Negative Poisson’s ratio and semi-soft elasticity of smectic-C liquid crystal elastomers

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Models of smectic-C liquid crystal elastomers predict that it can display soft elasticity, in which the shape of the elastomer changes at no energy cost. The amplitude of the soft mode and the accompanying shears are dependent on the orientation of the layer normal and the director with respect to the stretch axis. We demonstrate that in some geometries the director is forced to rotate perpendicular to the stretch axis, causing lateral expansion of the sample; a negative Poisson’s ratio. Current models do not include the effect of imperfections that must be present in the physical sample. We investigate the effect of a simple model of these imperfections on the soft modes in monodomain smectic-C elastomers in a variety of geometries. When stretching parallel to the layer normal (with imposed strain) the elastomer has a negative stiffness once the director starts to rotate. We show that this is a result of the negative Poisson’s ratio in this geometry through a simple scalar model.

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I. INTRODUCTION

Liquid crystal elastomers (LCEs) are soft solids composed of flexible polymers, with attached liquid crystalline mesogens, crosslinked into a network [1]. A variety of liquid crystalline phases of LCEs have been synthesized, including the nematic and smectic phases. The nematic phase undergoes deformation at no energy cost, known as soft elasticity [2] in both monodomain samples stretched perpendicular to the director [3], and in some types of polydomain samples [4–6]. Soft elasticity in nematic elastomers requires several sympathetic shears to develop during the deformation as the director rotates. The deformation of the sample must also obey the boundary conditions imposed by the clamps. Thus, the sample forms a striped microstructure on the micrometre length scale consisting of domains in which the director rotates in opposite directions in adjacent domains [7]. Without this microstructure soft deformations would not be possible. In nematics this microstructure has been observed in some detail experimentally [8], and its mathematical properties described [9]. Theoretically an ideal nematic LCE should be perfectly soft, however in practise a small force must be applied to deform the LCE. This semi-soft behaviour is due to various imperfections in the elastomer, and can be incorporated into theoretical models by the addition of a semi-soft energy term that penalises rotation of the director with respect to the rubber matrix [10].

Smectic LCEs have been fabricated in both the smectic-A (Sm-A) and smectic-C (Sm-C) phases, and with both main chain [11] and side chain [12] architectures. Their mechanical behaviour can be modelled by adding in the embedded smectic layers to the nematic elasticity free energy [13, 14]. Sm-A elastomers with a high degree of smectic order exhibit a sharp change in their elastic deformation when deformed parallel to the layer normal, and are extremely anisotropic materials, behaving as 2-D elastic materials [12, 15, 16]. However, the response of smectic elastomers depends on the chemistry, the crosslinking procedure, and domain sizes in the sample [17]. In contrast to the nematic phase the Sm-A phase does not show any soft elastic behaviour because the director is locked parallel to the layer normal. However, the elastic behaviour of Sm-C elastomers is predicted to be more complex. The director is free to rotate on a cone around the layer normal, with fixed tilt angle as shown fig. 1 a). As a consequence it is predicted to have a soft elastic mode just as in nematic elastomers [18, 19]. A more complicated combination of shears is required in Sm-C soft modes. As a result of the compatibility requirements between these deformations a far more restricted set of tensile geometries are predicted to deform softly with clamped boundary conditions [20].

To test these theoretical results experimentally, a monodomain must be produced which requires alignment of both the layer normal and the director. Using a two-stage crosslinking method, the director field can be uniformly aligned [21]. However, the layer normals are tilted at a fixed angle on a cone around the director. We will refer to this as a pseudo-monodomain (see fig. 1 b)) [22] in order to distinguish it from a monodomain, which has both the layer normal and the director uniformly aligned, and polydomain, which has random director and layer normal alignment. The layer normals in the pseudo-monodomain

FIG. 1. a) The layer normal and director in the Sm-C phase (polymer chains not shown), b) the director and layer normals in a pseudo-monodomain.
can be aligned by a second uniaxial deformation perpendicular to one of the layer normals [23], or alternatively by a shear deformation perpendicular to the director [24]. To our knowledge no mechanical experiments on monodomain Sm-\(C^\ast\) elastomers have been reported, perhaps because of the difficulty in aligning these samples. However, the spontaneous deformations associated with changing the phase of the elastomer from Sm-A to Sm-C have been observed [25]. Many more experiments have been carried out on the more accessible polydomain system [11] [26]. Unfortunately, as with many polydomain systems, this is more difficult to model theoretically.

The director reorientation in soft modes may be particularly important for the electromechanical properties of chiral Sm-\(C^\ast\) phase elastomers [27]. The liquid crystal rods have a permanent dipole moment that is aligned perpendicular to both the director and the layer normal. The coupling between the macroscopic mechanical deformations, and the microscopic orientation of these dipoles results in their piezoelectric properties. These materials show both the direct piezoelectric effect in nematic elastomers that will be used here [28], as well as the inverse piezoelectric effect [29]. Spontaneous polarization of pseudo-monodomains has also been reported [30].

This paper is organised as follows. We will describe the model of Sm-\(C^\ast\) elastomers that will be used in [11] and show that the soft modes in this model have negative incremental Poisson’s ratio in some geometries. In [11] we will illustrate the effect of the semi-soft elastic term in four different geometries. We will then summarise the effect of this term, and discuss the model predictions in relation to the mechanical experiments in polydomains in [11].

II. MODEL FREE ENERGY

The model of a Sm-\(C^\ast\) elastomer that will be used here is described in Refs. [30] [31]. The free energy has contributions from the nematic elasticity \(F_{nem}\), smectic layer spacing \(F_{sm}\), and the energy penalty for changing the tilt of the director with respect to the layer normal \(F_{tilt}\). The nematic elasticity is given by

\[
F_{nem} = \frac{1}{2} \mu \text{Tr} \left[ \lambda \cdot \xi_0 \cdot \lambda^T \cdot \xi^{-1} \right]
\]  

(1)

where \(\mu\) is the rubber modulus, and \(\lambda\) is the deformation gradient. The step length tensor before the deformation has been applied is \(\xi_0 = \hat{\kappa} + (r - 1) \mathbf{n}_0 \mathbf{n}_0\), with \(\mathbf{n}_0\) the initial director, \(\hat{\kappa}\) the unit tensor, and \(r\) the polymer anisotropy. The current step length tensor is denoted by \(\xi\), and its inverse by \(\xi^{-1} = \hat{\kappa} + (1/r - 1) \mathbf{n} \mathbf{n}\), with \(\mathbf{n}\) the final director. In principle a Sm-\(C^\ast\) elastomer should have a biaxial shape tensor for the polymer backbone because its shape may be affected by both the director alignment and the layer normal direction. For simplicity we will approximate it as uniaxial here, depending only on the director. We will also assume that the nematic and smectic order parameters remain fixed throughout the deformation.

It is assumed that the smectic layers are embedded in the rubber matrix, so that the corresponding layer normals \(\mathbf{k}\) will deform like embedded planes

\[
\mathbf{k} = \frac{\lambda - T \cdot \mathbf{k}_0}{|\lambda - T \cdot \mathbf{k}_0|}
\]

(2)

where \(\mathbf{k}_0\) is the initial layer normal. The layer spacing is penalised by the smectic liquid crystal modulus \(B\)

\[
F_{sm} = \frac{1}{2} B \left( \frac{d}{d_0} - \frac{\cos \theta}{\cos \theta_0} \right)^2
\]

(3)

where \(d\) is the final layer spacing, and \(d_0\) is the initial layer spacing, and \(d/d_0 = 1/|\lambda - T \cdot \mathbf{k}_0|\). \(F_{sm}\) describes the free energy penalty for deviations of the layer spacing away from that required to accommodate the smectic mesogens. For tilted smectic mesogens, the required layer spacing is \(\cos \theta / \cos \theta_0\), where their tilt angle with respect to the layer normal is \(\theta_0\) in the initial state, and \(\theta\) in the current state. The free energy term that penalises the deviation of the director from a tilt angle \(\theta_0\) is

\[
F_{tilt} = \frac{1}{2} a_4 \left( \cos^2 \theta_0 - (\mathbf{n} \cdot \mathbf{k})^2 \right)^2
\]

(4)

where \(a_4\) is the tilt modulus, and \(\mathbf{n} \cdot \mathbf{k} = \cos \theta\).

It will be assumed here that the bulk modulus of the rubber is much larger that the shear, tilt and smectic moduli, so that the deformation gradient obeys \(\det \lambda = 1\), hence it conserves volume. Typically the smectic layer modulus is very large compared to the rubber shear modulus, i.e. \(B \gg \mu\) (at least in smectic elastomers of a similar type to that of Nishikawa et al. [15]), so that the layer spacing remains almost fixed. The tilt modulus is also large compared to the shear modulus \(a_4 \gg \mu\), so that the tilt angle remains close to \(\theta_0\) [32].

A. Soft elasticity

The free energy outlined above permits the subset of the nematic soft modes that maintain the layer spacing. There is only one soft mode that satisfies this (up to a global rotation), and it corresponds to a rotation of the director about the layer normal [18] [19]. We summarise some of the properties of this soft mode here, as they are crucial in understanding the semi-soft response of the elastomer.

We assume that the layer normal points along the \(\mathbf{z}\) direction, and the director is tilted into the \(\mathbf{y}\) direction, i.e. \(\mathbf{k}_0 = \mathbf{z}\) and \(\mathbf{n}_0 = \mathbf{z} \cos \theta_0 + \mathbf{y} \sin \theta_0\) in the starting state. The soft modes can be parameterised by the angle \(\phi\) which gives the rotation of the director \(\mathbf{n}_0\) around the
layer normal towards the x direction. The deformation matrix is given by [18]

\[
\begin{pmatrix}
1 & a(\phi) & 0 \\
0 & (1 - \frac{r}{2}) \sin 2\phi & (r - 1) \sin 2\theta_0 \\
0 & \frac{(r - 1) \sin 2\theta_0}{2r} & 1
\end{pmatrix}
\]

where

\[
\rho = \sin^2 \theta_0 + r \cos^2 \theta_0 \quad \text{(6)}
\]

\[
a(\phi) = \sqrt{\cos^2 \phi + \frac{\rho}{r} \sin^2 \phi}. \quad \text{(7)}
\]

The deformation components as a function of rotation angle are illustrated in Fig. 2.

FIG. 2. For the parameter values \( r = 2 \) and \( \theta_0 = 0.5 \) radians a) shows the diagonal components of the deformation matrix, b) shows the shear components, and c) shows an illustration of the deformations on the LCE, together with the component of the director perpendicular to the layer normal, c.

The soft mode in Eq. (5), denoted by \( \lambda_{\text{soft}} \), can be transformed to different starting configurations of the director and layer normal by the following rotations

\[
\lambda_{k_0}^{\text{soft}} = P \cdot \lambda^{\text{soft}}(\phi) \cdot Q
\]

where the rotation matrix \( Q \) takes the general starting layer normal \( k_0 \) to the z direction, and \( n_0 \) into \( \cos \theta_0 z + y \sin \theta_0 \). The second rotation matrix \( P \) can be used to satisfy the requirements of the soft mode in target state, for example ensuring that the \( z \) shear component is zero. This transformation is described in Appendix A for the case of stretching parallel to the layer normal in the \( k_0 = x \) direction, when \( n_0 = \cos \theta_0 x + \sin \theta_0 y \). Although the result is analytic, the algebra is not instructive, and is not presented here. The components of the deformation matrix for this geometry are illustrated in Fig. 3. The \( \lambda_{zz} \) component increases with imposed \( \lambda_{xx} \), i.e. the sample expands in the direction perpendicular to the imposed elongation. This is because the constraint requiring a fixed angle between the layer normal and director results in the director rotating into the z direction. The sample then expands to accommodate the anisotropic chain shape, as shown in Fig. 4. This illustrates an unusual property of some Sm-C soft modes: their negative Poisson’s ratio. To our knowledge this mechanism for negative Poisson’s ratio has not been reported before. Alternative mechanisms of producing auxetic behaviour based on modifying the attachment of mesogens to the polymer backbone in smectic LCEs have been proposed and investigated experimentally [33, 34].

The incremental Poisson’s ratio (IPR) is defined by

\[
\nu_{zz} = \frac{-d\lambda_{zz}}{d\lambda_{xx}} \quad \text{(9)}
\]

where an elongation \( \lambda_{xx} \) is imposed and \( \lambda_{zz} \) is the transverse deformation. For isotropic materials, the Poisson’s ratio must be in the range \(-1 < \nu < 0.5 \). LCEs are anisotropic materials, so have Poisson’s ratios outside this range. As the materials considered here are volume conserving, the Poisson’s ratio in the y direction is

\[
\nu_{yy} \quad \text{(10)}
\]
FIG. 4. An illustration of the Sm-\textit{C} elastomer deformation when stretching parallel to the layer normal. The director (red) moves out into the z direction perpendicular to the stretch axis, maintaining its tilt angle with respect to the layer normal (white) causing the elastomer to expand in the perpendicular direction.

\[ \nu_{yy} = 1 - \nu_{zz}. \]  

When stretching parallel to the layer normal, the Poisson’s ratio at \( \lambda_{xx} = 1 \) is given by  
\[ \nu_{zz} = \left. \frac{d\lambda_{zz}}{d\lambda_{xx}} \right|_{\lambda_{xx}=1} = -\frac{1}{(r-1)\cos^2\theta_0}. \]  

Substituting in typical values of \( \theta_0 \sim 0.5 \) radians, and \( r \sim 2 \) for a side chain system produces \( \nu \sim -1.3 \). This corresponds to a larger expansion than is achieved in auxetic foam systems [35], albeit in only one direction. The extent of the soft mode in this geometry is  
\[ \lambda_{xx} = \sqrt{1 + \frac{(r-1)^2}{\rho^2} \sin^2 2\theta_0}, \]  

hence it has no extent when \( \theta_0 = 0 \), or when \( r = 1 \). Consequently the result in Eq. (10) cannot be used to calculate Poisson’s ratio for the Sm-\textit{A} phase which has no soft deformations.

B. Semi-soft elasticity

Soft modes in ideal LCEs have zero energy cost, and so the sample requires no force to deform. In practise these materials have several sources of non-ideal behaviour, such as compositional fluctuations and cross linking points that result in semi-soft behaviour. We will use the well known, and general form (up to quadratic order) of semi-soft elasticity in nematics [10]

\[ F_{ss} = \frac{1}{2} \alpha \mu \text{Tr} \left[ \mathbf{A} \cdot (\mathbf{A} - \mathbf{n}_0 \mathbf{n}_0^T) \cdot \mathbf{n} \mathbf{n}^T \right]. \]  

Eq. (12) is well founded in nematic LCEs, so serves as a starting point for smectic LCEs. However, in Sm-\textit{C} elastomers the semi-soft term in the free energy could in principle involve any of the directions in the problem including the director, and the layer normal, but we will neglect these effects here for consistency.

Typical values of \( \alpha \) are up to \( \sim 0.1 \) in nematic LCEs, but it may be even larger in smectic LCEs [31].

Some studies of semi-soft elasticity have used the following simplified form [9]

\[ F_{ss} = \frac{1}{2} \alpha \mu \text{Tr} \left[ \mathbf{A} \cdot \mathbf{A}^T \right], \]  

which is the neo-Hookean elasticity formula. This more general semi-soft term gives rise to the same qualitative behaviour as Eq. (12).

C. Numerical Method

The free energy described in Eq. (1), (3), (4), and (12), is subject to the non-linear constraints that the director remains of unit length and that the layer normal deforms as an embedded plane (Eq. 2). This constrained minimisation can only be performed analytically in a few circumstances. Numerical minimisation of this free energy using conventional methods often results in the location of only local minima. We have used a simulated annealing algorithm to minimise the total free energy, which finds the global free energy minimum more reliably. The constraint of the tilt angle of \( \theta \) between the layer normal

\[ n \]  

and
and the director can be encoded as
\[ \mathbf{n} = c \sin \theta + k \cos \theta, \]
where the vector \( c \) is perpendicular to \( k \). A particular basis is required to express \( c \). It is convenient to use \( c_0 \), the starting component of \( \mathbf{n}_0 \) perpendicular to \( k_0 \), and \( c_0 \times k_0 \). The vector \( c \) can be expressed as
\[ c = \hat{a} \cos \phi + \hat{b} \sin \phi \]
where \( \hat{a} \) is a unit vector constructed from the component of \( c_0 \) that is perpendicular to \( k \), and \( \hat{b} \) is perpendicular to both \( \hat{a} \) and \( k \), i.e. \( \hat{b} = k \times \hat{a} \). The simulated annealing algorithm then minimises the free energy over \( \phi, \theta \) and the required components of \( \lambda_0 \). The global minimum derived from this was then refined using a NAG sequential quadratic programming library routine. The imposed constraints are implemented using Lagrange multipliers. The results of this method are in good agreement with the results obtained from configurations that can be solved analytically.

III. ELONGATIONS OF SM-C ELASTOMERS

We will consider four elongations to illustrate some of the behaviour and to build up some intuition for semi-soft Sm-C elastomers. The orientation of the layer normal and director in each case is shown in fig. 5. The model considers an imposed deformation \( \lambda_{xx} \). In experiment, imposed stress ensembles are often used, which yield the same results when the stress-strain curve is monotonic. However, some of the stress-strain curves calculated here are non-monotonic, hence there are several strain values for a single stress value. In this case there is a difference between the fixed stress and fixed strain ensembles, and for fixed stress a Maxwell construction must be used to determine the strain. This is described in [36], and briefly in [IV].

The model has the parameters \( \mu, a_1, B, r \) and \( \theta_0 \). Typical, \( \theta_0 \sim 30^\circ \) [22], \( B/\mu = b \sim 60 \) in well ordered samples [12] [15] [17], \( a_1/\mu = c \gtrsim 1 \) and \( \alpha \sim 0.1 \) in smectics [31] [32], and \( r \sim 2 \) in side chain liquid crystalline polymers [11]. We will use these parameter values to illustrate the behaviour of the model in what follows.

A. Elongation perpendicular to \( n_0 \) and \( k_0 \)

First we consider an elongation deformation in the \( x \) direction, with the starting layer normal \( k_0 = z \) and the starting director \( n_0 = \cos \theta_0 z + \sin \theta_0 y \), as illustrated in fig. 5a). In the absence of the semi-soft term of Eq. (12) this deformation is as described in [11]. The full free energy can be minimised numerically as explained in [IV]. The resulting stress-strain curve, and the orientation of the director of this minimisation are shown in fig. 5b) by the thick (green) lines. For the ideal Sm-C elastomer, this plateau ends at \( \lambda_{xx} = \sqrt{\pi/2} \), as can be seen from the soft mode in Eq. (5). The plateau ends when the director has completed a rotation by \( \pi/2 \) around the layer normal. For non-zero values of \( \alpha \) the onset of rotation of the layer normal is delayed, and it never finishes a full \( \pi/2 \) rotation.
This is evident in the stress-strain curve, because the well defined stress plateau for \( \alpha = 0 \) becomes progressively less sharply defined. For \( \alpha \sim 0.01 \) there is a pronounced stress plateau, but for larger values of \( \alpha \sim 0.1 \) there is no plateau, merely a knee in the stress-strain curve. Fig. 6 also shows the effect of reducing the tilt modulus \( c \). The knee in the stress strain curve becomes less pronounced, and the rubber hardens more slowly for larger values of \( \lambda_{zz} \). The retardation of the director rotation may be significant for piezoelectric response of these materials. There would be no piezoelectric response until the strain was above the threshold. The potential difference across the sample would be lower in semi-soft samples because the alignment of the electric dipoles associated with director rotation is spread over a much larger deformation range.

The deformation components when stretching perpendicular to \( k \) are illustrated in Fig. 7. Note the sympathetic shears that accompany the director rotation are persistent, because the director rotation is never completed if \( \alpha > 0 \).

Numerically it is clear that with the inclusion of the semi-soft term there is a delay in the rotation of the director. Some analytical progress can be made in this geometry by decomposing the deformation into three parts; the initial hard deformation with fixed director and layer spacing denoted \( \Delta_{\text{hard}} \), the soft mode \( \Delta_{\text{soft}} \) and the subsequent shear and elongation after the soft mode \( \Delta' \).

\[
\Delta = \Delta' \cdot \Delta_{\text{soft}} \cdot \Delta_{\text{hard}}
\]  

where \( \Delta_{\text{hard}} = \text{diag}(\lambda_1, 1/\lambda_1, 1) \), \( \Delta_{\text{soft}} \) given in Eq. (5), and

\[
\Delta' = \begin{pmatrix}
\zeta & 0 & \eta \\
0 & 1/\zeta & 0 \\
0 & 0 & 1
\end{pmatrix}.
\]

This deformation matrix can be substituted into the free energy terms of Eq. (1), (4), and (12) (assuming that \( c \to \infty \), so that \( \theta = \theta_0 \)). The problem is then reduced to a minimisation over the variables \( \lambda_1, \zeta, \eta \) and \( \phi \), with the constraint that the total \( \lambda_{zz} \) is prescribed. The threshold before the onset of director rotation can be calculated by setting \( \zeta = 1 \) and \( \eta = 0 \), then performing a series expansion of the free energy in soft mode rotation angle \( \phi \). The leading term is \( O(\phi^2) \), and when this term becomes negative a non-zero value of \( \phi \) will lower the free energy. To leading order in \( (\lambda_1 - 1) \), this coefficient becomes negative when \( \lambda_1 \) is approximately

\[
\lambda_1 = 1 + 8r^2\alpha/(1 + 29r - 29r^2 - 3r^3 + r\alpha + 35r^2\alpha) + 4r^2\alpha \cos 2\theta + (r - 1)((r - 1)^2 + r\alpha) \cos 4\theta
\]

This value is slightly smaller than the corresponding threshold to director rotation in nematic elastomers of \( \lambda^2 = \frac{r - 1}{r - 2} \) [1]. Intuitively this is because in the Sm-C phase the deformation is restricted to two dimensions by the layer spacing constraint. Consequently there is a larger contraction in the direction perpendicular to the stretch which causes the elastic free energy to rise faster, and hence the director rotation to start earlier in Sm-C LCEs as compared to the nematic phase.
The minimisation of the free energy over $\lambda_1, \zeta, \eta$ and $\phi$ produces results that are in good agreement with the more general numerical method. The results are shown by the black lines in Fig. 6.

B. Elongation parallel to $k_0$

Elongation parallel to the layer normal is illustrated in Fig. 5 b). The initial layer normal is given by $k_0 = x$ and the director $n_0 = x \cos \theta_0 + z \sin \theta_0$. Using the form of deformation matrix described in Eq. (16), the free energy can again be minimised using the numerical technique described in § II C. The results for various values of the semi-soft parameter $\alpha$ are illustrated in fig. 8. For $\sigma_0 \rightarrow \infty$ the Poisson's ratio becomes less negative.

The rotation of the layer normal and director, and the deformation components are illustrated in Fig. 9. The expansion of the sample in the $z$ direction is clearly visible at the onset of rotation, as are the usual shear components that accompany a soft mode. For finite values of $c$, the deformation becomes more complicated; before the threshold the director rotates towards the layer normal and the sample shears, which itself results in movement of the layer normal. There is both an increase in the threshold to the start of rotation, and a reduction in the amplitude of the semi-soft deformation. This is because the shearing before director rotation results in rotation of the layer normal, and there is a reduction in the tilt angle before the onset of shearing.

FIG. 8. a) The stress-strain response for a semi-soft Sm-C elastomer stretched parallel to the layer normal. The model parameters are $b = 60$, $r = 2$ and $\theta_0 = 0.5$, and the values of $(\alpha, c)$ shown in the figure. b) The corresponding IPRs for the stress-strain curves.

the first part of the stress-strain curve is determined by the smectic layer modulus $B$. The semi-soft term prevents the rotation of the director, and the layer spacing increases. Once the force required to increase the layer spacing is comparable to that required to rotate the director, the semi-soft mode begins. The stress-strain curve has negative slope once director rotation starts. As explained in [II A] there is a negative IPR in this geometry as the director rotates around the layer normal into the direction perpendicular to the stretch axis (see Fig. 8 b)). This lateral expansion, combined free energy expression for the semi-soft elasticity, results in the negative stiffness. For larger values of $\alpha$ the Poisson’s ratio becomes

FIG. 9. For the parameter values $(\alpha, c) = (0.05, \infty)$ and $b = 60$, $r = 2$ and $\theta_0 = 0.5$ radians for stretching parallel to the layer normal. a) Shows the director and layer normal rotation, b) the shear components, and c) the diagonal components of the deformation tensor when stretching parallel to the layer normal.

The soft mode in this geometry can be calculated analytically, as explained in [II A] and its amplitude is given in Eq. (11). Some analytic results can be obtained by
decomposing the deformation as follows.

\[ \lambda = \lambda' \cdot \lambda_{\text{soft}} \cdot \lambda_{\text{hard}}. \] (20)

Both \( \lambda' \) and \( \lambda_{\text{hard}} \) have the form

\[
\begin{pmatrix}
\eta & 0 & \zeta \\
0 & \xi & 0 \\
0 & 0 & 1/(\eta \xi)
\end{pmatrix}.
\] (21)

The appropriate soft mode must be calculated based on the rotated layer normal, as the shear component \( \zeta \) will cause it to rotate.

The onset of director rotation can be obtained by substituting back into the free energy, expanding in terms of \( \phi \) up to quadratic order. When the coefficient of the \( O(\phi^2) \) term is negative, the soft mode becomes active. This happens when

\[ \lambda_1 \approx 1 + \frac{r^2 \alpha}{b(r - 1)^2 \cos^2 \theta_0} + \frac{3 \alpha r^2}{4 \rho^2 b^2 c \cos^2 \theta_0} + O\left(b^{-3}, c^{-2}, \alpha^2\right). \] (22)

Note for smaller values of \( c \) this is inaccurate because the shear is only expanded up to quadratic order. The occurrence of \( \alpha \) and \( b \) in this expression correspond to the competition between the stretching of the layer spacing, and the semi-soft elastic term keeping the director fixed in the matrix. The threshold predicted by this calculation is consistent with the numerical results for large \( b \) and \( c \).

1. **Scalar model of negative slope region**

   The unusual response above for the Sm-\( C \) soft mode can be illustrated for a much simpler deformation. Consider an elongation with a diagonal deformation matrix of an imposed \( \lambda_{xx}, \lambda_{zz} \) given by

\[ \lambda_{zz} = 1 - A \left( \lambda_{xx} - \frac{3}{2} \right)^2 + \frac{A}{4}, \] (23)

with \( \lambda_{yy} \) determined by volume conservation. The parameter \( A \) here controls the initial rate of expansion of the material. Its Poisson’s ratios are \(-A\), and \(1+A\). This is similar to the soft mode in a Sm-\( C \) illustrated in Fig. 3.

The deformation in Eq. (23) can be substituted into a neo-hookean model such as Eq. (13), which is broadly similar to the semi-soft elastic energy term. The resulting stress-strain curve is shown in fig. 10. It can be seen from this plot that for sufficiently large values of \( A \) the stress-strain curve has a negative slope similar to stretching the Sm-\( C \) LCE parallel to the layer normal. For some geometries the Poisson’s ratio is sufficiently negative to result in a negative stiffness. The configurational entropy of the perpendicular degrees of freedom decreases as the sample expands resulting in a positive contribution to the stress. Once lateral expansion starts to slow sufficiently there is a weaker contribution to stiffness of the sample from the perpendicular degrees of freedom and the stress starts to drop, which produces a negative slope in the stress-strain response. By tuning the parameter \( A \) in the model, the balance between the parallel and perpendicular degrees of freedom can be altered, and the stiffness changed from negative to positive.

This scalar model shows that the negative stiffness is a result of the lateral expansion during the Sm-\( C \) soft mode, and not due to the form of the semi-soft elastic term.

C. **Elongation perpendicular to \( n_0 \)**

Stretching perpendicular to the initial director, \( n_0 \) is illustrated in fig. 5c). The results for the numerical calculation of the stress-strain curve for this geometry are shown in Fig. 11. This geometry has the remarkable feature that \( \nu_{zz} \to -\infty \) when \( \alpha \to 0 \), as shown in Fig. 11. For larger values of \( \alpha \) the Poisson’s ratio becomes less negative. The jump in the director also causes a discontinuity in the IPR, and a sudden increase in the width of the sample. Note that in this geometry there is a discontinuity in the stress-strain curve, in addition to the negative stiffness. The discontinuity in the stress-strain curve is accompanied by a jump in the director as shown in Fig. 12. Intuitively the discontinuity arises
because when the director jumps the long axis of the polymer shape tensor jumps towards the elongation direction. Consequently the natural length of the rubber in this direction is increased, so there is corresponding drop in the stress.

The jump in the director can be understood from the properties of the soft mode in this geometry. We can approximate the first part of the total deformation (until the end of director rotation) as a hard deformation where there is no director rotation, followed by a soft mode

$$\lambda = \lambda_{\text{soft}} \cdot \lambda_{\text{hard}}.$$  \hfill (24)

The soft mode in this geometry can be calculated analytically as explained in appendix \textbf{A}. Whilst its analytic form is algebraically very long, the amplitude of the soft mode has a much simpler expression, and is given by

$$\lambda_{xx} = \left(3 + r(7r - 2) + 4(r^2 - 1) \cos 2\theta_0 + (1 + (2 - 3r)r) \cos 4\theta_0 \right)^{1/2} / (2\sqrt{2}\rho).$$ \hfill (25)

The hard part of the deformation has only diagonal elements, and an $xz$ shear component.

$$\lambda_{\text{hard}} = \begin{pmatrix} \lambda_{xx} & 0 & \lambda_{xz} \\ 0 & 1/(\lambda_{xx}\lambda_{zz}) & 0 \\ 0 & 0 & \lambda_{zz} \end{pmatrix}.$$ \hfill (26)

Substituting this into the full free energy density yields an approximate solution to the minimisation problem, where the director rotation is assumed to be continuous. The free energy density in this case is shown in Fig. 13. The analytic solution with continuous director rotation has higher free energy for the first part of the deformation. Hence, the elastomer initially stretches without director rotation. If the director were to start rotating, then the form of the soft mode results in rapid rotation of the director, and an infinite slope in the free energy. However, the rate of increase slows, and eventually the state with a rotated director is lower in free energy than that with a fixed director. At this point the director jumps to the new orientation. There is a discontinuity in the slope of the free energy at this point, or equivalently a jump in the stress.

This behaviour is not solely a result of the semi-soft energy term, but again is a result of the shape of the soft mode, combined with a general semi-soft elasticity term.
These calculations are based on an equilibrium model of a Sm-$C$ elastomer. In practise kinetic terms, such as viscosity would smooth out the sharp jump demonstrated here.

1. Scalar model describing stress discontinuity

The semi-soft behaviour of Sm-$C$ elastomers is characterised by two deformation modes; before the onset of director rotation, and afterwards. A scalar model that exhibits the same behaviour when stretching perpendicular to the director can be developed based on representing each of these deformation modes as a spring, and deforming the two springs in series. The total strain is the sum of two deformation modes corresponding to keeping a fixed director $\epsilon_U$, and rotating the director $\epsilon_{SM}$

$$\epsilon_T = \epsilon_U + \epsilon_{SM}. \quad (27)$$

The two modes of deformation have different energy penalties, the first arises from a simple uniaxial deformation, so in a neo-hookean energy model will result in a free energy term of the form

$$F_U = \frac{1}{2} K_1 \epsilon_U^2, \quad (28)$$

where $K_1$ corresponds to the shear modulus of the rubber. The second arises from the soft mode, which has a singular edge in the contraction of the rubber as it is stretched. The $zz$ component in the soft mode is initially of the form $\lambda_{zz} = 1/(1 + (\lambda_{xx} - 1)^\beta)$ (where here $\lambda_{xx} - 1 = \epsilon_{SM}$. When this is put into the neo-hookean free energy, it results in free energy terms to leading order in $\epsilon_{SM}$ of the form

$$F_{SM} = \frac{1}{2} K_2 \epsilon_{SM}^\beta \quad (29)$$

where $K_2$ is the corresponding shear modulus for this mode. In the case of the semi-soft Sm-$C$ elastomer, this term arises because of the rapid rotation of the director during the start of the soft mode.

The total free energy is then

$$F_T = \frac{1}{2} K(\epsilon_T - \epsilon_{SM})^2 + \frac{1}{2} K_2 \epsilon_{SM}^\beta, \quad (30)$$

where first spring in this system is hookean, and the second is non-linear, being infinitely stiff at zero strain for $0 < \beta < 1$, but softening rapidly as strain increases. This should be minimised over $\epsilon_{SM}$ to determine the distribution of strain between the two springs. It can be solved analytically for $\beta = 0.5$. The behaviour of this model is illustrated in Fig. 14. For small $\beta$ this system has a discontinuity in the stress-strain curve, but as $\beta$ is increased the stress-strain response becomes continuous. The free energy as a function of $\epsilon_{SM}$ is also illustrated in Fig. 14.
ity when stretched perpendicular to the director (where the soft mode has a singular edge). Larger values of $\beta$ correspond to stretching at a larger angle to the director, where the soft mode does not have such a rapid rotation of the director, and a corresponding sharp drop in the lateral dimension. If the angle between the director and the elongation direction is large enough, then the stress-strain response becomes continuous as we will see in the next section.

D. Elongation at an angle $\psi$ to the layer normal

The last deformation we consider is shown in fig. 5 d). The numerical solution of stress-strain curve associated with this geometry is shown in Fig. 15. The stress-strain curve is continuous in this geometry, but again has a pronounced negative slope. There is a negative IPR of $\sim -1.5$ that is roughly independent of the semi-soft parameter. The expansion of the sample that accompanies the rotation of the director can be seen in Fig. 16.

IV. DISCUSSION

The first three deformations considered above in Fig. 5 (a-c), when made with clamped boundary conditions, would not be soft even without the semi-soft elastic term.

This is because no microstructure can be constructed from the soft deformations that is compatible with the boundary conditions, due to the shear components in the Sm-C soft mode [20]. However, the properties of a long sheet of Sm-C LCE may approximate this behaviour as the centre of the sample could deform without rigid boundary conditions. The final deformation in Fig. 5 d) can be performed with clamped boundary conditions in the soft case. In the semi-soft case the sample starts to shear before the onset of rotation, which is not compatible with clamped boundaries, so in experiment it may be even stiffer initially due to this additional constraint on its deformation.

The maximum lateral expansion can be deduced from the soft mode presented in Fig. 15. The shear components are transformed, through a rotation, into an elongation. At $\phi = \pi/2$ the maximum lateral expansion occurs (in the $y$ direction for the example given in the text), and
has a value of $\sqrt{\frac{E}{\rho}}$.

The region of negative slope in the constitutive models reported here is typically explained by a Maxwell Construction. Similar behaviour occurs in the Van der Waals gas model which has a region of negative slope in the pressure-volume curve. Here there is a two phase region consisting of a mixture of the liquid and gas phases. In solids the two deformations on either side of the instability must be compatible to form a mixture [37]. The system should then disproportionate, adopting a mixture of the two deformations to achieve the externally imposed strain. The first order type phase transition seen in the example stretching perpendicular to the layer normal can result in hysteretic behaviour as the system jumps from one energy well to another. The rate of the deformation in comparison to the sample relaxation times may also result in hysteresis [38]. There is interest in negative stiffness materials [39] for applications such as sealants, stiffening composites, and creating meta-materials having a negative refractive index to sound waves.

Experimental work reporting mechanical testing on Sm-C monodomains has not been reported. Whilst it is anticipated that these monodomains should exhibit soft elasticity, the addition of the semi-soft elasticity term to the model suggests that these effects may be difficult to observe for large semi-soft parameter $\alpha$. When stretching perpendicular to both the layer normal and the director, the semi-soft term may prevent any stress plateau being observed, instead only a shoulder is visible in the stress-strain response.

Although we have only considered the deformations of monodomains here, the results inform model predictions for polydomains. Polydomains are difficult to model because of the requirement of ensuring that adjacent domains deform in a compatible way. A simplifying approximation used to model a polydomain is to assume that it consists of an array of monodomains that deform at the imposed external strain, but are independent from each other. If we deform the pseudo-monodomain shown in Fig. [1] by stretching in the $x$ direction, then deformation component $\lambda_{yy}$ averaged over all the domains is illustrated in fig. [17] for 50 domains. This figure shows that there is a negative IPR as the director in each of the domains jumps causing them to expand. The curve illustrated here is jagged because the alignment of each domain jumps at a slightly different threshold. The expansion of the film thickness, and the energy loss as a result of the jump in the director orientation in this geometry may be observable in experiments on pseudo-monodomains [11] [40]. The larger values of deformation reported in experiment before the knee in the stress-strain curve point to a much larger value of $\alpha$ than in the illustrative plot in Fig. [17].

The features of the smectic-C model described here would be present in a wide range of models that have soft modes of nematic elastomers but incorporate the constraint on the director to remain at a fixed angle to the layer normal. However, validation of these models await either experimental work on mechanical testing of Sm-C monodomains, or theoretical work on pseudo-monodomains to link up with existing mechanical experiments on pseudo-mododomains.

V. CONCLUSION

We have studied a model of monodomain Sm-C LCEs with the inclusion of a semi-soft elastic term to describe imperfections in the elastomer. As result of the negative incremental Poisson’s ratio inherent in the soft modes of a Sm-C monodomain, the mechanical properties of a semi-soft monodomain are unusual. When stretching perpendicular to the layer normal and the director, the response is reminiscent of a nematic elastomer. A finite force is required to deform the LCE and initial the rotation of the director. However, the stress plateau is less well defined for larger values of semi-soft parameter $\alpha$; it is reduced to a shoulder in the stress-strain response. When stretching parallel to the layer normal the elastomer again exhibits a threshold to director rotation. Once director rotation has started the elastomer has a negative incremental Poisson’s ratio, and a negative stiffness. A negative incremental Poisson’s ratio of up to $\nu \sim -1.5$ has been found for typical model parameters. This arises because the director rotates in a direction perpendicular to the stretch axis due to the constraint of the layer normal. This more detailed understanding of monodomain deformations of Sm-C elastomers might prove useful in understanding recent mechanical and piezoelectric experiments on polydomain Sm-C elastomers.

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Appendix A: Transforming the soft mode for different starting configurations

The soft mode given by Eq. (5) can be transformed to other geometries by a pair of rotation matrices. For example, consider the case of a Sm-C′ elastomer stretched parallel to the layer normal. Let us assume that starting layer normal is \( k_0 = x \) and the starting director is \( n_0 = \cos \theta_0 x + \sin \theta_0 y \). The soft mode for this configuration that is an upper triangular matrix, as described in Eq. (16), can be found as follows. From the reference configuration a body rotation is performed such that the layer normal \( k_0 \) is parallel to the \( z \) axis. In this case, a 90° rotation about the \( y \) axis

\[
Q = \begin{pmatrix}
0 & 0 & -1 \\
0 & 1 & 0 \\
1 & 0 & 0
\end{pmatrix}.
\] (A1)

After this rotation the director is given by \( n = z \cos \theta_0 + y \sin \theta_0 \). Note that in general an additional rotation around the \( z \) axis may be required to ensure the director is in this orientation. This is the initial configuration for the soft mode given in Eq. (5). The director now rotates by an angle \( \phi \) around the new layer normal, and the sample executes the soft mode. Finally a rotation of the target state is performed such that the deformation matrix has the form described in Eq. (10). This rotation matrix is in general simpler if we first undo the rotation \( Q \). The rotation matrix \( P \) is described by three angles:

\[
P = \begin{pmatrix}
\cos \psi_z & \sin \psi_z & 0 \\
-\sin \psi_z & \cos \psi_z & 0 \\
0 & 0 & 1
\end{pmatrix} \cdot \begin{pmatrix}
1 & 0 & 0 \\
0 & \cos \psi_x & \sin \psi_x \\
0 & -\sin \psi_x & \cos \psi_x
\end{pmatrix} \cdot \begin{pmatrix}
\cos \psi_y & 0 & \sin \psi_y \\
0 & 1 & 0 \\
-\sin \psi_y & 0 & \cos \psi_y
\end{pmatrix}.
\] (A2)

The three angles \( \psi_x, \psi_y \) and \( \psi_z \) can be calculated by substituting into the equation

\[
\Delta = P \cdot Q^T \cdot \Delta_{\text{soft}} \cdot Q
\] (A3)

and ensuring that the three lower triangular elements of \( \Delta \) are zero. In the case of stretching parallel to \( k_0 \) and perpendicular to \( n_0 \) the soft mode can be calculated analytically. The algebraic expressions for these soft modes is long, and unedifying so will not be presented here.
[33] W. T. Ren, Ph.D. thesis, Georgia Institute of Technology (2007).
[34] W. Ren, P. J. McMullan, and A. C. Griffin, Phys. Status Solidi B 9, 2124 (2009).
[35] R. Lakes, Science 235, 1039 (1987).
[36] J. M. Adams and M. Warner, Phys. Rev. E 77, 021702 (2008).
[37] J. M. Adams, M. Warner, O. Stenull, and T. C. Lubensky, Phys. Rev. E 78, 011703 (2008).
[38] G. S. Agarwal and S. R. Shenoy, Phys. Rev. A 23, 2719 (1981).
[39] R. S. Lakes, T. Lee, A. Bersie, and Y. C. Wang, Nature 410, 565 (2001).
[40] W. Ren, P. J. McMullan, and A. C. Griffin, Macromolecular Chemistry and Physics 209, 1896 (2008).