Liquid crystal elastomers

Theory and Applications

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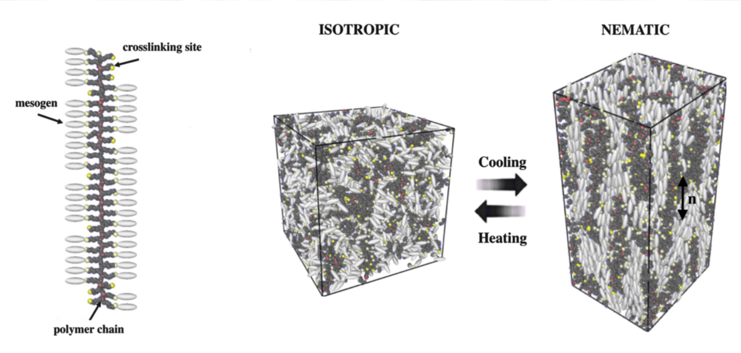
Liquid crystal elastomer (LCE)

Cross-linked networks of polymeric chains containing liquid crystal mesogens



Envisioned by P.G. de Gennes (1975)
Synthesised by H. Finkelmann, H.J. Kock & G. Rehage (1981)
Theoretical foundation by M. Warner & E.M. Terentjev (2003, 2007)
MD simulations by L.A.M., H. Wang, J. Guilleminot & A. Goriely (2021)

LCE natural response to heat, light, magnetic and electric fields
Can be made sustainable (biodegradable, recyclable, reprocessable)

The Gough-Joule effect

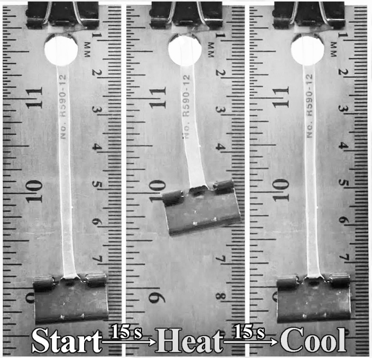
A tendency of stretched elastomers to contract when heated.

Observed in rubber by J. Gough (1802)
Studied by J.P. Joule in the 1850s

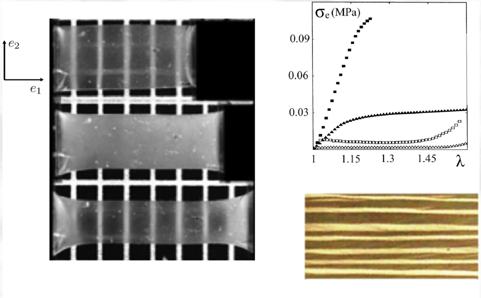
LCE monodomains

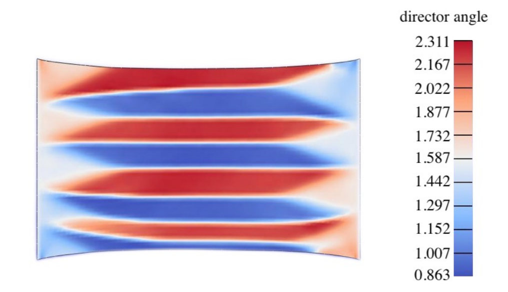
Nematic director well aligned.

Reliably synthesised by
J. Küpfer & H. Finkelmann (1991)



LCE shear striping
Large-strain deformation under uniaxial stress





J. Küpfer & H. Finkelmann (1991, 1994)
I. Kundler & H. Finkelmann (1995)

FEBio simulations by R. Poudel (2023)

LCE model function based on rubber elasticity

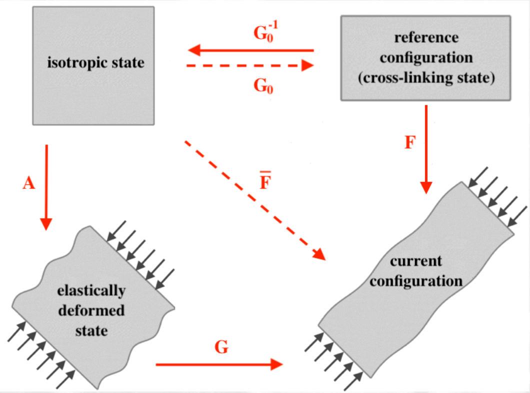
$$W^{(lce)}(\mathbf{F},\mathbf{Q}) = W^{(el)}(\mathbf{F},\mathbf{Q}) + W^{(lc)}(\mathbf{Q})$$

- $W^{(el)}(\mathbf{F},\mathbf{Q})$ is the elastic strain-energy density;
  - $\mathbf{F}$ is the deformation gradient from the reference configuration, $\det \mathbf{F} = 1$;
  - $\mathbf{Q} = \mathbf{Q}(\mathbf{n})$ describes orientational order in nematic liquid crystals;
  - $\mathbf{n}$ is the nematic director in the current configuration;
  - $\mathbf{n}_0$ is the nematic director in the reference configuration;
- $W^{(lc)}(\mathbf{Q}) = \frac{1}{3}\mathtt{A}\mathrm{tr}\left(\mathbf{Q}^2\right) - \frac{4}{9}\mathtt{B}\mathrm{tr}\left(\mathbf{Q}^3\right) + \frac{2}{9}\mathtt{C}\mathrm{tr}\left(\mathbf{Q}^4\right) + \cdots$ is the Landau-de Gennes expansion of the nematic free energy;
  - $\mathtt{A} = \mathtt{A}(T), \mathtt{B}, \mathtt{C}$ are material constants.

Early "theory on nematic networks" by M. Warner, K.P. Gelling & T.A. Vilgis (1988)
First models by P. Bladon, E.M. Terentjev & M. Warner (1993, 1994)

Deformation decomposition

$$\mathbf{F} = \mathbf{G}\mathbf{A}\mathbf{G}_0^{-1}, \qquad \mathbf{G}_0^2 = c_0\left(\mathbf{I} + 2\mathbf{Q}_0\right), \qquad \mathbf{G}^2 = c\left(\mathbf{I} + 2\mathbf{Q}\right)$$



Order parameter tensor

$$\mathbf{Q} = \text{diag}\left(-\frac{Q-b}{2}, -\frac{Q+b}{2}, Q\right)$$

Uniaxial order parameter

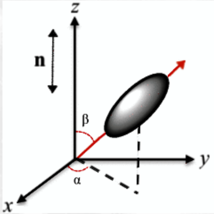
$$Q = \left\langle \frac{3}{2}\cos^2\beta - \frac{1}{2} \right\rangle$$

$Q = 1$ for perfect nematic;
$Q = 0$ for isotropic phase;

Biaxial order parameter

$$b = \frac{3}{2}\langle \sin^2\beta \cos(2\alpha) \rangle$$

$b \neq 0$ for biaxial systems;
$b = 0$ for uniaxial systems.



Requirements based on isotropic elasticity and liquid crystal theories

(C1) **Objectivity.** The constitutive equation is unaffected by a superimposed rigid-body transformation (which involves a change of position after deformation), i.e.,

$$W^{(lce)}(\mathbf{F}, \mathbf{Q}(\mathbf{n})) = W^{(lce)}(\mathbf{RF}, \mathbf{Q}(\mathbf{Rn}))$$

As $\mathbf{n}$ is defined with respect to the deformed configuration, it transforms when this configuration is rotated, whereas $\mathbf{n}_0$ does not. Material objectivity is guaranteed by defining strain-energy functions in terms of the scalar invariants.

(C2) **Isotropy.** The constitutive equation is unaffected by a rigid-body transformation prior to deformation, i.e.,

$$W^{(lce)}(\mathbf{F}, \mathbf{Q}(\mathbf{n})) = W^{(lce)}(\mathbf{FR}, \mathbf{Q}(\mathbf{n}))$$

As $\mathbf{n}$ is defined with respect to the deformed configuration, it does not change when the reference configuration is rotated, whereas $\mathbf{n}_0$ does. For isotropic materials, the strain-energy function is a symmetric function of the principal stretch ratios.

Stretch ratios have a clear kinematic interpretation

Ogden-type models

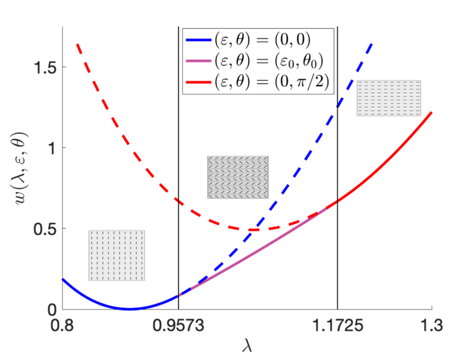
$$W^{(el)}(\lambda_1, \lambda_2, \lambda_3, \mathbf{Q}) = W^{(1)}(\lambda_1, \lambda_2, \lambda_3) + W^{(2)}(\alpha_1, \alpha_2, \alpha_3),$$

$$W^{(1)}(\lambda_1, \lambda_2, \lambda_3) = \sum_{j=1}^{m} \frac{c_j^{(1)}}{2\left(p_j^{(1)}\right)^2} \left(\lambda_1^{2p_j^{(1)}} + \lambda_2^{2p_j^{(1)}} + \lambda_3^{2p_j^{(1)}} - 3 \right)$$

$$W^{(2)}(\alpha_1, \alpha_2, \alpha_3) = \sum_{j=1}^{n} \frac{c_j^{(2)}}{2\left(p_j^{(2)}\right)^2} \left(\alpha_1^{2p_j^{(2)}} + \alpha_2^{2p_j^{(2)}} + \alpha_3^{2p_j^{(2)}} - 3 \right)$$

- $\{\lambda_1^2, \lambda_2^2, \lambda_3^2\}$ are the eigenvalues of $\mathbf{F}^T\mathbf{F}$, $\lambda_1\lambda_2\lambda_3 = 1$;
- $\{\alpha_1^2, \alpha_2^2, \alpha_3^2\}$ are the eigenvalues of $\mathbf{A}^T\mathbf{A}$, where $\mathbf{A} = \mathbf{G}^{-1}\mathbf{F}\mathbf{G}_0$, $\alpha_1\alpha_2\alpha_3 = 1$;
- Linear shear modulus is $\overline{\mu} = \overline{\mu}^{(1)} + \overline{\mu}^{(2)}$, with $\overline{\mu}^{(1)} = \sum_{j=1}^{m} c_j^{(1)}$, $\overline{\mu}^{(2)} = \sum_{j=1}^{n} c_j^{(2)}$.

Shear striping



A third equilibrium state is found when

$$\varepsilon_0=\pm\frac{\lambda(a-1)\sin(2\theta_0)}{2\sqrt{(\eta+1)(\eta+a)}}$$

$$\theta_0=\pm\arccos\sqrt{\frac{a^{1/6}\sqrt{(\eta+1)(\eta+a)}}{\lambda^2(a-1)}-\frac{\eta+1}{a-1}}$$

for $\quad a^{1/12}\left(\frac{\eta+1}{\eta+a}\right)^{1/4}<\lambda<a^{1/12}\left(\frac{\eta+a}{\eta+1}\right)^{1/4}$

where $\eta=\overline{\mu}^{(1)}/\overline{\mu}^{(2)}$.

L.A.M. & A. Goriely (2020)

Theorem. For ideal unconstrained uniaxial nematic LCEs described by

$$W^{(nc)}(\mathbf{F},\mathbf{n}) = W(\mathbf{A}),$$

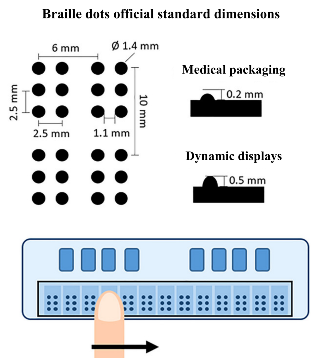
where $W(\mathbf{A})$ is the strain-energy density of the isotropic polymer network and $\mathbf{A} = \mathbf{G}^{-1}\mathbf{F}\mathbf{G}_0$, with $\mathbf{G}_0$ constant in Cartesian coordinates, a deformation with gradient $\mathbf{F}(\mathbf{X})$ which is piecewise of differentiability class $\mathcal{C}^2$, such that $\det\mathbf{F}(\mathbf{X}) > 0$, can be maintained for all $W^{(nc)}$ by the application of surface tractions only (without body forces) if and only if both $\mathbf{F}$ and $\mathbf{G}$ are piecewise constant in Cartesian coordinates. For geometric compaticility, in two adjacent subdomains, the deformation gradients $\mathbf{F}_+$ and $\mathbf{F}_-$, respectively, must be rank-one connected, i.e.,

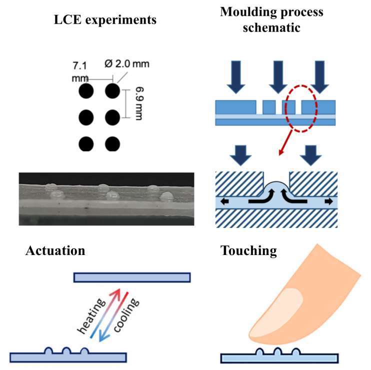
$$\operatorname{rank}(\mathbf{F}_+ - \mathbf{F}_-) = 1$$

L.A.M. & A. Goriely (2023)

APPLICATION 1

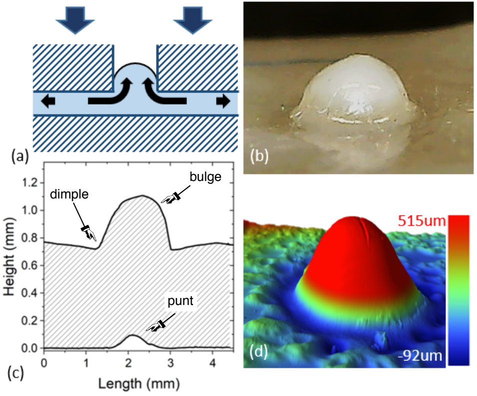
Haptic interfaces: Refreshable Braille displays

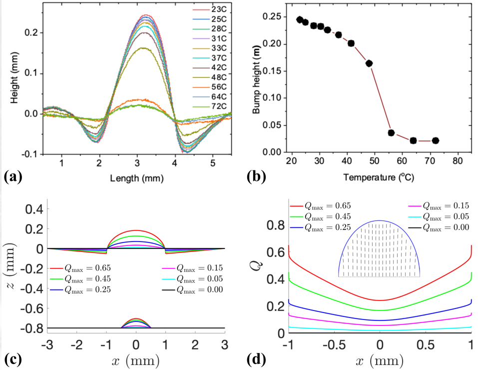




A. Gablier & E.M. Terentjev (2023)

Bulging and punting of actuated LCE

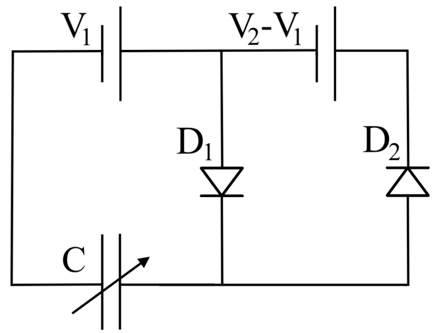




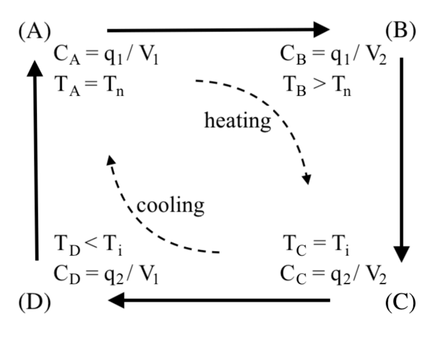
L.A.M., A. Gablier, E.M. Terentjev & A. Goriely (2023)

Energy harvesting via LCE actuation

Charge pump electrical circuit



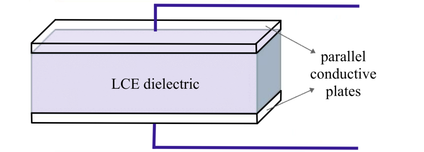
Operating cycle

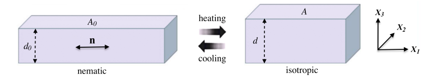


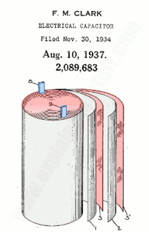
T. Hiscock, M. Warner & P. Palffy-Muhoray (2011)

Variable capacitor with LCE dielectric

Parallel compliant electrodes (other designs: multi-layer structure, concentric tubes, ...)







Courtesy US Patent & Trademark Office

Capacitance: $C(Q, \lambda) = q/V = \varepsilon\varepsilon_0 \Omega / d^2 = \varepsilon\varepsilon_0 \Omega / \left(\lambda^2 d_0^2\right)$

- $\Omega = Ad$ volume; A area of each plate; d distance between plates;
- q magnitude of charge stored when voltage across capacitor is V;
- ε permittivity of dielectric material;

Strain energy density

$$\mathcal{W}(Q,\lambda_1,\lambda) = \frac{\mu^{(1)}}{2}\left(\lambda_1^2 + \lambda_1^{-2}\lambda^{-2} + \lambda^2\right) + \frac{\mu^{(2)}}{2} a^{1/3} a_0^{-1/3}\left(\lambda_1^2 a^{-1} a_0 + \lambda_1^{-2}\lambda^{-2} + \lambda^2\right) - \frac{CV^2}{2Ad}$$

Net electrical energy generated by the cycle

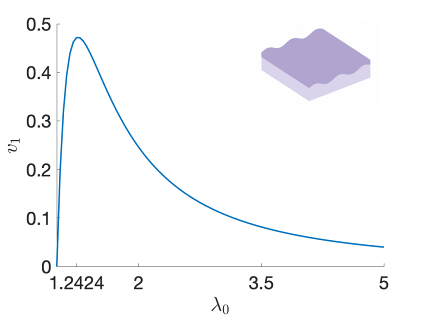
$$W = W_{out} - W_{in} = (V_2 - V_1)(q_1 - q_2) = -C_n V_1^2 \left(\frac{C_i}{C_B} - 1\right)\left(\frac{C_n}{C_B} - 1\right)$$

Maximum generated output per cycle

$$W_m = C_n V_1^2 \frac{(\xi - 1)^2}{4\xi},$$

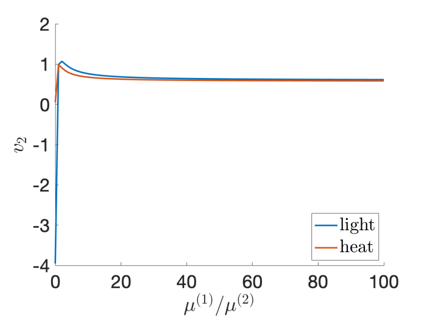
where $\xi = C_n/C_i > 1$.

INPUT WRINKLING VOLTAGE



(when pre-stretching parallel or perpendicular to the director)

OUTPUT WRINKLING VOLTAGE

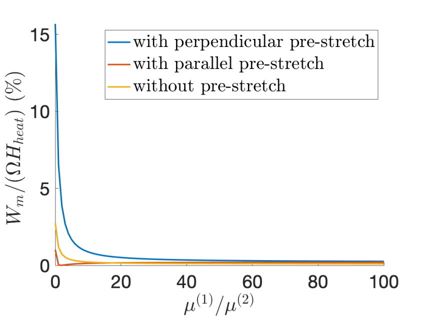


(when pre-stretching perpendicular to the director in the director plane)

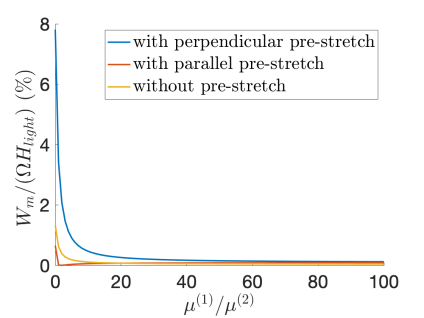
Energy efficiency

LCE nematic-isotropic transition requires $H_{heat} \approx 3 \cdot 10^6$ J/m^3 or $H_{light} \approx 10^7$ J/m^3

HEAT



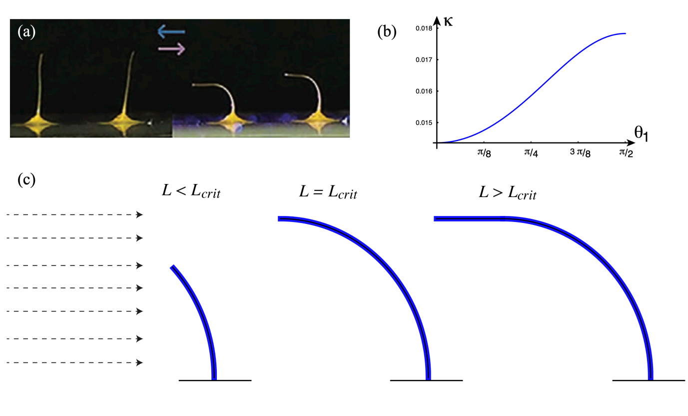
LIGHT



L.A.M. (2023)

APPLICATION 3

Light-induced actuation of phototropic LCE



A. Goriely, D. Moulton & L.A.M. (2021)

Tests: L. Liu, M. del Pozo, F. Mohseninejad, M.G. Debije, D.J. Broer & A.P.H.J. Schenning (2020)

Conclusion

- Developments in LCEs draw on understading from both elasticity and LC theories;
- In LCEs, mechanical strains give rise to changes in liquid crystalline order and, conversely, changes in orientational order generate mechanical stresses and strains;
- LCEs are top candidates for several important applications of mechanical actuation, including in biomedical engineering, power generation and flexible electronics.

THANK YOU

Engineering and Physical Sciences Research Council

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