We now consider the finite element implementation for the given constitutive equation. The aforementioned thin strip model of the LCP is discretized by a standard triangular element. Each element contains internal variables such as order parameters and $\vec{n}$, which may vary greatly depending on the condition upon synthesis and actuation, even though it is more natural to define such director by each node, as their persistent length, which is up to a few microns [2], is often not comparable to mesh size and thus they undergo spurious discontinuity that crosses the element interface. In this regard, we only consider the uniform director distribution by which the discontinuity is not severe or is nonexistent.

A tensorial description obtained by linearization is directly incorporated into the classical finite element formulation of the plate, which is analogous to that of the functionally graded material. We only briefly describe the formulation, as the detailed formulation can be found in the literature [32]. At each element, Eq. (16) must be evaluated prior to the matrix assembly.

$$\begin{aligned}\delta W &= 0 = \int \delta(\bar{\varepsilon}_{\alpha\beta}^o - z\bar{\kappa}_{\alpha\beta} + \bar{\omega}_{\alpha\beta})(\bar{\sigma}_{\alpha\beta}^o + \bar{\sigma}_{\alpha\beta}^{\text{ph}}) d\Omega \\ &= \delta \bar{\mathbf{d}}_d \cdot \bar{\mathbf{K}}^e \cdot \bar{\mathbf{d}}_d - \delta \bar{\mathbf{d}}_d \cdot \bar{\mathbf{\Sigma}}^{\text{ph}},\end{aligned}\tag{16}$$

where $\mathbf{K}^e$ is the element stiffness matrix, $\mathbf{d}$ is the vector storing nodal degree of freedom $\bar{u}_d$ (displacement) and $\bar{\theta}_d$ (rotation), and $\mathbf{\Sigma}^{\text{ph}}$ is the resultant vector. The overbar of the matrices indicates that the specified tensors are defined by the elementwise manner, while subscript d indicates they are related to the pure deformation of the element; this notation is consistent throughout the present paper. Strain-displacement tensors that associate ε^o (in-plane strain), κ (curvature), and rotation (ω) to the nodal degrees of freedom are unique to the linear element; the optimal triangular element (OPT element) suggested by Felippa *et al.* [35] and the discrete Kirchhoff element (DKT element) by Batoz *et al.* [36] are used to consider the membrane and bending behavior of the three-dimensional (3D) manifold, respectively. A thickness integration is obtained by the following Simpson's rule, with the integration number higher than that of the nematic solids [32], since the present case involves greater complexity due to the definition of the shape parameter.

Such elementwise linear description is further investigated in terms of geometric nonlinearity: The bending phenomenon, a dominant feature of photoinduced deflection, is followed by

large element rotation that requires the nonlinear consideration. In this work, element-independent corotational formulation (EICR) that kinematically filters out local deformation from total displacement and rotation is used for several reasons. Firstly, the higher order element is easily implemented in the finite element, which enhances the accuracy of the solutions and the removal of the numerical treatment (e.g., reduced integration to alleviate the locking phenomenon). Secondly, the conventional polar decomposition approach can hinder both computational efficiency and programming procedure due to the complex gradient of higher order elements. In addition, the EICR is also beneficial to stimulate future works in terms of the mechanical design of actuators as analytic sensitivity has been reported in terms of geometric nonlinearity [37]

The filter of rigid-body motion is given as

$$\delta \bar{\mathbf{d}}_d = \begin{Bmatrix} \delta \bar{\mathbf{u}}_d \\ \delta \bar{\theta}_d \end{Bmatrix} = \bar{\mathbf{H}} \bar{\mathbf{P}} \mathbf{T} \begin{Bmatrix} \delta \mathbf{u} \\ \delta \phi \end{Bmatrix} = \Lambda \begin{Bmatrix} \delta \mathbf{u} \\ \delta \phi \end{Bmatrix},\tag{17}$$

where $\mathbf{u}$ and ϕ indicate the displacement and pseudovector, respectively, that account for the rotation that is defined in the global coordinate. A tensor Λ acts as a filter that extracts deformation $\delta \bar{\mathbf{u}}_d$ and pure deflection $\delta \bar{\theta}_d$, consisting of auxiliary matrices that sequentially execute frame transformation from the global to the element coordinate ($\mathbf{T}$), extraction of deforming portion ($\bar{\mathbf{P}}$), and the removal of the spurious gap between two pseudovectors ϕ and θ ($\bar{\mathbf{H}}$). A detailed description of these auxiliary matrices and kinematics is found in Ref. [38]. The aforementioned kinematics, consistent tangent stiffness tensor $\mathbf{K}$, and local residual force $\mathbf{R}$ are calculated as follows.

$$\begin{aligned}\Delta \mathbf{f} &= \mathbf{f}^i - \mathbf{f}^e = \mathbf{T}^T \bar{\mathbf{P}}^T \bar{\mathbf{H}}^T \bar{\mathbf{K}}^e \bar{\mathbf{H}} \bar{\mathbf{P}} \mathbf{T} \bar{\mathbf{f}}^e - \mathbf{T}^T \bar{\mathbf{H}}^T \bar{\mathbf{f}}^{\text{ph}} \\ &= \mathbf{T}^T \bar{\mathbf{P}}^T \bar{\mathbf{H}}^T (\bar{\mathbf{K}}^e \bar{\mathbf{d}}_d) - \mathbf{T}^T \bar{\mathbf{H}}^T \bar{\mathbf{f}}^{\text{ph}},\end{aligned}\tag{18}$$

$$\begin{aligned}\mathbf{K} &= \mathbf{K}^i - \mathbf{K}^e = (\mathbf{K}_{\text{GR}}^i + \mathbf{K}_{\text{GP}}^i + \mathbf{K}_{\text{GM}}^i + \mathbf{K}_M^i) \\ &\quad - (\mathbf{K}_{\text{GR}}^e + \mathbf{K}_{\text{GM}}^e),\end{aligned}\tag{19a}$$

with

$$\begin{aligned}\mathbf{K}_M &= \mathbf{T}^T \bar{\mathbf{P}}^T \bar{\mathbf{H}}^T \bar{\mathbf{K}}^e \bar{\mathbf{H}} \bar{\mathbf{P}} \mathbf{T} \quad \mathbf{K}_{\text{GR}} = -\mathbf{T}^T \bar{\mathbf{F}}_{\text{nm}} \bar{\mathbf{G}} \mathbf{T}, \\ \mathbf{K}_{\text{GM}} &= \mathbf{T}^T \bar{\mathbf{P}}^T \bar{\mathbf{L}} \bar{\mathbf{P}} \mathbf{T} \quad \mathbf{K}_{\text{GP}} = -\mathbf{T}^T \bar{\mathbf{G}}^T \bar{\mathbf{F}}_n \bar{\mathbf{P}} \mathbf{T}, \\ \mathbf{K}_{\text{GM}}^e &= \mathbf{T}^T \bar{\mathbf{L}}^e \bar{\mathbf{P}} \mathbf{T} \quad \mathbf{K}_{\text{GR}}^e = -\mathbf{T}^T \bar{\mathbf{F}}_{\text{nm}}^e \bar{\mathbf{G}} \mathbf{T}.\end{aligned}\tag{19b}$$

Note that projection matrix $\bar{\mathbf{P}}$ is removed for the following force term ($\mathbf{f}^{\text{ext}}$) because the rigid-body part of the load must be retained.

III. RESULTS AND DISCUSSIONS

In this section, we present various aspects of the phase behaviors of smectic solids. Materials deform to accommodate the internally generated stress owing to the change of the order of the parameters (i.e., degree of symmetries and anisotropy of the microscopic conformation). Equation (20) is a paraphrased relation that computes deformation u (midplane displacement) and θ (midplane rotation) for given shape parameter r found in Eq. (15); being a stress-free configuration, the solution of the equation is essentially equivalent to the eigen-strain problem frequently found in numerous multiphysical studies.

$$\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^{el}(u, \theta; r, r_o) + \sigma_{\alpha\beta}^{ph}(r, r_o) = 0. \quad (20)$$

It is worth noting that the constitutive relationship does not converge to the nematic case [22] when neither the reference nor the current states are in the smectic- A phase, due to the violations of the assumptions imposed on the smectic layer: affine deformation of the normal vector, and nonzero layer modulus. Therefore, the phase behavior analysis of the non-smectic- A solid, of which the cross-linked and reference traction-free states are nematic or isotropic is not carried out herein. Accordingly, a deep-smectic phase is assumed to be created upon cross-linking in all simulations (i.e., $T_o = T_{NA} - 30 \text{ K} = 320 \text{ K}$), while the operating temperature $T \in [320, 360]$ and effective intensity of incident light $I_{\text{eff}} \in [0, 2]$ vary. The temperature-induced effects other than phase behavior are ignored herein, as the behavior of the LCP is dominantly governed by polymeric conformation change when compared to thermal expansion [2].

A. Homogeneous phase behavior

Without light, the temperature increment uniformly changes the shape parameters, as in the order parameters (s^* , ρ^* , q^*) found in all material points. The thin strip thereby undergoes uniaxial shrinkage as shown in Fig. 2.

Upon heating, the length of the specimen shows a non-monotonic decrease as found in the experiment [19], wherein pretransitional anomalies are found between the smectic- A and

nematic phase; such behavior is already depicted in the shape parameter, of which the relation to deformation is illustrated in the inset of Fig. 2(b). The uniaxial change also agrees well with the one-dimensional (1D) material behaviors (marked by dots) based on the nonlinear equation directly originating from $\partial f / \partial \lambda = 0$, combined with the uniaxial deformation gradient $\tilde{\lambda} = \text{diag}(\lambda^{-1/2}, \lambda^{-1/2}, \lambda)$, where λ is a scalar valued extension. This demonstrated that the effect from assumptions made during formulation and linearization are found to be virtually negligible when layer modulus B is higher than 20, so that dilatation does not significantly deviate from unity. It is also worth noting that mechanically induced layer undulation (i.e., CMHH instability [16]), is not provoked as the phase behavior is stress-free behavior, and the elongation mode thus does not compete with the shear modes.

B. Light-induced bending of smectic solids

As a primary objective of the present work, light-induced deformation is also investigated via numerical simulations. A combination of multiphysical consideration and FEA is shown in Fig. 3, which is similar to that in the previous study on the steady-state light-responsive behavior of nematic solids; modifications have been made in the phase-transition computations, conformations, and constitutive equations.

Provided that two temperatures (cross-linking T_o and operation T) and the intensity of light irradiation I_{eff} are specified, the spatial distribution of the order parameters can be computed via a dilute model and light decay profile, which in turn computes the shape of the polymer conformation. Figure 4 shows the normalized light intensity and light-affected change of the internal properties; the gradients in the transverse direction, which originated from light decay, are essential to compute the light-induced curvature of the specimen.

Note that light decay follows the classical Beer's law, which is often substituted by the nonlinear Lambert-W function that describes the photobleaching effect [39] as there is no experimental evidence of such phenomena in smectic solids. Nevertheless, the derivatives of light, such as n_{cis} and r , possess

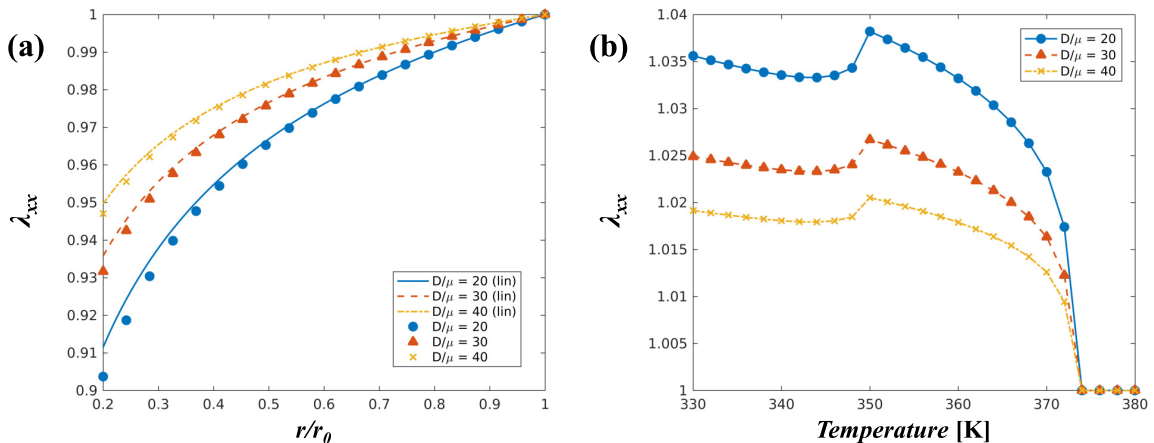


FIG. 2. Uniaxial shrinkage due to phase change of the smectic solids with different layer modulus D : (a) Length change vs changing shape parameter r ; (b) length change vs operating temperature. Nonmonotonic shrinkage is observed, as shown in the experiment [19,20].

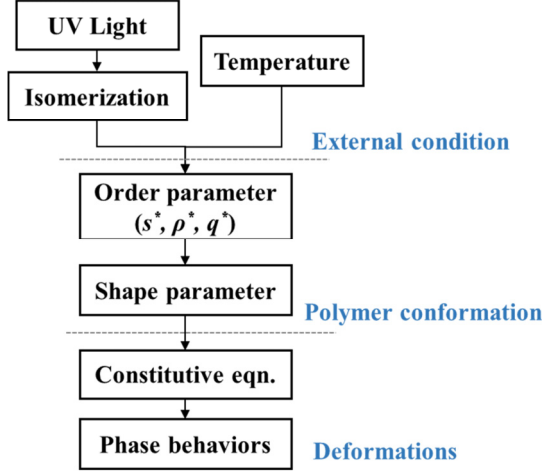


FIG. 3. Flowchart of the photomechanical analysis on smectic solids, which is a combination of microscopic polymeric conformation and finite element analysis (marked by deformations).

nonlinear thickness-varying profiles. In addition, a sigmoid term found in the shape parameter in the pretransitional regime generates a nonmonotonic form. The Simpson's numerical integration thus requires more integration points than in the nematic case, which is 150, in order to avoid smoothing of its characteristic profile and to preserve the physical quantities and gradients that are pivotal to determine the bending profile and its curvature. In this work, the integration point of more than 240 is proven to be sufficient to yield nondependency to a number of the points. However, the increase of the computational load is not significant since the material integration is only taken for each increment, which is at most 40 when we implement adaptive step length control [32].

The dimensions of the smectic-A strip are $20 \text{ mm} \times 1 \text{ mm} \times 500 \text{ }\mu\text{m}$ by length (L) $\times$ width (W) $\times$ thickness (h), respectively, in which the length-to-thickness ratio is higher than 20 to retain the validity of the thin-plate assumption. We use 1280 mesh, the size of which is assumed to be uniform. We assume that the left boundary ($x = 0$) is clamped, while the director vector is $\{1, 0, 0\}^T$, which is in the longitudinal direction. We also set $\mu = 1.5 \text{ GPa}$, $B/\mu = 20$, and $d/h = 0.4$; these material properties are fixed hereafter, unless otherwise specified.

1. Temperature-alternating bending direction

Due to the gradients generated in the out-of-plane direction, the thickness-varying modulus and the eigenstress are present, which are analogous to the functionally graded material (FGM). Consequently, an out-of-plane deflection in agreement with the boundary conditions is generated. Figure 5 illustrates the light-induced bending in terms of the curvature with various temperatures and penetration depths. A deflection curve evaluated at the middle of the width ($y/W = 0.5$) is well fitted using the quadratic polynomial function ($\|\text{goodness of fit}\| \sim 0.99$); Eq. (21) computes the principal curvature at the center of the specimen.

$$u_z = a_i x^i, \quad 0 \leq i \leq 3; i \in \mathbf{Z},$$

$$\kappa(x = L/2) = u''_z(x = L/2)/[1 + u'_z(x = L/2)^2]^{3/2}. \quad (21)$$

As shown in Figs. 5(a) and 5(b), the profiles of bending curvature with light increment exhibit salient nonlinearity and nonmonotonicity. In terms of the operating temperature T that ranges from $T_{NA} - 30 \text{ K}$ to $T_{NA} + 10 \text{ K}$, three different regimes are found as we increase the temperature: smectic dominant, pretranslational, and nematic dominant. If the diluted transition temperature remains higher than the operating temperature T ($T < 330 \text{ K}$), the curvature is proportional to the irradiation; an increase of the degree of symmetry is directly reflected in the shape parameter. Upon an increase of the temperature below T_{NA} , the curvature profile reverses: It first bends away from the incident direction at low intensity, and bends towards the light at a higher intensity. Such phenomenon originates from the assumption of the shape parameter that bears the sigmoid term which reflects the pretransitional state. Finally, the photomechanical behavior of the smectic solids operating above the T_{NA} exhibits a consistent bending direction. Such temperature-dependent bending phenomenon agrees well with the experimental reports on smectic-A liquid crystal polymer [19] that undergoes sequential phase transition from smectic-A, to nematic, and then to isotropic. The transition points of the slope also agree, whereby the T at the material points partially becomes higher than T_{NI} (i.e., isotropic) due to the dilution of the T_{NI} temperature. The curvature slope obtained thereafter is analogous to that of the nematic-isotropic photomechanical behaviors reported in previous work [32].

The penetration depth of the light is also investigated parametrically by fixing the operating temperature at 330 K,

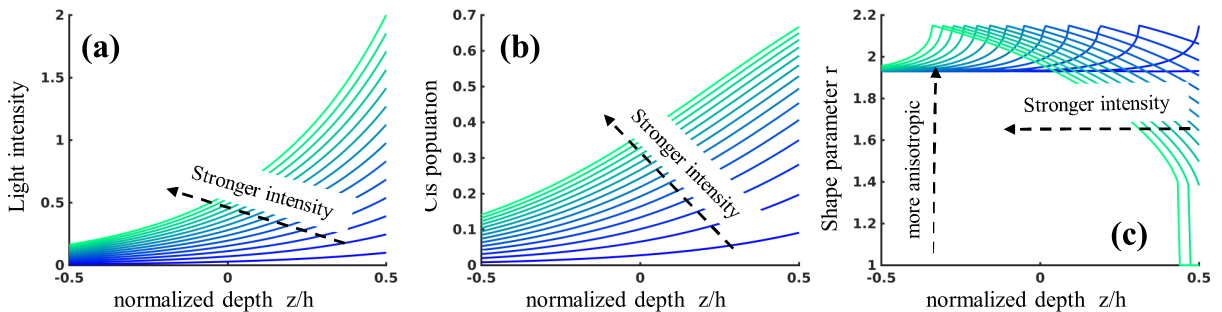


FIG. 4. Profile of light-induced derivatives in out-of-plane direction. (a) Decay of the light intensity depending on Beer's law; (b) steady-state *cis* population n_{cis} ; (c) shape parameter r , wherein monotonicity is observed.

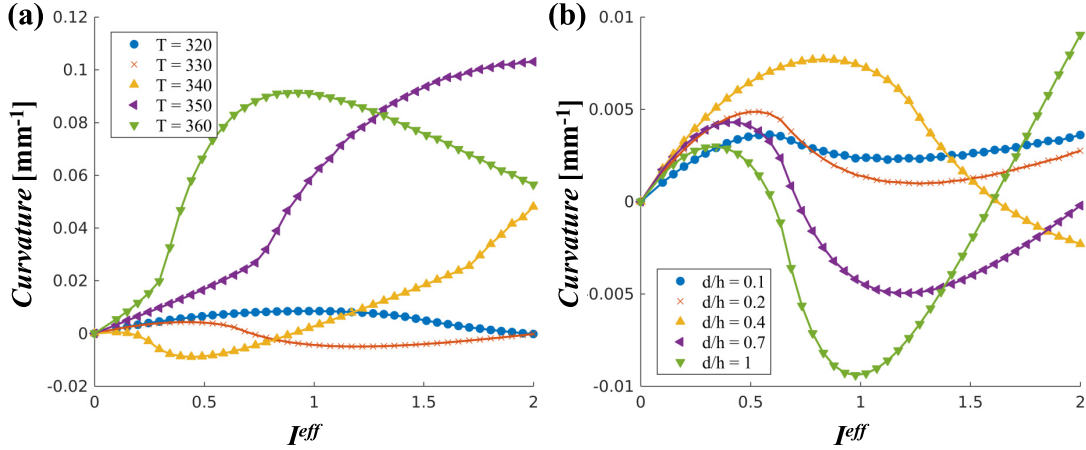


FIG. 5. Temperature dependence of photoresponsive behavior with increasing light intensity in terms of curvature. (a) Temperature variation with fixed penetration depth ($d/h = 0.4$) and (b) variation of penetration depth d with fixed temperature ($T = 330$ K).

which shows the aforementioned alternating bending direction as it is within the intermediate regime. Upon an increase in the penetration depth, by which light travels further into the material, a stronger gradient of the conformation is developed, as demonstrated by the large deviation between the two bending curvatures at the maximal bending away from and bending toward the light.

For each photomechanical computation, the local rotation of the layer normal (ϕ) as an auxiliary parameter is also investigated. It is not only an important observation in optics (e.g., polarized microscopy), but also serves well in

demonstrating the quasisoftness of the material [22]. Obtained from Eq. (22), the profile of ϕ with respect to the light intensity and spatial locations (A, B, and C) are plotted in Fig. 6. Note that the local rotation possibly changes the elasticity of the LC layers and alignments, which is often considered in terms of Frank elasticity, which is assumed to be negligible in the present work due to the infinitesimal rotation induced by phase transition and the nonconvex nature of the energy. If such elasticity is included within the model, we presume that the rotation is further restrained due to penalization. Hence the rotation presented in the present study must be considered as

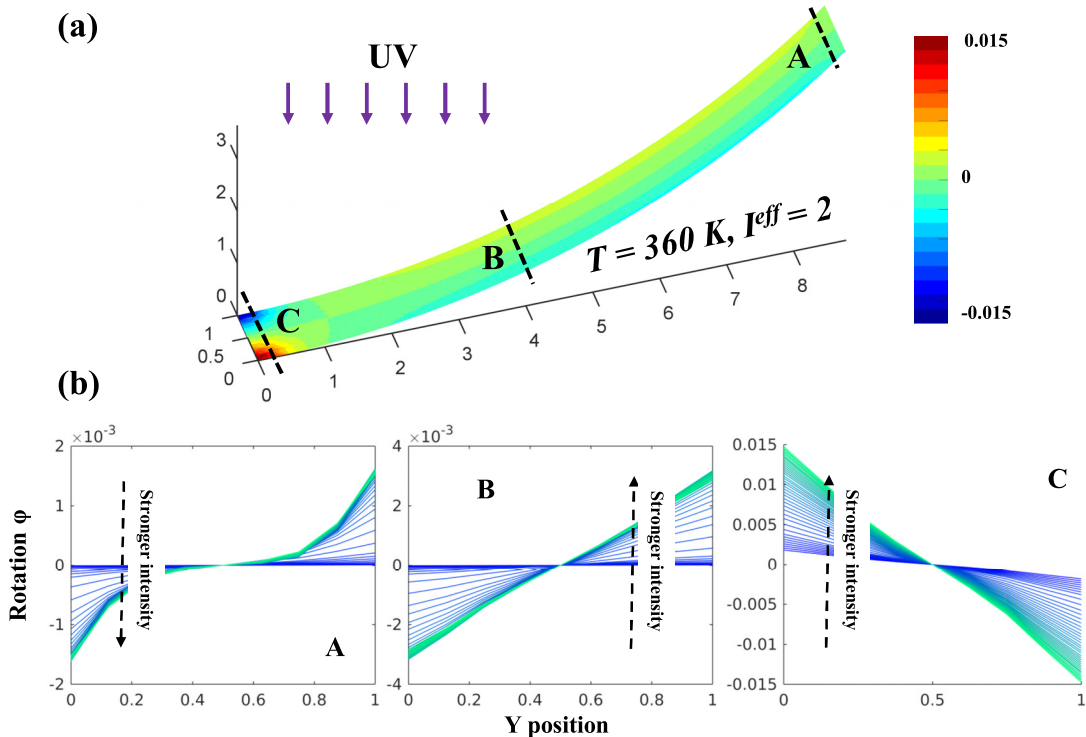


FIG. 6. (a) Deformed profile and the local rotation ϕ of the smectic solid with given stimuli ($T = 360$ K, $I^{\text{eff}} = 2$), and (b) profile of the rotation with increasing light intensity and greater nonlinearity.

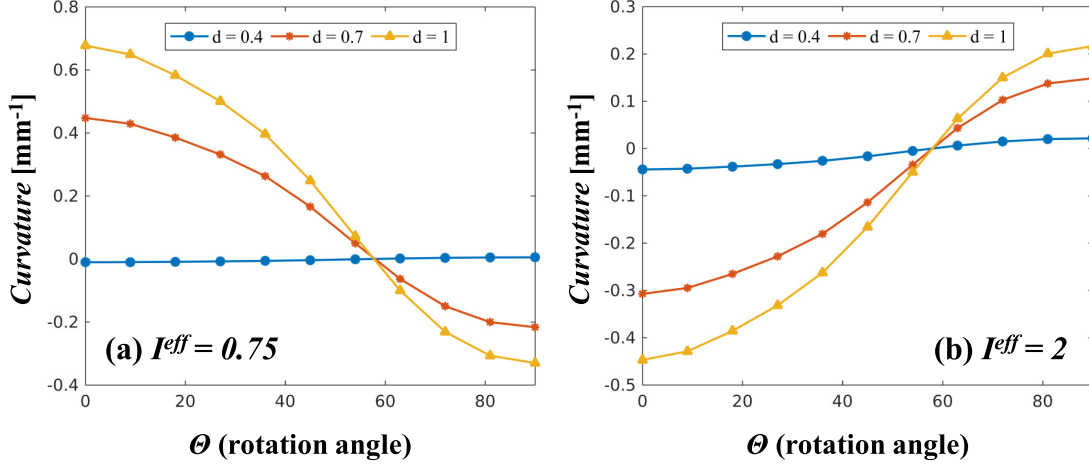


FIG. 7. Alternation of the bending curvature depending on the uniformly deviated angle θ between layer normal $\vec{n}$ and the longitudinal direction, with fixed temperature $T = 330$ K. The bending direction is found to be strongly dependent on intensity and θ .

the upper bound, given that only a phase behavior is provoked by either thermal or optical stimuli.

$$\begin{aligned}\vec{n} &= \{\cos \phi, \sin \phi\}^T \\ &= \hat{\lambda}^{-T} \vec{n}_o / |\hat{\lambda}^{-T} \vec{n}_o| \hat{=} (1 - \xi) \vec{n}_o / |(1 - \xi) \vec{n}_o|. \quad (22)\end{aligned}$$

As shown in Fig. 6(a), the rotation is found to be distributed inhomogeneously in the bent solid, where larger rotations (both positive and negative) are found near the clamped boundary. Such distribution accords with the shear strain distribution found in the bent plate that is subject to the clamped boundary, since ϕ is strongly dependent on the shear strain; such effects are therefore possibly analyzed only by considering the boundary conditions and not by the 1D beam model [22,31]. To further discuss the influence from the boundary condition, the three different locations [A: at the clamped base ($x/L = 0.1$); B: at the middle ($x/L = 0.5$); C: at the tip ($x/L = 1$)] are investigated. Upon the increase of light intensity, the rotation found at each position evolves. However, the gradient and signs of the rotation profile with respect to the y position (i.e., width direction) differ from each other. Especially, the profile found in position A has an inverse slope, and a magnitude that is one order higher than the others; such behavior demonstrates the boundary effect, which is analogous to the Saint-Venant boundary layer. It is worth again noting that such distribution of the rotation is one of the pivotal properties in optics, as it changes the amount of opacity of the material. Even though no experimental proof has been provided to date, the authors believe that (1) the opacity of the specimen is not evenly distributed after bombardment of the UV light, and (2) such distributions are strongly correlated with the boundary conditions, both of which are easily validated through a polarized microscope.

Conversely, the director change specified in the presynthesis state also produces prominent changes in deflection. As an anisotropic material, the longitudinal axis of the specimen may not necessarily be coaxial to the layer normal; such deviation, for example, is possibly created by cutting out the specimen that is in a nonparallel direction to the rubbing direction (i.e., monodomain direction). The change of principal bending

behavior is demonstrated in Fig. 7, where θ indicates the prescribed angle difference between the layer normal $\vec{n}_o$ and a longitudinal axis (i.e., $\vec{n}_o = \{\cos \theta, \sin \theta\}^T$). The magnitude of deflection is strongly alternated when θ changes from 0 to $\pi/2$, whereby the principal bending direction is rotated and thus bending-twisting coupling is generated. As discussed in Fig. 7, a deflection generally increases proportional to d , while the direction of deflection is determined by light intensity when the operating temperature is selected within a range that provokes the pretransitional effect. It is worth noting that such finding is analogous to the experimental results [19] and steady-state solution [32] of nematic solids, although the point where zero deflection (i.e., purely twisting deformation) differs due to the nonmonotonic profile of the shape parameter. The present findings suggest that the direction of cutting is an efficient design parameter to determine the mode of deflection, and the meticulous selection of temperature and light intensity is critical.

2. Effect of geometric nonlinearity

Finally, the influence of geometric nonlinearity on the solution is also demonstrated in Fig. 8, wherein the curvatures computed from linear (dot) and nonlinear (line) finite element solutions are presented.

Even though the curvature itself is within 0.1 mm^{-1} for all explored ranges of light intensity and temperature, its deviation in percentile is proven to be substantial, which means we might severely underestimate the curvature of the light-responsive smectic solid if a linear solution is employed. As in nematic solids, nonlinearity is generally proven to be substantial when the magnitude of curvature increases. The use of a nonlinear finite element solution is therefore recommended, regardless of the operating condition, as the direction and the magnitude are strongly nonmonotonic, and thus estimating their peak values is nontrivial. Otherwise, we might produce an incorrect estimation to the point where the sign of curvature changes. Moreover, such overestimation can produce error in the internal parameters as shown in the inset in Fig. 8, wherein the linear case shows a more dramatic contrast of the rotation as shear strain near the tip is strongly influenced by the rigid-body rotation. Considering that rotation

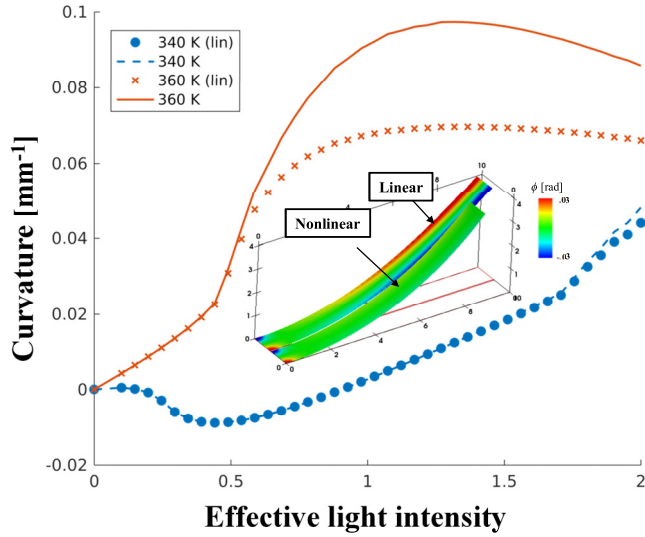


FIG. 8. Effect of nonlinearity depending on the temperature and intensity (inset) of the bent geometry of the smectic solid, where the rotation ϕ is marked by the color on the surface. The overestimation of the curvature and rotation is observed when nonlinearity is not taken into account.

ϕ is pivotal in the optical characterization of solids, the linear solution might cause severe degradation of the computation. Although not shown herein, this finding is in the same line with that of the curvature evaluated at the clamped end, and the maximal deflections are overestimated in the linear case. Moreover, these deviations are alleviated when simply supported boundary conditions are imposed.

IV. CONCLUSION

By transferring the geometric symmetries of rigid rods to the polymeric networks, liquid crystal polymers exhibit alternating anisotropy as a response to external photothermal stimuli. Such smart behaviors imply many attractive applications such as remote-controlled actuation, by which such polymer has been investigated thoroughly in both experimental and numerical analysis in the past decade. Concerning the design of the behavior of the liquid crystal polymer, many of these works have revealed a considerable relationship between the trait of incorporated mesogens and mechanical behavior; the change from nematic (rotational symmetry) to smectic (rotational and translational symmetry) molecules demonstrates dramatic changes to the heat-induced elongation and light-induced bending, whereby the nonmonotonicity of the behavior with imposed stimuli is observed.

In this work, we suggested a finite element framework designed for a smectic solid, wherein a multiphysical constitutive equation is combined with a geometric nonlinear solution. For the constitutive relation, the thermomechanical modeling that bridges the local degree of order (i.e., order parameters) to the stress-strain constitutive equation is formulated by the variational principle along with the shape parameter postulation and Landau model of smectic-nematic-isotropic phase transition. The issues related to the nonquasiconvexity of the nonlinear material behavior are circumvented by linearization; the present modeling becomes suitable for

macroscopic phase behavior that is equivalent to a stress-free configuration of the given photomechanical eigenstress. The geometric nonlinearity is also considered by means of EICR as a wrapper of the constitutive tensorial equation; the significant bending behavior induced by light is thereby attributed to the composition of the rigid-body motion and deformation. The comprehensive analysis is therefore facilitated, as the large-scale macroscopic shape change is successfully related to the macroscopic change determined by the increase or decrease of the polymeric conformation r . Several interrelated behaviors shown in the smectic solid are presented in this work in order to demonstrate the simulation capability to consider the presynthesis and postsynthesis conditions, and the response of the material from optical and mechanical viewpoints.

We first investigated the phase behavior of a smectic-solid model in general; the thermal-induced shrinkage and light-induced bending are simulated as we change the strength of stimuli and presynthesis material properties. This demonstrates that the addition of translational symmetry changes the behavior of the smectic solid completely and nontrivially as the material undergoes nontrivial phase changes between smectic, nematic, and isotropic, which accords with the experimental observations [19,20]. Such findings imply that the smectic solid under meticulously selected operating conditions can produce nontrivial actuation such as an alternating direction, which is in contrast to the photomechanical behavior of nematic solid that only shows unidirectional actuation.

Next, a bidirectional relationship between the deflection and mesogen director is also investigated. On the one hand, a global change of the mesogen director, e.g., induced by the deviation of the cutting direction and rubbing direction, is shown to significantly change the deflection, where the deformation with respect to angle deviation differs considerably when we change the operating incident light. In addition, a local perturbation of layer normal is simulated as actinic light is irradiated on the surface. The boundary condition has been proven to play a dominant role in the macroscopic deflection; the quasisofterness of the director is found to depend significantly on the location of the material with respect to the clamped region. Similarly, the nonlinearity of the solution is discussed by elucidating the gap between linear and nonlinear solutions. This finding suggests that the geometric nonlinearity should be considered in order to estimate not only the deflection and curvature, but also the internal parameters of the light-responsive behavior of liquid crystal polymer.

Based on both the suggested formulation and the simulation results, it is concluded that the comprehensive finite element model presented herein can be the basis of the photomechanical behavior of smectic solids by meeting the following criteria: (1) 3D full sheet with arbitrary shape, boundary condition, and easily modeled operating condition; (2) geometric nonlinearity dominant in bending behavior is considered, which is vital in correct estimation of deflection and internal parameters; (3) complex phase behavior ensuring the thermotropic phase change of the smectic liquid crystal is modeled with the aid of Landau modeling; (4) quasisofterness of the material has been considered by constitutive modeling. In addition, our proposed framework considers the photomechanical behavior of smectic solids, which relates to the preceding works on polymer physics, phase transition, and multiphysical FEA.

The present study also has some limitations as follows. First, the framework must depend on the assumption that the material should be a thin strip, and its rigid chromophores should be homogeneous to the free layer, in order to retain the validity of the assumptions on the Kirchhoff plate and plane stress. Otherwise, the stress conditions and resulting formulations need to be reformulated from the beginning. Moreover, the LC layer elasticity must be taken into account as well, when the inner coupling between mesogen and external loading is of interest other than the phase behavior of the material, where the affine deformation mode of the director $\vec{n}$ is violated. In addition, the assumed deep-smectic phase upon synthesis must also be preserved, as the layer modulus remains nonzero throughout the present formulation and thus yields fictitious constraints when the material is nematic, or isotropic in the reference state. The decay of the modulus by power law [40] during smectic-to-nematic transition, for example, must be considered in order to build more comprehensive formalism. Lastly, many material parameters are only assumed due to the lack of experimental reports; for example, the constitutive parameters of Landau modeling must be explained by experimental phase-transition analysis. In this regard, the outcomes of the present study should be further examined by experiments such as the combination of polarized microscopy and photomechanical observation, which is not possible at present. However, the authors expect these experimental reports will soon be of value, because of the growing interest in smart, novel materials and rapid improvement in the stabilization of the smectic phase within the polymer.

ACKNOWLEDGMENT

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIP) (Grant No. 2012R1A3A2048841).

APPENDIX A: CAUCHY-STRESS DERIVATION

The total potential energy functional is constructed by combining Eqs. (8) and (9).

$$\Pi = \frac{\mu}{2} \text{tr}(\tilde{l}^{-1} \tilde{l}_o \tilde{l}^T) + \frac{B}{2} (|\tilde{l}^{-T} \cdot \vec{n}_o|^{-1} - 1)^2 - p[\det(\tilde{l}) - 1], \quad (\text{A1})$$

where an elastic energy part [first term on the right-hand side (RHS)] is described only by $\tilde{l}$ and $\vec{n}_o$, by employing affine deformation condition from Eq. (10).

$$f_{el} = \frac{\mu r^{1/3}}{2} \text{tr}[\tilde{l}_o \tilde{l}^T + (r^{-1} - 1)(\vec{n} \otimes \vec{n}) \tilde{l}_o \tilde{l}^T]. \quad (\text{A2})$$

Differentiation by $\tilde{l}$ of elastic energy is therefore

$$\frac{\partial}{\partial \tilde{l}} \left\{ \frac{\mu}{2} \text{tr}(\tilde{l}^{-1} \tilde{l}_o \tilde{l}^T) \right\} = \mu \tilde{l}^{-1} \tilde{l}_o + \frac{\mu r^{1/3}(r^{-1} - 1)}{2} \frac{\partial(\vec{n} \otimes \vec{n})}{\partial \tilde{l}} \tilde{l}_o \tilde{l}^T, \quad (\text{A3})$$

where several equalities are required as described below ($\vec{x}$ denotes $\tilde{l}^{-T} \vec{n}_o$).

$$\frac{\partial \lambda_{ij}^{-1}}{\partial \lambda_{pq}} = -\lambda_{ip}^{-1} \lambda_{qj}^{-1} \rightarrow \frac{\partial \lambda_{ij}^{-T}}{\partial \lambda_{pq}} = \frac{\partial \lambda_{ji}^{-1}}{\partial \lambda_{pq}} = -\lambda_{jp}^{-1} \lambda_{qi}^{-1}, \quad (\text{A4a})$$

$$\begin{aligned} \frac{\partial n_i}{\partial \lambda_{pq}} &= \frac{\partial}{\partial \lambda_{pq}} \frac{x_i}{|\vec{x}|} = -x_i \frac{x_m}{|\vec{x}|^3} \frac{\partial x_m}{\partial \lambda_{pq}} + \frac{1}{|\vec{x}|} \frac{\partial x_i}{\partial \lambda_{pq}} \\ &= n_p \lambda_{qm}^{-1} n_m n_i - n_p \lambda_{qi}^{-1}, \end{aligned} \quad (\text{A4b})$$

$$\frac{\partial x_m}{\partial \lambda_{pq}} = \frac{\partial \lambda_{ma}^{-T}}{\partial \lambda_{pq}} n_a^o = -\lambda_{ap}^{-1} \lambda_{qm}^{-1} \vec{n}_a = -x_p \lambda_{qm}^{-1}. \quad (\text{A4c})$$

In short, the first order derivative of elastic energy becomes

$$\begin{aligned} \frac{\partial f_{el}}{\partial \tilde{l}} &= \mu \tilde{l}^{-1} \tilde{l}_o + \mu r^{1/3}(r^{-1} - 1) \\ &\quad \times [(\vec{n} \cdot \tilde{B}_{\text{eff}} \cdot \vec{n})(\vec{n} \otimes \vec{n}) \tilde{l}^{-T} - (\vec{n} \otimes \vec{n}) \tilde{B}_{\text{eff}} \tilde{l}^{-T}], \end{aligned} \quad (\text{A5})$$

where $\tilde{B}_{\text{eff}}$ indicates an effective strain measure $\tilde{l} \tilde{l}_o \tilde{l}^T$ found in the literature on nematics [21,29].

The second term of the RHS of Eq. (A1) is also derived by employing the aforementioned equalities [Eq. (A4)].

$$\frac{\partial}{\partial \lambda_{pq}} \frac{B}{2} \left(\frac{1}{|\vec{x}|} - 1 \right)^2 = B \left(\frac{1}{|\vec{x}|^2} - \frac{1}{|\vec{x}|} \right) (\vec{n} \otimes \vec{n}) \tilde{l}^{-T}. \quad (\text{A6})$$

The Cauchy stress, $\sigma = \tilde{P} \tilde{l}^T / \det(\tilde{l})$, is therefore

$$\sigma = \left[\mu \tilde{l}^{-1} \tilde{B}_{\text{eff}} + \mu r^{1/3}(r^{-1} - 1) \{ (\vec{n} \cdot \tilde{B}_{\text{eff}} \cdot \vec{n})(\vec{n} \otimes \vec{n}) - (\vec{n} \otimes \vec{n}) \tilde{B}_{\text{eff}} \} + D(|\tilde{l}^{-T} \vec{n}_o|^{-2} - |\tilde{l}^{-T} \vec{n}_o|^{-1})(\vec{n} \otimes \vec{n}) \right] - p \tilde{l}. \quad (\text{A7})$$

Note that Eq. (A7) is reduced to

$$\begin{aligned} \sigma &= \mu \left(\frac{r}{r_o} \right)^{1/3} \left[[\tilde{l} \tilde{l}^T + (r_o - 1) \tilde{l}(\vec{n}_o \otimes \vec{n}_o) \tilde{l}^T] + \frac{(r^{-1} - 1)r_o}{|\tilde{l}^{-T} \vec{n}_o|^4} [\tilde{l}^{-T}(\vec{n}_o \otimes \vec{n}_o) \tilde{l}^{-1}] \right] \\ &\quad + D(|\tilde{l}^{-T} \vec{n}_o|^{-4} - |\tilde{l}^{-T} \vec{n}_o|^{-3}) [\tilde{l}^{-T}(\vec{n}_o \otimes \vec{n}_o) \tilde{l}^{-1}] - p \tilde{l}, \end{aligned} \quad (\text{A8})$$

which is a function of initial parameters and deformation gradient.

Frame invariance is guaranteed as $\sigma(\hat{R} \tilde{l}) = \hat{R} \sigma \hat{R}^T$ where $\hat{R}$ is the rotation matrix.

APPENDIX B: UNDULATION CONDITION AND SHEAR-FREE EQUIVALENCE

Let layer normal be parallel to y , and in-plane condition is employed within the x - z plane. Following the undulation instability condition found in Ref. [17], the layer spacing and the shape parameter are assumed to be maintained throughout deformation.

Assuming incompressibility, the deformation gradient becomes Eq. (B1) without losing generality.

$$\begin{bmatrix} \lambda_{xx} & 0 & 0 \\ 0 & \frac{1}{\lambda_{xx}\lambda_{zz}} & 0 \\ \lambda_{zx} & 0 & \lambda_{zz} \end{bmatrix}. \quad (\text{B1})$$

Cauchy stress is therefore expressed as

$$\begin{aligned} \sigma_{11} &= -\frac{B\lambda_{xx}^3\lambda_{zx}^2\lambda_{zz}}{(\lambda_{xx}^2 + \lambda_{zx}^2)^{5/2}} - \frac{B\lambda_{xx}\lambda_{zx}^4\lambda_{zz}}{(\lambda_{xx}^2 + \lambda_{zx}^2)^{5/2}} + \lambda_{xx}^2 \left[\mu + \frac{(B + \mu - r\mu)\lambda_{zx}^2\lambda_{zz}^2}{(\lambda_{xx}^2 + \lambda_{zx}^2)^2} \right] - p, \\ \sigma_{22} &= \frac{\mu}{\lambda_{xx}^2\lambda_{zz}^2} - p, \\ \sigma_{33} &= -\frac{B\lambda_{xx}^3\lambda_{zz}(\lambda_{xx}^2 + \lambda_{zx}^2 - \lambda_{xx}\sqrt{\lambda_{xx}^2 + \lambda_{zx}^2}\lambda_{zz})}{(\lambda_{xx}^2 + \lambda_{zx}^2)^{5/2}} + \mu \left[\lambda_{zx}^2 + \frac{(\lambda_{xx}^4 + 2r\lambda_{xx}^2\lambda_{zx}^2 + r\lambda_{zx}^4)\lambda_{zz}^2}{(\lambda_{xx}^2 + \lambda_{zx}^2)^2} \right] - p, \\ \sigma_{13} &= \sigma_{31} = \mu\lambda_{xx}\lambda_{zx} \left[\mu + \frac{B\lambda_{xx}\lambda_{zz}}{(\lambda_{xx}^2 + \lambda_{zx}^2)^{3/2}} - \frac{(B + \mu - r\mu)\lambda_{xx}^2\lambda_{zz}^2}{(\lambda_{xx}^2 + \lambda_{zx}^2)^2} \right]. \end{aligned} \quad (\text{B2})$$

The plane stress condition is satisfied when $p = \mu/(\lambda_{xx}\lambda_{zz})^2$.

Onset of the instability is computed by letting $\{\lambda_{xx}, \lambda_{zx}\} = \{\sqrt{\lambda_c}/\lambda_{zz}, 0\}$.

The onset condition of the critical stretch ($\lambda_{zz} = \lambda_c$) is obtained through shear-free condition ($\sigma_{31} = 0$), which is reduced to

$$g(\lambda_c) = \frac{-B(-1 + \lambda_c)\lambda_c^2 + \mu[1 + (-1 + r)\lambda_c^3]}{\sqrt{\lambda_c}} = 0. \quad (\text{B3})$$

An equivalent condition is also found in Ref. [17], where the analytic solution is evaluated.

-
- [1] E. Nishikawa and H. Finkelmann, *Macromol. Chem. Phys.* **200**, 312 (1999).
- [2] E. M. Terentjev and M. Warner, *Liquid Crystal Elastomers* (Clarendon Press, Oxford, 2006).
- [3] Y. Li, C. Pruitt, O. Rios, L. Wei, M. Rock, J. K. Keum, A. G. McDonald, and M. R. Kessler, *Macromolecules* **48**, 2864 (2015).
- [4] M. Camacho-Lopez, H. Finkelmann, P. Palffy-Muhoray, and M. Shelley, *Nat. Mater.* **3**, 307 (2004).
- [5] M. Yamada, M. Kondo, J.-I. Mamiya, Y. Yu, M. Kinoshita, C. J. Barrett, and T. Ikeda, *Angew. Chem., Int. Ed. Engl.* **47**, 4986 (2008).
- [6] K. D. Harris, R. Cuypers, P. Scheibe, C. L. van Oosten, C. W. M. Bastiaansen, J. Lub, and D. J. Broer, *J. Mater. Chem.* **15**, 5043 (2005).
- [7] L. T. de Haan, A. P. H. J. Schenning, and D. J. Broer, *Polymer* **55**, 5885 (2014).
- [8] G. L. Nealon, R. Greget, C. Dominguez, Z. T. Nagy, D. Guillon, J. L. Gallani, and B. Donnio, *Beilstein J. Org. Chem.* **8**, 349 (2012).
- [9] A. Sánchez-Ferrer and H. Finkelmann, *Soft Matter* **9**, 4621 (2013).
- [10] A. P. Zakharov and L. M. Pismen, *Eur. Phys. J. E* **38**, 75 (2015).
- [11] J. M. Ilynyskyi, M. Saphiannikova, D. Neher, and M. P. Allen, *Soft Matter* **8**, 11123 (2012).
- [12] M. Knežević and M. Warner, *Phys. Rev. Appl.* **2**, 044017 (2014).
- [13] A. Komp and H. Finkelmann, *Macromol. Rapid Commun.* **28**, 55 (2007).
- [14] D. Kramer and H. Finkelmann, *Macromol. Rapid Commun.* **32**, 1539 (2011).
- [15] P.-G. de Gennes, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1975).
- [16] E. Nishikawa and H. Finkelmann, *Macromol. Chem. Phys.* **198**, 2531 (1997).
- [17] J. M. Adams and M. Warner, *Phys. Rev. E* **71**, 021708 (2005).
- [18] A. W. Brown and J. M. Adams, *Phys. Rev. E* **88**, 012512 (2013).
- [19] N. Abfalq and H. Finkelmann, *Macromol. Chem. Phys.* **202**, 794 (2001).
- [20] Y. Zhang, J. Xu, F. Cheng, R. Yin, C.-C. Yen, and Y. Yu, *J. Mater. Chem.* **20**, 7123 (2010).
- [21] L. Jin, Z. Zeng, and Y. Huo, *J. Mech. Phys. Solids* **58**, 1907 (2010).
- [22] Y. Lin, L. Jin, and Y. Huo, *Int. J. Solids Struct.* **49**, 2668 (2012).
- [23] P. M. Hogan, A. R. Tajbakhsh, and E. M. Terentjev, *Phys. Rev. E* **65**, 041720 (2002).
- [24] W. L. McMillan, *Phys. Rev. A* **8**, 328 (1973).
- [25] P. Biscari, M. C. Calderer, and E. M. Terentjev, *Phys. Rev. E* **75**, 051707 (2007).
- [26] P. K. Mukherjee, *J. Mol. Liq.* **190**, 99 (2014).
- [27] S. Conti, A. DeSimone, and G. Dolzmann, *J. Mech. Phys. Solids* **50**, 1431 (2002).

- [28] J. Adams, S. Conti, and A. De Simone, *Continuum Mech. Thermodyn.* **18**, 319 (2006).
- [29] B. L. Mbanga, F. Ye, J. V. Selinger, and R. L. B. Selinger, *Phys. Rev. E* **82**, 051701 (2010).
- [30] J. V. Selinger, H. G. Jeon, and B. R. Ratna, *Phys. Rev. Lett.* **89**, 225701 (2002).
- [31] J. Yun, C. Li, H. Chung, J. Choi, and M. Cho, *Chem. Phys. Lett.* **627**, 20 (2015).
- [32] H. Chung, J. Choi, J.-H. Yun, and M. Cho, *Phys. Rev. E* **91**, 042503 (2015).
- [33] H. Chung, J. Choi, J.-H. Yun, and M. Cho, *Sci. Rep.* **6**, 20026 (2016).
- [34] M. L. Dunn, *J. Appl. Phys.* **102**, 013506 (2007).
- [35] C. A. Felippa, *Comput. Methods Appl. Mech. Eng.* **192**, 2125 (2003).
- [36] J.-L. Batoz, K.-J. Bathe, and L.-W. Ho, *Int. J. Numer. Methods Eng.* **15**, 1771 (1980).
- [37] J. M. Pajot and K. Maute, *Finite Elem. Anal. Des.* **42**, 900 (2006).
- [38] C. A. Felippa and B. Haugen, *Comput. Methods Appl. Mech. Eng.* **194**, 2285 (2005).
- [39] D. Corbett and M. Warner, *Phys. Rev. Lett.* **99**, 174302 (2007).
- [40] S. Shibahara, J. Yamamoto, Y. Takanishi, K. Ishikawa, H. Takezoe, and H. Tanaka, *Phys. Rev. Lett.* **85**, 1670 (2000).