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Cite this article: Brighenti R, Cosma MP. 2023 Multiphysics modelling of light-actuated liquid crystal elastomers. Proc. R. Soc. A 479: 20220417. https://doi.org/10.1098/rspa.2022.0417

Received: 16 June 2022 Accepted: 15 December 2022

Subject Areas:

materials science

Keywords:

liquid crystal elastomerspolymersactive materialsphoto-thermal induced actuation

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Multiphysics modelling of light-actuated liquid crystal elastomers

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Liquid crystalline elastomers (LCEs) represent a promising class of responsive polymers whose physical properties are peculiar to both fluids and solids. Thanks to their microscale structure made of elongated rigid molecules (mesogens)characterized by their capability to reversibly switch from an isotropic to an ordered state-LCEs exhibit a number of remarkable physical effects, such as self-deformation and mechanical actuation triggered by external stimuli. Efficient and physics-based modelling, aimed at designing and optimizing LCEbased devices (such as artificial muscles, deployable structures, soft actuators, etc.), is a fundamental tool to quantitatively describe their mechanical behaviour in real applications. In the present study, we illustrate the multi-physics modelling of lightdriven deformation of LCEs, based on the photothermal energy conversion. The role played by the light diffusion and heat transfer within the medium is considered and their effect on the obtainable actuation is studied through numerical simulations based on the multi-physics theory developed.

Electronic supplementary material is available online at https://doi.org/10.6084/m9.figshare. c.6373107.

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Nomenclature

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microscale (molecular scale) quantities	
b	Kuhn's length of a chain segment
C _a	number of cross-links of the polymer network per unit volume (proportional to the concentration of active chains)
k _B	Boltzmann constant
ℓ ₀	step length tensor
$\ell_{0\parallel}, \ell_{0\perp}$	step lengths in the direction parallel and perpendicular to the mesogens alignment, respectively
n	unit vector defining the nematic order orientation in the three-dimensional space
N	number of segments in a polymer chain belonging to a single network
Q , Q	nematic order tensor and order parameter of the LCE, respectively
r	end-to-end distance of a polymer chain
8	entropy of a single chain
$\varphi_0(\mathbf{r}), \varphi(\mathbf{r})$	normalized distribution function of the polymer's chains in the stress-free and in the current state, respectively
$ ho_0(\mathbf{r}), ho(\mathbf{r})$	distribution function of the end-to-end vector in the stress- free and in the current state, respectively
$\mu_i, i = 1, 2, 3$	eigenvalues of the distribution tensor $oldsymbol{\mu}$
μ_0, μ, μ_n	chain distribution tensor corresponding to the chain distribution function in the stress-free, in a generic state, and of a nematic network, respectively
λ	stretch of the single polymer chain
ψ	deformation energy for a single chain
macroscale (continuum scale) quantities	
A	light absorbance of the material
C	specific heat of the material
D	dissipated energy per unit volume
Ε	Young modulus
ε	internal energy per unit volume
F , F _{ij}	deformation gradient tensor
h	heat flux vector crossing the boundary of the unit volume domain per unit time
$L = \dot{F}F^{-1}, l_{ij}$	velocity gradient tensor
J	volume change ratio, $J = V/V_0$
P	first Piola stress tensor related to the mechanical deformation of the network

heat generated per unit volume

(Continued.)

macroscale (continuum scale) quantities	
S	entropy per unit material volume
t	time
T	absolute temperature
T _{NI}	LCE phase transition absolute temperature
μ	shear modulus
Ψ_0, Ψ	network's deformation energy per unit volume in the stress-free and in the current configuration, respectively
$\Psi_{ m ext}$	mechanical energy associated with the external forces
Ξ_e	Helmholtz free energy per unit current volume
π	hydrostatic pressure
Π	total potential energy per unit volume
σ	Cauchy stress tensor

1. Introduction

Several types of responsive materials, such as polymers possessing functionalities conferred by particular embedded molecules or by their particular microstructure, have been synthesized in the last decades [1]. The availability of active materials paves the way to the development of new and unprecedented applications, where they can be exploited as untethered sensors or actuators whose driving energy is provided wirelessly [2,3].

Within the realm of active materials, liquid crystal elastomers (LCEs) are a promising class of responsive polymers gathering peculiar properties of fluids and solids at the same time. LCEs possess both liquid crystal orientational order and mechanical properties of a highly deformable amorphous polymer network, the latter coming from a sufficiently low cross-link density of the network.

The microstructure of an LCE material is made of elongated rigid molecules (mesogens) capable of reversibly switching from an isotropic (random chain orientation) to an anisotropic (preferential chain orientation) configuration, leading to a macroscopic spontaneous deformation of the material [4]. The resulting material possesses unique responsiveness capabilities to a variety of physical stimuli (heat, electric and magnetic fields, light, etc.) which can trigger huge reversible detectable deformations taking place in a short time interval [5–8]. The arising macroscopic deformation—usually associated with large force or torque outputs—makes them perfect candidates for designing artificial muscles, deployable structures, soft actuators, optical devices, adjustable microscopy and imaging systems, etc. [9–11]. Since the above-mentioned stimuli can be easily encountered in real situations, such as those related to environmental or bio applications, the use of LCE-based devices is of particular interest since they can be designed in order to smartly respond to accomplish a desirable task according to the surrounding environment [12,13].

LCEs are synthesized by cross-linking liquid crystal mesogen units to a highly deformable network: the high deformability of their entropic energy-dominated network microstructure and the reversible phase transformation of their nematic mesogens makes LCEs capable of displaying shape morphing at will when a proper mesogens ordering pattern is inferred to the material [14–21]. Various building approaches have recently been developed to create structures or LCE-based devices possessing a controlled mesoscale architecture suitable to produce the desired actuation [14–16]. The most promising production approaches are those based on three-dimensional printing technologies, such as the direct ink writing (DIW), enabling the director



Figure 1. Schematic of the reversible nematic to isotropic phase change in a main chain LCE upon crossing the transition temperature T_{M} by heating up or cooling down the material.

alignment and pattern within a two-dimensional or three-dimensional domain to be precisely controlled [18–21].

Basically, an LCE is made of polymer chains, mesogen units and cross-linker components, whose synthesis requires us to covalently link the three above-mentioned constituents. Mesogen molecules are 'rod-like' elements, with one axis appreciably longer than the other ones, containing a reactive group, a spacer unit separating the core of the mesogen from the polymer, and a core component. Most commonly, the synthesis technique for cross-linking the polymer chains to the mesogen units is through the hydrosilylation reaction or acrylate polymerization [22]. The process requires the mesogen units and cross-linker molecules to be properly functionalized, for instance by using vinyl groups for the hydrosilylation reaction and acrylate groups in the acrylate polymerization. The resulting elastomer has an amorphous structure, being the polymer chains randomly arranged in the three-dimensional space, and so the mesogen units do not have any preferential alignment direction. Once the LCE has been synthesized, the preferential orientation of the network is obtained by aligning the mesogen units; typically, this is obtained by mechanical-, magnetic- or three-dimensional printing-based orientation techniques. The preferential orientation is inferred to the material after it has been partially polymerized, i.e. when it is not fully solid. Finally, the polymerization process is completed to freeze the microstructure in the anisotropic state. It is worth recalling that, whereas mechanical- and magnetic-based orientations allow obtaining a simple uniaxial (monodomain) alignment, three-dimensional printing enables us to build complex alignment patterns in two or three dimensions.

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Two mesogen-network architectures can usually be found in LCEs, namely the so-called side chain LCEs (SCLCEs) and the main chain LCEs (MCLCEs); in the first case, the mesogen units are chemically attached to the linear polymer network backbone as side-groups, while in the second case the mesogen units are cross-linked as one of the constituents of the polymer forming the LC network. Nematic, smectic or cholesteric LCE can be obtained by using both side chain and MCLCEs [23]. Interesting mechanical behaviour and morphing capabilities arise because of the elastic anisotropy; a spontaneous contraction or elongation, induced for instance by a temperature change, allows the microstructure to switch from the ordered to the disordered state [24,25].

In fact, the coupling of the orientational order of the mesogen units with the polymer network is stable up to the so-called phase transition temperature while, if such a temperature is overcome, the network changes conformation, becoming isotropic (figure 1). Correspondingly, a macroscopic change in the sizes of the entire network emerges because of the contraction (expansion) along (normal to) the director axis. Size changes are particularly evident in MCLCEs. It is worth recalling that the deformation rate taking place when the phase transition occurs in temperature-responsive LCEs is mainly governed by the thermal heat conductivity of the material, and a fast actuation is usually possible [26].

The preferentially orientated structure is usually described by the director parameter (n), a unit vector indicating the average direction of the mesogen units [5,6]. The degree of scattering of the mesogens embedded in the polymer network, measured with respect to their mean preferential orientation, is quantified by the order degree whose magnitude is provided by the order parameter.

Beyond standard 'trial and testing' approaches, efficient physics-based modelling tools, suitable to quantitatively describe the behaviour of this class of materials, are of crucial importance for the design and optimization of new devices.

The precise knowledge and a full control of the molecular scale mechanisms taking place in LCEs are desirable when the material design is needed for high precision applications, such as small-scale sensors or actuators. Within this class of approaches, molecular-based simulations (lattice models) represent suitable tools [27]; moreover, molecular dynamics (MD) approaches—based on the intermolecular forces existing between the mesogens and the network molecules described by suitable interaction potentials—have been used for modelling LCEs from a molecular standpoint. These approaches allow understanding the molecular origin of the phase transition, the influence of the mechanical deformation and of the applied physical stimuli. It is worth mentioning that the use of molecular scale simulation tools has some limitations related to the huge computational resources needed even for studying very small LCE domains [28].

A continuum model—suitable to be implemented in a computational framework—is generally necessary to fully exploit the potentialities offered by modern fabrication technologies, enabling us to arrange the mesogen orientation in generic patterns. The use of continuum-level approaches and their computational coding in a robust finite-element (FE) framework, have been demonstrated to be a promising tool for simulating the order evolution induced by environmental stimuli [29,30]. It is also worth recalling that several structural models have been formulated to describe the deformation [31] and the mechanical response of simple LCE structural elements, such as plates and shells, in which a given order parameter field has been assumed to exist [15,32,33].

The goal of this study is to provide a comprehensive multi-physics framework suitable to describe the responsiveness of LCEs when exposed to external stimuli, such as light-induced heating. The network-scale mechanisms underlying the phase transition are first considered (§2), as well as some fundamental thermo-dynamical aspects relevant to the problem under study (§3). Since we are interested in providing a comprehensive framework encompassing the main physics involved in LCEs subjected to an external stimulus, we consider the light diffusion phenomenon and the related heat generation and transport to determine the evolving temperature field within the material (§4). The multi-physics theoretical model is finally coded into an FE framework whose details are briefly provided in §5. Section 6 is devoted to illustrating some relevant examples aimed at demonstrating the influence of the main parameters involved in light-driven LCEs. Finally, §7 depicts some final remarks and future perspectives in the field.

The proposed multi-physics approach is of general applicability and has no restrictions related to specific structural elements. It is suitable to describe elastomers characterized by multiple networks, allows accounting for strain-rate effects and damage mechanisms, and can be straightforwardly coded in a computational framework, enabling the simulation and design of real cases requiring—differently from molecular-based approaches [28]—a reduced computational effort. Moreover, the model's parameters have a clear physical meaning, enabling the design of the material starting from its molecular structure.

2. Mechanics of liquid crystalline elastomer network

(a) Basic concepts

Elastomers are characterized by a microstructure made of entangled chains, eventually reciprocally joined at discrete points to form a three-dimensional network; this disordered structure suggests adopting a statistical description of the network configuration. Because of

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the above-mentioned amorphous structure, the network state is dominated by entropic energy, while the enthalpic contribution becomes relevant only at very high deformation levels, when the stretched chains lose their randomness and start being roughly aligned along the stretch direction. In order to fully exploit the statistical-based description of the chain network, in the following we consider only the entropic contribution to the mechanical energy.

Within the so-called rubber elasticity theory, a single chain is assumed to be made of N identical rigid monomer units (Khun's segments) of length b, while their arrangement in the three-dimensional space is assumed to be described by the random-walk theory (freely jointed chain model, FJC). The chains' physical state is assumed to be provided by the so-called chain's end-to-end vector r [34]. Upon stretching, chains start uncoiling, thus the disorder level, and consequently the entropic energy, reduces. Because of the assumed rigidity of the Khun's segments, the extension of a chain is limited and the distance |r| between its endpoints cannot overcome the chain's contour length Nb; by following the affine deformation hypothesis, and being $|\bar{r}| = b\sqrt{N}$ the mean end-to-end distance of a network's chain in the stress-free state, the chain's stretch limit is equal to $\lambda_{max} = |r_{max}|/|r_0| = bN/b\sqrt{N} = \sqrt{N}$.

When the statistical mechanics approach is considered, one of the main issues relies on understanding how the statistics conformation of an individual chain is related to the mechanics of the entire polymer network and, in turn, on how to upscale it to the macroscopic level (continuum mechanics). To this end, various models have been proposed in the literature [35], such as the three-chain model [36], the four-chain model [37], the eight-chain model [38] and the full network model [39–41]. In this work, we adopt a mechanical description of the polymer network based on a full network model.

We now introduce the chain distribution function of the polymer network, quantifying the amount of chains per unit polymer volume characterized by a given end-to-end vector r; in the stress-free reference state (at the time t = 0) it is expressed as

$$\rho_0(\mathbf{r}) = c_a \varphi_0(\mathbf{r}). \tag{2.1}$$

The chain distribution function ρ_0 has been expressed as the number of mechanically active cross-links c_a (proportional to the number of chains that from the mechanical viewpoint are effectively joined to the network), times the normalized distribution function φ_0 , usually assumed to be described by the standard Gaussian distribution, $\varphi_0(|r|) = (3/2\pi Nb^2)^{3/2} \exp(-(3|r|^2/2Nb^2))$, with mean value r = 0 and standard deviation $b\sqrt{N/3}$ [34]. It is worth noticing that the integral $\int_{\Omega} \varphi_0 d\Omega = \langle \varphi_0 \rangle = \int_0^{2\pi} \int_0^{\pi} \left(\int_0^{Nb} \varphi_0(r) r^2 dr \right) \sin \theta d\theta d\omega = 1$ since it represents the cumulated probability of finding all the chain lengths and orientations in the unit volume; the integral of the distribution function over Ω thus leads to $\langle \rho_0(r) \rangle = c_a$.

It is worth recalling that the number of cross-links per unit volume is related to the shear modulus μ of the material through the well-known expression $\mu = c_a k_B T$, where k_B and T are the Boltzmann constant and the absolute temperature, respectively [34]. If the cross-link density is preserved during a generic deformation process, i.e. if we exclude the possibility to have breaking of chains, at any generic time instant t > 0 it happens to be $\langle \rho(\mathbf{r}, t) \rangle = c_a$.

The energy stored in a single chain is usually made to depend on its stretch, considering that the rest state of the chain corresponds to $|\mathbf{r}| = 0$. According to the Gaussian statistics, valid for moderate stretch values, the elastic energy of a single chain is expressed as $\psi(\mathbf{r}) = (3k_BT/2Nb^2)|\mathbf{r}|^2$, while the deformation energy density of the polymer is

$$\Delta \Psi = \Psi - \Psi_0 = c_a \left\langle [\varphi(\mathbf{r}, t) - \varphi_0(\mathbf{r})] \psi \right\rangle + \pi [\det(F) - 1], \tag{2.2}$$

where $\Psi_0 = [3c_a k_B T/(2Nb^2)]$ tr[($Nb^2/3$)1] is the non-zero energy density in the initial stress-free state of the material and π is the hydrostatic stress required to satisfy the isochoric deformation assumption, $J = \det(F) = 1$. In (2.2), F is the deformation gradient, $F = \partial x/\partial X$, being X, x the position vector in the reference and in the current deformed configuration, respectively, and $\varphi(r, t)$ is the actual dimensionless chain distribution function.

In equation (2.2), $\psi = -Ts$ is the energy per single chain, with s being its entropy. According to the Gaussian statistics, such an entropy is expressed as $s = -\frac{3 k_B}{2} \lambda^2$, while it is given by $s = -N k_B \left(\beta \frac{\lambda}{\sqrt{N}} + \ln \frac{\beta}{\sinh \beta}\right)$, when the Langevin statistic (suitable for large deformations) is adopted, being $\beta = \mathcal{L}^{-1} \left(\lambda/\sqrt{N}\right)$, where \mathcal{L} is the Langevin function defined as $\mathcal{L}(\blacksquare) = \coth(\blacksquare) - \blacksquare^{-1}$ [34].

It is worth recalling that, in general, the force in a chain is provided by the derivative of the chain energy with respect to its end-to-end vector, i.e. $|f| = |\partial \psi(r)/\partial r|$. Let us now introduce the chain distribution tensor defined as

$$\boldsymbol{\mu} = \int_{\Omega} \varphi(\boldsymbol{r}, t) \boldsymbol{r} \otimes \boldsymbol{r} \mathrm{d}\Omega = \langle \varphi(\boldsymbol{r}, t) \boldsymbol{r} \otimes \boldsymbol{r} \rangle, \qquad (2.3)$$

thus, the previous expression of the energy density evaluated by using the Gaussian statistics, equation (2.2), can be restated as [41]

$$\Delta \Psi = \frac{3c_a k_B T}{2Nb^2} \int_{\Omega} \left[\varphi(\mathbf{r}, t) - \varphi_0(\mathbf{r}) \right] |\mathbf{r}|^2 d\Omega + \pi \left[\det(F) - 1 \right]$$
$$= \frac{3c_a k_B T}{2Nb^2} \operatorname{tr}(\boldsymbol{\mu} - \boldsymbol{\mu}_0) + \pi (J - 1).$$
(2.4)

It can be easily demonstrated that for polymers whose network chain end-to-end distance obeys the Gaussian distribution in the stress-free state, the distribution tensor assumes the simple form $\mu_0 = \mu(F = 1, t = 0) = (Nb^2/3)\mathbf{1}$ [41]. The chain distribution tensor μ is characterized by three eigenvalues, μ_1, μ_2, μ_3 such that, in the principal direction frame of reference, it can be expressed in the diagonal form $\mu_p = \text{diag}(\mu_1, \mu_2, \mu_3)$.

(b) Application of chain configuration statistics to liquid crystalline elastomers

Dealing with nematic elastomers, it must be considered that the microstructure of the material is characterized by the field of the director direction, whose spatial rearrangement allows the material to show spontaneous deformations. The main physics-based theory based on a statistical description of the LCE's chain network relies on the fundamental developments of Warner & Terentjev [6]. They extended the classical rubber elasticity to LCEs by introducing the effect of the preferential orientation existing in the polymer network.

The present approach is based on the description of the LCE network through the chain distribution tensor, which enables a general physics-based modelling of the mechanisms taking place at the molecular level, in the present case being represented by the nematic–isotropic transition of the mesogen units. The approach is easily adaptable to describe the mechanics of elastomers characterized by multiple networks, as well as for describing other mechanisms taking place at the molecular level, such as strain-rate effects, chains uncoiling, damage, etc.

The distribution tensor, presented in the previous section for standard polymers, is hereafter extended to consider the preferential chain orientation induced by the nematic order of the embedded mesogen units. It is worth mentioning that the network description based on the chain distribution tensor can be extended to describe other mechanisms affecting the material responsiveness, such as the cross-link density coming from the LCE synthesis [40].

Typically, in the stress-free state standard polymers chains are uniformly oriented in all the directions of the three-dimensional space, i.e. the distribution function can be thought to have a spherical symmetry, and the corresponding distribution tensor μ_0 is characterized by three identical eigenvalues, $\mu_0 = \mu_{01} = \mu_{02} = \mu_{03}$, i.e. $\mu_0 = \text{diag}(\mu_0, \mu_0, \mu_0)$. Any mechanical deformations and/or nematic order change are responsible for the evolution of the distribution tensor, as will be illustrated in the following. Let's now start by considering the stress-free state of the network (at the time of cross-linking) to be characterized by a non-isotropic chain distribution;

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in this case, the Gaussian distribution function takes the form [6]:

$$\varphi_0(\mathbf{r}) = \frac{1}{\sqrt{\det \ell_0}} \sqrt{\left(\frac{3}{2\pi Nb}\right)^3} \exp\left[-\frac{3\mathbf{r} \cdot \boldsymbol{\ell}_0^{-1} \mathbf{r}}{2Nb}\right],\tag{2.5}$$

where the step length tensor of the chain distribution $\ell_0 = \ell_{0\perp} \mathbf{1} + (\ell_{0\parallel} - \ell_{0\perp})\mathbf{n} \otimes \mathbf{n}$ has been used. This tensor quantifies the anisotropy of the chain arrangement through the effective initial step lengths, $\ell_{0\perp}$ and $\ell_{0\parallel}$, measured parallel and perpendicular to the director \mathbf{n} of the mesogens, respectively, [7]. In a highly aligned chain network, it happens to be $\ell_{0\parallel} \gg \ell_{0\perp}$, while when the network is in the isotropic state the averaged square end-to-end chain distance is given by $\langle r_i^2 \rangle = Nb^2/3, i = 1, 2, 3, \ell_{0\parallel} \cong \ell_{0\perp}$ and the step length tensor reduces to $\ell_0 = b\mathbf{1}$.

By using the definition of the chain distribution tensor provided by equation (2.3), and adopting the non-isotropic chain distribution function (equation (2.5)), the following chain distribution tensor-step length tensor relationship can be established:

$$\boldsymbol{\mu}_{0n} = \frac{Nb}{3}\boldsymbol{\ell}_0. \tag{2.6}$$

It happens to be tr $(\mu_{0n}) = Nb^2$, irrespective of the nematic order parameter. It is worth noticing that the eigenvalues μ_{0ni} , i = 1, 2, 3 of the tensor μ_{0n} represent the standard deviation of the chain's end-to-end distance in the stress-free state, evaluated along the three principal directions of μ_{0n} , i.e. $\mu_{0ni} = \langle r_{0i}^2 \rangle$.

Let's assume that, at a generic time instant *t*, the principal directions of the distribution tensor $\mu_n(t)$ are aligned with those of the Cartesian coordinate frame of reference; in such a case, the distribution tensor can be related to the order parameter Q(t) as

$$\boldsymbol{\mu}_{n}(t) = \frac{Nb}{3}\boldsymbol{\ell}(t) = \frac{Nb}{3}b[(1 - Q(t))\mathbf{1} + 3Q(t)\mathbf{n} \otimes \mathbf{n}]$$

or in matrix form :
$$\boldsymbol{\mu}_{n}(t) = \frac{Nb}{3}b\begin{bmatrix} 1 - Q(t) & 0 & 0\\ 0 & 1 - Q(t) & 0\\ 0 & 0 & 1 + 2Q(t) \end{bmatrix}$$
(2.7)

where the well-known relationship between the step length tensor and the order tensor, $\ell(t) = b[(1 - Q(t)) \ 1 + 3Q(t) \ n \otimes n]$ or equivalently $\ell(t) = b[2Q(t) + 1]$ being $Q = Q/2(3n \otimes n - 1)$ the order tensor (or the de Gennes tensor [5]), has been exploited [6]. In equation (2.7), $Q(t) = \langle (3/2)\cos^2\theta(t) - (1/2) \rangle$ is the so-called order parameter, θ being the angle of mesogens orientation dispersion with respect to the director n here assumed to be parallel to the z-axis of the Cartesian coordinate frame of reference, $n \equiv z = (0, 0, 1)$. The mean deviation from such a preferential direction is mathematically assessed through the order parameter. The value Q = 1 indicates that all the mesogens are perfectly aligned with the z-axis, while if Q = 0 they are randomly oriented in the three-dimensional space; finally, if Q = -(1/2) the mesogen units lay on the x-y plane. When intermediate values of the order parameter are considered, 0 < Q < 1, an intermediate degree of alignment about the z-axis exists, while the dispersion degree increases as $Q \rightarrow 0$.

It is well-known that in LCEs $\theta(t) = \theta(T(t))$, i.e. the scattering angle depends on the temperature of the material. When $T < T_{NI}$ the material is in the nematic state, while when $T > T_{NI}$ the material undergoes a phase transformation and the mesogens switch to the isotropic state [6].

According to the classical theory of LCEs, an intimate relationship between the step length tensor and the order tensor, $\ell - Q$, exists. Since equation (2.7) relates the chain distribution tensor to the step length tensor ($\mu - \ell$ relationship), a relationship between the chain distribution tensor and the order tensor can be also established ($\mu - Q$ relationship) as follows:

$$Q(t) = \frac{1}{2} \left(\frac{\ell(t)}{b} - 1 \right) = \frac{1}{2} \left(3 \frac{\mu(t)}{Nb^2} - 1 \right).$$
(2.8)

In order for the present model to be suitable to describe the mechanics of LCEs, the mesogen units need to be properly and effectively bonded to the polymer network, i.e. their preferential orientation setting must be fully transmitted to the polymer chains.

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(c) Energy density of liquid crystalline elastomers

In order to determine the physical state of the network, its energy density is required to be evaluated along the applied deformation and/or stimuli paths; for this purpose, it is convenient to define the time rate of the energy density variation of an LCE provided by equation (2.4). The time rate of the energy density is given by [41]

$$\Delta \dot{\Psi} = \frac{3c_a k_B T}{2Nb^2} \left[\frac{\dot{T}}{T} \operatorname{tr}(\boldsymbol{\mu} - \boldsymbol{\mu}_0) + \operatorname{tr}\left(\underbrace{\dot{\boldsymbol{\mu}}_F + \dot{\boldsymbol{\mu}}_n}_{\dot{\boldsymbol{\mu}}} - \dot{\boldsymbol{\mu}}_0\right) \right] + J\pi \operatorname{tr}(L), \tag{2.9}$$

where both the temperature and the deformation have been assumed to depend on time; for simple isothermal processes, it happens to be $\dot{T} = 0$, while if the temperature varies slowly in time it is reasonable to assume that $\dot{T} \cong 0$ so the first term in parenthesis vanishes. In equation (2.9), the time rate of the distribution tensor $\dot{\mu}$ has been written as the sum of two different contributions: (i) the time rate provided by the contribution of the mechanical deformation, $\dot{\mu}_F$ and (ii) those coming from the time rate of the LCE nematic–isotropic phase transition, $\dot{\mu}_n$. In equation (2.9) L is the velocity gradient tensor, $L = \dot{F}F^{-1}$, whose trace happens to be zero for incompressible deformations, as we are assuming here. Splitting the energy density, or correspondingly its time rate, into a contribution coming from the mechanical deformation and one from the nematic–isotropic transition, i.e. $\Delta \Psi = \Delta \Psi_F + \Delta \Psi_n$, is usually adopted in molecular-statistical theory of nematic elastomers [42].

The above expression of the time rate of the energy density $\Delta \Psi$ has been obtained by applying the integration by part of the term $\langle [\dot{\varphi}(\mathbf{r},t) - \dot{\varphi}_0(\mathbf{r})] | \mathbf{r} |^2 \rangle$ in equation (2.4), and by expressing the time derivative of the chains' end-to-end distance probability distribution functions φ as [43]

$$\frac{\partial \varphi(\mathbf{r},t)}{\partial t} = -\nabla \varphi(\mathbf{r},t) \cdot L\mathbf{r} - 2\mathrm{tr}(L)\varphi(\mathbf{r},t), \qquad (2.10)$$

that simplifies to $\partial \varphi(\mathbf{r}, t) / \partial t = -(\nabla \varphi \otimes \mathbf{r}) : \mathbf{L}$ when an isochoric deformation is considered, being $\operatorname{tr}(\mathbf{L}) = 0$ in such a case. Since the chain distribution space is embedded within a single point of the material and we adopt the affine deformation hypothesis, the deformation gradient \mathbf{F} and the velocity gradient \mathbf{L} are homogeneous throughout the chain configuration space and the rate of the chain's deformation $\dot{\mathbf{r}}$ can be expressed as $\dot{\mathbf{r}} = \mathbf{L}\mathbf{r}$.

By recalling equation (2.8), in order to ensure the objectivity of the time rate of the distribution tensor associated with the nematic tensor field μ_n , it must be expressed as [43]

$$\dot{\boldsymbol{\mu}}_n = \frac{\partial \boldsymbol{\mu}_n}{\partial t} = \frac{Nb^2}{3} \frac{\partial (2Q+1)}{\partial t} = 2\frac{Nb^2}{3} (\dot{\boldsymbol{Q}} - \boldsymbol{W}\boldsymbol{Q} + \boldsymbol{Q}\boldsymbol{W}), \tag{2.11}$$

 $W = 1/2(\nabla \dot{u} - \nabla \dot{u}^T)$ being the spin tensor (with u the displacement field) [44], while the time derivative of the order tensor $\dot{Q} = \dot{Q}/2(3n \otimes n - 1)$ can be evaluated as follows:

$$\dot{Q}(t) = \begin{bmatrix} -\dot{Q}(t)/2 & 0 & 0\\ 0 & -\dot{Q}(t)/2 & 0\\ 0 & 0 & \dot{Q}(t) \end{bmatrix},$$
(2.12)

 \hat{Q} being the time derivative of the order parameter. The time derivative of the order tensor does not depend on the time derivative of the nematic director, since it does not change during the phase transformation. In fact, during the nematic–isotropic transition the alignment degree of the mesogen units reduces (the angle of scattering increases), without any change of their preferential direction *n* typically embedded in the material during the synthesis process. Since the nematic– isotropic transition is reversible, once the isotropic state has been achieved, the reverse transition occurs upon material cooling, and the mesogens re-orient recovering their initial preferential orientation. Since the order parameter Q(T) changes with the temperature, we adopt the following empirical relationship for its dependence on the temperature:

$$Q(T) = \frac{Q_0}{1 + \exp(\frac{T - T_{NI}}{p})},$$
(2.13)

p being a material-specific constant parameter, relevant only in the transient regime, controlling the steepness of the smooth nematic–isotropic phase transition with respect to the temperature variation upon crossing the temperature T_{NI} : when the temperature rises beyond T_{NI} , the order parameter value changes from the initial one (Q_0) tending toward zero (isotropic state). The reverse transformation takes place when the material is cooled down. The time rate of the order parameter is given by $\dot{Q} = (dQ/dT)\dot{T}$, with $dQ/dT = -(Q^2/pQ_0)\exp(\frac{T-T_{NI}}{p})$.

3. Thermodynamic considerations

A link between the microscale and the macroscale response of the polymer can be obtained by expressing macroscopic measures, such as the stress tensor and the energy variation, in terms of network-related quantities, such as the above-defined distribution tensor.

For a generic process, the time rate of the internal energy density \mathcal{E} is expressed as $\dot{\mathcal{E}} = \boldsymbol{\sigma} : \boldsymbol{L} - \nabla \cdot \boldsymbol{h} + \dot{q}$, where $\boldsymbol{\sigma}$ is the Cauchy stress, \boldsymbol{h} is the heat flux crossing the boundary of the unit volume domain per unit time and \dot{q} is the rate of the heat supplied to the unit volume of material. By introducing the Helmholtz free energy per unit current volume, Ξ_e , its time rate can be expressed as

$$\dot{\Xi}_e = (\boldsymbol{\sigma} : \boldsymbol{L} - \nabla \cdot \boldsymbol{h} + \dot{\boldsymbol{q}}) - \dot{T}\boldsymbol{s} - T\dot{\boldsymbol{s}} - \dot{\boldsymbol{D}}, \tag{3.1}$$

where D is the rate of the dissipated energy density, here introduced to account for nonconservative effects, and *s* is the entropy per unit volume. The Clausius–Duhem inequality, enforcing the second principle of thermodynamics, establishes a fundamental relationship between the rate of entropy per unit volume (\dot{s}) and the above-defined energy terms,

$$\dot{s} - \left(\frac{\dot{q}}{T} - \frac{1}{T}\nabla \cdot \boldsymbol{h} + \frac{1}{T^2}\boldsymbol{h} \cdot \nabla T\right) \ge 0.$$
(3.2)

By substituting the expression of \dot{s} obtained from equation (3.1) in equation (3.2), we obtain:

$$(\boldsymbol{\sigma}: \boldsymbol{L} - \dot{T}\boldsymbol{s} - \dot{\boldsymbol{\Xi}}_{\boldsymbol{\varrho}}) - \frac{1}{T}\boldsymbol{h} \cdot \nabla T \ge 0.$$
(3.3)

On the other hand, the Helmholtz free energy and its time rate, \dot{z}_e , have to be evaluated by taking into account the material heat absorption,

$$\Xi_{e} = \Delta \Psi + (c - s_{0})(T - T_{0}) - cT \ln \frac{T}{T_{0}}$$

$$\dot{\Xi}_{e} = \Delta \dot{\Psi} - \dot{T}s_{0} - c\dot{T} \ln \frac{T}{T_{0}}$$
(3.4)

and

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where *c* is the specific heat of the material assumed to be constant. By recalling equation (2.4), the time rate $\Delta \dot{\Psi}$ of the energy density assumes the following expression [41]:

$$\Delta \dot{\Psi} = \frac{3c_a k_B T}{2Nb^2} \left[(\mu_F - \mu_0) : L + \text{tr} \, \dot{\mu}_n + \frac{\dot{T}}{T} \, \text{tr}(\mu - \mu_0) \right] + \pi \, \text{tr}(L), \tag{3.5}$$

 $\mu_F(t) = \mu_0 + \int_0^t \dot{\mu}_F dt$ being the distribution tensor corresponding to the network in the actual state whose deformation comes from mechanical actions only. Similarly, we can define the distribution tensor related to the nematic–isotropic phase change as: $\mu_n(t) = \mu_0 + \int_0^t \dot{\mu}_n dt$. By using equations

(3.3), (3.4) and (3.5), the following inequality can be established:

$$\boldsymbol{\sigma}: \boldsymbol{L} - \dot{T}\boldsymbol{s} - \left[\Delta \dot{\boldsymbol{\Psi}} - \dot{T}\boldsymbol{s}_0 - c\dot{T}\ln\frac{T}{T_0}\right] - \frac{1}{T}\boldsymbol{h}\cdot\nabla T + \dot{\boldsymbol{D}} \ge 0, \tag{3.6}$$

where \dot{D} is now the time rate of the dissipated mechanical energy density due to the phase transition occurring in the LCE network.

Using equation (3.5) in equation (3.6) and rearranging the terms, we finally obtain the inequality:

$$\begin{bmatrix} \boldsymbol{\sigma} - \frac{3c_a k_B T}{2Nb^2} (\boldsymbol{\mu} - \boldsymbol{\mu}_0) - \boldsymbol{\pi} \mathbf{1} \end{bmatrix} : \boldsymbol{L} + \frac{3c_a k_B T}{2Nb^2} \operatorname{tr} \dot{\boldsymbol{\mu}}_n + - \dot{T} \begin{bmatrix} s - s_0 + \frac{3c_a k_B}{2Nb^2} \operatorname{tr} (\boldsymbol{\mu} - \boldsymbol{\mu}_0) - c \ln \frac{T}{T_0} \end{bmatrix} - \frac{1}{T} \boldsymbol{h} \cdot \nabla T \ge 0,$$
(3.7)

where $\dot{D} = (\frac{3c_a k_B T}{2Nb^2})$ tr $\dot{\mu}_n$ is the expression assumed by the mechanical energy density dissipation rate due to the phase transition taking place in the LCE, while the stress tensor can be recognized to be given by

$$\boldsymbol{\sigma}(t) = J^{-1} \boldsymbol{P} \boldsymbol{F}^{T} = \frac{\partial \Delta \Psi}{\partial \boldsymbol{F}} \boldsymbol{F}^{T} = \frac{3c_{a}k_{B}T}{Nb^{2}} [\boldsymbol{\mu}(t) - \boldsymbol{\mu}_{0}] + \boldsymbol{\pi}(t) \mathbf{1}$$
(3.8)

with **P** being the first Piola stress tensor, $\mu(t) = \mu_0 + \int_0^t (\dot{\mu}_F + \dot{\mu}_n) dt$, and J = 1.

It is worth recalling that statistical-based network models, like the one we are adopting, are suitable to assess the mechanics of highly deformable polymers whose chains conformation change is significant during the mechanical deformation process and so is the entropic energy variation. Too highly cross-linked and/or entangled (i.e. stiff) networks are not properly described by this class of model. Further, it has to be considered that in very highly stretched networks, the enthalpic energy also plays a role, so entropic energy does not suffice to fully describe the mechanical state of the material [36,45].

4. Stimuli-induced phase transition in liquid crystalline elastomers

Nematic to isotropic phase transition is reversible and maintains high efficiency even after many cycles; according to the underneath LCE chemistry, it can be induced by various stimuli—such as mechanical stress, heat, magnetic field, light, etc.—among which temperature variation can be considered the most important [46].

At room temperature, LCEs are in the nematic phase because of the high orientational order of mesogen units, while at temperatures greater than the transition temperature the mesogen units lose their orientational order leading to an isotropic state [47,48]. Because of its efficiency, speed of actuation and untethered nature, phase transformation induced by photo-thermal heating represents an interesting way of actuating LCEs, enabling the development of unprecedented applications [49,50].

(a) Photo-induced phase transition in liquid crystalline elastomers

Heating can be induced by harnessing the photo-thermal effect provided by particles—such as gold, iron and magnetite nanoparticles—embedded into the material, i.e. by exploiting the photon-heat energy conversion phenomenon. The potentialities offered by the use of nanoparticles as light-thermal converters have been studied in recent years because of their capability to speed up the heating process of a material, useful to improve the actuation velocity when a responsive material is concerned.

Light radiation is converted into heat when it encounters nanoparticles: a fraction of the generated heat energy spreads in the material by conduction, convection and radiation, while a fraction is dispersed (figure 2). For the sake of simplicity, in the following we consider that the heat generated by light remains entirely in the medium in which it propagates by conduction. The

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Figure 2. Heat generation due to light-thermal energy conversion in an LCE material with embedded photo-thermal nanoparticles. The incident light source, moving at a velocity ν and with the light direction forming the angle γ with the normal \boldsymbol{n} to the hit surface, is assumed to have a Gaussian-like intensity distribution on the top surface of the domain.

heat *q* generated by lighted nanoparticles embedded into a material is proportional to the light intensity *I* times the absorbance *A* of the material, i.e. [51–53]:

$$q(X,t) = A(X,t) I(X,t) \quad \text{for} \quad X \in \Omega_0.$$

$$(4.1)$$

Light diffusion in a semitransparent medium is an instantaneous phenomenon whose light intensity field depends on the value of the absorbance distribution in the material. We assume that the incoming light beam is characterized by its own intensity distribution, and by its inclination with respect to the normal to the hit surface (figure 2).

The light diffusion in a three-dimensional domain Ω_0 is governed by the Beer–Lambert law, equipped with the proper boundary conditions; by referring to the undeformed reference configuration, the governing PDEs are expressed as [54]

$$I(X, t) \cdot \nabla_X I(X, t) = -A(X, t) I(X, t), X \in \Omega_0$$

$$I(X, t) = I_0(X, t), X \in \partial \Omega_0,$$
(4.2)

I(X, t) being the light intensity at the position X and time t, while I(X, t) is the unit vector indicating the direction of the incoming light beam. In equation (4.2), ∇_X indicates the gradient operator in the reference configuration and A(X, t) is the light attenuation coefficient (or absorbance), providing the light intensity reduction while the light crosses the material, figure 2.

The simplest assumption for evaluating the absorbance is to adopt a constant value for such a parameter throughout the deformation process, i.e. the change of the nematic order is assumed to not influence the degree of light depletion when light crosses the material. On the other hand, the light absorbance can be reasonably made to depend on the angle formed by the light direction *l* with respect to the direction of the nematic director [55]. The parameter *A* can be simply estimated by accounting for the absorbance coming from the polymer backbone, A_{pol} , as well as for the absorbance induced by the photo-thermal particles (photo-absorbers) whose molar absorptivity is ϑ [56]

$$A(X,t) = A_{\text{pol}} + \vartheta C_n(X,t).$$
(4.3)

In equation (4.3) C_n is the concentration of photo-absorbers which can eventually vary in time if they are consumed in some chemical reactions, such as the photopolymerization, taking place in the material. If no chemical reactions take place and assuming incompressibility, the concentration C_n can be reasonably taken to be homogeneous and time-independent within the LCE domain. It is worth mentioning that the light absorbance of a material can be easily determined by Once the heat density generated per unit volume has been determined through equation (4.1), the temperature evolution in the material can be determined by solving the standard heat conduction Fourier equation, equipped with the related boundary conditions.

5. Computational aspects

The above illustrated multi-physics theoretical approach developed to model LCEs is here restated in view of its computational coding. To this end, the problem is formulated by adopting a variational approach for the mechanics, phase transition, as well as for the light diffusion problem. Let us consider an undeformed region \mathcal{B}_0 , bounded by $\partial \mathcal{B}_0$, occupied by the LCE; the first variation of the total potential energy Π with respect to the displacement field u reads:

$$\delta_u \Pi = \delta_u \left(\int_{\mathcal{B}_0} \Delta \Psi dV + \Psi_{\text{ext}} \right) =$$
(5.1*a*)

$$= \int_{\mathcal{B}_0} \frac{\partial \Psi}{\partial \nabla F} \frac{\partial F}{\partial \nabla u} \cdot \delta \nabla u \, dV - \int_{\mathcal{B}_0} \mathbf{b} \cdot \delta u \, dV - \int_{\partial \mathcal{B}_0} \mathbf{t} \cdot \delta u \, dA = \delta_u \Psi_{\text{int}} + \delta_u \Psi_{\text{ext}} =$$
(5.1b)

$$= \int_{\mathcal{B}_0} -\left[\nabla \cdot \mathbf{P}_F + \frac{3c_a k_B T}{Nb^2} \nabla \cdot \left(\mu_n F^{-T}\right) + b\right] \cdot \delta \mathbf{u} \, dV + \int_{\partial \mathcal{B}_{0 \sqcup}} \left(\mathbf{P} \, \mathbf{n} - \mathbf{t}\right) \cdot \delta \mathbf{u} \, dA = 0 \tag{5.1c}$$

where Ψ_{ext} is the energy associated with the external body force *b* and surface tractions *t*, and *n* is the unit outward normal to the boundary ∂B_0 . In equation (5.1*c*), obtained from (5.1*b*) by applying the divergence theorem, the first Piola stress tensor has been written as

$$P = \frac{\partial \Delta \Psi}{\partial F} = P_F + P_n = \underbrace{\frac{3c_a k_B T}{Nb^2} [\mu_F - \mu_0] F^{-T} + \pi F^{-T}}_{P_F} + \underbrace{\frac{3c_a k_B T}{Nb^2} \mu_n F^{-T}}_{P_n}.$$
(5.2)

where the two contributions, one coming from the mechanical deformation, P_F , and the other from the phase change, P_n , have been outlined. By introducing the standard FE discretization of the domain of interest, the interpolations of the nodal-related quantities reads:

$$u \cong \sum_{i=1}^{n_n} [N]_i \tilde{u}_i, \quad \nabla_X u \cong \nabla_X \sum_{i=1}^{n_n} [N]_i \tilde{u}_i = \sum_{i=1}^{n_n} [B]_i \tilde{u}_i,$$
(5.3)

where the interpolated displacements and their gradient have been expressed by using the corresponding nodal values \tilde{u}_i . In equation (5.3), $B = \nabla_X N$ is the standard compatibility matrix and N the shape function matrix (whose terms associated with the *i*-th node have been indicated with $[B]_i$ and $[N]_i$, respectively) and n_n is the number of nodes. By using the above interpolations and referring to the domain \mathcal{B}_{0e} (with boundary \mathcal{B}_{0e}) of a single FE, starting from equation (5.1*b*) we obtain the following equilibrium equation expressed in terms of the residual force vector \mathbf{R}^e :

$$\boldsymbol{R}^{e} = \boldsymbol{R}_{int}^{e} - \boldsymbol{R}_{ext}^{e} = \left[\int_{\mathcal{B}_{0e}} \boldsymbol{B}^{T} \boldsymbol{P}_{F} \, dV \right] - \left[\int_{\mathcal{B}_{0e}} \boldsymbol{N}^{T} \boldsymbol{b} \, dV + \int_{\partial \mathcal{B}_{0e \sqcup}} \boldsymbol{N}^{T} \boldsymbol{t} \, dA - \frac{3c_{a}k_{B}T}{Nb^{2}} \int_{\mathcal{B}_{0e}} \boldsymbol{B}^{T} \left(\boldsymbol{\mu}_{n} \boldsymbol{F}^{-T} \right) \, dV \right] = \boldsymbol{0}$$
(5.4)

where R_{ext}^e depends on the external mechanical forces and on the temperature of the material through the distribution tensor μ_n . By linearizing equation (5.4), the above-defined residual force vector is made to vanish at equilibrium by iteratively solving the following nodal displacement

incremental equations

$$K_T^j \Delta \tilde{\boldsymbol{u}}^j = -\boldsymbol{R}_i^j,$$

with $K_T^j = \mathbb{A}_{e=1}^{ne} K_T^{ej}$, and $\tilde{\boldsymbol{u}}_i^j = \tilde{\boldsymbol{u}}_{i-1} + \sum_{k=1}^j \Delta \tilde{\boldsymbol{u}}^k,$ (5.5)

that have been written at a generic mechanical load step *i* and iteration *j*, by considering the domain of the problem discretized with *ne* finite-elements. In (5.5), \tilde{u}_{i-1} is the converged solution at the previous step, $K_T^{ej} = \frac{\partial R_i^{ej}}{\partial u}$ is the standard tangent stiffness matrix of the finite-element *e* for the current step and iteration, and A is the assembly operator. It is worth mentioning that the micromechanical model presented in the previous sections is assumed to be adopted at the Gauss point level in the computational FE framework. The light diffusion and the heat conduction problems (namely the Beer–Lambert law [57] and the Fourier's heat conduction equation, respectively) are solved numerically, by adopting the same FE framework used for the mechanical problem, and whose equations are obtained through a weak formulation of the governing PDEs.

The solution of the light diffusion, heat conduction and mechanical problems, provided that the time step is sufficiently small, can be conveniently solved by adopting a staggered scheme to overcome the solution of a fully coupled problem. This approach is computationally convenient with respect to a fully coupled formulation; although the problem's unknowns are linked together, they can be evaluated directly by solving alternatively the corresponding subproblems. In more detail, the staggered solution procedure can be summarized as follows: (i) light diffusion problem (main unknowns: nodal light intensities). When the light intensity on the boundary is assigned in time, the light intensity within the domain is evaluated through the solution of the Beer–Lambert law (no iterations required) [57]. (ii) heat conduction problem (main unknowns: nodal temperatures). Once the heat generated per unit volume has been determined from the light intensity determined in (i), the temperature in the material is evaluated by solving the Fourier's heat conduction equation (no iterations required). (iii) mechanical problem (main unknowns: nodal displacements). Once the temperature in the material is known at a given time instant, the microscale quantities of the LCE (order tensor, step length tensor, etc.), and the chain distribution tensor, are updated. The solution is iteratively updated (equations (5.3)–(5.5)) until a proper convergence criterion is fulfilled. All the above-mentioned sub-problems are solved by accounting for the large displacements taking place in the material through the use of an updated Lagrangian approach.

6. Simulations of liquid crystalline elastomer elements actuated by lightinduced heating

In the following sections, we present some examples illustrating the morphing deformation of a LCE cantilever beam exposed to a light source. For all the presented cases, the following common geometrical, mechanical and chemical parameters have been assumed: beam sizes L = 8 mm, h = t = 0.5 mm, Young's modulus E = 1 kPa, Poisson's ratio v = 0.5, mass density of the LCE $\rho_{\text{LCE}} = 1000 \text{ kg m}^{-3}$, specific heat of the material $c = 1050 \text{ J kg}^{-1} \text{ K}$, initial value of the order parameter $Q_0 = 0.3$, phase transition temperature of the LCE $T_{NI} = 323 \text{ K}$, while the parameter controlling the steepness of the nematic–isotropic phase transition has been assumed to be p = 6. Further, the light absorbance of the polymer has been determined by equation (4.3) with $A_{\text{pol}} = 400 \text{ m}^{-1}$, and molar absorptivity of the photo-absorber units is equal to $\vartheta = 30 \text{ m}^2 \text{ mol}^{-1}$, while their concentration in the network has been assumed to be $C_n = 200 \text{ mol m}^{-3}$. The actuation capacity of LCEs is here assumed not to be dependent on the cross-link density of the polymer matrix, despite playing a general role [40]. The light source intensity distribution is assumed to be described by a Gaussian law as $I(X, t) = \alpha(t)I_0 \exp(-\frac{|X(t)-X_0|^2}{d^2})$, where I_0 is the maximum intensity occurring at $X = X_0$, and the parameter d defines the width of the distribution; in the

case of a moving light source, the position of the maximum light intensity is expressed through the translation speed v of the source as $|X_0| = v t$. No cooling is assumed to take place for all the cases examined, i.e. the beam is assumed to lose heat at a rate much slower than that of the heating.

The FE discretization of the LCE element has been performed by adopting (8×64) fournoded plane stress elements in which the nodal values of the field variables—namely the light intensity, temperature and displacement vector—have been determined working within an updated Lagrangian scheme, through the above-mentioned staggered scheme. The incompressibility constraint has been fulfilled by determining the hydrostatic stress enabling us to fulfil the volumetric constraint det F = 1 at each Gauss point of the discretized domain.

(a) Response of a light-driven monodomain liquid crystalline elastomer element under a uniform light source

In the first parametric simulations, we consider an LCE cantilever beam, whose nematic orientation is aligned with the *x*-axis, exposed to a fixed light source with a nearly uniform intensity characterized by $I(X, t) \cong I_0 = 200 \text{ mW cm}^{-2}$ and $d^2 = 10^{-3} \text{ m}^2$. The response of the LCE element is studied by adopting three different values of the thermal conductivity, namely $\lambda_T = 0.2$;0.8;1.5 W mK⁻¹.

In figure 3, the response of the beam is illustrated in three cases: firstly, the light is turned and kept on during the entire process (figure 3a, $\alpha(t) = 1$, $0 \le t \le 20$ s), in the second case the light intensity is made to vary linearly in the time interval $0 \le t \le 10 \le (\alpha_1(t) = t/10)$ and then maintained constantly on in the interval $10 \text{ s} \le t \le 20 \text{ s} (\alpha_1(t) = 1)$, while in the third case the light intensity is made to vary linearly in the whole time interval $0 \le t \le 20 \le (\alpha_2(t) = t/20, 0 \le t \le 20 \le)$ (figure 3e). The light intensity arising within the element when the light is on ($\alpha(t) = 1$) is illustrated in figure 3d. In figure 3b,c, the displacement path of the point P (figure 3b) and its vertical displacement history (figure 3c) are illustrated for three different thermal conductivity values λ_T ; it can be appreciated that low values of the heat conductivity allow a temperature difference between the top and bottom part of the beam to be maintained, so inducing a different order parameter change responsible for the beam morphing. On the contrary, high values of the heat conductivity lead to a more uniform temperature throughout the beam, causing a simple shortening of the beam itself (see red curves in figure $3b_{c}$). The second and third time-dependent light intensity histories induce a slower temperature increase in time with respect to the first case; the maximum deformation shown by the LCE element does not depend on the way the light is spread to the material, while the morphing of the element is delayed according to the way the light intensity varies in time.

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The temperature and the dimensionless order parameter maps, corresponding to the situations indicated with 1, 2 and 3 in figure 3c (corresponding to the maximum vertical displacement at point *P*), are illustrated in figure 4. It appears that a uniform temperature distribution across the element's height does not promote a significant nematic–isotropic distribution difference (see the maps of the order parameter on the right-hand side of figure 4) which is mainly responsible for the bending actuation.

It can be clearly appreciated that a uniform temperature distribution with values above the T_{NI} simply entails the shortening of the element because of the homogeneous contraction taking place along the initial nematic director direction.

(b) Simulation of a light-driven monodomain liquid crystalline elastomer element under a moving light source

In this second group of tests, we consider the LCE cantilever beam exposed to a moving light source (translating from left to right), whose intensity distribution is characterized by



Figure 3. LCE cantilever beam with different thermal conductivity values λ_T exposed to a uniform light coming from the top. Light on from t = 0 s until t = 20 s (*a*); dimensionless displacements at point P in the *x*-*y* plane (*b*) and corresponding time history of its vertical displacement (*c*). Schematic of the LCE cantilever beam and light intensity field within the domain, $\alpha = 1$ (*d*). Linear increase of the light intensity in the time interval $t = 0 \div 10$ s and in the time interval $t = 0 \div 20$ s (*e*); dimensionless displacements at point P in the *x*-*y* plane (*f*) and corresponding time history of its vertical displacement (*q*).

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Figure 4. Map of the temperature (left column) and of the dimensionless order parameter Q/Q_0 for the LCE cantilever beam of figure 3 for three different values of the thermal conductivity $\lambda_T = 0.2, 0.8, 1.5$ W mK⁻¹ adopted for the material; the deformed shapes illustrated correspond to the points 1 (*a*,*d*), 2 (*b*,*e*) and 3 (*c*,*f*) of the curves in figure 3*c* (from top to bottom, respectively).

 $I_0 = 800 \text{ mW cm}^{-2}$, $d^2 = 10^{-6} \text{ m}^2$ (for this choice of the parameter *d* the Gaussian distribution is far from being constant over the element's top surface) and velocity v = 0.5; 2 mm s^{-1} . The thermal conductivity of the material is assumed to be $\lambda_T = 0.2 \text{ W mK}^{-1}$ for all cases.

The purpose of the analyses is to study the effect of the speed of the moving light on the actuation response of the beam in the dimensionless time interval $0 \le t/t_c \le 1$, t_c being the

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Figure 5. Cantilever beam under a moving light source (*a*). Dimensionless vertical coordinate of the point P versus time for two different light velocities, v = 0.5 mm s⁻¹ and v = 2.0 mm s⁻¹ (*b*). Deformed shape of the centreline of the cantilever when the maximum intensity of the light is placed at X/L = 0.5 with the dimensionless order parameter map at the same time instant represented on the undeformed configuration (*c*). Deformed shape of the centreline of the LCE cantilever when the maximum intensity of the light is at X/L = 1.0 with the dimensionless order parameter map at the same time instant represented on the undeformed configuration (*d*).

time of the analysis, i.e. $t_c = L/v$. From figure 5b-d it can be appreciated that a light source moving sufficiently fast ($v = 2 \text{ mm s}^{-1}$) does not allow the material to heat up enough and the resulting actuation is very low; in fact, the point P moves upward by a small amount (figure 5b) and also the beam centreline displays a very limited deformation (see dotted red curve in figure 5b). On the contrary, when the light speed is small ($v = 0.5 \text{ mm s}^{-1}$) the heating process is most effective, and the actuation of the LCE element is clearly visible (black dot curves in figure 5b-d). In particular, when the maximum light intensity is located at the position X/L = 0.5 (i.e. at $t/t_c = 0.5$), the order parameter field is non-uniform, with the lowest values occurring in a small region located at the top of the beam, thus causing the appearance of a hinge-like deformed area (figure 5c); it must be noted that the hinged region is placed behind the maximum light intensity position because of the heat diffusion delay with respect to light diffusion.

Finally, when the light reaches the end of the beam $(t/t_c = 1)$, since the heat diffusion leads to an almost uniform temperature in the element, the order parameter is nearly constant in the vertical direction and no bending of the beam takes place (figure 5*d*).



Figure 6. LCE cantilever beam under a static light source with various intensity distributions (*a*–*c*). Corresponding deformed shapes of the element's centreline, and maps of the temperature and dimensionless order parameter plotted in the undeformed configurations at $t/t_c = 0.5$ (*d*–*f*) and at $t/t_c = 1$ (*g*,*h*,*i*).

(c) Response of a light-driven monodomain liquid crystalline elastomer element under a static light source with different intensity distributions

In this example, we investigate the effect of the spatial distribution of the light intensity on the morphing response of an LCE cantilever beam. The thermal conductivity of the material is $\lambda_T = 0.2 \text{ W mK}^{-1}$. The light source is assumed to be at rest, with a maximum intensity $I_0 = 200 \text{ mW cm}^{-2}$ placed at the middle of the element for the whole thermo-mechanical process whose duration is $t_c = 20 \text{ s}$. The response of the LCE element is studied by adopting three different values of the parameter defining the amplitude of the light intensity Gaussian distribution, namely $d^2 = 10^{-3}$; 10^{-5} ; 10^{-6} m^{-2} , figure 6a-c. The corresponding deformed shapes of the middle line of the LCE element are shown in figure 6d-f (at $t/t_c = 0.5$) and in figure 6g-i (at $t/t_c = 1$); the maps of the temperature and of the dimensionless order parameter, plotted on the undeformed configurations of the LCE element, are also reported in the figure.

In the case characterized by $d^2 = 10^{-3} \text{ m}^{-2}$ (the highest value considered), the Gaussian distribution is nearly constant along the upper boundary of the LCE element, i.e. $I(x)/I_0 \cong 1, \forall x \in [0, L]$, figure 6*a*. This corresponds to a uniform distribution of the light intensity along the LCE element, while the light intensity decreases through the element thickness because of the material's absorbance. Correspondingly, during the transient heat transfer phenomenon, a layered distribution of the temperature and of the order parameter across the height of the element take place, see maps in figure 6*d*,*g*. These fields are responsible for the morphing of the LCE element which shows a nearly uniform bending at $t/t_c = 0.5$, figure 6*d*, while it tends to simply contract at $t/t_c = 1$ when the heat diffusion leads to a nearly homogeneous temperature and order parameter fields, figure 6*g* (see §6a).

In the case $d^2 = 10^{-5}$ m², the amplitude of the Gaussian distribution is lower with respect to the case characterized by $d^2 = 10^{-3}$ m⁻², figure 6b. The temperature increase and the corresponding decrease of the order parameter take place locally, i.e. close to the location of the maximum light intensity, see maps in figure 6e,h. This induces the formation of a localized region having a non-uniform distribution of the temperature and of the order parameter, the latter being responsible for the bending deformation as shown in figure 6e,h (a highly deformed hinge-like region appears). Differently from the previous case where the LCE element was characterized by uniform bending, the presence of the hinge-like deformed region induces an actuation characterized by two nearly straight (undeformed) parts rotating about such a hinge centrepoint.

The results corresponding to the case $d^2 = 10^{-6} \text{ m}^2$ (narrowest light intensity distribution) are similar to the previous one but with a narrower width of the hinge-like region. In this case, the temperature in the material is lower than in the previous cases due to the more localized light intensity, and a longer time is required to heat up the whole domain. No deformation of the LCE element can be appreciated at $t/t_c = 0.5$ (figure 6*f*), while bending occurs at $t/t_c = 1$ due to the presence of a narrower (compared to the case $d^2 = 10^{-5} \text{ m}^2$, figure 6*i*), hinge-like deformed region.

7. Conclusion

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The multi-physics phenomena involved in the deformation of LCEs, whose actuation comes from the reversible switching from an isotropic to an ordered state triggered by light-induced heating, has been considered. The change of the order tensor, expressing the nematic order orientation, has been related to the so-called chain distribution tensor and its variation upon mechanical deformation and thermal-induced phase transformation have been quantified. The knowledge of the nematic–isotropic transition temperature allows us to determine the chain orientation distribution and, consequently, the deformation and the stress state of the material.

Light-induced actuation represents an interesting stimulus enabling us to obtain untethered actuators, whose response can be finely tuned through light control. Within this context, we have considered the generation of internal heat induced by an external light source due to the presence of photo-thermal particles embedded in the material. The involved multi-physics landscape requires the light diffusion and heat transfer phenomena, as well as the mechanics of the phase transition taking place in LCEs, to be properly described.

The lack of temperature uniformity has been shown to induce a bending-like deformation of the material, despite the mesogen units being aligned along a single preferential direction. Further investigations could elucidate the role played by the material absorbance on the time rate of the generated heat, enabling us to tune the actuation speed. Moreover, the change of the LCE optical properties during the thermo-mechanical process should also be investigated: understanding the absorbance-order parameter relationship will enable us to further exploit LCEs to obtain intriguing actuation capabilities.

The illustrated multi-physics theory has been implemented in an FE framework and several numerical examples have been performed to clarify the role of the main parameters involved, such as the thermal conductivity of the material, the light intensity distribution and the light speed when a moving source is considered.

A deep understanding and the availability of precise and efficient physics-based simulation tools, enable harnessing and optimizing the nematic arrangement through a precise material microstructure control, nowadays easily obtainable by advanced three-dimensional printing technologies. The inverse approach allows designing LCE-based elements and devices whose response, induced by suitable external stimuli, can be precisely tuned through proper mesogens arrangement patterns as well as cross-link density distribution within the material. This approach paves the way to the development of materials by designing their molecular scale structure, a strategy that offers an extremely wide design space for the optimization and the development of new devices with unprecedented responsive capabilities.

Data accessibility. Electronic supplementary material is available online [58].

Authors' contributions. R.B.: conceptualization, funding acquisition, methodology, software, writing—original draft, writing—review and editing; M.P.C.: investigation, software, visualization, writing—review and editing.

Both authors gave final approval for publication and agreed to be held accountable for the work performed therein.

Conflict of interest declaration. We declare we have no competing interests.

Funding. The support from the European Union's Horizon 2020 Spreading Excellence and Widening Participation program (H2020-WIDESPREAD-2018, SIRAMM), under grant agreement no. 857124 is greatly acknowledged.

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