

## **Phase Transitions in Liquid Crystalline Elastomers** *A Fundamental Aspect of LCEs as Artificial Muscles*

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**Key words:** Liquid Crystals, Elastomers, Phase Transitions, Microgravity

**Abstract:** Liquid crystalline elastomers (LCEs) are composed of low molecular weight mesogenic units tethered to a cross-linked polymer network. Because LCEs have remarkable shape-changing properties at the nematic-isotropic phase transition, it has been suggested that they could serve as generic large amplitude, low frequency actuators and sensors i.e. artificial muscles. As this transition does not exist in LCEs when the mesogenic side chains are uniformly oriented, the understanding of phase transitions in LCEs emerges as a topic of fundamental interest for their application as artificial muscles.

### **1. INTRODUCTION**

The understanding of phase transitions in liquid crystalline elastomers (LCEs), falls under several topics of fundamental interest. These include a deeper understanding of the role fluctuations play in modifying structural properties, the control of instabilities at traveling phase boundaries and situations where objects must be freely suspended. The study of phase transitions in liquid crystals has long been of interest to the general physics community [1] because it has enabled stringent tests of modern phase transition theories and revealed a wealth of new physics and symmetry breaking scenarios (see e.g. [2]) not anticipated by theory.

The structure of LCEs involves interactions between long range cooperative forces of low molecular weight liquid crystals (LMWLCs) with a cross linked polymer network. LCEs exhibit a dramatic shape change at the

nematic-isotropic phase transition of the low molecular weight liquid crystalline moiety chemically tethered to the cross-linked polymer network. In the absence of a liquid crystal moiety, the polymer network has no phase transition. This has led to the suggestion by de Gennes et al. that LCEs may be useful components in artificial muscles [3,4]. However, to turn the unusual shape changing properties of LCEs into a viable device, it is desirable to trigger such shape changes with weak electric fields rather than temperature changes. This in turn requires a deeper grasp of how liquid crystalline cooperative effects couple to the cross-linked polymer network.

We have observed a large spontaneous shape change associated with the nematic-isotropic phase transition in monodomain LCEs, that is, one where the orientational order is uniform. This is interesting because the nematic-isotropic phase transition no longer exists in the weakly cross-linked LCEs known at this time. In analogy to the usual critical point, the nematic-isotropic phase transition in monodomain LCEs is said to be “beyond the critical point” [5]. In low molecular weight liquid crystals and in liquid crystal polymers, this transition is first order.

While low molecular weight LCs and LC polymers are not birefringent in the isotropic state, monodomain nematic LCEs maintain birefringence in the isotropic state of the low molecular weight moiety [6-8]. On the other hand, monodomain smectic A LCEs, where there is a layered structure perpendicular to the direction of orientational order [9,10], are not birefringent when the liquid crystalline moieties lose long range orientational order. In addition, we have not observed a large spontaneous shape change associated with the smectic A-isotropic transition.

In this short report, we only discuss results observed at the nematic-isotropic phase transition of monodomain LCEs. The technique used is observations in a polarizing microscope with a video-camera whose output is fed to an image analysis system that we developed at Bell Labs about 10 years ago. This particular experimental strategy is particularly suited for obtaining qualitative and quantitative information related to liquid crystal phase transitions, traveling phase boundaries, defect dynamics and instabilities, see e.g. [11-17] – in short, topics of fundamental interest to materials behaviour in microgravity. To fine-tune LCE materials properties so that they may realize their full potential as reliable low frequency, large amplitude biomimetic sensors and actuators driven by weak electric fields, rather than temperature (at this time, the only known way to trigger LC cooperative effects on the network), we believe that such fundamental knowledge is crucial.

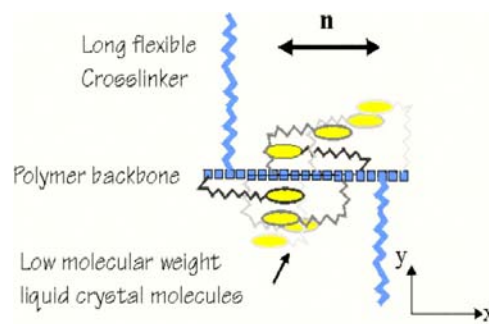
## 2. NEMATIC LCEs

Nematic liquid crystalline elastomers were first synthesized by Finkelmann et al. in 1981 [6]. These materials became accessible to physical studies in 1991 when Küpfer and Finkelmann synthesized the first nematic LCE where the orientational order of the low molecular weight liquid crystalline molecules is uniform and the material is transparent [7]. They called these uniformly oriented LCEs, Liquid Single Crystalline Elastomers or LSCEs. A great deal of work has been accomplished to document their unusual mechanical properties [8].

These mechanical properties are measured by applying a stress ( $\sigma$ ) parallel to  $\mathbf{n}$ , i.e. a load, then measuring SLCE extension ( $\lambda$ ). At the nematic-isotropic transition, extensions on the order of 50% are observed in side-chain LCEs. Even larger extensions ( $\sim 300\%$ ) have been measured in LCEs where the LMWLCs are part of the polymer network [18]. We note that such large deformations at the nematic-isotropic transition are not observed in polydomain LCEs.

The new physics as far as a macroscopic description of the nematic-isotropic transition in LCEs is concerned, is the coupling between the orientational order parameter ( $Q_{ij}$ ) of the nematogens (LMWLCs) and the cross-linked polymer network [19]. A model proposed to describe the role of the cross-linked polymer network is a static orientational order parameter,  $P_{ii}$ , associated with the orientational order frozen into the cross-linking sites during the synthetic process [7-10]. The lowest order coupling between  $P_{ii}$  and  $Q_{ij}$  is linear. Above a threshold value for  $P_{ii}$ , the discontinuity at the first order nematic-isotropic phase transition “disappears” giving rise to a continuous behaviour for  $Q_{ij}$  as the transition to the isotropic state takes place. This is a “minimal” theoretical picture to account for the nematic-isotropic transition “beyond the critical point” [19].

The deGennes et al. [3,4] model treats the nematic-isotropic transition in LCEs as being first order with two competing metastable regions, isotropic and nematic, separated by an interface that can be made to propagate either

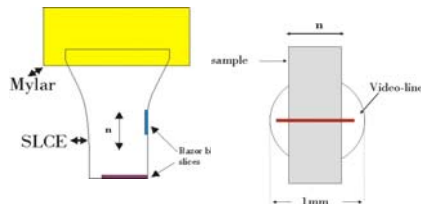


**Fig. 1:** Liquid Crystalline Elastomers are spatially homogeneous multi-component systems with novel mechanical properties. LCEs are composed of  $\sim 80\%$  low molecular weight liquid crystals (LMWLCs) and  $\sim 20\%$  polymer and cross linking agent. The direction of orientational order for the LMWLCs is shown as  $\mathbf{n}$ . ©ALCT

way depending on the temperature change [see e.g. 11]. They also invoke a propagating deformation wave traveling at twice the transverse speed of sound in these materials, that changes the shape of the elastomer at constant volume.

We cannot test the de Gennes et al. model because it turns out that all known liquid single crystalline elastomers have nematic-isotropic transitions that have “disappeared”.

## 2.1 Observation of Spontaneous Shape Change



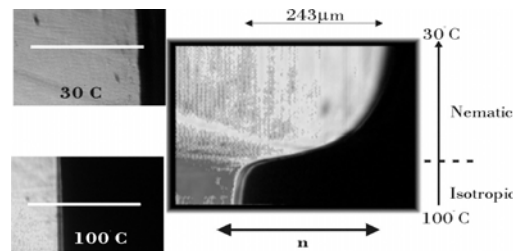
Figs. 2.1 (left) and 2.2 (right).

We look at the sample between crossed polarizers using a video-camera and image analysis. A feature of this image analysis system is that one line of a video frame (Figure 2.2) can be collected at fixed time intervals. After collection, the lines for each time interval are plotted in sequence to make another picture called an ST-plot - for Space-Time. While the ST-plot is running, the temperature is scanned at a fixed rate. The start and final temperatures are noted. In this way we convert time to temperature. A cooling result is shown in Figure 2.3.

In Figure 2.3, the total sample width is  $l = 1350\mu\text{m}$ . Assuming both sides expand equally (checked later on samples where both edges could be observed), the total

We cut slices from the nematic SLCE that Nicole Assfalg, at that time a PhD student in the laboratory of Professor H. Finkelmann, had sent us. Slices were made parallel and perpendicular to  $\mathbf{n}$  (Figure 2.1).

A sample is made by suspending a slice over a hole in a microscope



**Fig. 2.3.** *Left frame.* Two snapshots of the field of view in a polarizing microscope (polarizers crossed  $45^\circ$  to the picture borders) at the start of the run ( $100^\circ\text{C}$ ) where the elastomer is isotropic and at the end ( $30^\circ\text{C}$ ) where it is nematic. The direction of orientational order is marked  $\mathbf{n}$ . *Right frame.* The ST plot at one of the LSCE-air edges while the temperature is scanned from  $100^\circ\text{C}$  to  $30^\circ\text{C}$  at  $0.034\text{K/s}$ . Between crossed polarizers, the air is black. In the nematic phase (bulged part), the LSCE is brighter than it is in the isotropic liquid state at  $100^\circ\text{C}$  where it is nevertheless still birefringent. A very large change in position of the cut edge is evidenced at  $76.2^\circ\text{C}$ , the nematic-isotropic transition temperature. The transition is sharp but there is no evidence of front propagation. At this transition, the LCE-air edge moves about  $243\mu\text{m}$  in  $\sim 1\text{K}$  (or about  $3\text{s}$  i.e. its response time here is that of the scanning rate).©ALCT

extension is  $\Delta l \sim 500 \mu\text{m}$  or  $\Delta l/l \sim 0.35$ . This is a large extension but consistent with thermoelastic measurements. We stress that this shape change is a spontaneous temperature response independent of gravity.

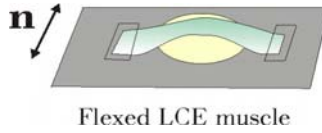
## 2.2 LCEs as Artificial Muscles

The realization that large displacements of the elastomer boundary can take place at the nematic-isotropic transition prompted de Gennes et al. [3,4] to suggest liquid crystalline elastomers as promising candidates for artificial muscles.

For example, in Figure 2.3, the ends of the sample on the substrate are nearly free. In Figure 2.4, we show the result when the elastomer ends are clamped to the sample substrate at room temperature (where it is nematic) then heated to the isotropic state. Scotch tape is the clamping device (empty rectangles in Figure 2.4).

While the sample thins along  $\mathbf{n}$ , it expands perpendicular to  $\mathbf{n}$ . The sample is clearly seen arching over the substrate hole. The “muscle” has flexed.

*Conclusion:* At the bulk nematic-isotropic transition, the orientational order of low molecular weight liquid crystal side-chains controls the network shape. This is a remarkable result posing many open fundamental questions. Figure 2.3 shows that despite being constrained by attachments to the cross-linked polymer network, working cooperatively, the low molecular weight nematogens can influence the network shape even when the nematic-isotropic transition has “disappeared”.



**Fig. 2.4.** Flexed sample made by fixing the LSCE ends to the substrate then heating to the isotropic state.  
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## 3. QUASI-ISOTROPIC MODEL

A *quasi-isotropic* model for LSCEs (Eq. 1) has been developed by Weilepp and Brand (the WB model) [20] to account for the appearance of a threshold stress,  $\sigma_c$  (Eq. 2), for reorientation of  $\mathbf{n}$  when  $\boldsymbol{\sigma}$  is applied at an LSCE at an angle to  $\mathbf{n}$  [21]. We discuss this model here as it is the only theoretical analysis we know that discusses the coupling between liquid crystalline cooperative effects, as embodied by the direction of orientational order,  $\mathbf{n}$ , and the elastomer network. The WB model nicely summarizes the situation where long range orientational cooperative effects are important and gives a sense of the measurable parameters to test the model. In the example presented here, the analysis of the WB model finds that the observed

threshold field is a forward bifurcation with the external mechanical stress,  $\sigma$ , as the control parameter [20].

Up to terms quadratic in the strain field,  $\varepsilon_{ij}$ , and the rotation of the network relative to  $\mathbf{n}$ ,  $\tilde{\Omega}_i$ , WB write for the generalized energy,  $E = E_0 + \tilde{E}$ .  $E_0$  contains terms present in a simple liquid and  $\tilde{E}$  has the following terms:

$$\tilde{E} = \int d\mathbf{r} \left\{ \begin{array}{l} \frac{1}{2} (C_1 \varepsilon_{ij}^2 + C_2 \varepsilon_{ii}^2) + \text{Isotropic elastic medium with shear modulus, } C_1, \text{ and bulk modulus, } C_2. \\ \frac{1}{2} (D_1 \tilde{\Omega}_i \tilde{\Omega}_j + 2D_2 \tilde{\Omega}_i \varepsilon_{jk} n_j \delta_{ik}^{\text{tr}}) + \Omega_i = \delta n_i - \Omega_i^\perp: \text{ rotation of the network relative to } \mathbf{n} \\ K/2[(\text{div } \mathbf{n})^2 + (\mathbf{n} \times \text{curl } \mathbf{n})^2] \text{ Frank elastic energy with planar variations in } \mathbf{n}. \end{array} \right. \quad [1]$$

In Equation 1,  $\mathbf{n}$  is the usual LC director with  $n_i \delta n_i = 0$ . The geometry is 2-dimensional with thickness,  $\ell$ , in the third dimension. With variations of  $\mathbf{n}$  confined to a plane, only splay ( $\text{div } \mathbf{n}$ ) and bend deformations ( $\mathbf{n} \times \text{curl } \mathbf{n}$ ) for  $\mathbf{n}$  are needed. The Frank elastic constant for splay,  $K_1$ , and bend,  $K_3$ , are set equal to  $K$ . In the isotropic state,  $K = 0$ .

As LCEs have a finite static shear modulus, the WB model includes solid state elastic effects, the  $C_i$ . While a uniaxial solid has 5 coefficients, an approximately isotropic elastic medium has only two: a shear modulus,  $C_1$ , and a bulk modulus,  $C_2$ .

In addition to the strain tensor,  $\varepsilon_{ij} = \frac{1}{2}(\nabla_i u_j + \nabla_j u_i)$ , where the  $u_i$  are components of a displacement vector,  $\mathbf{u}$ , they take into account relative rotations between the network and  $\mathbf{n}$  in the following way. In a theory linearized with respect to elastic effects, the rotations of the network take the form:  $\Omega_i^\perp = n_j \Omega_{ij}$  where  $\Omega_{ij}$  is the linearized rotation tensor,  $\Omega_{ij} = \frac{1}{2}(\nabla_i u_j - \nabla_j u_i)$ . The rotation of the network relative to  $\mathbf{n}$  is then:  $\Omega_i = \delta n_i - \Omega_i^\perp$ . These terms are controlled by the relative rotation constants,  $D_i$ .

The external mechanical stress sets up deformations via Hooke's Law. Then, the competition between the relative rotations and the strains leads to an optically detectable director rotation with respect to the network. The two solutions to the WB model are  $\varphi = 0$  when  $\sigma < \sigma_c$  and  $\varphi \propto (\sigma - \sigma_c)^{1/2}$  when  $\sigma > \sigma_c$  where  $\sigma_c$  is given by:

$$\sigma_c = \frac{\pi}{\ell D_2} \sqrt{K C_1 (D_1 C_1 - D_2^2/2)} \quad [2]$$

In the linear limit, where  $\sigma - \sigma_c \propto \lambda - \lambda_c$ , the WB model gives a nice comparison between theory [20] and the data of Kundler and Finkelmann who measured the reorientation angle,  $\varphi$ , as a function of  $\lambda$  [21].

That  $D_2$  is crucial for director reorientation can be seen in Equation 2: when  $D_2 \rightarrow 0$ ,  $\sigma_c \rightarrow \infty$ . In addition, when  $K \rightarrow 0$ ,  $\sigma_c \rightarrow 0$ . A study of  $\sigma_c$  as a function of temperature and cross-linking density in LSCEs would be a stringent test of the WB model with development potential for novel methods to control cooperative effects with weak electric fields in LC elastomers.

## 4. CONCLUSION

The study of Phase Transitions in liquid crystalline elastomers falls under several areas of fundamental interest for Physics and BioPhysics in microgravity. It is a new field just opening up to physical studies. The probability is therefore large that qualitatively new directions as well as novel applications such as artificial muscles, could emerge.

### References

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