## Statistical models of elasticity in main chain and smectic liquid crystal elastomers

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Liquid crystal systems typically consist of rod like molecules that spontaneously align along a chosen direction (the director) below a certain temperature or above a certain concentration. When these molecules are connected to polymers, the alignment of the molecules can alter the conformation of the polymer backbone. This effect can be seen on a macroscopic level by cross-linking the polymer chains together to form a liquid crystal elastomer (LCE). In this thesis the elastic properties of main chain and smectic liquid crystal elastomers are modelled, and a mechanism of piezoelectricity in LCEs is explored. These three projects are summarised below.

In the strongly nematic state main chain liquid crystalline polymers have hairpin defects along their length. When these chains are cross-linked together they show unusual soft elastic properties experimentally. The elastic properties of a main chain elastomer are modelled here by calculating the stiffness of chains with hairpin defects and of those without. The dramatically different spring constants motivate a non-affine model for deformation of the resulting elastomer. The chains with hairpin defects are less stiff than those without and so take up more of the macroscopic strain. As the elastomer is stretched the macroscopic strain becomes more concentrated in the elastically weaker hairpinned chains, and so the rubber shows a plateau in its stress-strain curve.

A mechanism of developing a polarisation in chiral main chain LCE is analysed. In this mechanism the dipoles of the chiral monomers can be aligned by a shear deformation. It is shown that the polarisation of a pure LCE is zero in equilibrium due to rotation of the director. The response of the director must be altered in a specific way in order to realise a non-zero result. Three methods of circumventing this result are explored: oscillating shear, pinning the director with smectic layers, and using a mixture of chiral and non-chiral chains. Each of these methods is shown to produce a polarisation which is much larger per unit stress than that of quartz crystal.

A fully non-linear model of elasticity in smectic A elastomers is developed from a phantom network model. The rigid constraints required by the layered smectic system are analysed from a geometric perspective. The results of this model are then compared to a wide range of experimental observations: extreme Poisson ratios, in-plane modulus, modulus before and after threshold when the elastomer is stretched along the layer normal. This model is then used to look for soft modes in biaxial smectic A elastomers and smectic C elastomers. A general procedure for the calculation of soft modes is developed and specific examples of soft modes given.

## Preface

In this thesis the elastic properties of two different types of liquid crystal elastomer are modelled: main chain liquid crystal elastomers in part I and smectic liquid crystal elastomers in part II. The first chapter of part I, chapter 2, addresses the questions; What is the distribution of end-to-end spans in main chains? How does this affect the way a main chain elastomer deforms? What are the resulting stress-strain characteristics of a main chain elastomer? At the time of writing there are only a few experimental groups synthesising main chain elastomers and investigating their elastic properties. The results produced are not in agreement, having different stress-strain characteristics, and some theoretical guidance is required. In chapter 3 an unusual mechanism of polarisation in amorphous materials is explored. This mechanism raises the question; how does the director of a liquid crystal elastomer respond to a deformation? For the polarisation mechanism to work, the response of the director must be altered in a specific way. Three different mechanisms are discussed for this alteration.

In part II smectic elastomers become the focus of the discussion. In chapter 4 a model motivated by the Gaussian phantom network is constructed to describe the elastic properties of smectic elastomers. However, because smectic elastomers are layered systems with the layer spacing being extremely stiff, there are rigid constraints that must be obeyed as the smectic elastomer deforms. The predictions of this model are explored and compared to the available experimental data. Chapter 5 explores two different smectic phases and in particular the soft elastic response of smectic elastomers, that is the modes of deformation that cost no energy in smectic elastomers.

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## Word Limit

This dissertation does not exceed 60,000 words, including tables, footnotes, bibliography and appendices, but excluding photographs and diagrams.

## Declaration of originality

This dissertation is my own work and contains nothing which is the outcome of work done in collaboration with others, except as specified in the text and Acknowledgements.

James M Adams

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## Chapter One

# Introduction

The subject of this thesis is the elastic properties of two different types of polymer networks: main chain nematic elastomers and smectic elastomers. Both of these systems are anisotropic, and the molecular theories used to describe them here are in the same vein as previous phantom chain models of rubber elasticity.

## 1.1 Classical rubber elasticity

The classical theory of rubber elasticity, based on a phantom network of Gaussian chains, is surprisingly successful. Modelling the cross-link points of rubbery materials as deforming affinely with the external strain  $(\mathbf{R} \to \underline{\lambda} \cdot \mathbf{R})$  one obtains the free energy density of a Gaussian phantom network as

$$f = \frac{1}{2}\mu \operatorname{Tr}\left(\underline{\lambda}^T \cdot \underline{\lambda}\right),$$

where  $\mu$  is the shear modulus of the network [1]. For a rubber network the constraint of incompressibility  $(\det(\underline{\lambda}) = 1)$  is usually imposed. Despite the successes of the phantom network model it neglects, amongst other things, entanglements of the network strands and non-Gaussian nature of the chains, for example their finite extensibility. One way to correct for these failings is the Mooney-Rivlin approach. The free energy density should be invariant under rotation of the target and reference states, so can only be a function of the rotational invariants of the Cauchy-Green deformation tensor  $\underline{C} = \underline{\lambda}^T \cdot \underline{\lambda}$  [2]. These invariants can be added together to phenomenologically fit the deviations from the phantom network model. However, this approach does not provide any insight to the microscopic details of the network. Other attempts have also been made to include entanglements (e.g. [3]), but such corrections will be neglected here.

## **1.2** Neo-classical rubber elasticity

In 1969 de Gennes proposed that if an elastomer was cross-linked in the presence of a liquid crystalline solvent then the resulting polymer network should show anisotropic properties as a consequence [4]. For example, if the network was cross-linked in a nematic solvent then the polymer chains should elongate along the director. Polymer liquid crystals (PLCs) offer a more direct way of combining the anisotropic properties of liquid crystals with a polymer backbone. The liquid crystalline molecules can be coupled in several different ways to the polymer as illustrated in Fig. 1.1. If these PLCs are cross-linked into



Figure 1.1: Three examples of polymer liquid crystals: a) main chain , b) prolate back bone side chain and c) oblate back bone side chain [5].

a network, then the coupling between the mesogenic units and the polymer backbone will result in an elastomer that exhibits the anisotropic properties referred to by de Gennes. An important advance was the synthesis of polymer liquid crystal networks using polysiloxane backbones [6]. This enabled exploration of a several parameters in the construction of the network, for example the spacer length and the influence of the mesogenic units. Initially the samples made were not globally aligned: they were polydomains. Two approaches have been successfully employed to align the separate domains, and hence prepare monodomain elastomers. The first is to pre-align the polymers in a magnetic field and then cross-link them [7]. On heating these samples to the isotropic state and returning them to the nematic state, they show complete recovery of the globally aligned nematic phase. The second method is to carry out a light cross-linking stage of an unaligned elastomer, and then load the sample before carrying out a second cross-linking stage [8]. The elastic properties of the resulting monodomains can then be investigated without the complication of the polydomain structure. The anisotropic properties of the nematic monodomain described above can be modelled using the phantom network model for anisotropic chains (see e.g. [9]). The resulting free energy density is

$$f = \frac{1}{2}\mu \operatorname{Tr}\left(\underline{\underline{\ell}}_0 \cdot \underline{\underline{\lambda}}^T \cdot \underline{\underline{\ell}}^{-1} \cdot \underline{\underline{\lambda}}\right),\,$$

where  $\underline{\ell}_0$  and  $\underline{\ell}$  are the matrices of effective step lengths before and after the deformation by  $\underline{\lambda}$ , respectively. This theory has proved remarkably successful in describing, amongst other things, the spontaneous elongation of a nematic elastomer on cooling into the nematic state. Some main chain polymers (see Fig. 1.1 a)) show particularly large spontaneous elongation due to the strong nematic state that they form. The unusual elastic properties of main chain liquid crystalline elastomers will be discussed in part I.

Cholesteric liquid crystals have a helical structure in their director fields. A cholesteric liquid crystal elastomer also has a twisted director field that is cross-linked into the elastomer. However, by the use of a cholesteric solvent and a nematic elastomer, a twist can be cross-linked into the elastomer and can be adjusted by the concentration of the cholesteric solvent present during cross-linking. The more concentrated the cholesteric solvent, the more tightly twisted is the director field on cross-linking. This director field is imprinted on the network by the cross-linking process and remains after the solvent has been removed. These chirally imprinted elastomers show a fascinating twisted-untwisted transition as the solvent concentration is varied [10, 11]. Cholesteric elastomers show a remarkable ability to separate chiral isomers by preferentially absorbing one handedness over the other [12, 13].

The smectic phase was also discussed by de Gennes and was expected to have extremely anisotropic mechanical properties. This is because the layered structure of smectic liquid crystals was expected to force the polymer chains to concentrate in between layers, and as a result the elastomer structure is strongly anisotropic. The elastic properties of smectic elastomers will be discussed in part II.

An interesting attempt to connect together the classical theory of rubber elasticity and the neo-classical theory of rubber elasticity has been made by Xing *et al.* [14]. They follow the replica-based approach of Deam and Edwards [15] and construct a Landau theory of the vulcanization transition. Their work also promises to shed light on properties of polydomain liquid crystal elastomers [16–19].

## **1.3** Applications for liquid crystal elastomers

Liquid crystal elastomers are an exciting system academically because of their many unusual elastic and optical properties for example [20]. Their practical usefulness is currently limited because of the small quantities available. However, there are many interesting prospective applications including the sifting of chiral molecules mentioned above. One application that has attracted particular interest is that of an actuator or artificial muscle. Typical stress and strain values for skeletal muscles are of the order of 350kPa and 25%. By adjusting the cross-linking density and the polymer backbone it is possible to make a liquid crystal elastomer with similar characteristics [21, 22]. However the limiting factor is the response to a stimulus as the thermal conductivity of an elastomer is low. One possible solution to this with a sufficiently fast response is to incorporate dye molecules into the elastomer that undergo a transition from *trans* to *cis* on illumination.

The applications of liquid crystal elastomers is expected to grow when their piezoelectric and ferroelectric properties have been fully developed.

# — Part I—

# Main chain liquid crystal elastomers

# — Chapter Two — — —

# The elasticity of hairpin chain elastomers

IN THIS CHAPTER a simple model of a main chain liquid crystalline elastomer is presented. This model is based on the calculation of the partition function for a 1-D model of polymer chain with hairpin defects along its length. Calculation of the chain's spring constants motivates a non-affine method for stretching the polymer network. The nominal stress-strain curves for this model are then calculated and discussed.

## 2.1 Introduction

## 2.1.1 Semi-flexible polymers

Mesogenic polymers can be divided into two classes: main chain and side chain polymers. The focus here is main chain polymers. These polymers exhibit hairpin defects where the chain switches from following the nematic field direction on average to following the nematic field in the opposite sense. The transition is achieved by bending the polymer (penalised by the bending energy if done rapidly) and having sections of the chain misaligned with the nematic field (penalised by the nematic field energy if done too slowly). Hairpin defects are responsible for the transition from a rod like conformation of main chain polymers in strong nematic field, to a coil in weak nematic field [23]. The statics and dynamics of these defects has been calculated in [24]. At low temperatures it is found that exponentially rapid growth of chain dimension occurs as a function of inverse temperature. This is confirmed by small angle neutron scattering measurements of the chain dimension as a function of temperature [25]. A rigid cylinder model of the chain extent fitted to small angle neutron scattering is also consistent with the hairpin bend picture. A nematic main chain polyester with 28 monomers exhibits on average 2.45 hairpins on average according to the rigid cylinder model [26]. The worm-like chain model of semi-flexible chains in ensembles of fixed end-to-end length have attracted interest recently because it is now technologically possible to measure force extension curves of individual strands of DNA for example [27]. Consequently, the details of this model has been explored in 1, 2 and 3 dimensions using the Fokker-Planck equation [28]. The 1-D model of a semi-flexible chain is particularly relevant to the main chain elastomers considered here.

### 2.1.2 Main chain elastomers

Main chain liquid crystalline polymers can be cross-linked together to form an elastomer. One of the remarkable properties of this elastomer is the softness that it exhibits. When an aligned monodomain is stretched perpendicular to the director, the elastomer deforms at no energy cost because the increase in macroscopic length demanded by the stretching is provided by rotation of the director, rather than by stretching the polymer. This is called soft elasticity.

Polydomain materials also show plateaux in their stress strain curves, due to the rotation of the domains in the material aligning their local directors, which is accompanied by a soft elastic response [17]. The alignment of adjacent domains can be studied experimentally by measuring the order parameter of the sample as a function of the deformation. When the order parameter becomes saturated, the stress begins to rise again as the deformation applied increases, i.e. the material becomes much harder. The length of the plateau is controlled by the anisotropy of the polymers that make up the elastomer ( $\sqrt{r}$ ). The shape anisotropy is governed by the coupling between the mesogenic units and the polymer backbone. Consequently, main chain polymers have a much higher anisotropy than side chain polymers, so exhibit more exaggerated effects in the main chain samples.

Experimentally, main chain elastomers have proved much more difficult to fabricate and work with than side chain elastomers. Recent stress-strain experiments on main chain polydomain samples have shown that the plateau in the stress-strain curves persists after the order parameter has saturated. Wermter *et al.* [29, 30] carried out stress-strain experiments on three different polydomain samples. The samples were made by using long main chain polymers (with up to ~ 60 rod like monomers per chain) to cross-link side chain polymers together. However, the main chain cross-linkers dominate the rubber elasticity of the samples. The samples were made with three different molar percentages of main chain cross-linker: 1.9%, 4.0% and 9.1% denoted by samples 5a, 5b and 5c. The first two samples do not show a compelling extended plateau. In the third sample with the highest proportion of main chain cross-linkers, the plateau is clearly extended. The results of the stress-strain experiment and corresponding order parameter measurements are shown in



Fig. 2.1. This behaviour was only seen in the polydomain samples of Wermter *et al.*; no monodomain samples were tested.

Figure 2.1: The stress-strain curve and the order parameter for sample 5c of Wermter *et al.* [30]. The order parameter saturates at around  $\lambda = 3$  whilst the stress-strain curve still exhibits a plateau up to  $\Lambda = 4.5$ .

Similar experiments, but on monodomains, were performed by Clarke *et al.* [31]. They investigated three different types of cross-linker; short siloxane (SiF), short aliphatic (SiH) and long main-chain (SiMC). Mechanical experiments show that when the elastomer is stretched perpendicular to the director, there is a plateau in the stress-strain curves [31] (Fig. 2.2). The length of this plateau is in agreement with the predictions of soft elasticity [32]. However when stretched along the director there is no weak response as in [30], the modulus is enormously greater, see Fig. 2.2. A possible explanation of the lack of an extended plateau during stretch along  $\mathbf{n}$  is that during the aligning of the monodomain, thermal expansion occurs leaving no scope for further chain extension, and very few hairpins.

In the following sections the stretching of a monodomain elastomer composed of main chains parallel to the director is modelled. The hairpin defects on the main chain polymers form the basis of this model. First the properties of a single hairpin chain in the direction parallel and perpendicular to the nematic field are considered. The probability distribution of the span length of a hairpin chain parallel to the nematic field is, surprisingly, very close to a Gaussian distribution for very small numbers of hairpin defects. Then the stretching mechanism of an elastomer composed of hairpin chains is motivated by the properties of the individual chains. The elastic response of this model,



Figure 2.2: Stress-strain curve of a monodomain main chain elastomer, (a) stretched parallel to the director and (b) stretched perpendicular to the director [31].

using both the stretching mechanism and the model of main chain polymers, is then calculated.

## 2.2 Model of hairpin chains

The energy of a single semi-flexible polymer chain in a strong nematic environment can be written down in terms of the bend modulus, B, which is a measure of local flexibility of the chain (length  $\cdot$  energy) and J which measures the nematic coupling between the local chain alignment and the alignment of the surroundings of the chain (length<sup>-1</sup>  $\cdot$  energy). The energy of the chain in terms of the local tangent at arc length s,  $\mathbf{u}(s)$  is then

$$E = \int_0^L ds_{\frac{1}{2}} \left[ B \left| \frac{\partial \mathbf{u}}{\partial s} \right|^2 - J u_z^2 \right]$$
(2.1)

Two different mechanisms by which the chain can gain configurational entropy are considered: via positioning of hairpin defects and via fluctuations of the alignment of the monomers about the nematic director.

## 2.2.1 Hairpin defects

An illustration of a chain with two hairpins is shown in Fig. 2.3. At zero temperature the thermal fluctuations of the polymer chain can be ignored and the shape of single hairpin defect on an infinite chain calculated (§2.A). The energy associated with a hairpin defect and the associated length scale are given by

$$u_{\rm h} = 2\sqrt{BJ} ; \ l_{\rm h} = \sqrt{(B/J)} \tag{2.2}$$

de Gennes was the first to calculate the energy of the hairpin defect in the continuum limit of the liquid crystalline polymer [33]. Several hairpin defects



Figure 2.3: An illustration of two hairpin defects.

on a polymer chain can be treated as thermal excitations, each of energy  $u_{\rm h}$  with the corresponding Boltzmann weight. The hairpins are also exponentially localized to the length  $l_{\rm h}$  so do not take up much of the arc length of the chain. They are also treated as non-interacting as explained below. In the model considered here it does not matter whether a discrete or continuum picture of a nematic polymer is used (this is a question of whether the hairpin scale is larger or smaller than the persistence length [34]), we simply use the hairpin energy,  $u_{\rm h}$ .

## 2.2.2 Undulations



Figure 2.4: A polymer chain in a strong nematic field makes small excursions away from the nematic director, **n**.

An undulating section of a polymer chain is illustrated in Fig. 2.4. It is assumed that the chain is so stiff and in such a strong nematic field, or under such a large force, that each monomer can only undergo small deviations from the nematic direction. It can be shown that the free energy of the undulations on the chain is roughly proportional to the length of the chain (§2.B). Consequently, if a hairpin is put into an undulating chain then the free energies of the undulating sections just add. The undulations contribute to the end-toend distance of the chain in the direction perpendicular to the nematic field. The end-to-end length projected down onto a plane perpendicular to the nematic director,  $\mathbf{n}$  is Gaussian distributed and has a mean square displacement given by (§2.B)

$$\left\langle \mathbf{R}_{\perp}^{2} \right\rangle = \frac{Lk_{\mathrm{B}}T}{J}.\tag{2.3}$$

Note that the mean square extent does not depend explicitly on the bend constant. This is because although an increase in the bend constant results in an increase in the persistence length of each unit, this dependence is exactly cancelled out by the fact that the segments will have a smaller average tilt angle to the nematic field, and hence a smaller transverse component, as a result of the increase cost of bending the polymer.

### 2.2.3 Partition function for 1-D model

Parallel to the nematic field, the end-to-end distance of the hairpin chain is principally governed by hairpins. The end-to-end distribution can be found by calculating the partition function of the hairpin chain. First imagine putting n hairpin defects onto the polymer chain as shown in Fig. 2.5, using the following procedure: Begin creating a polymer chain in a highly ordered nematic environment, starting with the chain pointing in the up direction. Lay down the polymer for a distance  $s_1$  and then insert the first hairpin by changing to the down direction. Then lay down a distance  $s_2 - s_1$  and put in the second hairpin by changing direction. This process is continued until all n hairpins are been put in. Then put in the remaining piece of polymer so that the total arc length is L. Repeat the process for all possible positions of the defects along the chain provided:  $s_1 < s_2 < s_3 < ... < s_n < L$ .

All defects are identical and so do pass through each other (to prevent over-counting). This procedure can be expressed in an integral which gives the number of configurations with a fixed end-to-end separation of R. Each configuration that has the required end-to-end separation is counted as 1 by using the delta function to impose the constraint

$$R = s_1 - (s_2 - s_1) \dots + (-1)^n (L - s_n).$$
(2.4)

Integrating this constraint over all hairpin positions, and remembering that the chain can start in either the up or the down directions results in the following

$$\Omega_{\pm}^{(n)} = \int_{0}^{L} \frac{ds_{n}}{l} \int_{0}^{s_{n}} \frac{ds_{n-1}}{l} \dots \int_{0}^{s_{2}} \frac{ds_{1}}{l} \\
\times \delta\left(\frac{1}{2l} \left[s_{1} - (s_{2} - s_{1}) \dots + (-1)^{n} (L - s_{n}) \mp R\right]\right), \quad (2.5)$$

where  $\Omega_{\pm}^{(n)}$  denotes the number of configurations starting from the up (+) and down (-) directions, L is the total arc length of the polymer and l is some



Figure 2.5: Two illustrations showing how the counting of the number of configurations of hairpins is carried out. a) starts by moving up and b) by moving down. R is the z-component of the end-to-end separation.

characteristic length scale of the polymer  $(l = B/k_BT)$ . The problem can be rendered dimensionless by using the following definitions

$$N = \frac{L}{l} ; y_n = \frac{s_n}{l} ; z = \frac{R}{l}.$$
 (2.6)

The integral of Eq. (2.5) can be evaluated for small values of n (up to about 3) using the appropriate hyper-volume. For example when n = 2

$$\Omega_{+}^{(2)} = \int_{0}^{N} dy_2 \int_{0}^{y_2} \delta\left(y_1 - y_2 + \frac{N - R}{2}\right) dy_1 \tag{2.7}$$

$$= \int_{\frac{N-R}{2}}^{N} dy_2 = \frac{N+R}{2}.$$
 (2.8)

Similarly starting in the (-) direction

$$\Omega_{-}^{(2)} = \frac{N - R}{2}.$$
(2.9)

Summing the two contributions to the configurations results in

$$\Omega^{(2)} = N. \tag{2.10}$$

This method of evaluation of the number of configurations becomes increasingly difficult for higher n. An alternative method of evaluating the number of configurations is to express the delta function in terms of its Fourier representation

$$\Omega_{\pm}^{(n)} = 2 \int_{-\infty}^{\infty} \frac{dk}{2\pi} \int_{0}^{N} dy_n \int_{0}^{y_n} dy_{n-1} \dots \int_{0}^{y_2} dy_1 \\ \times e^{-ik[y_1 - (y_2 - y_1)\dots + (-1)^n (N - y_n) \mp z]}.$$
(2.11)

These integrals can be decoupled using the following property of the Laplace transform of a convolution [35]

$$\mathcal{L}^{-1}\{f_1(q)f_2(q)\} = \int_0^\tau F_1(\tau - \sigma)F_2(\sigma)d\sigma, \qquad (2.12)$$

where  $f_i(q)$  is the Laplace transform of the function  $F_i(y)$ , denoted by  $f_i(q) = \mathcal{L} \{F_i(y)\}$ . The Laplace transforms required are

$$\mathcal{L}\left\{e^{iky}\right\} = f_+(q) = \frac{1}{q - ik}$$
(2.13)

$$\mathcal{L}\left\{e^{-iky}\right\} = f_{-}(q) = \frac{1}{q+ik}.$$
(2.14)

The result of using Eq. (2.12) is

$$\Omega_{\pm}^{(n)} = 2 \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{\pm ikz} \mathcal{L}^{-1} \{ W(q) \} , \qquad (2.15)$$

where the variable conjugate to q in the Laplace transform is N and W is given by

$$W(q) = \begin{cases} f_{+}^{\frac{n}{2}}(q)f_{-}^{\frac{n}{2}+1}(q) & \text{even } n\\ f_{+}^{\frac{n+1}{2}}(q)f_{-}^{\frac{n+1}{2}}(q) & \text{odd } n. \end{cases}$$
(2.16)

The inverse Laplace transform can be carried out by using the Bromwich inversion formula

$$F(N) = \frac{1}{2\pi i} \int_{\lambda - i\infty}^{\lambda + i\infty} e^{Nq} f(q).$$
(2.17)

Here the integration limits are chosen so that all the poles reside to the left of the contour of integration. The inverse Laplace transform are thus given by the residues of the function

$$W(q)e^{Nq} = \begin{cases} \left(\frac{1}{q-ik}\right)^{\frac{n}{2}} \left(\frac{1}{q+ik}\right)^{\frac{n}{2}+1} e^{Nq} & \text{even } n\\ \left(\frac{1}{q-ik}\right)^{\frac{n+1}{2}} \left(\frac{1}{q+ik}\right)^{\frac{n+1}{2}} e^{Nq} & \text{odd } n \end{cases}$$
(2.18)

The most direct way to calculate the number of configurations is to evaluate the residues of this expression. An alternative method by induction is given

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in §2.C. The general formula for calculating the residue at an  $m^{th}$  order pole at  $\xi = \xi_o$  is

Res 
$$F(\xi)|_{\xi=\xi_o} = \frac{1}{(m-1)!} \left(\frac{d}{d\xi}\right)_{\xi=\xi_o}^{m-1} \left(F(\xi)(\xi-\xi_o)^m\right).$$
 (2.19)

Once the inverse Laplace transform has been calculated, the Fourier transform of the resulting expression with respect to k is required to find the partition function. This requires evaluation of integrals of the type

$$I_{\pm} = \mathcal{P} \int_{-\infty}^{\infty} \frac{1}{k^n} e^{\pm ikz}.$$
 (2.20)

 $\mathcal{P}$  denotes the Cauchy principal value of the integral — the pole on the contour of integration is excluded from the value of the integral. The integral can be computed using by Jordan's lemma, giving the result

$$I_{\pm} = \frac{\pm i}{2(n-1)!} (\pm iz)^{n-1}.$$
(2.21)

The residues and the Fourier transforms are now calculated starting with an even number of hairpins. The Leibniz formula for differentiating a product is useful in calculating the residues

$$\frac{d^n}{dx^n}A(x)B(x) = \sum_{s=0}^n {}^nC_s \frac{d^s}{dx^s}A(x)\frac{d^{(n-s)}}{dx^{(n-s)}}B(x).$$
(2.22)

The residue of the pole at q = ik is found to be

$$\operatorname{Res}_{q=ik}(\Theta(q)e^{Nq}) = \frac{1}{(\frac{n}{2}-1)!} \sum_{s=0}^{\frac{n}{2}-1} C_s e^{ikN} N^{\frac{n}{2}-s-1} \left(\frac{n}{2}+1\right) \dots \left(\frac{n}{2}+s\right)$$
$$\times \frac{(-1)^s}{(2ik)^{\frac{n}{2}+s+1}}$$
$$= \frac{1}{(\frac{n}{2}-1)!(\frac{n}{2})!} \sum_{s=0}^{\frac{n}{2}-1} C_s e^{ikN} N^{\frac{n}{2}-s-1} \left(\frac{n}{2}+s\right)!$$
$$\times \frac{(-1)^s}{(2ik)^{\frac{n}{2}+s+1}}.$$

Similarly for the pole at q = -ik

$$\operatorname{Res}_{q=-ik}(\Theta(q)e^{Nq}) = \frac{1}{\left(\frac{n}{2}\right)!} \sum_{s=0}^{\frac{n}{2}} C_s e^{-ikN} N^{\frac{n}{2}-s} \left(\frac{n}{2}\right) \dots \left(\frac{n}{2}+s-1\right) \\ \times \frac{(-1)^s}{(-2ik)^{\frac{n}{2}+s}}$$

$$= \frac{1}{(\frac{n}{2}-1)!(\frac{n}{2})!} \sum_{s=0}^{\frac{n}{2}} C_s e^{-ikN} N^{\frac{n}{2}-s-1} \left(\frac{n}{2}+s-1\right)!$$
  
 
$$\times \frac{(-1)^s}{(-2ik)^{\frac{n}{2}+s}}.$$

The number of configurations can be found by summing the residues at the two poles and calculating the integral transforms Eq. (2.15) and then summing the results for starting in the up and down directions. First the integral transforms of the residue at q = ik is calculated, followed by the corresponding result at q = -ik. Denoting these two results as  $\omega^+$  and  $\omega^-$  we have

$$\begin{split} \omega^{+} &= \frac{2}{\left(\frac{n}{2}-1\right)! \left(\frac{n}{2}\right)!} \sum_{s=0}^{\frac{n}{2}-1} C_{s} \left(\frac{n}{2}+s\right)! \frac{(-1)^{s}}{(2i)^{\frac{n}{2}+s+1}} \times \\ &\times \left\{ \frac{i}{\left(\frac{n}{2}+s\right)!} \left(\left(i(1+\frac{z}{N})\right)^{\frac{n}{2}+s}+\left(i(1-\frac{z}{N})\right)^{\frac{n}{2}+s}\right) \right\} N^{\frac{n}{2}-1} \\ &= \frac{1}{2\left(\frac{n}{2}-1\right)! \left(\frac{n}{2}\right)!} \\ &\times \left( \left(\frac{1+\frac{z}{N}}{2}\right)^{\frac{n}{2}} \left(\frac{1-\frac{z}{N}}{2}\right)^{\frac{n}{2}-1} + \left(\frac{1-\frac{z}{N}}{2}\right)^{\frac{n}{2}} \left(\frac{1+\frac{z}{N}}{2}\right)^{\frac{n}{2}-1} \right) N^{n-1}, \end{split}$$

and at the other pole

$$\begin{split} \omega^{-} &= \frac{2}{\left(\frac{n}{2}-1\right)! \left(\frac{n}{2}\right)!} \sum_{s=0}^{\frac{n}{2}} C_{s} \left(\frac{n}{2}+s-1\right)! \frac{(-1)^{s}}{(-2i)^{\frac{n}{2}+s}} \times \\ &\times \left\{\frac{-i}{2\left(\frac{n}{2}+s-1\right)!} \left(\left(-i\left(1-\frac{z}{N}\right)\right)^{\frac{n}{2}+s-1}+\left(-i\left(1+\frac{z}{N}\right)\right)^{\frac{n}{2}+s-1}\right)\right\} N^{n-1} \\ &= \frac{1}{2\left(\frac{n}{2}-1\right)! \left(\frac{n}{2}\right)!} \\ &\times \left(\left(\frac{1+\frac{z}{N}}{2}\right)^{\frac{n}{2}} \left(\frac{1-\frac{z}{N}}{2}\right)^{\frac{n}{2}-1}+\left(\frac{1-\frac{z}{N}}{2}\right)^{\frac{n}{2}} \left(\frac{1+\frac{z}{N}}{2}\right)^{\frac{n}{2}-1}\right) N^{n-1}. \end{split}$$

Summing these two results gives the number of configurations for even  $\boldsymbol{n}$ 

$$\Omega^{(n)} = \omega^- + \omega^+ \tag{2.23}$$

$$= \frac{2N}{n(n-2)!!^2} \left(N^2 - z^2\right)^{\frac{n}{2}-1}.$$
 (2.24)

A similar analysis can be done for the odd case. The result for the number of configurations of the defects on the chain is

$$\Omega^{(n)} = \begin{cases} \frac{2}{n(n-2)!!^2} N(N^2 - z^2)^{\frac{n-2}{2}} & \text{even } n\\ \frac{2}{(n-1)!!^2} (N^2 - z^2)^{\frac{n-1}{2}} & \text{odd } n. \end{cases}$$
(2.25)

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The number of hairpins on the chain is governed by the temperature of the system and the energy of a hairpin defect. The partition function can be calculated by summing all the configurations multiplied by their associated Boltzmann factors. This is most naturally done by splitting up the sums for even and odd numbers of defects.

$$Z_{\rm hp} = Z_{\rm even} + Z_{\rm odd}$$

$$(2.26)$$

$$Z_{\text{even}} = \sum_{\text{even } n} \frac{2N^{n-1}}{n(n-2)!!^2} \left(1 - \left(\frac{z}{N}\right)^2\right)^{\frac{n-2}{2}} e^{-n\beta u_h}$$
(2.27)

$$Z_{\text{odd}} = \sum_{\text{odd } n} \frac{2N^{n-1}}{(n-1)!!^2} \left(1 - \left(\frac{z}{N}\right)^2\right)^{\frac{n-1}{2}} e^{-n\beta u_h}.$$
 (2.28)

Fortunately these series can be summed up to infinity resulting in modified Bessel functions. The power series expansion of modified Bessel function is given by

$$I_{\nu}(z) = e^{-\frac{\pi}{2}\nu i} J_{\nu}(iz) = \sum_{k=0}^{\infty} \frac{(z/2)^{\nu+2k}}{(k!)(\nu+k)!}$$
(2.29)

In summing the odd series, the following result is useful

$$(n-1)!! = 2.4...(n-1)$$
 (2.30)

$$= 2^{\frac{n-1}{2}} \left(\frac{n-1}{2}\right)! \tag{2.31}$$

Substituting n = 2p + 1 reduces the odd part of the partition function to

$$Z_{\text{odd}} = 2\sum_{p=0}^{\infty} \frac{\left(1 - \left(\frac{z}{N}\right)^2\right)^p N^{2p}}{(p!)^2 2^{2p}} e^{-(2p+1)\beta u_h}$$
(2.32)

$$= 2e^{-\beta u_h} I_0 \left( e^{-\beta u_h} N \sqrt{1 - \left(\frac{z}{N}\right)^2} \right).$$
 (2.33)

Similarly for the even series, the result

$$(n-2)!! = 2^{\frac{n-2}{2}} \left(\frac{n-2}{2}\right)! \tag{2.34}$$

enables the series to be summed. Substituting n = 2p gives

$$Z_{\text{even}} = 2\sum_{p=1}^{\infty} \frac{N^{2p-1}}{2(p-1)!p!} \left(\frac{1-\left(\frac{z}{N}\right)^2}{4}\right)^{p-1} e^{-2p\beta u_h}.$$
 (2.35)

Substituting p' = p - 1 enables this expression to be rewritten as

$$Z_{\text{even}} = 2\sum_{p'=0}^{\infty} \frac{N^{2p'+1}}{2(p'+1)!p'!} \left(\frac{1-\left(\frac{z}{N}\right)^2}{4}\right)^{p'} e^{-2(p'+1)\beta u_h}$$
(2.36)

$$= 2\sqrt{\frac{4}{1-\left(\frac{z}{N}\right)^2}} \sum_{p'=0}^{\infty} \frac{N^{2p'+1}e^{-2(p'+1)\beta u_h}}{2(p'+1)!p'!} \left(\frac{1-\left(\frac{z}{N}\right)^2}{4}\right)^{p'+1/2} (2.37)$$

$$= 2 \frac{e^{-\beta u_h}}{\sqrt{1 - \left(\frac{z}{N}\right)^2}} I_1\left(e^{-\beta u_h} N \sqrt{1 - \left(\frac{z}{N}\right)^2}\right).$$
(2.38)

Combining both of these results together with the delta functions that represent the chain in its fully stretched out configuration gives the full partition for the 1-D hairpin chains

$$Z_{\rm hp}(z) = \frac{2}{N} (fN) \left[ I_0 \left( fN \sqrt{1 - \left(\frac{z}{N}\right)^2} \right) + \frac{1}{\sqrt{1 - \left(\frac{z}{N}\right)^2}} I_1 \left( fN \sqrt{1 - \left(\frac{z}{N}\right)^2} \right) \right] + \delta(z - N) + \delta(z + N)$$

$$(2.39)$$

where f is the Boltzmann factor of a single hairpin  $f = e^{-\beta u_h}$ , and the partition function has been expressed in terms of the natural variable fN. The partition function is of the form

$$Z_{\rm hp}(z) = \frac{1}{N} h(fN, z/N).$$
 (2.40)

The combination fN can be interpreted as approximately the average number of hairpins on a hairpinned chain with z = 0 (§2.D). Alternatively specification of f gives the ratio of  $u_{\rm h}$  to  $k_{\rm B}T$  as  $\beta u_{\rm h} = -\ln f$ . The expression for  $Z_{\rm hp}(z \to N)$  is given by

$$Z_{\rm hp}(z \to N) \to 2f + f^2 N$$
 (2.41)

This is simply the sum of one and two hairpin contributions. The other hairpin formulae depend on the end-to-end distance whereas the one and two hairpin results have no dependence on the end-to-end distance. When approximating this partition function, it is useful to know the value of  $Z_{\rm hp}(0)$ 

$$Z_{\rm hp}(0) = 2f I_0(fN) + 2f I_1(fN)$$
(2.42)

Fig. 2.6 compares the end-to-end distributions for different temperatures expressed in the fN parameter. A comparison between the partition function summed over all hairpins and the partition function summed over only a finite number of hairpins is shown in Fig. 2.7. It shows that the partition function converges very quickly with the number of hairpin defects included in the sum for small fN. At larger fN many terms are required for any sort of convergence. To develop a better intuition for this partition function and calculate some of its limits it is useful to develop an approximation.



Figure 2.6: A comparison between the partition function,  $Z_{\rm hp}$ , for different values of fN (all normalised to  $Z_{\rm hp}(z=0)=1$ ). The curves shown are for fN=1,2,5,10,50. The distribution is flatter for low fN as it consists of mostly the one and two hairpin contributions. It should be remembered that there are also two delta function spikes at  $z=\pm N$ .

#### Asymptotic Approximation

It is difficult to integrate the partition function in Eq. (2.39). It is much easier to work with an asymptotic approximation to this expression. The modified Bessel function has the asymptotic approximation [36]

$$I_{\nu}(x) \sim \frac{1}{\sqrt{2\pi x}} e^x. \tag{2.43}$$

There is no  $\nu$  dependence in the leading behaviour. However, the coefficients of the next terms in the asymptotic expansion do depend on  $\nu$ . This approximation will become more accurate when  $z \ll N$  and  $fN \gg 1$ . Substituting Eq. (2.43) into Eq. (2.39) we obtain

$$Z_{\rm hp}(z) \sim \frac{2}{N} \sqrt{\frac{2fN}{\pi}} e^{fN} e^{-\frac{fN}{2} \left(\frac{z}{N}\right)^2}.$$
 (2.44)

Thus for  $fN \to \infty$  and  $z \to 0$  the partition function is asymptotic to a Gaussian distribution, as expected from the central limit theorem [37]. The scaling of  $\langle z^2 \rangle$  with N is dependent on temperature

$$\langle z^2 \rangle = \frac{N}{f} \equiv \frac{N^2}{fN}$$
 (2.45)



Figure 2.7: A comparison between the partition function summed to infinity and just the first few terms. This is at a temperature satisfying fN = 8. The distribution is truncated at  $z = \pm N$ , the stretched out length of the chain.

where the latter expression emphasises that the chains become rod like  $\langle z^2 \rangle \sim N^2$  unless the number of hairpins, fN, is large. At high temperature  $fN \sim N$  and on average there is a hairpin on every persistence length. In this temperature region the end-to-end span shows Gaussian scaling. At low temperatures where there are very few hairpins per chain  $fN \sim 1$  and the scaling is rod like. Fitting a Gaussian to the partition function provides a better estimate than working with the asymptotic approximation. The amplitude of the Gaussian is easily fixed by forcing agreement when z = 0

$$Z_{\rm GA}(z) = Z_{\rm hp}(0)e^{-\alpha N^2(\frac{z}{N})^2},$$
(2.46)

where  $Z_{\rm hp}(0) = 2f I_0(fN) + 2f I_1(fN)$ . To fit the curvature we need the following property of modified Bessel functions

$$\frac{d\mathbf{I}_{n}(x)}{dx} = \frac{1}{2} \left( \mathbf{I}_{n-1}(x) + \mathbf{I}_{n+1}(x) \right).$$
(2.47)

For  $I_0(x)$  we recall that:  $I_n(x) = I_{-n}(x)$ . Fitting the curvature gives  $\alpha = -\frac{Z''(0)}{2Z(0)}$ . The following expression for  $\alpha$  is obtained

$$N^{2}\alpha = \frac{1}{(fN)I_{0}(fN) + (fN)I_{1}(fN)} \left(\frac{(fN)^{2}}{4}I_{0}(fN) + \left(\frac{(fN)^{2}}{2} - \frac{fN}{2}\right)I_{1}(fN) + \frac{(fN)^{2}}{4}I_{2}(fN)\right).$$
(2.48)

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This expression simplifies considerably by the use of the identity  $I_1(x) - \frac{x}{2}I_0(x) = -\frac{x}{2}I_2(x)$ 

$$N^{2}\alpha = \frac{fN}{2} \frac{I_{1}(fN) + I_{2}(fN)}{I_{0}(fN) + I_{1}(fN)}.$$
(2.49)

An alternative method of fitting with a Gaussian is to match the areas under the curves. This method requires calculation of the area under the curve numerically. The value of  $\alpha$  can be calculated by solving the following equation

$$A = 2 \int_0^\infty Z_{\rm hp}(z) dz = Z_{\rm hp}(0) \sqrt{\frac{\pi}{\alpha}} \operatorname{erf}(N\sqrt{\alpha}).$$
 (2.50)

The first equality is the actual area under the curve and the second is the area calculated using a Gaussian distribution approximation. The integral is of an truncated Gaussian since  $Z_{\rm hp}(z)$  cuts off at  $z = \pm \sqrt{\alpha}N$  and is thus in terms of the error function

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt.$$
 (2.51)

It is easy to solve Eq. (2.50) by numerical iteration once the area under the actual partition function  $Z_{\rm hp}(z)$  has been calculated. A useful starting point can be calculated by expanding the error function for large values of its argument

$$\operatorname{erf}(x) \approx 1 - \frac{e^{-x^2}}{x\sqrt{\pi}}.$$
(2.52)

The first approximation for  $\alpha$  in this method is given by

$$\alpha \approx \frac{Z_{\rm hp}^2(0)\pi}{A^2}.$$
(2.53)

Within the Gaussian approximation the initial fraction of inert chains can be calculated. The full partition function has both  $Z_{hp}(z)$  and the terms corresponding to straight chains:  $\delta(z-N)+\delta(z+N)$ . In this model the straight chains thus have a weight 2 relative to the hairpin chains since by the same counting procedure they can point in either the up or down directions. The fraction of inert chains is denoted by  $g(\lambda)$ , where  $\lambda$  denotes the deformation. Initially  $\lambda = 1$  and the fraction of inert chains is

$$g(1) = \frac{2}{2 + \int_{-N}^{N} Z_{\rm hp}(z) dz} \approx \frac{2}{2 + Z_{\rm hp}(0) \sqrt{\frac{\pi}{\alpha}} \mathrm{erf}(N\sqrt{\alpha})}$$
(2.54)

The probability distribution of the hairpin chains, excluding the straight chains in terms of the chain's end-to-end distance is given by

$$P(z) = [1 - g(1)] \sqrt{\frac{\alpha}{\pi}} \frac{e^{-\alpha N^2 (\frac{z}{N})^2}}{\operatorname{erf}(N\sqrt{\alpha})}.$$
 (2.55)

Fig. 2.8 shows a comparison between the different approximations to the partition function for the hairpin chain. It shows two different Gaussian approximations as well as the asymptotic approximation. The asymptotic approximation is not as good as the others because it requires a larger fN value before it becomes accurate. As with most asymptotic results it is difficult to predict at what values of fN the asymptotic approximation will improve. The



Figure 2.8: A comparison of the actual partition function of hairpinned chains at fN = 3 to two Gaussian approximations and to an asymptotic approximation.

approximations are all of remarkable power when one considers that there are distributions that one truncated at extents where they are still large. Moreover the mean number of hairpins is very small in the example chosen (fN = 3). The strong Gaussian character arises because despite there being few steps in the random walk they are of variable, random lengths.

## 2.2.4 Comparison of spring constants

A main chain elastomer is made up of polymer chains of different character. It is important to estimate the moduli of the different types of chains so that the way in which the rubber stretches can be modelled. To this end a comparison of the spring constants, k, of three different chain is now made. These chains are; the Gaussian chain, the hairpin chain, and the undulating chain. For the Gaussian chain

$$F_{\rm g} = -k_{\rm B}T \frac{R^2}{2l^2N} \tag{2.56}$$

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$$f_{\rm g} = -\frac{\partial F_{\rm g}}{\partial R} = \frac{k_{\rm B}TR}{l^2N}$$
(2.57)

$$\Rightarrow k_{\rm g} = \frac{k_{\rm B}T}{l^2 N}.$$
(2.58)

For the hairpin chain the asymptotic limit is used. This will provide an overestimate of the spring constant for smaller values of fN.

$$F_{\rm hp} \approx -k_{\rm B}T \frac{R^2 f N}{2N^2 l^2} \tag{2.59}$$

$$f_{\rm hp} \approx k_{\rm B}T \frac{fN}{N^2 l^2} R$$
 (2.60)

$$\Rightarrow k_{\rm hp} = k_{\rm B} T \frac{fN}{l^2 N^2} \tag{2.61}$$

This shows that when  $fN \sim 5$  the Gaussian chains are much stiffer than the hairpin chains. The estimate of the spring constant of the undulating chain is given in §2.E. The result obtained is

$$f_{\rm z} \approx \frac{4u_{\rm h}}{k_{\rm B}T} \frac{J}{L} \delta R$$
 (2.62)

$$\Rightarrow k_{\rm u} = \frac{4u_{\rm h}J}{k_{\rm B}TL} \tag{2.63}$$

$$\approx \frac{4u_{\rm h}}{Nl^2}$$
 (2.64)

The ratio of moduli of chains is

$$k_{\rm u}: k_{\rm g}: k_{\rm hp} = \frac{4u_{\rm h}}{Bl^2}: \frac{k_{\rm B}T}{Nl^2}: \frac{k_{\rm B}TfN}{N^2l^2}$$
(2.65)

here the combination fN is retained since it is an estimate of the number of hairpins per chain,  $n_{\rm hp}$ . Then  $\frac{u_{\rm h}}{k_{\rm B}T} \approx \ln \frac{N}{n_{\rm hp}}$ , using the definition of f. In any event, one expects  $u_{\rm h} > k_{\rm B}T$  because hairpins are well-defined and relatively infrequent events. Thus the ratio of the spring constants becomes

$$k_{\rm u}: k_{\rm g}: k_{\rm hp} = 4\ln\frac{N}{n_{\rm hp}}: 1: \frac{n_{\rm hp}}{N}$$
 (2.66)

From these estimates it is clear that when the hairpins are removed from a chain it becomes significantly harder to stretch. The chains in this state can only have their end-to-end distance increased by a small amount because their longitudinal spatial extent is near to their arc length.

### 2.2.5 Perpendicular direction

In the plane perpendicular to the nematic direction the hairpin chains have two sources that can give rise to an end-to-end distance: Gaussian distributed undulations and the position of individual hairpin steps. In §2.B the mean square displacement of the undulations is calculated as

$$\langle R^2 \rangle_{\rm und} = \frac{Lk_BT}{J}.$$
 (2.67)

The mean square distance due to the width of a hairpin in the perpendicular plane can be estimated from the result of §2.D: the average number of steps in a hairpin chain is  $\sim fN$ . Assuming the span distribution to be approximately Gaussian then it follows that

$$\langle R^2 \rangle_{\rm hp} \approx (fN) w^2$$
 (2.68)

where w is the characteristic width of the hairpin. In the hairpin regime when  $fN \ll N$  the undulations dominate the transverse direction. The transverse excursions are thus dominated by the Gaussian excursions of the undulations. Henceforth it is assumed that the entire perpendicular extent is due to the undulations and can be modelled as being Gaussian distributed.

## 2.3 Non-affine deformation model

Imagine many hairpinned chains connected together to form a network. The mechanism of stretching of the chains is motivated by the properties of the individual hairpinned chains and will be modelled as follows. At first when the network is deformed, the hairpinned chains will deform quasi-affinely. The undulating, non-hairpinned chains will not deform significantly because their modulus is much higher than that of the undulating chains. Once a chain has reached its maximum extent (lost its hairpins) because of the extension of the network, it is inert as far as strain accommodation is concerned and passes on the requirement of taking up its share of the strain to neighbouring slack chains. These then take up the slack until they too become inert. The deformation of the hairpin chains is regarded as super-affine because they are suffering a deformation progressively larger than that of the bulk. The chains form a 3-D network because they have a transverse extent. The finite lateral extent of each hairpin and the transverse random walk due to undulations generate this three dimensionality. These two processes add incoherently so that the rubber is almost Gaussian in its transverse extent. In the hairpin regime the undulations dominate the finite lateral extent of the hairpins. Locally we assume that the network can be regarded as a one dimensional series of polymer strands. In extending this to a 3-D model we assume that the connections in the network allow the slack to be taken up by the neighbouring chains in the way described above. The elongation of the network is illustrated in Fig. 2.9. When modelling this mechanism of extension it is important to keep track of two populations of chains in the rubber: those containing hairpins and those without. It is assumed that the latter, straight chains, are completely



Figure 2.9: The figure illustrates the elongation of the network of hairpin chains. a) shows an undeformed section and b) shows the same section after a small deformation. The central strand has taken up most of the deformation leaving the surrounding two unchanged.

inert. As the rubber is stretched the inert chains remain unchanged whilst the hairpinned strands have their lengths changed in proportion to their current length so that this population takes up all the macroscopic strain, and the sample as a whole accommodates the required macroscopic strain. Those that are at their maximum length are not able to stretch any more and so do not contribute to the total length change of the rubber. Two measures of the deformation are thus required: the microscopic deformation,  $\lambda$ , and the macroscopic deformation,  $\Lambda$ . Chains cannot deform affinely with the bulk,  $\Lambda$ , since some do not extend at all and others must take up more than their share of deformation. To describe a hairpin chain we adopt the following reduced units (as in §2.2.3) for arc length L and end-to-end distance parallel to the nematic field, R, in terms of a persistence length, l

$$z = \frac{R}{l} ; N = \frac{L}{l}$$
(2.69)

The macroscopic deformation,  $\Lambda$ , can be related to the microscopic deformation,  $\lambda$  as follows. The fraction of chains with an initial end-to-end distance z is given by P(z), excluding the straight chains. The fraction of straight chains is denoted by  $g(\lambda)$ . The normalisation condition for P(z) is thus

$$1 = g(1) + 2\int_0^N P(z)dz,$$
(2.70)

where g(1) is the initial fraction of the chains that are straight, and the symmetry of P(z) has been used to halve the interval of integration. As the sample is stretched, chains from the hairpinned population with lengths initially in the interval  $\left[\frac{N}{\lambda}, N\right]$  fall into the straight population so the increased fraction

of straight chains,  $g(\lambda)$ , is given by

$$g(\lambda) = g(1) + 2 \int_{N/\lambda}^{N} P(z) dz. \qquad (2.71)$$

The macroscopic deformation can then be identified with the new mean span  $R_{\Lambda}$  with respect to the initial mean span,  $R_1$ :

$$R_{\Lambda} = g(\lambda)N + [1 - g(\lambda)]\lambda\langle z \rangle_{\rm hp}$$
(2.72)

$$\Lambda R_1 = g(\lambda)N + [1 - g(\lambda)]2 \int_0^{N/\lambda} \lambda z \left(\frac{P(z)}{1 - g(\lambda)}\right) dz.$$
 (2.73)

The length of an average chain is defined as the weighted average of the straightened chain length and the length of the hairpinned chains. The latter,  $\lambda \langle z \rangle_{\rm hp}$  consists of the average  $\langle z \rangle_{\rm hp}$  of the population initially in the interval  $z = (0, \frac{N}{\lambda})$  that is still hairpinned after extension  $\lambda$ , taken to its current average length by multiplication by  $\lambda$ . The normalisation of the part of the probability distribution for the hairpinned chains has been written explicitly for clarity. The average initial length of the chains is defined as above but with  $\Lambda = \lambda = 1$ 

$$R_1 = Ng(1) + 2\int_0^N zP(z)dz.$$
 (2.74)

In both Eq. (2.74) and Eq. (2.73) the first term on the right hand side is the length taken up by the fully extended chains and the second term is the length taken up by the remaining chains which are at various degrees of extension and have varying numbers of hairpins in them. Eq. (2.73) determines  $\Lambda[P(z), \lambda]$ in terms of the internal microscopic deformation and the initial span distribution. This is a departure from the usual affine deformation approximation for networks because of the hard constraints met when the hairpins are absent or are eliminated. The macroscopic deformation, defined in Eq. (2.73), can be rewritten as

$$\Lambda = \frac{\left[\left\{(g(1) + 2\int_{N/\lambda}^{N} P(z)dz\right\}N + 2\lambda\int_{0}^{N/\lambda} zP(z)dz\right]}{Ng(1) + 2\int_{0}^{N} zP(z)dz}.$$
(2.75)

The asymptotics of  $\Lambda$  can be calculated as follows

$$\frac{d\Lambda}{d\lambda} = \frac{2}{R_1} \int_0^{\frac{N}{\lambda}} z P(z) dz.$$
(2.76)

It is clear that the gradient goes to zero as  $\lambda \to \infty$ . The value of  $\Lambda$ , from Eq. (2.75), is then

$$\Lambda(\infty) = \frac{2N \int_0^N P(z) dz + g_1 N}{Ng_1 + 2 \int_0^N z P(z) dz}$$
$$= \frac{N}{Ng_1 + 2\int_0^N zP(z)dz}$$
  
$$\equiv \frac{N}{Ng_1 + (1 - g_1)\langle z \rangle_{\rm hp}(\lambda = 1)}.$$
 (2.77)

The average (reduced) extent of the hairpinned chains before deformation is denoted by  $\langle z \rangle_{\rm hp} (\lambda = 1)$ . Intuitively this result simply gives the maximum macroscopic deformation as the ratio of the length of the sample when all the chains are stretched to their full extent, to that when all chains are at their initial lengths. To calculate how  $\Lambda$  reaches its asymptotic value the following general result is applied to Eq. (2.75)

$$\frac{\partial}{\partial z} \int_{a(z)}^{b(z)} f(x,z) dx = \int_{a(z)}^{b(z)} \frac{\partial f}{\partial z} dx + f(b(z),z) \frac{\partial b}{\partial z} - f(a(z),z) \frac{\partial a}{\partial z}.$$
 (2.78)

The following is obtained on applying l'Hôpital's rule to the result

$$\Lambda = \frac{1}{R_1} \left( Ng_1 + 2N \int_0^N P(z)dz - \frac{N^2 P(0)}{\lambda} + O\left(\frac{1}{\lambda}\right)^2 \right).$$
(2.79)

Rearranging this expression results in

$$\lambda \approx \frac{N^2 P(0)}{R_1} \frac{1}{\Lambda(\infty) - \Lambda}.$$
(2.80)

This expression indicates that the microscopic deformation diverges at  $\Lambda(\infty)$  corresponding to stretching all the hairpin chains. Only those that were initially of very small length are still in the hairpin population, hence the P(0) factor. These chains of vanishing end-to-end extent require a very large  $\lambda$  locally to attain z = N, i.e. full extension. Interestingly, the hairpins with zero end-to-end distance are never stretched but since they constitute a set of zero measure, their contribution is vanishingly small for very large deformations. At  $\Lambda \geq \Lambda(\infty)$  this model suggests that the hairpin rubber should become very rigid since one is now deforming the undulations that represent the limited disorder remaining in chains. The approach to  $\Lambda(\infty)$  has been crudely modelled — for instance as soon as there is a percolating path of inert chains in the network, the modulus should abruptly rise and the remaining hairpin population have little further relevance.

Initially, at  $\lambda = 1$ 

$$\left(\frac{d\Lambda}{d\lambda}\right)_{\lambda=1} = 1 - \frac{Ng(1)}{R_1} \tag{2.81}$$

Thus expanding close to  $\lambda = 1$ 

$$\Lambda \approx 1 + (\lambda - 1) \left( 1 - \frac{Ng(1)}{R_1} \right) = \lambda - (\lambda - 1) \frac{Ng(1)}{R_1}$$
(2.82)

After the rubber has been deformed by  $\Lambda > 1$  and the stress is released the rubber contracts back to its initial equilibrium position. This is because each of the extended chains has recorded its initial position via cross-linking, so chains that were moved into the inert population by the deformation know how to re-enter the hairpin population.

#### 2.3.1 Macroscopic strain in the asymptotic approximation

A Gaussian approximation to the partition function can be used to calculate the macroscopic deformation. In what follows the curvature approximation will be used for numerical illustrations but the formulae are equally applicable to other Gaussian approximations, differing merely by the method of calculating the parameter  $\alpha$ . This results in the following formula for the macroscopic deformation

$$\Lambda = \frac{N\left[g(1) + (1 - g(1))(1 - \frac{\operatorname{erf}(N\sqrt{\alpha}/\lambda)}{\operatorname{erf}(N\sqrt{\alpha})})\right] + \frac{\lambda(1 - g(1))}{\operatorname{erf}(N\sqrt{\alpha})\sqrt{\alpha\pi}}(1 - e^{-N^2\alpha/\lambda^2})}{Ng(1) + \frac{1 - g(1)}{\operatorname{erf}(N\sqrt{\alpha})\sqrt{\pi\alpha}}(1 - e^{-N^2\alpha})}$$

The conversion between microscopic and macroscopic deformation is shown in Fig. 2.10. Note the curves only depend on fN and not on N. Each of the curves illustrates the divergence in microscopic strain when most of the chains have been moved into the inert population. There is then a very small fraction of chains that are deforming by a huge amount to achieve the required macroscopic strain.

# 2.4 Hairpin chain network free energy

In an elastomer the ends of the polymer chains are cross-linked to other chains so the end-to-end distance is a quenched variable. However, for a sufficiently large block of rubber the probability distribution of end-to-end distances of the chains can be averaged over. In contrast the hairpins are annealed degrees of freedom. For a polymer chain with a fixed end-to-end distance the number of hairpins on the chain can fluctuate around the equilibrium number of hairpins. The difference between quenched (qd) and annealed (ad) degrees of freedom is clear in the partitions functions. Suppose X represents a degree of freedom which can be annealed or quenched and Y represents all the other degrees of freedom in the problem then [38]

$$Z_{\rm qd} = e^{-\beta F_{\rm qd}} = Tr_Y \left[ e^{-\beta H(X,Y)} \right]$$
(2.83)

$$Z_{\rm ad} = e^{-\beta F_{\rm ad}} = Tr_{X,Y} \left[ e^{-\beta H(X,Y)} \right]$$
(2.84)

For the quenched degree of freedom it is assumed that the system is sufficiently large so that all of the different values of X can be realised. The probability



Figure 2.10: The microscopic to macroscopic deformation conversion curves for temperatures of fN = 1, 2, 5, 10, 50 going from left to right with  $\Lambda(\infty) = 1.7, 2.0, 2.8, 3.8, 8.8$  respectively. The Gaussian approximation to the hairpin partition function using a fit to the curvature was employed.

of the different values of X can then be used to calculate the free energy

$$F = \int P(X)F_{\rm qd}(X)dX, \qquad (2.85)$$

where P(X) is the probability distribution of the quenched degree of freedom X. For the hairpin rubber the network free energy per strand associated with the direction parallel to the nematic field as can be expressed as

$$F_{\parallel}(\lambda) = -2k_{B}T \int_{0}^{N/\lambda} P(z) \ln [Z_{\text{und}} Z_{\text{hp}}(\lambda z)] dz -2k_{B}T \int_{N/\lambda}^{N} P(z) \ln [Z_{\text{und}}] dz - k_{B}Tg(1) \ln [Z_{\text{und}}] , \quad (2.86)$$

where the first integral calculates the free energy of the hairpin chains and treats their undulations and hairpin degrees of freedom as independent so the partition functions can be multiplied. The second integral calculates the energy of the chains that are moved to the straightened population as a result of stretching. The last term is the free energy of those chains that were initially straight. This expression can be simplified by splitting up the logarithm in the first term. The resulting expression is

$$F_{\parallel} = -2k_BT \int_0^{N/\lambda} P(z) \ln Z_{\rm hp}(\lambda z) dz$$
  
$$-2k_BT \int_0^N P(z) \ln Z_{\rm und} dz - k_BTg(1) \ln Z_{\rm und},$$
  
$$= -2k_BT \int_0^{N/\lambda} P(z) \ln Z_{\rm hp}(\lambda z) dz - k_BT \ln Z_{\rm und}. \qquad (2.87)$$

The assumption that the hairpin and undulating parts are independent results in the separation of the undulating part of the problem. Since the undulating degree of freedom only contributes a constant to the free energy in the parallel direction it can be neglected. Expanding the free energy expression for large  $\lambda$  yields the result

$$F_{\parallel} \approx -\frac{2k_B T P(0)}{\lambda} \left( N \ln Z_{\rm hp}(N) - \int_0^N \frac{Z_{\rm hp}'(z)}{Z_{\rm hp}(z)} z dz \right) + O\left(\frac{1}{\lambda^2}\right)$$
(2.88)

Substituting the expansion of  $\Lambda$  for large  $\lambda$  from Eq. (2.80) into this expression it is clear that  $F_{\parallel}$  increases linearly with  $\Lambda$ 

$$F_{\parallel} \approx \frac{2k_B T R_1 (\Lambda - \Lambda(\infty))}{N} \left( \ln Z_{\rm hp}(N) - \int_0^N \frac{Z_{\rm hp}'(z)z}{Z_{\rm hp}(z)N} dz \right)$$
(2.89)

Note that the dependence on P(0) cancels out. The integral in this expression can be evaluated easily using the Gaussian approximation. The linear dependence of the free energy on  $\Lambda$  will produce a plateau in the nominal stress as the macroscopic deformation approaches its maximum value. After this plateau is reached the nominal stress will rise very quickly because the system now consists mainly of undulating chains. Note that this result is due to the mechanism of stretching. It arises because we have two separate populations, one of which is inert. As we gradually shift all chains to the second population fewer and fewer chains are accommodating the strain and the material becomes very weak. For the hairpin rubber the Gaussian approximation to the partition function can be substituted in and the integrals of Eq. (2.87) completed.

$$F_{\parallel} = -2k_BT \int_0^{N/\lambda} P(z) \ln Z_{\rm hp}(\lambda z) dz$$
  
$$= -2k_BT \frac{[1-g(1)]}{\operatorname{erf}(N\sqrt{\alpha})} \sqrt{\frac{\alpha}{\pi}} \left\{ \int_0^{N/\lambda} (\ln Z_{\rm hp}(0) - \alpha z^2 \lambda^2) e^{-\alpha z^2} dz \right\}$$
  
$$= -k_BT \frac{[1-g(1)]}{\operatorname{erf}(N\sqrt{\alpha})} \frac{2}{\sqrt{\pi}} \left\{ \int_0^{\frac{N\sqrt{\alpha}}{\lambda}} \ln Z_{\rm hp}(0) e^{-x^2} dx - \lambda^2 \int_0^{\frac{N\sqrt{\alpha}}{\lambda}} x^2 e^{-x^2} dx \right\}$$

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$$= -k_B T \frac{[1-g(1)]}{\operatorname{erf}(N\sqrt{\alpha})} \left[ \left\{ \ln Z_{\rm hp}(0) - \frac{\lambda^2}{2} \right\} \operatorname{erf}(N\sqrt{\alpha}/\lambda) + N\sqrt{\frac{\alpha}{\pi}} \lambda e^{-N^2 \alpha/\lambda^2} \right].$$
(2.90)

The behaviour of the rubber at  $\lambda = 1$  is important because it tells us how stiff the rubber is initially. It can be found by looking at the gradient of the free energy there

$$\left(\frac{dF_{\parallel}}{d\lambda}\right)_{\lambda=1} = k_B T (1-g(1)) \left\{ 1 + N \frac{Z_{\rm hp}(N)}{\int_0^N Z_{\rm hp}(x) dx} (\ln Z_{\rm hp}(N) - 1) \right\}.$$
(2.91)

The behaviour of this expression can be analysed most easily for large fN by using the asymptotic expression for the partition function given in Eq. (2.44). Using this equation produces the following in the limit  $fN \to \infty$ 

$$\int_0^N Z_{\rm hp}(z) dz \approx e^{fN} \tag{2.92}$$

$$g(1) \approx \frac{1}{1 + 2e^{fN}}.$$
 (2.93)

Thus using the above equations for large fN together with Eq. (2.41), then Eq. (2.91) becomes

$$\left(\frac{dF_{\parallel}}{d\Lambda}\right)_{\lambda=1} \approx k_B T \left\{ 1 + e^{-fN} (2fN + (fN)^2) \ln \frac{2fN + (fN)^2}{Ne} \right\}.$$
 (2.94)

Thus in the limit of large fN the hairpin rubber is slightly harder than the Gaussian rubber by an exponentially small amount. Note that this difference is due to the cost of each direction change  $(u_h)$  and that as  $f \to \infty$  the parallel direction becomes as hard as a Gaussian rubber. The exponential dependence on fN means that this expression is valid for even moderately large fN i.e. when there are only about three hairpins. This expression can be expanded for very small fN, that is low T

$$\int_{0}^{N} Z_{\rm hp}(z) dz \approx 2fN + (fN)^{2}$$
(2.95)

$$g(1) \approx \frac{1}{1 + 2fN + (fN)^2}.$$
 (2.96)

Substituting these expressions into the gradient of the free energy results in

$$\left(\frac{dF_{\parallel}}{d\Lambda}\right)_{\lambda=1} \approx 2k_B T \ln \frac{2fN + (fN)^2}{N}$$
  
= -2u<sub>h</sub>. (2.97)

Thus for small fN the hairpin part of the rubber will spontaneously elongate as it has a negative nominal stress and hence has no mechanism for competing with the transverse degrees of freedom. Note that the hairpin degrees of freedom on their own undergo spontaneous expansion here. The transverse degrees of freedom have not yet been included, but will cause the rubber to elongate via volume conservation.

# 2.4.1 Transverse degrees of freedom

In the transverse direction there are contributions from both the small undulations about the nematic direction and the transverse extent of the hairpins. As mentioned previously, these processes will be treated together, producing a Gaussian distribution of end-to-end distances in the perpendicular plane and hence a Gaussian rubber in the perpendicular direction. As a result the free energy in the transverse direction depends on the macroscopic deformation like a Gaussian rubber

$$F_{\perp} = 2\left(\frac{1}{2}k_B T \Lambda_{\perp}^2\right), \qquad (2.98)$$

the factor of 2 coming from the two transverse dimensions. For a volume conserving uniaxial deformation then

$$1 = \Lambda_{\parallel} \Lambda_{\perp}^2. \tag{2.99}$$

For uniaxial deformations writing  $\Lambda_{\parallel}=\Lambda$  gives the free energy expression as

$$F_{\perp} = \frac{k_B T}{\Lambda}.$$
 (2.100)

Thus as the elastomer is elongated, the free energy of the perpendicular degrees of freedom is reduced because the initial and final points of strands are brought into line and as a result the conformational entropy increases.

# 2.4.2 Free energy curves

To calculate the total free energy of the rubber the transverse Gaussian degrees of freedom and the hairpin degrees of freedom parallel to the nematic field are combined. The free energy depends on weakly on the length N of the polymer chains. The N dependence is logarithmic in Eq. (2.89) because it only enters  $Z_{\rm hp}$ . Fig. 2.11 shows the free energy as a function of the macroscopic deformation  $\Lambda$ . For the purposes of numerical illustrations the value N =100 is used (experimentally it is difficult to work with very long main chains because of their slow dynamics). The minimum in the free energy is at a  $\Lambda$ greater than one when there are a few hairpins, and the hairpin degrees of freedom are weak. As the number of hairpins is increased the minima moves slightly below  $\Lambda = 1$  and then back to  $\Lambda = 1$  for very large fN. This shows that on cross-linking the rubber will elongate to a new equilibrium value. As



Figure 2.11: The free energy of a hairpin rubber as a function of the macroscopic deformation for temperatures such that fN = 4.5, 5, 6, 7 and for a chain of length N = 100. The curves are calculated up to the end of the stress plateau,  $\Lambda(\infty)$ . After this the rubber rapidly attains the modulus of extended worm chains.

the rubber is deformed further, the free energy gradually becomes linear in the deformation  $\Lambda$  because more of the chains are now inert with the result that the microscopic deformation,  $\lambda$ , is concentrated in very few chains. The number of chains where energy is being stored reduces with  $\Lambda$  and the deformation becomes easier subsequently. This linear increase with  $\Lambda$  contrasts with the quadratic  $\Lambda^2$  response of a Gaussian rubber.

# 2.4.3 Nominal stress curves

The spontaneous elongation is even clearer on the nominal stress curves. Fig. 2.12 shows the nominal stress  $\frac{dF}{d\Lambda}$  as a function of the macroscopic deformation  $\Lambda$ . Each of the curves shows the nominal stress beginning to plateau as hairpins are pulled out. After all the hairpins have been pulled out, then only the stiff undulating chains remain so the nominal stress will then increase very rapidly (not modelled here). As the temperature of the rubber is reduced the average number of hairpins on a chain reduces. This causes the parallel direction to become weaker and hence the spontaneous elongation on cross-linking increases. Eventually the hairpin degrees of freedom will be so weak that the rubber will immediately elongate to its maximum extent so that it consists of undulating chains alone. The very large modulus of the undulating chains will then resist the transverse Gaussian degrees of freedom so that the rubber can find its equilibrium. The average number of hairpins on a chain



Figure 2.12: The nominal stress as a function of the macroscopic deformation of a hairpin rubber for chains of length N = 100.

when the rubber first elongates to its maximum extent can be calculated as follows. If the rubber just reaches its maximum extent then as  $\lambda \to \infty$  the nominal stress will be zero at this point. Using Eq. (2.89) and replacing the integral using the Gaussian approximation then

$$\frac{dF}{d\Lambda}_{\lambda \to \infty} = \frac{2k_B T}{\Lambda(\infty)} \left( \ln Z_{\rm hp}(N) + \frac{2N^2 \alpha}{3} \right) - \frac{k_B T}{\Lambda(\infty)^2}$$
(2.101)

Using the simplest approximation for  $N^2 \alpha = \frac{fN}{2}$  from the asymptotic expansion yields a value of approximately fN = 4.3 when N = 100. This corresponds to the lowest average number of hairpins possible on the chain before the chain spontaneously extends to its maximum extent on cross-linking. In practise it will not elongate to its maximum extent because there will be more and more percolating paths of inert chains which will gradually make the rubber harder. However, before this situation is reached the above model applies.

The spontaneous elongation on cross-linking the polymer chains has to be taken into account in subsequent measurements. The initial spontaneous elongation of  $\Lambda_s$  occurs on cross-linking. After this elongation any further deformation carried out will be in addition to this deformation. Fig. 2.13 shows the nominal stress curves plotted as a function of the experimentally measured deformation,  $\Lambda'$ 

$$\Lambda' \Lambda_s = \Lambda. \tag{2.102}$$

Thus networks with hairpins should have a longer stress-strain plateau, terminated by the final removal of hairpins. Networks that spontaneously deform to their limit  $\Lambda(\infty)$  will be instantly strong in extension but rubbery in compression along the director — most unusual materials.



Figure 2.13: The nominal stress as a function of the measured macroscopic deformation of a hairpin rubber for chains of length N = 100.

The spontaneous extension shown in this model may be a consequence of the way in which the chains are split up into non-hairpinned and hairpinned chains in the deformation mechanism. Since the non-hairpinned chains are separated out from the hairpinned chains then the remaining hairpinned chains will try to achieve their equilibrium distribution. Consequently the sample extends. In order to explore this effect in more detail the splitting up of the deformation between the chains should be done in a less singular way, such that the non-hairpinned chains experience some small elongation depending on their stiffness. The limit of infinite chain stiffness should then be taken.

# 2.5 Conclusions

An elastomer composed of main chain liquid crystalline polymers was considered. The strong nematic field results in creation of hairpin defects. The statistics of these hairpin chains can be calculated and can be approximated well by a truncated Gaussian distribution. The transverse degrees of freedom that accompany the hairpins are undulations of the chains about the nematic director. These undulations produce a Gaussian distribution for the transverse extent. The difference in the spring constants of undulating and hairpinned chains motivated a non-affine stretching mechanism of the rubber. Cross-linking the chains results in a rubber that spontaneously extends at low temperatures. As the rubber is deformed along the director it exhibits a plateau in its nominal stress. This is because the number of active chains that are being stretched is gradually depleted so that fewer and fewer chains are accommodating the stretch. Experimentally it is possible that both the extremes of main chain elastomers can be found. In the experiments of Wermter *et al.* [30] a polydomain main chain rubber showed a very long plateau (up to  $\Lambda \sim 5$ ) even after it had been aligned by the initial strain. Order parameter measurements confirmed that initially the plateau is due to director reorientation with its associated soft elastic response. An effective monodomain situation is achieved by  $\lambda \sim 3.5$ , leaving an extended soft plateau, possibly due to a hairpin rubber response modelled here.

Clarke *et al.* [31] found that monodomain main chain elastomers suffered a large spontaneous thermal deformation of  $\Lambda \sim 4.5$ . These were then very stiff along the director. Perpendicular extensions were very soft, presumably associated with the director rotation, conventional soft elasticity in nematic rubber. It is possible that hairpins were eliminated during thermal expansion and cooling from the isotropic synthesis to the lower experimental temperature. It would be interesting to know if such elastomers were soft along their director if extended at more elevated temperatures.

An interesting aspect of the data of Wermter *et al.* [30] that was not modelled here is the behaviour after the plateau. The plateau in the stress is higher as we decrease the temperature and the modulus of the elastomer after the plateau is higher as temperature is reduced. This indicates that modulus of the rubber may be dependent on the dynamics of the system [39]. At higher temperatures it is possible for the sharp hairpin defects to reptate in their tubes and thus move allowing the rubber to deform.

# 2.A Geometry of a hairpin at zero temperature

A polymer chain with a bend constant, B, in a nematic field with strength J has a free energy of the form

$$F = F_0 + \int_0^L ds \left[ \frac{1}{2} B \left( \frac{d\theta}{ds} \right)^2 + \frac{1}{2} J \sin^2 \theta \right].$$
 (2.103)

The hairpin configuration which has the minimum free energy and obeys the following boundary conditions is required

$$\begin{array}{rcl} \theta & = & 0 \; ; \; s \to -\infty \\ \theta & = & \pi \; ; \; s \to \infty \end{array}$$

Minimising the free energy expression Eq. (2.103) with respect to  $\theta$  results in the Euler-Lagrange equation:

$$\frac{d^2\theta}{ds^2} = \frac{1}{2l_{\rm h}^2}\sin 2\theta, \qquad (2.104)$$

where  $l_{\rm h} = \sqrt{(B/J)}$ . This equation has the solution:

$$\theta = 2 \tan^{-1} \left[ e^{s/l_{\rm h}} \right]. \tag{2.105}$$

This shows that the hairpin has a size of order  $l_{\rm h}$ . The misalignment dies away exponentially from the hairpin thereafter. As a result hairpins have a separable character. The size becomes very large if the nematic field gets weak or if the bending energy cost becomes very high. Substituting this expression back into the expression for the energy of the hairpin gives the result:

$$u_{\rm h} = 2(BJ)^{1/2}.$$
 (2.106)

# 2.B Undulating chain statistics

### The free energy of an undulating chain with free ends.

The worm-like chain model of a polymer can be used to write down the partition function of a polymer in a nematic field as:

$$Z = \int \mathcal{D}\mathbf{u}(s) \exp\left\{-\beta \frac{1}{2} \int_0^L ds \left[B \left|\frac{\partial \mathbf{u}}{\partial s}\right|^2 - Ju_z^2\right]\right\},\tag{2.107}$$

where  $\mathbf{u}$  is the tangent vector to the polymer. In strong fields the tangent vector only makes small deviations away from the nematic direction,  $\mathbf{z}$ ,  $\mathbf{u}$  can be written as:

$$\mathbf{u} pprox \mathbf{z} - oldsymbol{\sigma}$$

where  $\sigma$  is perpendicular to z. The rare and isolated hairpin events are ignored. Using the above expansion to second order in  $\sigma$  reduces the partition function to

$$Z = \int \mathcal{D}\boldsymbol{\sigma}(s) \exp\left\{-\beta \frac{1}{2} \int_0^L ds \left[B \left|\frac{\partial \boldsymbol{\sigma}}{\partial s}\right|^2 + J\boldsymbol{\sigma}^2\right]\right\}.$$
 (2.108)

To evaluate this Gaussian functional integral the Fourier representation is required

$$f(x) = \sum_{q} e^{iqx} f(q) \tag{2.109}$$

$$f(q) = \frac{1}{L} \int_0^L dx e^{-iqx} f(x),$$
 (2.110)

where  $q = \frac{2\pi n}{L}$  and n is an integer. The partition function can then be written as

$$Z = \int \mathcal{D}\sigma_q \exp\left\{-\frac{\beta L}{2} \sum_q \left(Bq^2 + J\right) |\sigma_q|^2\right\}.$$
 (2.111)

The result of this integration is the product

$$Z = A \prod_{q} \frac{2}{\beta L \left( Bq^2 + J \right)} \tag{2.112}$$

here A is a multiplicative constant from the path integral. This expression can be evaluated in two ways. The first requires the formula

$$\prod_{n=1}^{\infty} \frac{1}{1 + \left(\frac{x}{n\pi}\right)^2} = \frac{x}{\sinh x}$$
(2.113)

#### 2.B. UNDULATING CHAIN STATISTICS

The result is

$$Z \propto \frac{\frac{L}{2l_{\rm h}}}{\sinh(\frac{L}{2l_{\rm h}})} \tag{2.114}$$

The free energy associated with this partition function is then

$$F = F_0 - k_B T \left[ \ln \frac{L}{2l_{\rm h}} - \ln \sinh \left( \frac{L}{2l_{\rm h}} \right) \right]$$
(2.115)

If  $L/l_{\rm h}$  is large then this expression shows that the free energy is approximately linear in L and hence that the free energy of an undulating chain is proportional to its length. The alternative way to evaluate Eq. (2.112) is to write the product as

$$Z = A \exp\left\{-\int_{q_{min}}^{q_{max}} \frac{Ldq}{2\pi} \left(\ln\left(Bq^2 + J\right) + \ln\frac{\beta L}{2}\right)\right\}.$$
 (2.116)

This integral can be evaluated by substituting  $q_{min} = 0$  and  $q_{max} = \frac{2\pi}{l_{\rm h}}$ . The associated free energy is

$$F = F_0 + k_B T \left( \frac{L}{l_h} \ln \frac{J\beta L}{2} - \frac{2L}{l_h} + \frac{L}{l_h} \ln \left( 1 + 4\pi^2 \right) \right)$$
(2.117)

This expression is also essentially linear in L. This justifies the assumption that the hairpin defects and the undulating chain sections are very weakly coupled. An hairpin defect essentially acts as a node as regards undulations of a chain because of the extreme cost of additional bend around a hairpin defect. Thus if an undulating chain is divided up into segments separated by hairpins then the free energy of the undulating sections is the same as that of the reassembled sections.

#### The end-to-end distribution of undulating chains.

Using the same small angle approximation as above the probability distribution for end-to-end vectors projected onto the perpendicular plane,  $\mathbf{R}_{\perp}$  can be calculated.

$$P(\mathbf{R}_{\perp}) = \left\langle \delta \left( \mathbf{R}_{\perp} - \int_{0}^{L} ds \sigma(s) \right) \right\rangle$$

$$= \int \mathcal{D}\sigma(s) \int \frac{d^{2}\mathbf{p}}{(2\pi)^{2}} \exp \left\{ i\mathbf{p} \cdot \mathbf{R}_{\perp} - i\mathbf{p} \cdot \int ds \sigma(s)$$

$$- \frac{\beta}{2} \int_{0}^{L} ds \left( B \left| \frac{\partial \sigma(s)}{\partial s} \right|^{2} + J\sigma(s)^{2} \right) \right\}$$

$$(2.118)$$

This integral can be evaluated by using the Fourier representation. The result is

$$P(\mathbf{R}_{\perp}) \propto e^{-\frac{\beta J}{2L}\mathbf{R}_{\perp}^2} \tag{2.120}$$

The mean square end-to-end distance in the perpendicular plane of the ends of the undulating chain is

$$\langle \mathbf{R}_{\perp}^2 \rangle = \frac{Lk_B T}{J} \tag{2.121}$$

This result does not depend on the bend constant. This is because increasing the bend constant whilst increasing the persistence length of each segment, reduces the tilt angle. These two effects cancel out and as a result the projected length is the same so the mean square distance travelled in the perpendicular plane is independent of the bend constant.

# 2.C Induction method to count number of chain configurations

The Laplace transform method can be used to calculate the number of configurations of hairpins for the first ten terms. The results of this calculation are shown in table 2.1. From this table the general form for the number of config-

Number of defects	Number of Configurations $\Omega_n(z)$
0	$\delta(z+N) + \delta(z-N)$
1	2
2	N
3	$N^2(1-\left(\frac{z}{N}\right)^2)/2$
4	$N^3(1-\left(rac{z}{N} ight)^2)/8$
5	$N^4(1-\left(\frac{z}{N}\right)^2)^2/32$
6	$N^5(1-\left(\frac{z}{N}\right)^2)^2/192$
7	$N^{6}(1-\left(\frac{z}{N}\right)^{2})^{3}/1152$
8	$N^7 (1 - \left(\frac{z}{N}\right)^2)^3 / 9216$
9	$N^8(1-\left(\frac{z}{N}\right)^2)^4/73728$
10	$N^9(1-\left(\frac{z}{N}\right)^2)^4/737280$

Table 2.1: The number of configurations of arranging n hairpins on a polymer chain calculated as a function of end to end distance for the first 10 hairpins.

urations of n defects on a chain can be guessed and then proven by induction. For the odd case the guess is

$$G_n(z,N) = \frac{2}{(n-1)!!^2} (N^2 - z^2)^{\frac{n-1}{2}},$$
(2.122)

and for the even n case

$$G_n(z,N) = \frac{2}{n(n-2)!!^2} N(N^2 - z^2)^{\frac{n-2}{2}},$$
(2.123)

where !! denotes the usual double factorial function. To use the method of induction we proceed as follows. First it is necessary to split the sums up into parts: those which started by taking a step up the z-axis and those which started by taking a step down. Start with an even number of defects on a chain that started in the up direction and denote the number of configurations of the chain as a function of arc length N and end-to-end distance z as  $G_{n+}(z, N)$ . Another hairpin can then be added in by combining this with another section

of chain of length N' with no hairpins that started out in the down direction:  $G_{0-}(z, N')$ . This is illustrated in Fig. 2.14. To calculate all the possible



Figure 2.14: The two diagrams show the two different ways of adding one hairpin onto a chain that already has n hairpins on it. Direction reversal (hence another hairpin) occurs at the join. a) Shows the (n + 1) hairpin chain starting up and b) starting down.

configurations of this new chain it is necessary to integrate over all possible positions of the join with all possible partitions of arc length between the two sections

$$G_{(n+1)-}(z,N) = \int \int dz' dN' G_{n+}(z',N') G_{0-}(z-z',N-N')$$
(2.124)

The limits for the integrals follow from conservation of arc length. Applying conservation of arc length for each segment results in

$$N - N' \geq |z - z'| \tag{2.125}$$

$$N' \geq |z'| \tag{2.126}$$

Applying conservation of arc length to the whole chain then

$$N \geq -z' + (z - z') = z - 2z' \tag{2.127}$$

$$N \ge z - (z - z') = 2z' - z$$
 (2.128)

The first inequality is obtained by considering the extreme case where the new added on segment of chain goes entirely down a distance z' and then the existing part of the chain has to go up a distance z - z' (assuming the

hairpins use up a negligible amount of the end-to-end distance) to meet the end-to-end distance constraint. Similarly the second inequality is obtained by considering the case when the added segment goes up a distance z' and the existing segment must then come down a distance z - z'. Then the two quantities must be added with the correct sign to obtain the arc length which must be less that the total available arc length. Thus Eq. (2.124) can be evaluated as follows: first we assert the form of  $G_{n+}(z, N)$ 

$$G_{n+}(z,N) = \frac{1}{n(n-2)!!^2} (N+z)^{\frac{n}{2}} (N-z)^{\frac{n-2}{2}}.$$
 (2.129)

Then use this, together with the previous result that  $G_{0-}(z, N) = \delta(z + N)$  to obtain

$$G_{(n+1)+}(z,N) = \int dz' \int dN' \frac{1}{n(n-2)!!^2} (N-N'+z-z')^{\frac{n}{2}} \\ \times (N-N'-z+z')^{\frac{n-2}{2}} \delta(z'+N') \\ = \int_{\frac{z-N}{2}}^{0} dz' \frac{1}{n(n-2)!!^2} (N+z)^{\frac{n}{2}} (N+2z'-z)^{\frac{n-2}{2}} \\ = \frac{1}{n!!^2} (N^2-z^2)^{\frac{n}{2}}$$
(2.130)

Another defect can be added on in a similar way using the G that we have just derived

$$G_{(n+2)+}(z,N) = \int dz' \int dN' \frac{1}{n!!^2} (N - N' - z + z')^{\frac{n}{2}} \times (N - N' + z - z')^{\frac{n}{2}} \delta(z' - N') = \int_0^{\frac{z+N}{2}} dz' \frac{1}{n!!^2} (N - z)^{\frac{n}{2}} (N - 2z' + z)^{\frac{n}{2}} = \frac{1}{(n+2)(n)!!^2} (N + z)^{\frac{n+2}{2}} (N - z)^{\frac{n}{2}}$$
(2.131)

This is now the original form for the  $G_{n+}(z, N)$  so if it is true for n then it is also true for n + 2. A similar analysis can be carried out for the  $G_{n+}(z, N)$ (Fig. 2.14 a))which goes through in the same way, except with  $z \to -z$ . Thus on combining the two results for the even case

$$G_{n+}(z,N) = \frac{1}{n(n-2)!!^2} (N+z)^{\frac{n}{2}} (N-z)^{\frac{n-2}{2}}$$

$$G_{n-}(z,N) = \frac{1}{n(n-2)!!^2} (N-z)^{\frac{n}{2}} (N+z)^{\frac{n-2}{2}}$$

$$G_n(z,N) = G_{n-}(z,N) + G_{n+}(z,N)$$

$$= \frac{2}{n(n-2)!!^2} N (N^2 - z^2)^{\frac{n-2}{2}}$$
(2.132)

The odd result then follows by combining the intermediate result when only one hairpin had been added to an even number of hairpins

$$G_{n+}(z,N) = \frac{1}{(n-1)!!^2} (N^2 - z^2)^{\frac{n-1}{2}}$$

$$G_{n-}(z,N) = \frac{1}{(n-1)!!^2} (N^2 - z^2)^{\frac{n-1}{2}}$$

$$G_n(z,N) = G_{n-}(z,N) + G_{n+}(z,N)$$

$$= \frac{2}{(n-1)!!^2} (N^2 - z^2)^{\frac{n-1}{2}}$$
(2.133)

This method agrees with the calculation via the use of the exponentiation of the delta function/Laplace transform.

# **2.D** Interpretation of fN

The average number of hairpins on a chain at zero end-to-end distance can be calculated as follows.

$$\langle n \rangle(0) = \frac{1}{Z_{\rm hp}(0)} \sum_{n=0}^{\infty} n G_n(0, N) e^{-\beta u_h n}$$
 (2.134)

$$= -\frac{\partial \ln Z_{\rm hp}}{\partial (\beta u_h)} \tag{2.135}$$

The number of hairpins on a chain with zero end-to-end distance must always be greater than or equal to one because a straightened chain cannot have zero end-to-end distance. The mean number of hairpins on the chain can be calculated using

$$Z_{\rm hp}(0) = f(I_0(fN) + I_1(fN))$$
(2.136)

Using the chain rule results in the following

$$\langle n \rangle(0) = (fN) \frac{\partial \ln Z_{\rm hp}}{\partial (fN)}$$
 (2.137)

$$= fN + \frac{I_0(fN)}{I_0(fN) + I_1(fN)}$$
(2.138)

Since the modified Bessel function is asymptotic to  $x^{-1/2}e^x$  then for moderately large fN it follows that

$$\langle n \rangle (z=0) \approx fN + \frac{1}{2}$$
 (2.139)

Thus fN can be interpreted as the average number of hairpins on a polymer chain with span of z = 0.

# 2.E Spring constant of an extended worm-like chain

The spring constant of an extended worm can be calculated as follows. The partition function of a worm chain in a nematic field can be written as

$$Z(\mathbf{f}) = \int \mathcal{D}\mathbf{u}(s) \exp\left\{-\beta \frac{1}{2} \int_0^L ds \left[B \left|\frac{\partial \mathbf{u}}{\partial s}\right|^2 - Ju_z^2\right] + \beta \mathbf{f} \cdot \mathbf{R}\right\},\,$$

where **f** is the applied tension. In a strong nematic field it is assumed that the direction of the polymer segments fluctuate around the director direction  $(\hat{\mathbf{z}})$ . A small angle approximation can then be used by defining

$$\mathbf{u} = \hat{\mathbf{z}} + \boldsymbol{\sigma} + O(\sigma^2),$$

where  $\sigma$  is a vector perpendicular to  $\hat{\mathbf{z}}$ , required to keep  $\mathbf{u}$  a unit vector. Using this substitution and working to first order in  $\sigma$  the partition function can be calculated as

$$Z = \int \mathcal{D}\boldsymbol{\sigma}(s) \exp\left\{-\beta \frac{1}{2} \int_0^L ds \left[B\left(\frac{\partial \boldsymbol{\sigma}}{\partial s}\right)^2 + J\boldsymbol{\sigma}^2 + f_z \sigma^2\right]\right\},\,$$

Where the delta function constraint has now been satisfied. Now a discrete Fourier transform is performed on  $\sigma$  using

$$\boldsymbol{\sigma}(s) = \sum_{q} \boldsymbol{\sigma}(q) e^{iqs}$$

where q is a scalar. The partition function is then given by

$$Z = \int \mathcal{D}\boldsymbol{\sigma}(q) \exp\left\{-\beta \frac{1}{2} \sum_{q} \left[Bq^2 + J + f_z\right] |\boldsymbol{\sigma}(q)|^2\right\}.$$

From the principle of equipartition of energy we have that each of the modes has energy  $\frac{k_BT}{2}$ . Consequently

$$|\boldsymbol{\sigma}(q)|^2 = \frac{k_B T}{Bq^2 + J + f_z}$$

By integrating over all q values the average value of  $|\sigma|^2$  can be calculated

$$\langle |\boldsymbol{\sigma}|^2 \rangle = k_B T \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{1}{Bq^2 + J + f_z} = \frac{k_B T}{2\sqrt{B(J + f_z)}}$$

Here it is assumed that the summation can be converted to an integral because the q values are so closely spaced. The limits of the integrand are taken to be

# 2.E. SPRING CONSTANT OF AN EXTENDED WORM-LIKE CHAIN 47

infinity because the integrand decays very quickly. This result can be related to the average length of the chain as follows

$$\langle R_z \rangle = \int_0^L ds \ u_z \approx \int_0^L ds \left( 1 - \frac{\sigma(s)}{2} \right) = L \left( 1 - \frac{k_B T}{4\sqrt{B(J+f_z)}} \right)$$

Denoting  $\delta R_z = R_z(f_z) - R_z(f_z = 0)$  results in the following formula for the force as a function of extension

$$f_z = \frac{8\sqrt{BJ}J}{k_BTL}\delta R_z \tag{2.140}$$

This formula provides a useful estimate of the spring constant of a worm chain in a strong nematic field.

# -Chapter Three

# Polarisation of chiral liquid crystal elastomer

The subject of this chapter is piezoelectricity in liquid crystal elastomers. Whilst there are mechanisms of piezoelectricity in liquid crystal elastomers that do not require chirality, such as the flexoelectric effect, here a mechanism that relies on chirality is considered. This mechanism is based on a polymer chain of chiral monomers being deformed so that a binormal bias develops. The resulting polarisation relaxes away even in a non-ideal rubber due to the relaxation of the director,  $\mathbf{n}$ . After looking at two non-ideal cases: an elastomer composed of a random mixture of polymer chains of different lengths, and a network formed by a two stage cross-linking process using rod cross linkers for the second stage, three ways around this problem are suggested:

- (i) Dynamics where the director, **n**, responds more slowly than the polymer network,
- (ii) Rigid anchoring of the director e.g. in the smectic A phase,
- (iii) Binary mixtures of chiral and non-chiral chains.

# 3.1 Introduction

# 3.1.1 Piezoelectricity in Crystals

In 1880 Pierre and Jacques Curie published their experimental discovery of piezoelectricity. They discovered that certain crystals when subjected to a mechanical stress developed a surface charge. The name piezoelectricity is derived from the Greek word *piezein* meaning to squeeze or press, and has

two manifestations: the direct piezoelectric effect in which an applied mechanical stress results in an electric field across the material, and the converse effect in which an applied electric field results in a mechanical deformation. Only non-centrosymmetric crystals can be piezoelectric. This is because if the crystal were centro-symmetric then no combination of uniform stresses would produce a separation of the centres of positive and negative charge and thus a polarisation. The crystal structure should also define at least one axis along which the polarisation points. This axis need not be unique, and defines the direction the polarisation points in response to, for example, an elongation. There are 21 non-centrosymmetric crystal symmetry classes of which 20 have at least one polar axis in their structure (see for example [40]). Pyroelectric materials, which develop a polarisation in response to temperature change, further require that the polar axis is unique and thus only 10 of the 20 piezoelectric crystal symmetry classes are pyroelectric. A large variety of materials are now known to exhibit piezoelectricity including modern materials such as lithium niobate, biological materials such as bone and tendon, and polymers such as polyvinlidene fluoride. They have several useful applications including generating sparks, sensing vibrations, actuators to move precisely controlled small distances, and transducers for converting electrical energy into vibrational energy (often ultrasound ~ 50kHz).

The relationship between the polarisation and the mechanical stress can be expressed as

$$P_i = d_{ijk}\sigma_{jk},\tag{3.1}$$

where  $P_i$  is the polarisation in direction i,  $\sigma_{jk}$  is the stress, with force in the j direction on the face with normal in the k direction and  $d_{ijk}$  are the coupling constants. The coupling constants connecting polarisations in the  $\mathbf{x}, \mathbf{y}$  and  $\mathbf{z}$  directions with stresses applied along the  $\mathbf{x}, \mathbf{y}$  and  $\mathbf{z}$  directions and shears about the x, y and z axes. Since  $\sigma_{jk}$  is a symmetric tensor, the antisymmetric part of  $d_{ijk}$  in jk is not meaningful because it produces no polarisation. Thus  $d_{ijk}$  is symmetric under interchange of j and k and has 18 independent components as a result. As the symmetry of the crystal increases the number of independent constants decreases.

In crystalline materials the piezoelectric effect can be understood as resulting from the underlying crystal symmetry. However, piezoelectric-like effects have been predicted and discovered in less ordered materials.

### 3.1.2 Piezoelectricity in liquid crystals

In liquid crystals an effect similar to piezoelectricity was predicted by Meyer [41], however, due to its very different microscopic origin it is now known as the flexoelectric effect. It is not a consequence of chirality and thus is present even in centrosymmetric systems. Consider a liquid crystal composed of molecules that possess a large shape polarity as well as a large permanent dipole moment parallel to their long dimension (Fig. 3.1 (a)). There is no net

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polarisation in the uniform state because the molecules point randomly up or down. On applying a splay or bend deformation, a polarisation is externally induced. This arises because the geometry of packing now requires a bias in the molecular orientations, and thus an imbalance in the number of dipoles up and down. The converse effect is also possible. The required strains are curvatures of the director field rather than bulk stresses and shear strains as in crystals. The polarisation is given by

$$\mathbf{P} = e_1 \mathbf{n} (\nabla \cdot \mathbf{n}) + e_2 \mathbf{n} \times (\nabla \times \mathbf{n}), \qquad (3.2)$$

where  $e_1$  and  $e_2$  are splay and bend flexoelectric coefficients respectively, **P** is the polarisation, and **n** is the director. Fig. 3.1 (b) and (d) illustrates this for both the splay and bend deformation of tear drop and banana shaped molecules respectively.



Figure 3.1: Polar molecules with (a) teardrop shape and (c) banana shape give rise to an external polarisation after imposing a curvature strain (b), (d), [41].

The complex geometrical requirements mean that it is very difficult to study in nematic materials. However the required alternating bands of splay and bend can be produced in a cholesteric liquid crystal relatively easily by rotating the director out of the plane perpendicular to the helix axis using an electric field [42] as shown in Fig. 3.2.



Figure 3.2: An electric field when applied to a cholesteric liquid crystal results in a required director pattern for the flexoelectric effect. The splay and bend pattern illustrated here would be produced if an electric field was applied to a cholesteric, parallel to the helical axis. After Meyer [41].

# 3.1.3 Piezoelectricity of cholesteric liquid crystal elastomers

A liquid crystal elastomer, unlike a liquid crystal, can support a static shear stress. It can display a piezoelectric effect as a result of imposed strains like a true crystal, rather than curvatures of the director field as in liquid crystals. This is because of the coupling between the liquid crystal degrees of freedom and the strain. An analysis of the symmetry properties of the free energy of a cholesteric liquid crystal phase was presented in [43], including possible couplings between the electric field, **E**, the gradients of the director,  $\nabla \mathbf{n}$ , and the deformation tensor,  $\underline{\lambda}$ . The results of this analysis indicate that the allowed terms in the free energy are

$$Q_1\left(\mathbf{E}\times\mathbf{n}\cdot\underline{\lambda}^s\cdot\mathbf{n}\right) + Q_2\mathbf{E}\cdot\boldsymbol{\omega} + Q_3(\mathbf{E}\cdot\mathbf{n})(\boldsymbol{\omega}\cdot\mathbf{n}), \qquad (3.3)$$

where  $\boldsymbol{\omega}$  denotes the rotational component of the deformation and  $\underline{\lambda}^s$  denotes the symmetric part of the deformation. The first of these terms leads to the incorrect conclusion that there should be a polarisation under a compression. However, from the coarse grained approach of Pelcovits *et al.* [44] it can be concluded that the first term is a result of the flexoelectric effect.

The symmetry argument presented by Pelcovits *et al.* was used to construct the free energy in terms of the pitch axis around which the helix winds. The free energy density of a cholesteric elastomers produces three terms coupling the deformation to the electric field. The authors identify the three terms that produce a polarisation which are in agreement with the results of

[43] provided that the correct coarse graining procedure is applied there. The first term of Eq. (3.3) is directly related to the flexoelectric effect because the applied shear results in the director pattern depicted in Fig. 3.2. In this case the mechanical deformation takes the place of the electric field. The other two terms are connected with local rotations of the director. Although this effect is regarded as a piezoelectric effect because it is induced by a mechanical strain, its origins are as in Fig. 3.1, i.e. nothing intrinsically to do with chirality, or the lack of a centre of symmetry. The predictions of this coarse grained theory have been verified experimentally by Chang et al. by forming a cholesteric elastomer between two glass plates coated with indium tin oxide electrodes [45]. An oscillating shear field was then applied to the elastomer which produces the director pattern required for the flexoelectric effect. The resulting induced voltage from the piezoelectricity is measured. The experimental results were fitted to the theory of [44] using separate characteristic times for the polymer network and the director. Although it is possible to assign a relaxation time to a particular polymer strand, for example the Rouse time scale  $\tau_{\rm R} \sim 10^{-5} - 10^{-6}$ s, when the whole polymer network is considered the relaxation follows a power law. Thus there is no characteristic time scale. The director is expected to respond much more slowly  $\tau_{\rm LC} \sim 10^{-2} - 10^{-3}$ s. The significance of the relaxation time of Chang et al. is thus questionable. The characteristic time scale assigned to the polymer network, denoted by  $\tau_p$ , was  $\tau_p = 5$ ms. This is much slower than the director response. The liquid crystal molecules then follow the strain of the polymer network with a characteristic time  $\tau_{LC} = 0.3$ ms, which is in the region we expect. Thus the polymer network responds more slowly than the director, so the director tends to sit in its equilibrium orientation. This is contrary to the typical situation where the polymer network relaxes very quickly and the director lags behind [46].

# 3.1.4 A chiral mechanism for piezoelectricity in liquid crystal elastomers

Another mechanism for piezoelectricity in liquid crystal elastomers is the coupling of chiral chain elements to the mechanical distortions of the elastomer [47, 48]. This mechanism is truly piezoelectric in the sense that both a strain and the absence of a centre of symmetry are required. It is now described, and the derivation of the main results is outlined. The main chains considered there consist of chiral units as illustrated in Fig. 3.3. Each monomer consists of two arms that have different lengths. A third direction along which a dipole could point is then assigned to each unit based on the *same* rule so that each unit is, say, right handed. Only the long axis is affected by the nematic field. This is the key to the mechanism of the polarisation. The axis of the nematic field and the elastic axes are not parallel. A deformation could then be applied to the rubber so that it causes all of the dipole axes to align. To achieve this, a deformation that defines a direction is required. Of the simple deforma-



Figure 3.3: A single monomer of a chiral main chain polymer. The monomer has two arms of different lengths a, and b. Each monomer is then assigned a dipole using the right hand rule (in this case out of the page) so that each one is chiral.

tions only simple shear defines a direction for the polarisation to point along. The effect of a shear on a rubber consisting of nematic, chiral main chains is illustrated in Fig. 3.4.



Figure 3.4: A shear deformation applied to a network of chiral molecules (a) can cause an overall binormal vector (b) and hence a polarisation to develop (schematic only).

The joint probability distribution of end-to-end distance of a long chiral main chain, **R**, and the total binormal, **V**, is now calculated. The two directions for the long and the short arms of each monomer can be defined as **u** and **v** as shown in Fig. 3.3, so that the end-to-end distance of a monomer is given by:  $\mathbf{w}^{\alpha} = a\mathbf{u}^{\alpha} + b\mathbf{v}^{\alpha}$  where  $\alpha$  labels the monomer. The end-to-end distance of the chain and the chain binormal are then given by

$$\mathbf{R} = \sum_{\alpha} \mathbf{w}^{\alpha} \tag{3.4}$$

$$\mathbf{V} = \sum_{\alpha} \mathbf{u}^{\alpha} \times \mathbf{v}^{\alpha} \tag{3.5}$$

Since the  $\mathbf{u}^{\alpha}$  of each monomer is on average parallel or anti-parallel to the nematic field  $(Q \neq 1)$  and each monomer is independent, then it has the quadrupolar average

$$\langle u_i^{\alpha} u_j^{\beta} \rangle_u = \delta_{\alpha\beta} q_{ij}, \qquad (3.6)$$

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where the tensor order parameter is given by:  $q_{ij} = q_{\perp} \delta_{ij} + (q_{\parallel} - q_{\perp}) n_i n_j$ . If  $\theta$  is the angle that a monomer makes with the nematic direction, **n**, then  $q_{\parallel} = \langle \cos^2 \theta \rangle$  and  $q_{\perp} = \frac{1}{2} \langle \sin^2 \theta \rangle$ . Since **v** is perpendicular to **u** it has the average

$$\langle v_i^{\alpha} v_j^{\beta} \rangle_{vu} = \frac{1}{2} \delta_{\alpha\beta} (\delta_{ij} - q_{ij}) = \frac{1}{2} \delta_{\alpha\beta} M_{ij}$$
(3.7)

These averages can be used to evaluate the joint probability distribution by averaging over delta functions used to count the configurations. Exponentiating these delta functions and expanding down from the resulting exponent allows their evaluation. The result is

$$W(\mathbf{R}, \mathbf{V}) = \left\langle \delta \left( \mathbf{R} - \sum_{\alpha} \left( a \mathbf{u}^{\alpha} + b \mathbf{v}^{\alpha} \right) \right) \delta \left( \mathbf{V} - \sum_{\alpha} \mathbf{u}^{\alpha} \times \mathbf{v}^{\alpha} \right) \right\rangle$$
  
$$= \int \int \frac{d \boldsymbol{\eta} d \boldsymbol{\zeta}}{(2\pi)^{6}} \exp(\mathrm{i} \boldsymbol{\eta} \cdot \mathbf{R} + \mathrm{i} \boldsymbol{\zeta} \cdot \mathbf{V})$$
  
$$\times \left\langle 1 - \mathrm{i} \left( \sum_{\alpha} \boldsymbol{\eta} \cdot \left( a \mathbf{u}^{\alpha} + b \mathbf{v}^{\alpha} \right) + \boldsymbol{\zeta} \cdot \left( \mathbf{u}^{\alpha} \times \mathbf{v}^{\alpha} \right) \right) - \frac{1}{2} \left( \cdots \right)^{2} + \cdots \right\rangle.$$

The first few averages of this expansion can be evaluated, ignoring terms of order  $\left(\frac{b}{a}\right)^2$ , and then re-exponentiate and using the method of steepest descents to evaluate the integral. An iterative method can be used to solve for the points of steepest descent. The most interesting term comes from the cubic part. The resulting distribution function is

$$W(\mathbf{R}, \mathbf{V}) \propto \exp\left(\frac{-3}{2La}\mathbf{R}^T \cdot \underline{\ell}^{-1} \cdot \mathbf{R} - \frac{1}{N}\mathbf{V}^T \cdot \underline{\underline{M}}^{-1} \cdot \mathbf{V}\right) \\ \times \left(1 + \frac{3b}{aL^2} \left[\mathbf{R} \times \underline{\ell}^{-1} \cdot \mathbf{R}\right] \cdot \underline{\underline{M}}^{-1} \cdot \mathbf{V} + O(R^4, R^2 V^2)\right),$$

where  $\underline{\ell} = \underline{\delta} + (r-1) \mathbf{nn} \approx 3\underline{q}$ . This tensor provides information on the anisotropy of the chain shape. The anisotropy of the chains is given by  $r = l_{\parallel}/l_{\perp}$ . The important correction term is the coupling between  $\mathbf{R}$  and  $\mathbf{V}$ . Using this probability distribution the average binormal,  $\mathbf{V}$ , can be calculated.

$$\begin{split} \langle \mathbf{V} \rangle &\propto \int d\mathbf{V} \exp\left(-\frac{1}{N}\mathbf{V}^T \cdot \underline{M}^{-1} \cdot \mathbf{V}\right) \mathbf{V} \left(1 + \frac{3b}{aL^2} \left[\mathbf{R} \times \underline{\ell}^{-1} \cdot \mathbf{R}\right] \cdot \underline{M}^{-1} \cdot \mathbf{V}\right) \\ &= \frac{3bN}{2aL^2} \mathbf{R} \times \underline{\ell}^{-1} \cdot \mathbf{R}, \end{split}$$

where clearly in the  $\int d\mathbf{V}$  the first (linear) term gives zero, so the  $O(\mathbf{V}^2)$  terms must be evaluated. In a rubber the polymer chains will have their ends fixed. It is assumed that deformations move these ends affinely. If the quenched-in end-to-end vector is denoted by  $\mathbf{R}_0$  then after a deformation,  $\underline{\lambda}$ , the end-toend distance becomes  $\mathbf{R} = \underline{\lambda} \cdot \mathbf{R}_0$ . The quenched-in binormal vector, after averaging over formation conditions, is given by

$$\begin{aligned} \langle \mathbf{V} \rangle_{\mathbf{R}_{0}} &\propto \int d\mathbf{R}_{0} \exp\left(-\frac{3}{2La}\mathbf{R}_{0}^{T} \cdot \underline{\ell}_{0}^{-1} \cdot \mathbf{R}_{0}\right) \left(\frac{3bN}{2aL^{2}} \left(\underline{\lambda} \cdot \mathbf{R}_{0}\right) \times \underline{\ell}^{-1} \cdot \left(\underline{\lambda} \cdot \mathbf{R}_{0}\right)\right) \\ &= \frac{b}{2a} \left[\underline{\lambda}^{T} \times \underline{\ell}^{-1} \cdot \underline{\lambda} \cdot \underline{\ell}_{0}\right] \end{aligned}$$

This resulting binormal can now be summed over all the network strands,  $n_{\rm s}$  per unit volume. After weighting each elementary binormal vector by the dipole moment d that it carries, the resulting expression for the polarisation is

$$P_i = n_s d\langle V_i \rangle_{\mathbf{R}_0} = \frac{1}{2} n_s d(b/a) \epsilon_{ijk} (\underline{\underline{\lambda}} \cdot \underline{\underline{\ell}}_0 \cdot \underline{\underline{\lambda}}^T \cdot \underline{\underline{\ell}}^{-1})_{jk}, \qquad (3.8)$$

where  $P_i$  is the component of the polarisation in the *i* direction and  $n_s$  is the number of strands per unit volume. To evaluate this expression after the rubber has been deformed, the new equilibrium orientation of the director must be calculated. This is explored in the next section.

# 3.2 Equilibrium orientation of the director

The free energy density of a liquid crystal elastomer is given by

$$f = \frac{1}{2}\mu\lambda_{ij}\ell_{0jk}\lambda_{kl}^{T}\ell_{li}^{-1}.$$
(3.9)

Given the initial director orientation and the applied deformation, the equilibrium orientation of the director can be calculated after the deformation has been applied by minimising the free energy density with respect to the director **n** whilst keeping its magnitude fixed via a Lagrange multiplier,  $\chi$ . Thus the following quantity should be minimised w.r.t. **n** 

$$g = \mu \frac{1}{2} \left( \lambda_{ij} \ell_{0jk} \lambda_{kl}^T \ell_{li}^{-1} + \chi \left[ 1 - n_i n_i \right] \right)$$
(3.10)

Note that when the constraint is satisfied g and f are equal. On differentiation with respect to  $n_{\alpha}$  the result is

$$\frac{\partial g}{\partial n_{\alpha}} = \frac{1}{2}\mu\left(\frac{1}{r}-1\right)\left(n_{i}\lambda_{ij}\ell_{0jk}\lambda_{k\alpha}^{T}+\lambda_{\alpha j}\ell_{0jk}\lambda_{kl}^{T}n_{l}\right)-\mu\chi\delta_{i\alpha}n_{i}$$

The stationary points in the free energy density occur when  ${\bf n}$  obeys the condition

$$\left(\frac{1}{r}-1\right)\underline{\mathcal{M}}\cdot\mathbf{n} = \chi\mathbf{n} \tag{3.11}$$

$$\chi = \left(\frac{1}{r} - 1\right) n_i \lambda_{ik} \ell_{0kj} \lambda_{j\alpha}^T n_\alpha \qquad (3.12)$$

where  $\mathcal{M}_{i\alpha} = \lambda_{ij} \ell_{0jk} \lambda_{k\alpha}^T$ . This equation provides a useful general way of determining the final orientation of the director at equilibrium. From Eq. (3.11), **n** is a principal axis of  $\underline{\mathcal{M}}$ . The free energy will be stationary when the director is aligned with any one of the three principal axes of  $\underline{\mathcal{M}}$ .

#### **3.2.1** Nature of the stationary points

The free energy density minimum corresponds to putting the director **n** along the principal axis of  $\underline{\mathcal{M}}$  with largest principal value when r > 1 and along the principal axis with smallest principal value when r < 1. This follows from writing the free energy density as

$$f = \frac{1}{2}\mu \left[\frac{1}{r}m_1 + m_2 + m_3\right], \qquad (3.13)$$

where  $m_1$ ,  $m_2$  and  $m_3$  are the principal values of the  $\underline{\mathcal{M}}$  tensor and 1, 1 and  $\frac{1}{r}$  are the principal values of the  $\underline{\ell}^{-1}$  tensor. For r > 1 then  $m_1$  must be the largest principal value for the free energy density to be minimal. Similarly for r < 1 then  $m_1$  must be the smallest principal value for the free energy density to be minimal. The stability of aligning the director  $\mathbf{n}$  with each of the principal axes of  $\underline{\mathcal{M}}$  can be analysed by looking at the derivatives of the free energy density

$$\frac{\partial g}{\partial \mathbf{n}} = \frac{1}{2}\mu \left[ \left( \frac{1}{r} - 1 \right) \left( \mathbf{n} \cdot \underline{\mathcal{M}} + \underline{\mathcal{M}} \cdot \mathbf{n} \right) - 2\chi_k \mathbf{n} \right]$$
$$\frac{\partial^2 g}{\partial \mathbf{n}^2} = \frac{1}{2}\mu \left[ \left( \frac{1}{r} - 1 \right) 2\underline{\mathcal{M}} - 2\chi_k \underline{\delta} \right]$$

where the label k corresponds to the principal axis under consideration. The principal values of the second derivative matrix will dictate the stability of the direction  $\mathbf{n}_k$ . If all the principal values are positive then the point is a minimum, if they are all negative then the point is a maximum, and no conclusion can be drawn if they are neither all positive nor all negative. In the principal frame it is clear that for r < 1 all the  $\chi_k$  are positive. In this frame the matrix  $(\frac{1}{r} - 1) \underline{\mathcal{M}}$  has only diagonal entries of  $\chi_1, \chi_2$  and  $\chi_3$ . If the  $\chi_k$  are non-degenerate then the second derivative matrix has the following properties:

- Two negative principal values and one zero when k corresponds to the largest  $\chi$  value.
- One positive, one zero and one negative principal value when k corresponds to the middle  $\chi$  value.
- Two positive principal values and one zero when k corresponds to the smallest  $\chi$  value.

Note that there is always one zero in the tensor because fluctuations along the director do not keep the director of length unity. When r > 1 all the  $\chi$ acquire a minus sign so the behaviour of the stationary points swap. Thus the stable axis swaps from the axis with the smallest m principal value to that with the largest m principal value. The system has one stable axis along which the director lies, one saddle point, and one unstable axis. When considering a soft mode, then two of the principal values are degenerate. In this case it still follows that the axis along which the director lies is stable, but the other two axes have degenerate values of  $\chi$  and so will have two zeros in the matrix determining their stability, which cannot be classified as a maximum or a minimum.

# 3.3 The polarisation of a pure liquid crystal elastomers

Once the equilibrium orientation of the director is known, the polarisation of the elastomer can be calculated. The tensor  $\underline{\mathcal{M}}$  commutes with the tensor  $\underline{\ell}^{-1}$  because the director lies along one of the principal axes of  $\underline{\mathcal{M}}$ . The object  $\underline{\mathcal{M}} \cdot \underline{\ell}^{-1}$  is thus symmetric and as a result the polarisation of the elastomer is zero since it is the contraction of this symmetric tensor with the antisymmetric tensor  $\epsilon_{ijk}$ . Two more arguments that produce the same result are now presented.

# 3.3.1 Linearization of the polarisation expression

It is useful to look at small, symmetric deformations and rotations of the rubber matrix in which the rods are held. The deformation tensor can be broken up into the sum of the Kronecker delta, a symmetric tensor,  $\epsilon_{ij}$ , and an antisymmetric tensor  $W_{ij}$ . The antisymmetric tensor has the property that

$$\underline{W} \cdot \mathbf{a} = \mathbf{\Omega} \times \mathbf{a}. \tag{3.14}$$

This matrix performs rotations about the axis  $\hat{\Omega}$  of magnitude  $\Omega$  for small rotations. It is convenient to rewrite the antisymmetric tensor in terms of its axial vector,  $\Omega$ 

$$W_{ij} = \epsilon_{ikj} \Omega_k. \tag{3.15}$$

The strain tensor then becomes

$$\lambda_{ij} = \delta_{ij} + \epsilon_{ij} + \epsilon_{ikj}\Omega_k, \qquad (3.16)$$

where  $\underline{\epsilon}$  is a symmetric second rank tensor and  $\Omega$  is a vector parallel to the rotation axis and has a magnitude equal to the angle of rotation,  $\Omega$ . There should be no confusion between the Levi-Civita symbol,  $\epsilon_{ijk}$ , and the symmetric tensor  $\epsilon_{ij}$  here because of the number of indices. This decomposition can be used in the expressions for free energy and polarisation (dropping the prefactors in both cases for simplicity)

$$f = \operatorname{Tr}\left[\underline{\ell}_{0} \cdot \underline{\ell}^{-1} + \underline{\ell}_{0} \cdot \underline{\epsilon} \cdot \underline{\ell}^{-1} + \underline{\epsilon} \cdot \underline{\ell}_{0} \cdot \underline{\ell}^{-1} + \underline{\epsilon} \cdot \underline{\ell}_{0} \cdot \underline{\epsilon} \cdot \underline{\ell}^{-1}\right]$$

$$- \underline{\ell}_{0} \cdot \underline{W} \cdot \underline{\ell}^{-1} + \underline{W} \cdot \underline{\ell}_{0} \cdot \underline{\ell}^{-1} - \underline{W} \cdot \underline{\ell}_{0} \cdot \underline{W} \cdot \underline{\ell}^{-1} + \underline{W} \cdot \underline{\ell}_{0} \cdot \underline{\epsilon} \cdot \underline{\ell}^{-1} - \underline{\epsilon} \cdot \underline{\ell}_{0} \cdot \underline{W} \cdot \underline{\ell}^{-1}$$

$$(3.17)$$

$$P_{i} = \epsilon_{ijk} \left[ \underline{\ell}_{0} \cdot \underline{\ell}^{-1} + \underline{\ell}_{0} \cdot \underline{\epsilon} \cdot \underline{\ell}^{-1} + \underline{\epsilon} \cdot \underline{\ell}_{0} \cdot \underline{\ell}^{-1} + \underline{\epsilon} \cdot \underline{\ell}_{0} \cdot \underline{\epsilon} \cdot \underline{\ell}^{-1} - \underline{\ell}_{0} \cdot \underline{W} \cdot \underline{\ell}^{-1} + \underline{W} \cdot \underline{\ell}_{0} \cdot \underline{\ell}^{-1} - \underline{W} \cdot \underline{\ell}_{0} \cdot \underline{W} \cdot \underline{\ell}^{-1} + \underline{W} \cdot \underline{\ell}_{0} \cdot \underline{\ell}^{-1} - \underline{K} \cdot \underline{\ell}_{0} \cdot \underline{W} \cdot \underline{\ell}^{-1} + \underline{W} \cdot \underline{\ell}_{0} \cdot \underline{\ell}^{-1} - \underline{\epsilon} \cdot \underline{\ell}_{0} \cdot \underline{W} \cdot \underline{\ell}^{-1} \right]_{jk}.$$

$$(3.18)$$

[Note that the linear terms in  $\underline{\epsilon}$  cancel out due to the identity:  $(r-1) + (\frac{1}{r}-1) + (r-1)(\frac{1}{r}-1) = 0$ ]. Suppose now that  $\Omega$  and  $\underline{\epsilon}$  are small so that second order effects in these quantities may be neglected. The resulting free energy density and polarisation are

$$f \approx \operatorname{Tr}\left[\underline{\underline{\ell}}_{0} \cdot \underline{\underline{\ell}}^{-1} + \underline{\underline{\ell}}_{0} \cdot \underline{\underline{\epsilon}} \cdot \underline{\underline{\ell}}^{-1} + \underline{\underline{\epsilon}} \cdot \underline{\underline{\ell}}_{0} \cdot \underline{\underline{\ell}}^{-1} - \underline{\underline{\ell}}_{0} \cdot \underline{\underline{W}} \cdot \underline{\underline{\ell}}^{-1} + \underline{\underline{W}} \cdot \underline{\underline{\ell}}_{0} \cdot \underline{\underline{\ell}}^{-1}\right]$$
(3.19)

$$P_{i} \approx \epsilon_{ijk} \left[ \underline{\ell}_{0} \cdot \underline{\ell}^{-1} + \underline{\ell}_{0} \cdot \underline{\epsilon} \cdot \underline{\ell}^{-1} + \underline{\epsilon} \cdot \underline{\ell}_{0} \cdot \underline{\ell}^{-1} - \underline{\ell}_{0} \cdot \underline{W} \cdot \underline{\ell}^{-1} + \underline{W} \cdot \underline{\ell}_{0} \cdot \underline{\ell}^{-1} \right]_{jk}.$$
(3.20)

To show that the first order shift in the director cancels out the polarisation, consider minimisation of the free energy density with respect to variations in the order parameter that maintain the normalisation of the director  $\mathbf{n} \cdot \mathbf{n} = 1$ . Differentiation of the free energy density expression above, Eq. (3.19), w.r.t.  $\mathbf{n}$  and using a Lagrange multiplier,  $\chi$ , to maintain the constraint results in

$$\underline{\ell}_{0} \cdot \mathbf{n} + (\underline{\ell}_{0} \cdot \underline{\epsilon} + \underline{\epsilon} \cdot \underline{\ell}_{0}) \cdot \mathbf{n} + (\underline{W} \cdot \underline{\ell}_{0} - \underline{\ell}_{0} \cdot \underline{W}) \cdot \mathbf{n} = \chi \mathbf{n}$$
(3.21)

Perturbation theory can be used to calculate the shift in the principal axis (i.e. the director **n**) to first order. If  $\underline{\epsilon}$  and  $\underline{W}$  are small then the terms containing them on the left had side of Eq. (3.21) can be written as a perturbation  $\underline{\ell}' = (\underline{\ell}_0 \cdot \underline{\epsilon} + \underline{\epsilon} \cdot \underline{\ell}_0) + (\underline{W} \cdot \underline{\ell}_0 - \underline{\ell}_0 \cdot \underline{W})$  with a parameter  $\xi$  to control the "strength" of the perturbation and keep track of its order. Using this substitution and writing  $\chi = r + \xi r^{(1)} + \dots$  and similarly for **n** results in

$$(\underline{\ell}_0 + \xi \underline{\ell}')(\mathbf{n}_0 + \xi \delta \mathbf{n}^{(1)} + \ldots) = (r + \xi r^{(1)} + \ldots)(\mathbf{n}_0 + \xi \delta \mathbf{n}^{(1)} + \ldots).(3.22)$$

Collecting powers of  $\xi$  produces the following for the  $0^{th}$  and the  $1^{st}$  order shifts

$$\underline{\ell}_0 \cdot \mathbf{n}_0 = r \mathbf{n}_0 \tag{3.23}$$

$$\underline{\underline{\ell}}_0 \cdot \delta \mathbf{n}^{(1)} + \underline{\underline{\ell}}' \cdot \mathbf{n}_0 = r \delta \mathbf{n}^{(1)} + r^{(1)} \mathbf{n}_0$$
(3.24)

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The first of these is recognisable from the definition of  $\underline{\ell}_0$ . Using the fact that the first order shift in the principal axis is orthogonal to  $\mathbf{n}_0$  produces the following

$$r^{(1)} = \mathbf{n}_0 \cdot \underline{\ell}' \cdot \mathbf{n}_0 \tag{3.25}$$

$$\delta \mathbf{n}^{(1)} = \frac{\underline{\ell}' \cdot \mathbf{n}_0 - (\mathbf{n}_0 \cdot \underline{\ell}' \cdot \mathbf{n}_0) \mathbf{n}_0}{(r-1)}.$$
 (3.26)

When this first order shift is substituted into the polarisation expression the following result is obtained

$$P_{i} \approx \epsilon_{ijk} \left[ \left( \underline{\underline{\ell}}_{0} + \underline{\underline{\ell}}' \right) \cdot \underline{\underline{\ell}}^{-1} \right]_{jk}$$

$$= \epsilon_{ijk} \left[ \left( \underline{\underline{\delta}}_{+} + (r-1)\mathbf{n}_{0}\mathbf{n}_{0} + \underline{\underline{\ell}}' \right) \cdot \left( \underline{\underline{\delta}}_{+} + \left( \frac{1}{r+r^{(1)}} - 1 \right) (\mathbf{n}_{0} + \delta \mathbf{n}) (\mathbf{n}_{0} + \delta \mathbf{n}) \right) \right]_{jk}$$

$$\approx \left( \frac{1}{r} - 1 \right) \epsilon_{ijk} \left[ \underline{\underline{\ell}}' \cdot \mathbf{n}_{0}\mathbf{n}_{0} + (r-1)\mathbf{n}_{0}\delta \mathbf{n} \right]_{jk}$$

$$= \left( \frac{1}{r} - 1 \right) \epsilon_{ijk} \left[ \underline{\underline{\ell}}' \cdot \mathbf{n}_{0}\mathbf{n}_{0} + \mathbf{n}_{0} \left( \underline{\underline{\ell}}' \cdot \mathbf{n}_{0} - (\mathbf{n}_{0} \cdot \underline{\underline{\ell}}' \cdot \mathbf{n}_{0})\mathbf{n}_{0} \right) \right]_{jk}$$
(3.27)

Where use has been made of the fact that  $\underline{\ell'}$  is symmetric. The last term here vanishes by symmetry and the remaining two terms cancel out on interchange of the suffixes j and k due to the total antisymmetry of the Levi-Civita symbol. Thus it is clear that the rotation of the director means that there is no polarisation in equilibrium for a pure (i.e. not semi-soft) chiral elastomer.

#### 3.3.2 Vector properties from quadrupoles

A more general argument as to why there is no polarisation can also be constructed. Consider two quadrupolar objects represented by the vectors  $\mathbf{k}$  and  $\mathbf{n}$ . A pseudo-vector can be made out of these two quadrupolar objects as follows

$$\mathbf{p} = \alpha(\mathbf{n} \cdot \mathbf{k})(\mathbf{n} \times \mathbf{k}). \tag{3.28}$$

Note that even powers of the two vectors are required by their quadrupolar symmetry. It is clear from this object that if a pseudo-vector can be defined from the quadrupolar objects then the quadrupolar objects must not be either parallel or orthogonal to each other.

The specific case of a piezoelectric response of a liquid crystalline elastomer is now considered. In this case the two quadrupolar objects are: the liquid crystal order, as specified by the director **n** and a quadrupolar object defined by the elastic deformation we apply,  $\underline{\mathcal{M}}$ . To develop a polarisation the axes of these two objects must not be orthogonal. On minimising the free energy density it is found that the director must sit along a principal axis of the

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quadrupolar object  $\underline{\mathcal{M}}$ . Hence the two quadrupolar objects are always either parallel or orthogonal to one another so there can never be any polarisation.

From the analysis of the symmetry properties of the chiral elastomer it is clear that there is no underlying reason that prevents the system developing a polarisation. The coupling between the different elements in the energy of the elastomer prevents any polarisation developing. Two more detailed models of elastomers are now considered, together with their effect on this mechanism of polarisation.

#### 3.3.3 Random mixture of anisotropies

In the preceding sections the relaxation of the director and the remaining strain variables when a strain is imposed was shown to relax away the polarisation,  $\mathbf{P}$  in an ideal system. Semi-softness is one non-ideality and the possibility of a residual polarisation  $\mathbf{P}$  in a system where the optimal director orientation cannot be attained is now considered.

One route to a semi-soft elastomer is to include a mixture of polymer chains that do not all have the same anisotropy tensor. The anisotropy tensor for a given chain is denoted by  $\underline{\ell}^{(\nu)}$ , and the anisotropy by  $r^{(\nu)}$ . The free energy density is then calculated by averaging over all the different anisotropy tensors of chains. The result of this averaging is given by the expression

$$\frac{2f_{SS}}{\mu} = \operatorname{Tr}\left[\underline{\underline{\lambda}} \cdot \underline{\underline{\ell}}_{0} \cdot \underline{\underline{\lambda}}^{T} \cdot \underline{\underline{\ell}}^{-1}\right] + \alpha \operatorname{Tr}\left[\underline{\underline{\delta}}^{(tr)} \cdot \underline{\underline{\lambda}}^{T} \cdot \mathbf{nn} \cdot \underline{\underline{\lambda}}\right], \qquad (3.29)$$

where it is understood that it is the average of r values that occur in the chain shape anisotropy tensors,  $\underline{\ell}$ . The constant  $\alpha$  is given by:  $\alpha = \left(\langle \frac{1}{r} \rangle - \frac{1}{\langle r \rangle}\right)$ , and  $\underline{\delta}^{(tr)} = \underline{\delta} - \mathbf{n}_0 \mathbf{n}_0$ . The value of  $\langle r \rangle$  dictates the way that the system responds to a deformation. If  $\langle r \rangle > 1$  then the director responds in the same way as a prolate system, aligning along the extensional axis. If  $\langle r \rangle < 1$  then the system responds in the same way as an oblate system, i.e. along the compressional axis. When  $\langle r \rangle = 1$  then the system must consist of mixture of oblate and prolate chains. The competition between the rotation to the compressional axis of one chain type and the extensional axis for the other type completely cancel out.

Assuming that all the polymer chains in the system are chiral and hence polarisable, then the polarisation is also to be averaged over all the different chains and similar result for the polarisation formula is obtained

$$P_{i} = \frac{1}{2} n_{s} d(b/a) \epsilon_{ijk} (\underline{\lambda} \cdot \underline{\ell}_{0} \cdot \underline{\lambda}^{T} \cdot \underline{\ell}^{-1} + \alpha \underline{\lambda} \cdot \underline{\delta}^{(tr)} \cdot \underline{\lambda}^{T} \cdot \mathbf{nn})_{jk}$$
(3.30)

The analysis of §3.2 can be performed on this formula by minimising the free energy density  $f_{SS}$  with the constraint  $\mathbf{n} \cdot \mathbf{n} = 1$ . This results in the equation

$$\left(\frac{1}{r}-1\right)\underline{\lambda}\cdot\left(\underline{\ell}_{0}+\beta\underline{\delta}^{(tr)}\right)\cdot\underline{\lambda}^{T}\mathbf{n}=\chi\mathbf{n},$$
(3.31)

where

$$\beta = \frac{\alpha r}{1 - r} \tag{3.32}$$

$$\chi = \left(\frac{1}{r} - 1\right) \mathbf{n} \cdot \underline{\underline{\lambda}} \cdot \left(\underline{\underline{\ell}}_0 + \beta \underline{\underline{\delta}}^{(tr)}\right) \cdot \underline{\underline{\lambda}}^T \cdot \mathbf{n}.$$
(3.33)

Eq. (3.31) can then be substituted back in to the expression for the polarisation. The result of this yields

$$P_{i} = \frac{1}{2} n_{s} d(b/a) \left(\frac{1}{r} - 1\right) \epsilon_{ijk} (\underline{\lambda} \cdot (\underline{\ell}_{0} + \beta \underline{\delta}^{(tr)}) \cdot \underline{\lambda}^{T} \cdot \mathbf{nn})_{jk}$$
(3.34)

This is zero because **n** is a principal axis of the tensor  $\underline{\lambda} \cdot (\underline{\ell}_0 + \beta \underline{\delta}^{(tr)}) \cdot \underline{\lambda}^T$ , so it is a contraction of an antisymmetric tensor with a symmetric tensor.

# 3.3.4 Rod cross-linkers introducing semi-softness

Typically, elastomers are aligned by a two-stage cross-linking process resulting in a monodomain. A model of this multistage cross-linking process [49] shows that Gaussian chains do not remember the details of the strains imposed during the cross-linking process, indeed a multistage cross-linked network should exhibit the same behaviour as a single-stage system. This extended the ideas of Scanlan [50] into nematic elastomers. The process of multistage crosslinking may allow some extra orientational information to be imprinted into the elastomer. A model of this process presented in [51] is now summarised, where the second stage is carried out using rod cross-linkers. The polarisation of the rubber within this model with this second stage of cross-linking will subsequently be calculated.

#### Two-stage cross-linking

Consider two separate strands of n monomers that have already been crosslinked into a matrix. These strands are then cross-linked together as shown in Fig. 3.5. Initially the polymer chain was cross-linked with its ends at  $\mathbf{r}_0$  and  $\mathbf{r}_n$ . The rod cross-linker is joined to this original chain at the *j*th monomer down its length. If we denote the position of the *j*th monomer by  $\mathbf{r}_j$ , and the distance from the end to the *j*th monomer as:  $\mathbf{r}_{j0} = \mathbf{r}_j - \mathbf{r}_0$ , then the free energy of the strand with its new cross-linking point can be written as the sum of the two Gaussian strands

$$\frac{f}{k_B T} = \frac{3}{2a^2} \left( \frac{\mathbf{r}_{j0}^T \cdot \underline{\ell}^{-1} \cdot \mathbf{r}_{j0}}{j} + \frac{\mathbf{r}_{nj}^T \cdot \underline{\ell}^{-1} \cdot \mathbf{r}_{nj}}{n-j} \right).$$
(3.35)
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Figure 3.5: A rod like cross-linker is used in the second stage of the cross-linking to join together two of the strands. Here  $\mathbf{g}_n$  is the span of the polymer chain from the cross-linker to the first stage cross-link,  $\mathbf{a}_n$  is the span from the centre of the cross-link to the first stage cross-link,  $\mathbf{z}$  is the vector from the span between the two first stage cross-link points to the new cross-linked point,  $\mathbf{x}$  is the position of the rod cross link,  $\mathbf{c}$  is the director of the rod cross-link and 2t is the length of the rod cross-link.

The strand free energy can be re-expressed in terms of  $\mathbf{z}$  (see Fig. 3.5) by substituting in  $\mathbf{z}$  using the definitions

$$\mathbf{z} = \mathbf{r}_{j0} - \frac{j}{n} \mathbf{r}_{n0}$$
$$\mathbf{z} = \frac{n-j}{n} \mathbf{r}_{n0} - \mathbf{r}_{nj}$$

The strand free energy is then given by

$$\frac{f}{k_B T} = \frac{3}{2a^2} \left( \frac{n}{j(n-j)} \mathbf{z}^T \cdot \underline{\ell}^{-1} \cdot \mathbf{z} + \frac{\mathbf{r}_{n0}^T \cdot \underline{\ell}^{-1} \cdot \mathbf{r}_{n0}}{n} \right).$$
(3.36)

The two parts of this free energy can be recognised as the cost of localising the strand and that of the strand alone. The deformation of the network can be defined as follows: the total network deformation since its genesis is given by  $\underline{\lambda}$ , the network deformation from its genesis to the first stage of cross linking is given by  $\underline{\lambda}_f$ . A superscript f will be used to denote vector quantities at the second stage of cross-linking, whilst a superscript o will be used to denote

vector quantities at the first stage of cross-linking. The fact that  $\mathbf{a}_n$  and  $\mathbf{r}_{n0}$  deform affinely can be used to express  $\mathbf{z}$  as follows

$$\mathbf{z} = \underline{\lambda} \cdot \underline{\lambda}_{f}^{-1} \mathbf{z}^{f} - t \underline{\lambda} \cdot \underline{\lambda}_{f}^{-1} \mathbf{c}^{f} + t \mathbf{c}.$$
(3.37)

This expression can then be substituted into the expression for the free energy and the variables  $\mathbf{r}_{n0}$ ,  $\mathbf{z}^{f}$ , and  $\mathbf{c}^{f}$  quench-averaged over, whilst annealing over **c**. The required averages of the distribution are denoted as follows

$$\langle \mathbf{z}^f \mathbf{z}^f \rangle = \frac{1}{3} j(n-j) \frac{a^2}{n} \underline{\ell}_f$$
 (3.38)

$$\langle \mathbf{r}_{n0}^{o} \mathbf{r}_{n0}^{o} \rangle = \frac{1}{3} n a^{2} \underline{\ell}_{0}$$
(3.39)

$$\langle \mathbf{c}^f \mathbf{c}^f \rangle = \frac{1}{3} \underline{\underline{C}}^f.$$
 (3.40)

These averages are used to evaluate the expression

$$\frac{f_{el}}{k_B T} = -\int d\mathbf{c}^f P(\mathbf{c}^f) \int d\mathbf{r}_{n0} P(\mathbf{r}_{n0}) \int d\mathbf{z}^f P(\mathbf{z}^f) \ln\left[\int d\mathbf{c} e^{-\frac{F}{k_B T}}\right].$$
 (3.41)

Since the rigid-rod cross-link is short compared to the span of a Gaussian chain then the small elastic contribution of the rigid rod to the free energy is neglected. Terms linear in  $\mathbf{c}^f$  average to zero, terms in  $\mathbf{c}$  and  $\mathbf{c}^f$  are small, and terms in  $\mathbf{c}$  and  $\mathbf{z}^f$  are expanded down from the exponential and then averaged over w.r.t  $\mathbf{c}$  and the resulting logarithmic term expanded.

After evaluating these integrals the second stage of the cross-linking occurs at a random point along the polymer chain, and consequently the randomly chosen j is averaged over. The expression for the free energy density obtained is given by

$$f_{el} = \frac{1}{2} n_s k_B T \left( \operatorname{Tr} \left[ \underline{\lambda} \cdot \underline{A} \cdot \underline{\lambda}^T \cdot \underline{\ell}^{-1} \right] - \operatorname{Tr} \left[ \underline{\lambda} \cdot \underline{B} \cdot \underline{\lambda}^T \cdot \underline{\ell}^{*-1} \right] \right)$$
  

$$\underline{\ell}^* = \underline{\ell} \cdot \underline{C}^{-1} \cdot \underline{\ell}$$
  

$$\underline{A} = (1 - \alpha) \underline{\ell}_0 + \alpha \underline{\lambda}_f^{-1} \cdot \underline{\ell}_f \cdot \underline{\lambda}_f^{-T} + \alpha d \underline{\lambda}_f^{-1} \cdot \underline{C}_f \cdot \underline{\lambda}_f^{-T}$$
  

$$\underline{B} = \alpha d \underline{\lambda}_f^{-1} \cdot \underline{\ell}_f \cdot \underline{\lambda}_f^{-T}$$

Here  $\alpha = n_{\text{rigid}}/(n_1 + n_{\text{rigid}})$  where  $n_{\text{rigid}}$  is the number density of second stage cross-links and  $n_1$  is the number density of first stage cross-links. Thus  $\alpha$  is the fraction of second stage cross-links. The constant d arises from averaging over the position j that the rod linker is bonded, and is given by  $d = \left[2\ln(n-1)t^2\right] / \left[(n-1)a^2\right]$ . After this second stage of cross-linking, the rubber then relaxes to the optimal deformation. The total relaxation of the rubber from its first cross-linking state to its current relaxed state is denoted by  $\underline{\lambda}_r$ . This relaxation is chosen so as to minimise the free energy density.

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After this relaxation, a further deformation on the rubber can be imposed, which corresponds to the deformation applied experimentally after the second stage cross-linking process. A prime (') is now used to denote quantities such as  $\underline{X}' = \underline{\lambda}_r \cdot \underline{X} \cdot \underline{\lambda}_r^T$ . The imposed deformation after the relaxation is denoted by  $\underline{\lambda}$ . The final formula for the free energy density is thus

$$f_{el} = \frac{1}{2} n_s k_B T \left( \operatorname{Tr} \left[ \underline{\underline{\lambda}} \cdot \underline{\underline{A}}' \cdot \underline{\underline{\lambda}}^T \cdot \underline{\underline{\ell}}^{-1} \right] - \operatorname{Tr} \left[ \underline{\underline{\lambda}} \cdot \underline{\underline{B}}' \cdot \underline{\underline{\lambda}}^T \cdot \underline{\underline{\ell}}^{*-1} \right] \right)$$
(3.42)

#### Polarisation of two-stage cross-linked material

The polarisation of an elastomer composed of chiral main chains after a two stage cross-linking process is now calculated. The polymer chains have chiral monomers that carry a dipole moment, but the rod cross-linkers carry no dipole moment. The average binormal vector can be calculated as shown in §3.1.4. The original strand is split into two strands after the rod cross-linker is attached to the polymer chain. The end-to-end vector of these two strands is denoted by  $\mathbf{g}_o$  and  $\mathbf{g}_n$  as shown in Fig. 3.6. The total total binormal vector



Figure 3.6: The two end-to-end vectors of the polymer chain after it has been cross-linked to the rod.

for each strand can then be calculated using

$$\langle \mathbf{V} \rangle = \frac{3bN}{2aL^2} \left\langle \mathbf{g} \times \underline{\ell}^{-1} \times \mathbf{g} \right\rangle \tag{3.43}$$

This average can be calculated by first substituting for  $\mathbf{g}$  in terms of  $\mathbf{z}$  and  $\mathbf{r}_{n0}$ 

$$\mathbf{g}_0 + \frac{j}{n}\mathbf{r}_{n0} + \mathbf{z} = 0$$
$$\mathbf{g}_n - \left(1 - \frac{j}{n}\right)\mathbf{r}_{n0} + \mathbf{z} = 0$$

These two quantities can be related to the quantities at the second cross-link stage as follows

$$\mathbf{g}_{0} = -\frac{j}{n}\underline{\underline{\lambda}}\cdot\underline{\underline{\lambda}}_{f}^{-1}\cdot\mathbf{r}_{n0}^{f} - \underline{\underline{\lambda}}\cdot\underline{\underline{\lambda}}_{f}^{-1}\cdot\mathbf{z}^{f} + t\underline{\underline{\lambda}}\cdot\underline{\underline{\lambda}}_{f}^{-1}\mathbf{c}^{f} - t\mathbf{c}$$
$$\mathbf{g}_{n} = \frac{n-j}{n}\underline{\underline{\lambda}}\cdot\underline{\underline{\lambda}}_{f}^{-1}\cdot\mathbf{r}_{n0}^{f} - \underline{\underline{\lambda}}\cdot\underline{\underline{\lambda}}_{f}^{-1}\cdot\mathbf{z}^{f} + t\underline{\underline{\lambda}}\cdot\underline{\underline{\lambda}}_{f}^{-1}\mathbf{c}^{f} - t\mathbf{c}$$

The binormal average for the two strands  $\mathbf{g}_0$  and  $\mathbf{g}_n$  can be evaluated by substituting these expressions into the formula for the binormal vector. The average is slightly simpler than that of the free energy density because no annealed terms have to be expanded. Note that  $\mathbf{z}_f$  and  $\mathbf{r}_f$  are un-correlated; also  $\mathbf{c} \cdot (-) \cdot \mathbf{c}$  terms are ignored as are  $\mathbf{c} \cdot (-) \cdot \mathbf{z}^f$ ,  $\mathbf{c}^f \cdot (-) \cdot \mathbf{c}$  and  $\mathbf{c}_f \cdot (-) \cdot \mathbf{r}_{n0}$ . After using these averages the following expressions for the binormals of each strand are obtained

$$\begin{split} \langle \mathbf{V}_{\mathbf{g}_{0}} \rangle_{f} &= \frac{b}{2a} \epsilon_{ijk} \left[ \frac{j}{n} \underline{\lambda} \cdot \underline{\ell}_{0} \cdot \underline{\lambda}^{T} \cdot \underline{\ell}^{-1} + \frac{n-j}{n} \underline{\lambda} \cdot \left( \underline{\lambda}_{f}^{-1} \cdot \underline{\ell}_{f} \cdot \underline{\lambda}_{f}^{-T} \right) \cdot \underline{\lambda}^{T} \cdot \underline{\ell}^{-1} \\ &+ \frac{t^{2}}{ja^{2}} \underline{\lambda} \cdot \underline{\lambda}_{f}^{-1} \cdot \underline{C}_{f} \cdot \underline{\lambda}_{f}^{-T} \cdot \underline{\lambda}^{T} \cdot \underline{\ell}^{-1} \right] \\ \langle \mathbf{V}_{\mathbf{g}_{n}} \rangle_{f} &= \frac{b}{2a} \epsilon_{ijk} \left[ \frac{n-j}{n} \underline{\lambda} \cdot \underline{\ell}_{0} \cdot \underline{\lambda}^{T} \cdot \underline{\ell}^{-1} + \frac{j}{n} \underline{\lambda} \cdot \left( \underline{\lambda}_{f}^{-1} \cdot \underline{\ell}_{f} \cdot \underline{\lambda}_{f}^{-T} \right) \cdot \underline{\lambda}^{T} \cdot \underline{\ell}^{-1} \\ &+ \frac{t^{2}}{(n-j)a^{2}} \underline{\lambda} \cdot \underline{\lambda}_{f}^{-1} \cdot \underline{C}_{f} \cdot \underline{\lambda}_{f}^{-T} \cdot \underline{\lambda}^{T} \cdot \underline{\ell}^{-1} \right]. \end{split}$$

Summing the contributions from each chain and then average over the position, j, to which the rod molecule is bonded, with equal probability for each site, and summing the result over all strands results in the following expression

$$P_{i} = \frac{n_{s}d(b/a)}{2} \epsilon_{ijk} \left[ \underline{\lambda} \cdot \underline{A}' \cdot \underline{\lambda}^{T} \cdot \underline{\ell}^{-1} \right]$$
(3.44)

This is a polarisation formula but with a different matrix compared to the free energy density. The minimum of the free energy density can be found as in §3.2, assuming that  $\underline{\ell}^*$  has the same principal axes as  $\underline{\ell}$ . This follows because  $\underline{C}$  and  $\underline{\ell}$  have the same principal axes as a result of being in the same nematic environment. In order to develop a polarisation it is required that  $\underline{A}'$  and  $\underline{B}'$  have different principal axes. However, this cannot be the case because the anisotropy tensor  $\underline{\ell}_f$  is related to the original anisotropy tensor by the conventional trace formula so  $\underline{\ell}_o$  and  $\underline{\lambda}_f^{-1} \cdot \underline{\ell}_f \cdot \underline{\lambda}_f^{-T}$  have the same principal axes and hence  $\underline{A}'$  and  $\underline{B}'$  have the same principal axes. As a result the trace formula is still the contraction of a symmetric with an antisymmetric tensor and so again the polarisation is zero.

#### 3.4 Systems where a polarisation results

#### 3.4.1 Oscillating shear

The dynamics of liquid crystal elastomers are complicated because of the coupling between the liquid crystalline degrees of freedom and the underlying polymer matrix. As stated already, it is possible to identify several time scales in the elastomer. A single free polymer strand has an associated relaxation time called the Rouse time  $\tau_{\rm p} \sim 10^{-4} - 10^{-6}$ s, and the mesogenic units have an associated relaxation time  $\tau_{\rm LC} \sim 10^{-1} - 10^{-2}$ s. However the polymer network as a whole relaxes according to a power law and so has no associated scale. The polarisation associated with the dynamics of a liquid crystal elastomer is now calculated under the assumption that the polymer network responds very quickly and then the director relaxes much more slowly into its equilibrium orientation. For an elastomer that displays such a separation of time scales the relaxation of the polymer can be neglected (it is assumed to be instantaneous) and the slower dynamics of the director focused upon [52]. In this case the system can be modelled as an over-damped oscillator with a damping constant  $\gamma$  associated with the return to equilibrium of the director. The force causing the return to equilibrium is governed by the gradient of the equilibrium free energy density

$$\gamma \dot{\mathbf{n}} = -\frac{\partial (f - \chi \mathbf{n} \cdot \mathbf{n})}{\partial \mathbf{n}},\tag{3.45}$$

where the Lagrange multiplier has again been included to prevent changing of the length of the director during the motion. Using the the small deformation form for the free energy density given previously and then applying the constraint  $\mathbf{n} \cdot \mathbf{n} = 1$  to find  $\chi$  as before, then in the notation of section §3.3.1, the resulting equation is

$$\gamma \dot{\mathbf{n}} = -\mu \left(\frac{1}{r} - 1\right) \left( \left(\underline{\ell}_0 + \underline{\ell}'\right) \cdot \mathbf{n} - \mathbf{n} \left(\mathbf{n} \cdot \left(\underline{\ell}_0 + \underline{\ell}'\right) \cdot \mathbf{n}\right) \right)$$
(3.46)

To pick out the symmetric and antisymmetric contributions to this expression consider a deformation of the form

$$\underline{\underline{\lambda}} = \begin{pmatrix} 1 & 0 & \eta + \delta \\ 0 & 1 & 0 \\ \eta - \delta & 0 & 1 \end{pmatrix}.$$
 (3.47)

On substituting this deformation into Eq. (3.46) the following expression for the angle of the director is obtained

$$\gamma \dot{\theta} = \mu \left(\frac{1-r}{r}\right) \left( \left( (r-1)\delta - (r+1)\eta \right) \cos 2\theta + (r-1)\sin 2\theta \right) (3.48)$$

$$= -D_1 \sin 2\theta - (2D_1\delta(t) + D_2\eta(t)) \cos 2\theta, \qquad (3.49)$$

where de Gennes elastic constants  $D_1 = \frac{\mu}{2r}(1-r)^2$  and  $D_2 = \frac{\mu}{r}(1-r^2)$ [33] have been substituted in. Note the separation of the symmetric and the antisymmetric parts together with the appropriate de Gennes elastic constant.

For the case of an oscillating  $\lambda_{xz}$  component

$$\underline{\underline{\lambda}} = \begin{pmatrix} 1 & 0 & \epsilon \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{3.50}$$

the resulting perturbation can be calculated by breaking up the above  $\underline{\lambda}$  into its symmetric and antisymmetric parts, and then using the expression for  $\underline{\ell}'$ . The result is

$$\underline{\ell}' = \begin{pmatrix} 0 & 0 & \epsilon r \\ 0 & 0 & 0 \\ \epsilon r & 0 & 0 \end{pmatrix}.$$
(3.51)

The initial orientation of the director is  $\mathbf{n}_0 = (0, 0, 1)$  and the current director orientation can be written as  $\mathbf{n} = (\sin \theta, 0, \cos \theta)$ , then all the components of the equation of motion reduce to

$$\gamma \dot{\theta} = -D_1 \sin 2\theta - \left(\frac{D_2}{2} - D_1\right) \epsilon(t) \cos 2\theta \tag{3.52}$$

where the de Gennes elastic constants have again been substituted in. For small oscillations this reduces to a linear, driven, over-damped oscillator equation. The driving deformation is assumed to be  $\epsilon(t) = \epsilon e^{i\omega t}$ . The amplitude in complex notation is then

$$A(\omega) = \frac{\frac{\epsilon}{2} \left(1 - \frac{D_2}{2D_1}\right)}{1 + i\omega\tau_c},\tag{3.53}$$

where  $\tau_c = \frac{\gamma}{2D_1}$ . The polarisation of the liquid crystal elastomer can be calculated by using the orientation of the director and Eq. (3.8). Although this formula is derived entirely from equilibrium statistical mechanics, it is used here for a system that is considered locally close to equilibrium at each stage of its relaxation

$$P_y = \frac{1}{2} n_s d(b/a) \left( (r-1)\epsilon e^{i\omega t} - \frac{(r-1)^2}{r} A(\omega) e^{i\omega t} \right).$$
(3.54)

Denoting  $P_{\infty} = \frac{1}{2}n_s d(b/a)(r-1)\epsilon$  (the  $\infty$  denoting the large frequency response) and use the explicit forms above for  $D_1$  and  $D_2$ , then this simplifies to

$$P_y = P_\infty \frac{i\omega\tau_c}{1+i\omega\tau_c} e^{i\omega t}.$$
(3.55)

The amplitude of this response is given by

$$\left|\frac{P_y}{P_{\infty}}\right| = \frac{\omega\tau_c}{\sqrt{1 + (\omega\tau_c)^2}}.$$
(3.56)



Figure 3.7: The polarisation of a chiral liquid crystal elastomer under an oscillating shear.

The response of the polarisation is illustrated in Fig. 3.7. The maximum size of the response is given by  $P_{\infty}$ . The size of the maximum polarisation can be calculated by using the following estimates:  $n_s \sim 10^{26} \text{m}^{-3}$ ,  $d \sim 10^{-30} \text{Cm}$ ,  $\frac{b}{a} \sim \frac{1}{10}$ ,  $r \sim 50$  and  $\epsilon \sim 10\%$ . From these estimates the value:  $P_{\infty} \sim 25 \times 10^{-6} \text{Cm}^{-2}$  is obtained. Note that this method only yields a polarisation when the relaxation time for the director is slower than the response time of the polymer network. As a result it provides a probe of the response times of the network and the director.

#### 3.4.2 Smectic anchoring

The molecules that a smectic liquid crystal is made up of experience short range interactions that causes them to condense into layers. This can be modelled using a similar method to Maier-Saupe theory of nematic liquid crystals [53], using a mean field theory. In a smectic-A phase the director is anchored perpendicular to the layers (chapter 4). Similarly in a smectic liquid crystal elastomers the director can be treated as rigidly anchored perpendicular to the smectic layers, in the first approximation. As a result of the layer anchoring, when the polarisation of a chiral main chain elastomer is calculated, then a polarisation is obtained because the director cannot rotate without reducing the layer spacing. To illustrate this we now calculate the polarisation of a smectic-A<sup>\*</sup> elastomer that has its director aligned along the z-axis and a  $\lambda_{xz}$ shear imposed on it (Fig. 3.8 (a)). The polarisation can be calculated in this case simply by substituting the following deformation into the polarisation



Figure 3.8: (a) A  $\lambda_{xz}$  shear applied to a smectic liquid crystal elastomer. (b) A schematic sketch of the microscopic structure of the main chain smectic elastomer before shearing the layers.

formula with the initial and final director fixed parallel to the z-axis

$$\underline{\lambda} = \begin{pmatrix} 1 & 0 & \lambda \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{3.57}$$

The resulting polarisation is in the y direction and is given by

$$\mathbf{P} = \frac{1}{2}n_s d\frac{b}{a}(1-r)\lambda\hat{\mathbf{y}} \tag{3.58}$$

This expression is similar to that obtained for the case of an oscillating shear applied to a nematic and thus has a similar size.

#### 3.4.3 Binary Mixtures

Consider a binary mixture of polymer chains of different shape anisotropies,  $r_1$  and  $r_2$ . The elastomer has two different chain shape tensors that respond differently to the imposed deformation but are coupled by the nematic field. Since the system contains a mix of two components then the principal axes of the tensor along which the director lies to minimise the free energy density are different to the principal axes for each of the pure components. As a result, if one of the two components is made out of chiral chains that are polarisable, then the system has a polarisation because of the equilibrium orientation adopted by the chiral chains. Although this is a complicated system

to synthesise, similar systems have already been synthesised. For example, mixtures of main chain cross-linker elements with side chain polymers. The introduction of an extra component means that the reorientation of the director as the system deforms can be controlled. Mixtures of chains have already been studied in the context of liquid crystal elastomers as a source of semisoftness. The starting point used here is the free energy density of a mixture of polymer chains as shown in section  $\S3.3.3$ . The effect of the binary mixture on the orientation can be calculated from this formula. Once the orientation of the director is known, then the polarisation can be calculated from the model of the polarisation discussed earlier. Two cases are considered here: a shear with, and a shear without relaxation of the other deformation tensor components. In each case a mixture of prolate side chains and main chains is used as an illustration. Whilst it is possible to mix oblate and prolate chains in principle, in practise the formation of an aligned monodomain is not possible by the typical method of stretching the sample and then using a second crosslinking stage. The oblate and prolate chains respond by rotating in opposite directions to each other and so would not become aligned.

#### Shear with relaxation of deformation

A  $\lambda_{xz}$  shear is imposed on a block of rubber. To find a soft mode we allow the  $\lambda_{xx}$  and  $\lambda_{zz}$  deformations to relax. The third diagonal component  $\lambda_{yy}$  is unchanged during the rotation of the director, but once softness is finished it starts to shrink. An illustration of the deformation and the accompanying relaxations is shown in Fig. 3.9. To determine the trajectory of the director the



Figure 3.9: The imposed xz shear is accompanied by relaxations in the x and z directions so that the overall deformation is soft.

free energy density expression should be minimised. The deformation tensor

is

$$\underline{\underline{\lambda}} = \begin{pmatrix} \lambda_{\mathrm{xx}} & 0 & \delta \\ 0 & \frac{1}{\lambda_{\mathrm{zz}}\lambda_{\mathrm{xx}}} & 0 \\ 0 & 0 & \lambda_{\mathrm{zz}} \end{pmatrix}$$
(3.59)

where  $\lambda_{xz}$  is denoted simply by  $\delta$  and volume constraint has been included. The  $\lambda_{xz}$  component has been suppressed on geometric grounds, since a  $\lambda_{zx}$  deformation is being applied by plates attached to the sample. The free energy density of the mixture of chains is given by

$$f_{ss} = \frac{1}{2}\mu \operatorname{Tr}\left[\underline{\underline{\lambda}} \cdot \underline{\underline{\ell}}_{0} \cdot \underline{\underline{\lambda}}^{T} \cdot \underline{\underline{\ell}}^{-1} + \alpha \underline{\underline{\delta}}^{(tr)} \cdot \underline{\underline{\lambda}}^{T} \cdot \mathbf{nn} \cdot \underline{\underline{\lambda}}\right], \qquad (3.60)$$

where as usual  $\alpha = \langle \frac{1}{r} \rangle - \frac{1}{\langle r \rangle}$  and the  $\underline{\ell}_0$  and  $\underline{\ell}^{-1}$  are in terms of  $\langle r \rangle$ . The average value for the binary mixture of chains considered here is given by:  $\langle r \rangle = qr_1 + (1-q)r_2$ , where q is the fraction of main chains of anisotropy  $r_1$  and 1-q is the fraction of side chains of anisotropy  $r_2$ . On substituting into this formula the director orientations  $\mathbf{n}_0 = (0, 0, 1)$  and  $\mathbf{n} = (\sin \theta, 0, \cos \theta)$ , then the following expression for the free energy density is obtained

$$\frac{2f_{ss}}{\mu} = \frac{1}{\lambda_{xx}^2 \lambda_{zz}^2} + \lambda_{zz}^2 (1 + (r - 1)\sin^2\theta) + (r\delta^2 + \lambda_{xx}^2) \left(1 + \left(\frac{1}{r} - 1\right)\sin^2\theta\right) - (r - 1)\lambda_{zz}^2 \delta \sin 2\theta + \alpha \lambda_{xx}^2 \sin^2\theta$$
(3.61)

This free energy density is very similar to the case where the driving deformation is a stretch along the x axis and a shear is induced as a result of the rotation of the director. As a result it is possible to re-express some of the results for the imposed stretch case to apply here. For the case where there is no semi-softness the following solution is obtained

$$\lambda_{\rm xx}^2 = \frac{1}{2} \left\{ (r+1-\delta^2 r) - \sqrt{(r+1-\delta^2 r)^2 - 4r} \right\}$$
(3.62)

$$\lambda_{\rm yy} = 1 \tag{3.63}$$

$$\lambda_{\rm zz} = 1/\lambda_{\rm xx} \tag{3.64}$$

$$\sin^2 \theta = \frac{r}{r-1} \frac{\lambda_{\rm xx}^2 - 1}{\lambda_{\rm xx}^2}.$$
 (3.65)

This is the solution up to the end of softness which occurs at  $\delta_{\rm cr} = 1 - \frac{1}{\sqrt{r}}$ . After this point, minimisation of the free energy density becomes very difficult analytically. The solution also becomes rapidly intractable when we have a finite value of  $\alpha$ . To calculate the size of the polarisation in these cases a numerical procedure was used to minimise the free energy density. A simplex algorithm provides a convenient and robust method for minimisation of the free energy density. Fig. 3.10 shows a plot of the relaxation of  $\lambda_{\rm xx}$ ,  $\lambda_{\rm yy}$  and  $\lambda_{\rm zz}$  for an elastomer consisting of only one type of chain, and for an elastomer made of a mixture of two sorts of chains. Note that the pure elastomers,  $\alpha = 0$  exhibit softness, with an abrupt end to the relaxation once all the chains have rotated, whereas the semi-soft system has no such abrupt end because there is no deformation that can be soft for all the chains. As an example, a mixture of side chains with r = 2 and main chains with r = 50 is used. The angle of the



Figure 3.10: The figure shows a plot of the relaxation of the deformation as a function of applied shear,  $\delta$ . The different curves correspond to different mixtures of the main chain (r = 50) and side chain (r = 2) polymers. The fraction of main chain is denoted by q.

director to the z-axis is shown in Fig. 3.11. This figure shows that the director singularity for the two pure cases occurs at the critical value  $\delta_{\rm cr} = 1 - \frac{1}{\sqrt{r}}$ . Fig. 3.11 also shows that the director behaviour in the sample is dominated by the long chains; after  $q \sim 0.1$ . After this the director behaviour tends to follow the behaviour of the main chain system.

#### Polarisation

In the elastomer made of the mixed side chains and chiral main chains, each of the main chains can be polarised according to the model of [48]. The side chains will enable control of the rotation of the director. The polarisation of the system is then given by

$$P_{i} = \frac{1}{2}qn_{s}d\left(\frac{b}{a}\right)\epsilon_{ijk}\left(\underline{\underline{\lambda}}\cdot\underline{\underline{\ell}}_{0}\cdot\underline{\underline{\lambda}}^{T}\cdot\underline{\underline{\ell}}^{-1}\right)_{jk},$$
(3.66)

where an extra factor of q, the fraction of polarisable main chains in the system, has been inserted as compared to [48] which was for a pure system.



Figure 3.11: The figure shows a plot of the angle of the director to the z direction as a function of the applied shear,  $\delta$ during the soft deformation. The different curves correspond to different mixtures of the main chain and side chain polymers. The fraction of main chain is denoted by q. The r values are as in Fig. 3.10.

As in §3.1.4, b and a give the dimensions of the chiral units, d is the dipole moment of each monomer and  $n_s$  is the density of cross-linked strand in the network. The anisotropy tensors used here refer to the anisotropy of the <u>chiral</u> chains only because these chains are polarisable. However, because of the mixed-in side chains, the final director orientation is not solely determined by the polarisable main chains. For the deformation tensor of Eq. (3.59) the polarisation expression of Eq. (3.66) reduces to

$$P_{\rm y} = -\frac{1}{2}qn_{\rm s}d\left(\frac{b}{a}\right)\frac{r_{\rm I}-1}{2r_{\rm I}}\left(-2r_{\rm I}\lambda_{\rm zz}\delta\cos2\theta - \left(\lambda_{\rm xx}^2 + r_{\rm I}(\delta^2 - \lambda_{\rm zz})\sin2\theta\right)\right) \quad (3.67)$$

Using the orientation of the director determined above, the polarisation of the system can be calculated. A plot of the polarisation in the **y** direction in units of  $\frac{1}{2}qn_{\rm s}d\left(\frac{b}{a}\right)$  is shown in Fig. 3.12. The polarisation shows a minimum typically at around  $\lambda \approx 1$ . To understand this consider the q = 1 curve of the angle of the director. This is the trajectory that the director should follow for the polarisation to be zero, with the particular form of  $\delta$ . The further away from this trajectory the director is, then the larger the polarisation (Fig. 3.11). For very large shears the director orientation tends to be independent of the anisotropy of the chains so the polarisation goes to zero. Also for small shears the difference between the soft trajectory and the semi-soft trajectories is small so the polarisation is small.



Figure 3.12: The figure shows a plot of the polarisation as a function of the applied shear,  $\lambda$  during the soft deformation.  $P_y$  is in units of  $\frac{1}{2}n_s\frac{b}{a}d$ . The different curves correspond to different mixtures of the main chain and side chain polymers. The fraction of main chain is denoted by q.

#### Shear without relaxation of deformation

In practise it is more realistic to prohibit any relaxation of the system. This is because to impose the shear the sample will have to be glued to two plates and then the plates sheared. In this case the deformation tensor is given by

$$\underline{\underline{\lambda}} = \begin{pmatrix} 1 & 0 & \lambda \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$
(3.68)

This can be substituted directly into the free energy density, which can then be minimised w.r.t. the director orientation to calculate the angle of the director to the z axis,  $\theta$ . In this case the instabilities reported in [54] are expected. The orientation of the director is given by

$$\tan 2\theta = -\frac{2\langle r \rangle \lambda}{1 + \langle r \rangle (\lambda^2 - 1) + \frac{\alpha \langle r \rangle}{1 - \langle r \rangle}}.$$
(3.69)

Plots of this function for different compositions are shown in Fig. 3.13. Only two different compositions are shown because as soon as a small amount,  $q \sim 0.1$ , of main chains, are introduced to the system then it switches to being very close to the curve of q = 1.0. This can then be substituted into the formula for the polarisation as in the previous section. The resulting polarisation is illustrated in Fig. 3.14. An expression for the polarisation can



Figure 3.13: The figure shows a plot of the angle of the director to the z axis as a function of the applied shear,  $\lambda$  when no relaxation is allowed. The different curves correspond to different mixtures of the main chain and side chain polymers. The fraction of main chain is denoted by q.

be calculated and is given by the expression

$$\frac{2P_y}{n_s d_a^{\underline{b}}} = \frac{q(1-q)(r_1-1)(r_2-1)(r_1-r_2)\langle r \rangle \lambda}{r_1 r_2(\langle r \rangle - 1) \left\{ 4\langle r \rangle^2 \lambda^2 + \left(1 - \frac{q(1-q)(r_1-r_2)^2}{r_1 r_2(\langle r \rangle - 1)} + \langle r \rangle (\lambda^2 - 1)\right)^2 \right\}_{(3.70)}^{\underline{12}}}$$

where  $\langle r \rangle = qr_1 + (1-q)r_2$ . This expression tends to have a maximum around  $\lambda = 1$ . The expression also simplifies markedly for the composition such that  $\langle r \rangle = 1$ . In this case the director does not move under the shear. The polarisation expression then simplifies to

$$\frac{2P_y}{n_s d\frac{b}{a}} = \frac{(r_1 - 1)(r_2 - 1)\lambda}{(r_1 - r_2)}$$
(3.71)

The director now remains fixed along the z-axis in this case as the shear is carried out. This is now very similar to the toy model of [48].

#### 3.5 Conclusions

Analysis of the symmetry of the free energy density of a chiral liquid crystal elastomer shows that the elastomer can develop a polarisation. One way it can do this is similar to the flexoelectric effect in liquid crystals. An alternative mechanism is via a main chain polymer composed of chiral monomers.



Figure 3.14: The figure shows a plot of the polarisation as a function of the applied shear,  $\lambda$  when no relaxation is allowed. The different curves correspond to different mixtures of the main chain and side chain polymers. The fraction of main chain is denoted by q.

However, the polarisation of a sheared pure chiral liquid crystalline elastomer relaxes to zero. This result is robust and cannot be changed by considering a semi-soft elastomer or by introducing rod cross linkers into the elastomer. Another direction is required in the problem. Three methods by which a polarisation can develop have been suggested. The first relies the slow response of the director and a rapid response of the network so that the director lags behind its equilibrium orientation. The second method is to anchor the director to the layer normal in a smectic. The third method changes how the chiral main chain monomers relax by considering a binary mixture of polymer chains. This effect was illustrated here for a mixture of chains of different degrees of prolate anisotropy. If the rubber is allowed to relax, then it has little effect on the polarisation. We can estimate the resulting polarisation as follows:  $d \sim 1.6 \times 10^{-19} \text{ C} \cdot 1\text{\AA}$ ,  $\frac{b}{a} \sim \frac{1}{10}$  and  $n_{\rm s} \sim 3 \times 10^{26} \text{ m}^{-3}$ . Thus  $\frac{fn_{\rm s}d}{2} \left(\frac{b}{a}\right) \sim 50 \times 10^{-6} \text{Cm}^{-2}$  or  $\frac{P}{\sigma} \sim 50 \times 10^{-12} \text{C} \text{ N}^{-1}$ . This can be compared to the polarisation of  $\alpha$ -quartz:  $P_1 = e_{11}x$  where  $P_1$  is the polarisation, x is the applied strain and  $e_{11}$  is the required coefficient and has a value  $e_{11} \approx 0.173 \mathrm{Cm}^{-2}$ . Thus the  $\alpha$ -quartz has a much greater polarisation per unit strain. However the typical applied strain is much smaller:  $x \sim 0.2\%$ , so we expect a polarization of  $P \sim 340 \times 10^{-6} \text{ Cm}^{-2}$ . Alternatively the Young's modulus of quartz is  $E \sim 70$  GPa so:  $\frac{P}{\sigma} \sim 5 \times 10^{-15}$  C N<sup>-1</sup>. Thus although this mechanism of polarisation for a rubber produces a polarisation that is, per unit strain, much smaller than in a crystal, a rubber can be subjected to

a much larger strain so can obtain a polarisation only an order of magnitude less. If we carry out the same analysis for mixtures of prolate and oblate chains then it may be possible to increase the polarisation of the rubber by a factor of  $\sim 10$ .

# — Part II —

# Smectic liquid crystal elastomers

## -Chapter Four ——

# The elasticity of smectic-A elastomers

A model of smectic elastomers is developed in this chapter, starting from a microscopic model that is used calculate the properties of an average chain, and then using the affine approximation to build up the properties of the whole elastomer.

#### 4.1 Introduction

Smectic liquid single crystal elastomers share properties with both smectic liquid crystals and nematic elastomers. In this introduction some of the properties of smectic liquid crystals are discussed, aswell as methods used to describe them. In particular the Helfrich-Hurault effect, observed experimentally in smectic A (SmA) liquid crystals by Clark and Meyer [55], is examined. Some of the experimentally measured properties of SmA elastomers are then reviewed, and the terms used in the continuum model to describe smectic elastomers summarised.

#### 4.1.1 Smectic liquid crystal order parameter

Smectic and nematic liquid crystals are both composed of rod like molecules. However in the case of smectic liquid crystals, a short range anisotropic attractive interaction causes a modulation in the density of the rods in addition to the alignment of the rods along a particular direction. This modulation in the density distinguishes the smectic phase from the nematic phase and can be used to define an order parameter for the smectic phase. The density can be expressed as

$$\rho(\mathbf{x}) = \rho_0 + \sum_n \left[ \langle \psi_n \rangle \mathrm{e}^{in\mathbf{q}_0 \cdot \mathbf{x}} + \mathrm{c.c.} \right], \qquad (4.1)$$

where the sum over all integer values, n, and  $\mathbf{q}_0 = \frac{2\pi}{d_0}\hat{\mathbf{z}}$  is the wave vector of the layers. Typically only the n = 1 component is required. An order parameter can be defined from the oscillations in the density which can be written as

$$\langle \psi_1 \rangle = |\langle \psi_1 \rangle| \mathrm{e}^{-iq_0 u} \tag{4.2}$$

where  $|\langle \psi_1 \rangle|$  gives the size of the density modulations and  $e^{-iq_0u}$  gives the phase of the modulations relative to a defined origin. Planes of constant density within the smectic can be identified with planes of constant phase of the order parameter

$$\phi = \mathbf{q}_0 \cdot \mathbf{x} - q_0 u, \tag{4.3}$$

where u can be interpreted as giving the displacement along the old layer normal from the reference layer position to the current position of the layer as shown in Fig. 4.1. The equation for the layer planes in terms of the old layer



Figure 4.1: The figure shows the interpretation of the variable u as the vertical displacement of a layer with respect to its reference position (dashed lines).

normal,  $\mathbf{n}_0$ , and their spacing,  $d_0$ , in the reference frame coordinate  $\mathbf{x}$  is

$$\mathbf{n}_0 \cdot \mathbf{x} - u = nd_0 \tag{4.4}$$

#### 4.1.2 Microscopic model of the N/I – SmA phase transition

The ordering of the smectic phase can be understood by an extension of the Maier-Saupe model of the nematic phase [56, 57] carried out by McMillan [53]. These models are mean field models of the ordering in liquid crystals. In the Maier-Saupe model the rods that make up the liquid crystal are in an effective potential that depends on their angle to the average direction of all the other rods. In McMillan's model of an SmA liquid crystal, the potential is also dependent on the distance between the rods. The anisotropic part of the interaction is assumed to be proportional to

$$e^{-(r_{12}/r_0)^2} \left(\frac{3}{2}\cos^2\theta_{12} - \frac{1}{2}\right),$$
(4.5)

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where  $r_{12}$  is the distance between the centres of mass,  $r_0$  is roughly a molecular length, and  $\theta_{12}$  is the angle between the two rods. The attractive force between molecules results in a density wave in the mean field picture that can be described by the order parameter

$$\sigma = \langle \cos(\mathbf{x} \cdot \mathbf{q}) \left( \frac{3}{2} \cos^2 \theta_{12} - \frac{1}{2} \right) \rangle, \qquad (4.6)$$

where  $\mathbf{q}$  is the wave vector associated with the smectic layers. The system still has the orientational order described by the order parameter

$$\eta = \langle \frac{3}{2}\cos^2\theta - \frac{1}{2} \rangle. \tag{4.7}$$

The one-particle self-consistent potential is assumed to be of the form

$$V_1(z,\theta) = -V_0\eta \left(1 + \alpha\sigma \cos\left(\frac{2\pi z}{d}\right)\right) \left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right),\tag{4.8}$$

where d is the layer spacing and  $\alpha = 2e^{-(\pi r_0/d)^2}$ . The one-particle distribution function is given by

$$p(\theta, z) = \frac{1}{Z} e^{-\frac{V_1(z,\theta)}{k_B T}}$$

$$(4.9)$$

$$Z = \int_0^d dz \int_0^\pi e^{-\frac{V_1(z,\theta)}{k_B T}} \sin \theta d\theta.$$
 (4.10)

The entropy and internal energy of N molecules can then be evaluated to find the free energy of the system

$$-TS = NV_0(\eta^2 + \alpha\sigma^2) - Nk_BT\ln Z \qquad (4.11)$$

$$U = -\frac{1}{2}NV_0(\eta^2 + \alpha\sigma^2)$$
 (4.12)

$$F = U - TS. (4.13)$$

The free energy can then be minimised w.r.t. the order parameters and solved self-consistently for  $\eta$  and  $\sigma$  given values of T and  $\alpha$ . This model provides a useful conceptual basis for the SmA phase transition. However, it predicts that the transition is first order. McMillan completed several experimental studies in which he found evidence for both first [58] and second order [59] smectic phase transitions. For a more detailed discussion of the nematic SmA phase transition see, *inter alia*, [60].

#### 4.1.3 Smectic liquid crystal free energy

The terms in the free energy that describe the SmA phase differ from those of the nematic phase primarily by the addition of a term pertaining to the compression (and dilatation) of the layers. Assuming that the smectogens always remain normal to the layers, it is possible to calculate the orientation of the director from the layer displacement. The layer normal is parallel to  $\nabla \phi$  where  $\phi$  is defined in Eq. (4.3). The free energy cost of bending the layers can be calculated from the Frank elastic term associated with splay, but with renormalised elastic constants compared with a nematic because of the layer formation. Assuming that  $\nabla u$  is small then the following results are obtained

$$n_{\rm x} = -\frac{\partial u}{\partial x} \tag{4.14}$$

$$n_{\rm y} = -\frac{\partial u}{\partial y} \tag{4.15}$$

$$f = \frac{1}{2}B\left(\frac{\partial u}{\partial z}\right)^2 + \frac{1}{2}K_1\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right)^2.$$
(4.16)

Note that the associated length scale  $\xi = (K_1/B)^{1/2}$  is of the order of the layer thickness, and that there can be no twist deformation because  $\mathbf{n} \cdot \nabla \times \mathbf{n} = 0$  by the commutative property of the partial derivatives for sufficiently smooth functions. Typically, the Frank elastic constant,  $K_1$ , is larger than that of nematics because of the higher degree of order in smectics.

The Helfrich-Hurault effect requires the calculation of the contribution of the magnetic field to the free energy. The susceptibility tensor  $\underline{\chi}$  is uniaxial with its principal axis along the director  $\mathbf{n}$ , so the magnetisation (induced by the external magnetic field) is given by:  $\mathbf{M} = \underline{\chi} \cdot \mathbf{H} = \chi_{\perp} \mathbf{H} + (\chi_{\parallel} - \chi_{\perp}) (\mathbf{H} \cdot \mathbf{n}) \mathbf{n}$ . The part of the magnetic free energy density that depends on the director is thus given by

$$f_{\text{mag}} = -\frac{1}{2}\mu_0 \chi_a \left(\mathbf{n} \cdot \mathbf{H}\right)^2, \qquad (4.17)$$

where  $\chi_a = \chi_{\parallel} - \chi_{\perp}$  is the anisotropy in the susceptibility of the rods.

#### 4.1.4 The Helfrich-Hurault effect in smectic liquid crystals

The Helfrich-Hurault effect has been analysed in [61] as follows. Consider an SmA liquid crystal between two plates, with the layers parallel to the walls. Applying a magnetic field to the system (Fig. 4.2) in the plane of the layers generates a torque that acts to turn the layers. The clamping at the walls will prevent the rotation of layers occurring because as soon as the layer rotation starts there is an infinite energy cost as the layers pile up at the walls, and their spacing there collapses.

An alternative to this bulk rotation is local rotation of different parts of layers in opposite directions, so that the layers lower their energy with respect to the magnetic field whilst avoiding the cost associated with reducing the layer spacing, as well as any global layer movement. Above a certain threshold magnetic field, **H**, the layers start to rotate. This can represented in terms of the layer displacement variable

$$u(x,z) = u_0(z)\cos kx.$$
 (4.18)



Figure 4.2: An illustration of the magnetic field configuration required to see the Helfrich-Hurault effect. After the field is applied in the direction shown we can either rotate all the layers or locally rotate different parts of layers in opposite directions.

This is subject to the constraint that the amplitude of the displacement is zero at the edges of the sample, z = 0, L. Only the first harmonic is considered here as an illustration

$$u_0(z) = u_0 \sin k_z z, \tag{4.19}$$

where  $k_z = \pi/L$ . The director can be calculated from the layer displacement because it remains normal to the layers

$$n_{\rm x} \approx -\frac{\partial u}{\partial x} = \epsilon \sin(k_{\rm z} z) \sin(k x)$$
 (4.20)

$$n_{\rm y} = 0 \tag{4.21}$$

$$n_{\rm z} \approx 1,$$
 (4.22)

where  $\epsilon = u_0 k$ . Substituting this expression for the layer displacement into the Frank elastic and magnetic energy densities of the liquid crystal the following is obtained

$$\langle f_{\rm el} \rangle = \frac{1}{2} \epsilon^2 \left[ B \frac{k_z^2}{k^2} \langle \cos^2 k_z z \rangle \langle \cos^2 kx \rangle + K_1 k^2 \langle \sin^2 k_z z \rangle \langle \sin^2 kx \rangle \right] (4.23)$$

$$\langle f_{\rm mag} \rangle = -\frac{1}{2} \chi_a \mu_0 H^2 \langle n_x^2 \rangle = -\frac{1}{2} \chi_a \mu_0 H^2 \epsilon^2 \langle \sin^2 k_z z \rangle \langle \sin^2 kx \rangle.$$
(4.24)

The minimum in the total free energy occurs when  $k^2 = \pi/(\xi L)$ , where  $\xi^2 = \frac{K}{B}$ . This is the optimal wavelength of the distortion that reaches a compromise between bending the layers and keeping their spacing fixed. The critical magnetic field can be calculated from the condition that the elastic and the magnetic terms exactly cancel

$$\chi_{\rm a}\mu_0 H_{\rm c}^2 = \frac{2\pi B\xi}{L}.$$
(4.25)

The strength of the field required to see this transition is extremely strong, and the required sample must be extremely uniform. However, this transition can be seen in a simpler, mechanical context.

#### 4.1.5 Mechanical Helfrich-Hurault effect in smectic liquids

When a slab of SmA liquid crystal is put under mechanical tension by moving apart the bounding plates, then periodic undulations are observed in the layers as in the Helfrich-Hurault transition induced by a magnetic field. This effect is only observed under tension. To understand this effect it is necessary to improve the approximation to the layer spacing used in calculation of the free energy. If the layers are rotated by a small amount then the distance between the new layer position and the old layer position is  $\xi \cos n_x$ . There is thus a second order correction to the dilatation energy density of the layers

$$f_{\rm dil} = \frac{1}{2} B \left( \frac{\partial u}{\partial z} - \frac{1}{2} \left( \frac{\partial u}{\partial x} \right)^2 \right)^2.$$
(4.26)

The layer displacement can be broken up into two parts:  $u = \epsilon z + u_0(z, x)$ . The first part is the uniform displacement and the second part describes the undulation. Near the threshold  $u_0$  will be infinitesimal. Thus expanding the free energy density up to order  $u_0^2$  results in

$$f = \frac{1}{2}B\left(\epsilon^2 - \epsilon n_{\rm x}^2 + 2\epsilon \frac{\partial u_0}{\partial z}\right) + \frac{1}{2}K_1\left(\frac{\partial^2 u_0}{\partial x^2}\right)^2.$$
 (4.27)

The linear term in  $u_0$  gives zero on averaging over z. The resulting expression has the same form as the free energy in a magnetic field with the identification

$$-\frac{1}{2}\chi_a\mu_0 H^2 n_{\rm x}^2 = -\frac{1}{2}B\epsilon n_{\rm x}^2.$$
(4.28)

Thus a critical deformation can be identified, at which the undulations in the layers start to develop. The critical deformation is given by

$$\epsilon_{\rm c} = \frac{2\pi\xi}{L}.\tag{4.29}$$

Note that a similar buckling instability is found in numerous other fields including thermoplastics and structural geology [62].

#### 4.1.6 The physical properties of smectic elastomers

SmA and SmC elastomers have been aligned into monodomain samples via first making a polydomain elastomer film, loading with a small stress, heating into the isotropic state and then allowed to cool slowly into the smectic state [63, 64]. The alignment of these samples and the formation of the layers was confirmed by x-ray scattering data.

The elastic properties of these films show several interesting effects. Firstly, when the films are stretched in the plane of the layers, contraction only occurs in the perpendicular direction and not along the layer normal. Hence for small



Figure 4.3: The experimental results of [65] show that when the SmA elastomer is stretched perpendicular to the layer normal the sample width does not change, indicating that the Poisson ratios in the y and z directions are (1,0).

deformations where the Poisson ratios are defined, they take extreme values of (1,0) [65]. This is illustrated in Fig. 4.3.

When stretched parallel to the layer normal, smectic elastomers show a remarkably different response. In the experiments of Nishikawa and Finkelmann [66] the smectic elastomer film initially had a modulus  $3.2 \times 10^6 \text{Nm}^{-2}$ . The sample also contracted equally in the two perpendicular directions, that is it had Poisson ratios (1/2, 1/2). Once the strain reaches a value of approximately 3% the mechanical behaviour changes remarkably. The modulus drops to  $1.3 \times 10^5 \text{Nm}^{-2}$  and the sample immediately becomes opaque. It still maintains the same Poisson ratios, that is it keeps contracting equally in the two perpendicular directions. The modulus before threshold is comparable to that of the compression modulus *B* of layers of the liquid crystal SmA phase. After the threshold the modulus is comparable to the rubber modulus measured on stretching parallel to the layer planes. The elastic data for this experiment and photographs of the smectic elastomer film are shown in Fig. 4.4(a) and (b) respectively.

In the same paper Nishikawa and Finkelmann report x-ray scattering patterns of the smectic film as it is stretched along the layer normal. The x-ray scattering patterns show clear evidence for the onset of layer rotation at the threshold strain. However, there is a rapid loss of x-ray scattering intensity from the layer scattering peaks attributed to the melting of the smectic phase. These experimental features are returned to in §4.4 to compare them with the predictions of the model developed in §4.2.

Since large deformations are required to see the threshold behaviour in these samples, a non-linear model of a smectic elastomer is required.

An alternative method of measuring the elastic properties of smectic elastomer films was reported in [67]. In this case a smectic elastomer film is formed as a balloon across the end of a capillary tube. The pressure inside



Figure 4.4: a) The experimental results of [66] for a smectic elastomer stretched parallel to the layer normal, b) a photograph of the elastomer before the threshold (clear) and after (opaque).

the balloon can be altered and the change in radius measured yielding the stress strain characteristics of the film. In these experiments it was observed that in weakly coupled smectic elastomers there is no signature of the smectic layer system [68] and [69]. These systems are not considered here.

#### 4.1.7 Continuum model of a smectic elastomer

The elastic properties of smectic liquid crystals can be calculated for small deformations based on the continuum free energy. The terms that are included in this free energy are the sum of the contributions for the ordinary nematic, the ordinary smectic, and the elastomer. These different degrees of freedom are then coupled together. The different contributions to the continuum free energy will be pointed out here. A full discussion can be found in [46]. The contributions to the free energy density will be denoted as:  $f_{\rm elastic}$  for the uniaxial elastic energy density,  $f_{\rm nem}$  for the Frank elastic terms and the coupling between the elastomer and the director,  $f_{\rm smA}$  for the Landau-de Gennes smectic order terms and  $f_{\rm smA-el}$  for the terms pertaining to the coupling between the layers and the rubber matrix

$$f_{\text{elastic}} = C_1 (\mathbf{n} \cdot \underline{\epsilon} \cdot \mathbf{n})^2 + 2C_2 \operatorname{Tr}[\underline{\tilde{\epsilon}}] (\mathbf{n} \cdot \underline{\epsilon} \cdot \mathbf{n}) + C_3 \left( \operatorname{Tr}[\underline{\tilde{\epsilon}}] \right)^2 + 2C_4 [\mathbf{n} \times \underline{\epsilon} \times \mathbf{n}]^2 + 4C_5 [\mathbf{n} \times \underline{\epsilon} \cdot \mathbf{n}]^2.$$
(4.30)

In this equation  $\underline{\tilde{\epsilon}}$  denotes the symmetric part of the deformation tensor  $\underline{\lambda}$ , and  $\underline{\epsilon}$  denotes the same symmetric part after the non-volume preserving parts have been removed (i.e. it has been made traceless). Note  $C_1, C_4$  and  $C_5$  are of order  $\mu$  whereas  $C_3$  is of order the bulk modulus and  $C_2$  is smaller that  $\mu$ .

$$f_{\text{nem}} = \frac{1}{2}D_1 \left[ (v_{xz}^{(a)} - \delta n_x)^2 + (v_{yz}^{(a)} - \delta n_y)^2 \right]$$

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$$-D_2 \left[ (v_{xz}^{(a)} - \delta n_x) \epsilon_{xz} + (v_{yz}^{(a)} - \delta n_y) \epsilon_{yz} \right] + \frac{1}{2} K_1 (\operatorname{div} \delta \mathbf{n})^2 + \frac{1}{2} K_2 (\operatorname{curl} \delta \mathbf{n})^2 + \frac{1}{2} K_3 (\partial_z \delta \mathbf{n})^2 \qquad (4.31)$$

where  $v_{ij}^{(a)}$  is the antisymmetric part of the deformation tensor,  $\underline{\lambda}$ .

$$f_{\rm smA} = \frac{1}{2} \left( \tau |\psi|^2 + \frac{1}{2}\beta |\psi|^4 + g_{\parallel} |\partial_z \psi|^2 + g_{\perp} |(\nabla_{\perp} - iq_0 \delta \mathbf{n})\psi|^2 \right)$$
(4.32)

where  $\psi(\mathbf{r}) = |\psi(T)| e^{-iq_0 u(\mathbf{r})}$  is the smectic order parameter. The first gradient term expresses the rigidity of the smectic layers:  $B = g_{\parallel} q_0^2 |\psi|^2$  and the second gradient term expresses the coupling of the director to the layer normal.

$$f_{\rm smA-el} = \Lambda \left[ V_z(\mathbf{r}) - u(\mathbf{r}) \right]^2$$
  
 
$$\sim \Lambda \left[ V_z(0) - u(0) \right]^2 + \Lambda L^2 \sum_j \left[ \nabla_j u(0) - v_{zj} \right]^2$$
  
 
$$+ \Lambda \int [\tilde{u}(\mathbf{r}) - \tilde{V}_z(\mathbf{r})]^2 \qquad (4.33)$$

where u denotes the layer displacement,  $V_z$  denotes the displacement of the elastic matrix in the z direction  $(\mathbf{r} \to \mathbf{r} + \mathbf{V})$ ,  $v_{zj}$  is defined by the expansion of  $\mathbf{V}$ :  $V_j(\mathbf{r}) = V_j(0) + r_i v_{ji} + \tilde{V}_j$  and  $\tilde{u}(\mathbf{r})$  and  $\tilde{V}_z(\mathbf{r})$  denote the fluctuating components of the layer displacement and the matrix displacement in the z direction respectively. It is remarkable that the system size  $\mathcal{L}$  occurs in the second term. This term is a very rigid constraint which is derived and discussed below. This contribution to the free energy density is studied in [70].

The free energy terms outlined above are used in the continuum theory of smectic elastomers. To study the elastic properties of the network one can average over the nematic director position, and to study the nematic director one can average over the elastic degrees of freedom (see [46] for more details). In addition to the above terms the effects of the cross-links have also been considered close to the smectic-nematic transition. In elastomers the volume fraction of cross-links is much smaller than that of the backbone and mesogenic groups so the cross-links exist in a mesogenic environment. The cross-link's effect on the smectic order is to enhance smectic order and locally fix its phase. This has a free energy density contribution

$$f_{\rm RF} = \sum_{\alpha} \gamma |\psi(\mathbf{R}_{\alpha})| \cos \left\{ q_0 [z_{\alpha} - u(\mathbf{R}_{\alpha})] \right\}$$
(4.34)

where  $\mathbf{R}_{\alpha}$  is the position of the  $\alpha$ th cross-link point, and  $\gamma$  is the coupling constant. The effects of this term on the N-SmA transition have been studied in detail in [71].

The interplay of these free energy terms has been studied in [72], where it was reported that this coupling destroys the conditions required for soft nematic elasticity. It was also found that the smectic layer modulus is responsible for the large anisotropy found by Nishikawa and Finkelmann [66].

The undulation instability in SmA liquid single crystal elastomers has been studied using this continuum theory [73]. A technique very similar to that outlined in §4.1.4 was used to calculate the threshold strain and the critical wavenumber to compare with the experiments of [66]. The results obtained were  $10^{-3}$  cm $< \lambda_c < 10^{-2}$  cm (here  $\lambda_c$  refers to the length scale of the stripes not to the imposed strain) together with a threshold strain of  $\epsilon_c \approx \frac{1}{2} \frac{C_1}{B} \approx 1\%$ .

# 4.2 Microscopic, finite deformation model of the smectic elastomer

A microscopic model of a nematic elastomer can be formulated from analysing the probability distribution of the occurrence of particular end-to-end spans of a polymer. This average end-to-end distribution gives the average properties of all chains, and is used as a representative of the elastomer as a whole. This approach works particularly well for nematic elastomers.

For a smectic elastomer both the span of a polymer chain and its position relative to the smectic layers are significant. This interaction between the polymer chains and the smectic order is modelled here as follows. The smectic order presents a series of potential wells, forming a corrugated potential, in which the cross-link points sit as illustrated in Fig. 4.5. Deviation of the crosslink points from these wells is penalised because it disrupts the smectic order of the layers, and because of the steric repulsion between the cross-link point and the mesogens.

The probability distribution as a function of the positions of the ends of the chain,  $\mathbf{R}_1$  and  $\mathbf{R}_2$  is given by

$$P_{0}(\mathbf{R}_{1}, \mathbf{R}_{2}) \propto \exp\left\{-\frac{3}{2L}\mathbf{R}_{12}^{T} \cdot \underline{\ell}_{0}^{-1} \cdot \mathbf{R}_{12} + 2\beta \cos(\alpha - \mathbf{q}_{0}^{T} \cdot \mathbf{R}_{1}) + 2\beta \cos(\alpha - \mathbf{q}_{0}^{T} \cdot \mathbf{R}_{2})\right\}$$

$$\approx \sum_{n,m} \exp\left\{-\frac{3}{2L}\mathbf{R}_{12}^{T} \cdot \underline{\ell}_{0}^{-1} \cdot \mathbf{R}_{12} - \beta(2\pi n - \mathbf{q}_{0}^{T} \cdot \mathbf{R}_{1} + \alpha)^{2} - \beta(2\pi m - \mathbf{q}_{0}^{T} \cdot \mathbf{R}_{2} + \alpha)^{2}\right\}$$

$$(4.36)$$

$$= \sum_{m,n} P_{0(m,n)}(\mathbf{R}_1, \mathbf{R}_2), \qquad (4.37)$$

where  $\mathbf{R}_{12} = \mathbf{R}_1 - \mathbf{R}_2$ , *L* is the arc length of a polymer,  $\mathbf{q}_0$  is the wave vector of the smectic layers,  $\beta$  defines the strength of the potential in which the layers are sitting and we use the definition

$$\underline{\underline{\ell}}_{0} = \ell_{\perp} \underline{\underline{\delta}} + (\ell_{\parallel} - \ell_{\perp}) \mathbf{n}_{0} \mathbf{n}_{0}^{T}$$

$$(4.38)$$



Figure 4.5: The figure shows an illustration of the microscopic model of a smectic elastomer, in which the cross-link points sit in a periodic potential as a result of the smectic ordering. Note the smectogens are not shown for clarity.

Note that this probability distribution does not penalise the polymer chain for moving across layers (see for example [74]). This effect could be partially taken into account by using a different value of the anisotropy, r. It is assumed, without loss of generality, that the first layer in the system sits at the origin  $\alpha = 0$ , i.e. there is no displacement w.r.t. the background. In Eq. (4.36) the limit of  $\beta \gg 1$  has been taken and the probability distribution written as a sum over all the layers labelled by n and m in which the two different ends can sit. The cosine functions have been written as a power series and, since  $\beta \gg 1$ , only the first term taken. The summation sign can then be brought down from the exponent because since,  $\beta$  is so large, all the wells of the potential are effectively decoupled. This expression is useful in calculating the quenched average since each cross-link point has to be quenched into a particular layer. A one dimensional version of this probability distribution is shown in Fig. 4.6, for  $P_{0(m,n)}(0, \mathbf{R}_2)$  where  $\mathbf{R}_2$  is parallel to  $\mathbf{q}_0$ .

It is useful to convert to centre of mass and span coordinates as follows

$$\mathbf{P} = \frac{1}{2}(\mathbf{R}_1 + \mathbf{R}_2) \tag{4.39}$$



Figure 4.6: An illustration of the smectic chain probability distribution:  $f(x) \propto e^{-\frac{x^2}{10}-20\cos(2x)}$ . Each one of the peaks is separated so this function can be replaced by a sum over Gaussian peak shapes displaced from the origin.

$$\mathbf{Q} = (\mathbf{R}_1 - \mathbf{R}_2) \tag{4.40}$$

$$x = (n+m) \tag{4.41}$$

$$y = (n-m).$$
 (4.42)

Any change in the Jacobian from this change of variables for the following integrals is cancelled out in the normalisation factor. The exponent in Eq. (4.36)then contains the following

$$-\frac{3}{2L}\mathbf{Q}\cdot\underline{\underline{\ell}}_{0}^{-1}\cdot\mathbf{Q}-\frac{1}{2}\beta(2\pi y-\mathbf{q}_{0}^{T}\cdot\mathbf{Q})^{2}-2\beta(\pi x-\mathbf{q}_{0}^{T}\cdot\mathbf{P})^{2}.$$
(4.43)

When the smectic elastomer is formed deep in the smectic phase, the specific layer that the cross-link points are in will be a quenched variable, that is both x and y are quenched variables. When the cross-links are formed the span of the polymer,  $\mathbf{Q}$ , is quenched in, and since both the ends of the chain are fixed into a network then the coordinate  $\mathbf{P}$  must also be quenched. To calculate the free energy density of the system after deforming the matrix by  $\underline{\lambda}$ , translating the matrix by  $\mathbf{b}$  and translating the smectic layers by  $\mathbf{t}$  the following quenched average must be performed

$$f = -k_B T \int d\mathbf{P} \int d\mathbf{Q} \sum_x \sum_y P_{0(x,y)}(\mathbf{P}, \mathbf{Q}) \ln P_{(x,y)}(\underline{\lambda} \cdot \mathbf{P} + \mathbf{b}, \underline{\lambda} \cdot \mathbf{Q})$$
$$= \frac{k_B T}{\mathcal{N}} \int \int d\mathbf{P} d\mathbf{Q} \sum_x \sum_y \exp\left\{-\frac{3}{2L}\mathbf{Q} \cdot \underline{\ell}_0^{-1} \cdot \mathbf{Q} - \frac{1}{2}\beta(2\pi y - \mathbf{q}_0^T \cdot \mathbf{Q})^2\right\}$$

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$$-2\beta(\pi x - \mathbf{q}_{0}^{T} \cdot \mathbf{P})^{2} \bigg\} \cdot \bigg[ \frac{3}{2L} \mathbf{Q}^{T} \cdot \underline{\lambda}^{T} \cdot \underline{\ell}^{-1} \cdot \underline{\lambda} \cdot \mathbf{Q} + \frac{\beta}{2} (2\pi y - \mathbf{q}^{T} \cdot \underline{\lambda} \cdot \mathbf{Q})^{2} +2\beta(\mathbf{q}^{T} \cdot \mathbf{t} + \pi x - \mathbf{q}^{T} \cdot (\underline{\lambda} \cdot \mathbf{P} + \mathbf{b}))^{2} \bigg], \qquad (4.44)$$

where  $\mathcal{N}$  is the normalisation constant for the probability distribution. This integral can be separated out into an integral over  $\mathbf{P}$  and an integral over  $\mathbf{Q}$ . These two integrals are now performed one at a time, dealing first with the  $\mathbf{P}$  integral

$$\frac{1}{\mathcal{N}} \int d\mathbf{P} \sum_{x} \exp\left\{-2\beta (\mathbf{q}_{0}^{T} \cdot \mathbf{P} - \pi x)^{2}\right\} \left[2\beta (\mathbf{q}^{T} \cdot \mathbf{t} + \pi x - \mathbf{q}^{T} \cdot (\underline{\lambda} \cdot \mathbf{P} + \mathbf{b}))^{2}\right].$$

To perform the sum over x, note that  $\beta \gg 1$  so that it is a very narrow Gaussian distribution in x. As a result the sum over x picks out a particular value of  $x = \frac{1}{\pi} \mathbf{q}_0^T \cdot \mathbf{P}$ . The resulting expression is

$$\frac{1}{\mathcal{N}} \int d\mathbf{P} \left( 2\beta \left[ \mathbf{q}^T \cdot \mathbf{t} - \mathbf{q}^T \cdot (\underline{\lambda} \cdot \mathbf{P} + \mathbf{b}) + \mathbf{q}_0^T \cdot \mathbf{P} \right]^2 \right) = 2\beta \left[ (\mathbf{q}^T \cdot (\mathbf{t} - \mathbf{b}))^2 + \frac{\mathcal{L}_i^2}{12} (\mathbf{q}^T \cdot \underline{\lambda} - \mathbf{q}_0^T)_i^2 \right], \qquad (4.45)$$

on completing the **P** integral as well. This expression, though an energy density, contains the size of the system in the *i*th direction,  $\mathcal{L}_i$ , since the integral is not governed. This is because if the layers were to rotate relative to the network in such a way as to not be commensurate with the cross-link points, then all of the cross-links throughout the whole sample would be displaced from the minimum in the smectic potential by an amount scaling with the lineal dimension of the system, resulting in a massive energy cost. This term can be made zero (minimised) only if  $\mathbf{q}^T \cdot \underline{\lambda}$  and  $\mathbf{q}_0^T$  are parallel. Their magnitudes can be made to agree by modifying *d* which is penalised separately by the modulus *B*. Thus the rotation of the layers with the applied deformation is a rigid constraint

$$\mathbf{q} = \underline{\lambda}^{-T} \cdot \mathbf{q}_0 \tag{4.46}$$

The first term of Eq. (4.45) describes the penalty associated with a mismatch between the smectic layers and the matrix arising from translation of one relative to the other. These two terms arise in the continuum model of layer-matrix coupling in Eq. (4.33) and in [70].

The integral over the variable  $\mathbf{Q}$  is now considered

$$\frac{1}{\mathcal{N}} \int d\mathbf{Q} \sum_{y} \exp\left\{-\frac{3}{2L}\mathbf{Q} \cdot \underline{\underline{\ell}}_{0}^{-1} \cdot \mathbf{Q} - \frac{1}{2}\beta(2\pi y - \mathbf{q}_{0}^{T} \cdot \mathbf{Q})^{2}\right\}$$
$$\cdot \left[\frac{3}{2L}\mathbf{Q}^{T} \cdot \underline{\underline{\lambda}}^{T} \cdot \underline{\underline{\ell}}^{-1} \cdot \underline{\underline{\lambda}} \cdot \mathbf{Q} + \frac{\beta}{2}(2\pi y - \mathbf{q}^{T} \cdot \lambda \cdot \mathbf{Q})^{2}\right]$$
(4.47)

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The same procedure as that used for the previous integral is used; first the sum over y is evaluated picking out the particular value  $y = \frac{1}{2\pi} \mathbf{q}_0^T \cdot \mathbf{Q}$ , and then the integral over  $\mathbf{Q}$  performed. After carrying out the sum over y the result is

$$\frac{1}{\mathcal{N}} \int d\mathbf{Q} \exp\left\{-\frac{3}{2L}\mathbf{Q} \cdot \underline{\ell}_{0}^{-1} \cdot \mathbf{Q}\right\}$$
$$\cdot \left[\frac{3}{2L}\mathbf{Q}^{T} \cdot \underline{\lambda}^{T} \cdot \underline{\ell}^{-1} \cdot \underline{\lambda} \cdot \mathbf{Q} + \frac{\beta}{2}(\mathbf{q}_{0}^{T} \cdot \mathbf{Q} - \mathbf{q}^{T} \cdot \underline{\lambda} \cdot \mathbf{Q})^{2}\right] \qquad (4.48)$$

The integral over  $\mathbf{Q}$  can then be performed. The first term results in the usual trace formula expression. The second term can be evaluated using the average:  $\langle \mathbf{Q}^T \mathbf{Q} \rangle = \frac{1}{3} L \underline{l}_0$ . The result is then

$$\frac{L\beta}{6} \operatorname{Tr} \left[ \underline{\ell}_0 \cdot \left( \mathbf{q}_0 \cdot \mathbf{q}_0^T + \underline{\lambda}^T \cdot \mathbf{q} \cdot \mathbf{q}^T \cdot \underline{\lambda} - \underline{\lambda}^T \cdot \mathbf{q} \cdot \mathbf{q}_0^T - \mathbf{q}_0 \cdot \mathbf{q}^T \cdot \underline{\lambda} \right) \right]$$
(4.49)

This expression can be simplified by using the following definition of  $\underline{\ell}_0$  given in Eq. (4.38). Since  $\mathbf{n}_0$  and  $\mathbf{q}_0$  are parallel this simplifies to

$$\frac{L\beta}{6} \operatorname{Tr}\left[\left(\frac{2\pi}{d_0}\right)^2 \ell_{\parallel} \underline{\delta} + \underline{\ell}_0 \cdot \underline{\lambda}^T \cdot \mathbf{q} \cdot \mathbf{q}^T \cdot \underline{\lambda} - \underline{\lambda}^T \cdot \mathbf{q} \cdot \mathbf{n}_0^T \frac{2\pi}{d_0} \ell_{\parallel} - \frac{2\pi}{d_0} \ell_{\parallel} \mathbf{n}_0 \cdot \mathbf{q}^T \cdot \underline{\lambda}\right]$$

This expression can be rearranged into

$$\frac{L\beta}{6} \left( (\underline{\ell}_0^{1/2} \cdot \underline{\lambda}^T \cdot \mathbf{q}) - \frac{2\pi}{d_0} \mathbf{n}_0 \sqrt{\ell_{\parallel}} \right)^2 \tag{4.50}$$

It can be seen from this expression that this constraint penalises  $\mathbf{q}$  if it is not equal to  $\underline{\lambda}^{-T} \cdot \mathbf{q}_0$ . The resulting terms from the  $\mathbf{Q}$  integral are thus

$$\frac{1}{2} \left\{ \operatorname{Tr}\left[\underline{\underline{\lambda}} \cdot \underline{\ell}_{0} \cdot \underline{\underline{\lambda}}^{T} \cdot \underline{\ell}^{-1}\right] + \frac{L\beta}{3} \left( (\underline{\underline{\ell}}_{0}^{1/2} \cdot \underline{\underline{\lambda}}^{T} \cdot \mathbf{q}) - \frac{2\pi}{d_{0}} \mathbf{n}_{0} \sqrt{\ell_{\parallel}} \right)^{2} \right\}$$
(4.51)

Thus our final microscopic model for the smectic liquid crystal elastomer is of the form

$$f = \frac{\mu}{2} \operatorname{Tr} \left[ \underline{\lambda} \cdot \underline{\ell}_0 \cdot \underline{\lambda}^T \cdot \underline{\ell}^{-1} \right] + \frac{1}{2} B \left( \frac{d}{d_0} - 1 \right)^2, \qquad (4.52)$$

where  $\mu = k_B T n_s$ . The second term is the layer compression penalty from the smectic free energy density. The identification of the layer normal, **q** with the director, **n**, is rigidly made here, that is in the notation of [72]  $b_{\perp} \to \infty$ . The constraint:  $\mathbf{q} = \underline{\lambda}^{-T} \cdot \mathbf{q}_0$  is rigidly imposed.

## 4.2. MICROSCOPIC, FINITE DEFORMATION MODEL OF THE SMECTIC ELASTOMER

#### 4.2.1 Affine layer model

The constraint on the smectic layer normal can be understood geometrically, by calculating how the layer deforms if it moves affinely with the matrix. Consider the affine deformation of a system such that

$$\mathbf{x} \to \underline{\lambda} \cdot \mathbf{x}. \tag{4.53}$$

To calculate the new layer normal take two vectors that lie in the plane of the smectic layer and calculate how they deform with  $\underline{\lambda}$ . Then take the cross product of these two vectors to find the new normal, **n**. This is illustrated in Fig. 4.7.



Figure 4.7: The figure shows how the normal to the layer deforms when the vectors in the layer deform according to  $\mathbf{x} \to \underline{\lambda} \cdot \mathbf{x}$ .

The new normal is thus given by

$$\mathbf{n} = \frac{(\underline{\lambda} \cdot \mathbf{k}) \times (\underline{\lambda} \cdot \mathbf{m})}{|(\underline{\lambda} \cdot \mathbf{k}) \times (\underline{\lambda} \cdot \mathbf{m})|}$$
(4.54)

This expression can be rewritten in a more familiar form by using the properties of the cofactor matrix. The matrix of cofactors can be written as  $\det(\underline{\lambda})\underline{\lambda}^{-T}$ , i.e. the determinant multiplied by the inverse transpose of the matrix. The determinant can be calculated from the expression

$$\det(\underline{\lambda})\epsilon_{ijk} = \epsilon_{\alpha\beta\gamma}\lambda_{\alpha i}\lambda_{\beta j}\lambda_{\gamma k}.$$
(4.55)

The deformations considered here are volume conserving deformations so  $det(\underline{\lambda}) = 1$ . Multiplying from the right by  $(\underline{\lambda}^{-1})_{kp}$  gives

$$\epsilon_{\alpha\beta p}\lambda_{\alpha i}\lambda_{\beta j} = \lambda_{kp}^{-1}\epsilon_{ijk} = \lambda_{pk}^{-T}\epsilon_{ijk}.$$
(4.56)

Substituting this expression into that for **n** above and setting  $\mathbf{k} \times \mathbf{m} = \mathbf{n}_0$ , results in the following

$$\mathbf{n} = \frac{\underline{\lambda}^{-T} \cdot \mathbf{n}_0}{|\underline{\lambda}^{-T} \cdot \mathbf{n}_0|}.$$
(4.57)

From this expression it is clear that the layer normal should deform according to the transpose of the inverse matrix, i.e. the matrix of cofactors.

The layer spacing for this affine model can also be calculated. Consider two adjacent planes in the deformed system, the first of which contains the point  $\mathbf{p}$  and the second contains the point  $\mathbf{q}$  as illustrated in Fig. 4.8. From



Figure 4.8: The figure shows the required vectors to calculate the spacing between the layers as the elastomer is deformed.

Fig. 4.8 it is clear that

$$\mathbf{p} = \underline{\lambda} \cdot \mathbf{x} \tag{4.58}$$

$$\mathbf{q} = \underline{\lambda} \cdot \mathbf{x} + d_0 \underline{\lambda} \cdot \mathbf{n}_0 \tag{4.59}$$

The displacement between these points resolved along the layer normal gives the spacing between the smectic layers

$$d = (\mathbf{q} - \mathbf{p}) \cdot \mathbf{n} \tag{4.60}$$

$$= d_0(\underline{\lambda} \cdot \mathbf{n}_0) \cdot \mathbf{n}. \tag{4.61}$$

Assuming that the normal is initially parallel to the z axis then the layer spacing can be written as

$$\frac{d}{d_0} = (\underline{\lambda} \cdot \mathbf{n}_0) \cdot \frac{\underline{\lambda}^{-T} \cdot \mathbf{n}_0}{|\epsilon_{ijk} \lambda_{jx} \lambda_{ky}|}$$
(4.62)

$$= \frac{1}{|\epsilon_{ijk}\lambda_{jx}\lambda_{ky}|} \tag{4.63}$$

where Eq. (4.54) has been used to substitute for **n** and the denominator rewritten by identifying  $\mathbf{k} = \hat{\mathbf{x}}$  and  $\mathbf{m} = \hat{\mathbf{y}}$ . The cross product expression that produces the new layer normal can be thought of geometrically as calculating the distance along the normal between two planes, or equivalently as calculating the area of the plane. These two statements are equivalent because the system is volume conserving.

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#### 4.3 Finite deformation examples

The elastic properties of a smectic elastomer are now explored for various different deformations using the free energy density

$$f = \frac{1}{2}\mu \operatorname{Tr}\left[\underline{\underline{\lambda}} \cdot \underline{\underline{\ell}}_0 \cdot \underline{\underline{\lambda}}^T \cdot \underline{\underline{\ell}}^{-1}\right] + \frac{1}{2}B\left(\frac{d}{d_0} - 1\right)^2, \qquad (4.64)$$

which was derived in §4.2. First the case where the layer spacing is rigidly fixed  $(B \to \infty)$  is examined in §4.3.1, then this constraint is relaxed in §4.3.3. The four cases depicted in Fig. 4.9 are examined.



Figure 4.9: Imposed deformation; a) stretching parallel to the layer normal, b) stretching perpendicular to the layer normal, c) shearing the layers in their plane and d) shear out of the planes.

#### 4.3.1 $B \rightarrow \infty$

In this section the layer modulus is so large that there are effectively two constraints to incorporate into the calculation: constant volume and constant layer spacing. Note that in the following section the director and the layer spacing can be calculated in the following way: take the initial director along z, that is  $\mathbf{n}_0 = \hat{\mathbf{z}}$  and thus from Eq. (4.57) the director is given by

$$n_i = \lambda_{iz}^{-T}.\tag{4.65}$$

Since the layer spacing does not change there is no need to calculate the normalisation factor. The layer spacing can then be calculated from the same cofactor elements that appear in this expression for the director

$$\frac{d}{d_0} = \frac{1}{\left(\lambda_{iz}^{-T} \lambda_{iz}^{-T}\right)^{1/2}}.$$
(4.66)

In the following sections  $d/d_0 = 1$  because of the large *B* value so the above equation provides a method for calculating this constraint. The convention that  $\lambda$  denotes the imposed element of the deformation matrix is also adopted.

#### Imposed $\lambda_{zz}$

In the first case illustrated in Fig. 4.9 a), the following form of the deformation tensor will be considered

$$\underline{\underline{\lambda}} = \begin{pmatrix} \lambda_{\rm xx} & 0 & 0\\ 0 & \lambda_{\rm yy} & 0\\ \lambda_{\rm zx} & 0 & \lambda \end{pmatrix}.$$
(4.67)

The shear component  $\lambda_{zx}$  is allowed to relax because, when the layers are constrained to move with the matrix, it allows rotation away from the stretch axis. The constraints of constant volume and constant layer spacing can be expressed respectively as

$$1 = \lambda_{\rm xx} \lambda_{\rm yy} \lambda \tag{4.68}$$

$$1 = \lambda_{yy}^2 (\lambda_{xx}^2 + \lambda_{zx}^2). \tag{4.69}$$

The director can be calculated from Eq. (4.57) using the tensor  $\underline{\lambda}$  given in Eq. (4.67). The resulting director orientation can be written as

$$\mathbf{n} = (-\lambda_{yy}\lambda_{zx}, 0, \lambda_{xx}\lambda_{yy}). \tag{4.70}$$

Note that this is normalised because of the constraint of constant layer spacing, Eq. (4.69). Substituting these expressions into the free energy density results in

$$f = \frac{1}{2}\mu \left\{ 1 + \lambda_{\rm xx}^2 \lambda^2 + \frac{1}{\lambda_{\rm xx}^2 \lambda^2} + r\left(\lambda^2 - 1\right) \right\}.$$
 (4.71)

This expression can be minimized w.r.t.  $\lambda_{xx}$  and has a minimum when  $\lambda_{xx} = \frac{1}{\lambda}$ . The resulting relaxed deformation gradient tensor and director are given by

$$\underline{\underline{\lambda}} = \begin{pmatrix} \frac{1}{\lambda} & 0 & 0\\ 0 & 1 & 0\\ \frac{\sqrt{\lambda^2 - 1}}{\lambda} & 0 & \lambda \end{pmatrix} \quad ; \quad \mathbf{n} = \left(-\frac{\sqrt{\lambda^2 - 1}}{\lambda}, 0, \frac{1}{\lambda}\right) \tag{4.72}$$

Note that this deformation is exactly that required to preserve the areas of the layers, as can be seen by looking at the projected area and comparing it to  $\mathbf{n} \cdot \mathbf{z}$ . Using this deformation and director, the free energy is given by

$$f = \frac{1}{2}\mu \left\{ 3 + r(\lambda^2 - 1) \right\}.$$
 (4.73)

This expression for the free energy density is pathological in that it does not have zero slope at  $\lambda = 1$ . However at this point the material cannot be compressed along the layer normal due to the infinite value of B (we can never achieve  $\lambda < 1$ ). The free energy thus does have a minimum at  $\lambda = 1$  although it is not smooth there. This is illustrated in Fig. 4.10 together with diagrams of the deformed layers at the different deformation values. Also note that the transition to the sheared state is not possible in compression because the layer spacing in the **z** direction can only be increased by a  $\lambda_{zx}$  shear.


Figure 4.10: The figure shows the free energy density of a smectic elastomer with  $B \to \infty$  as a  $\lambda_{zz}$  deformation is applied, together with illustrations of the deformed state at  $\lambda_{zz} = 1$  and 1.3.

## Imposed $\lambda_{xx}$

This deformation is illustrated in Fig. 4.9 b). For a stretch in the plane the following deformation tensor is used

$$\underline{\underline{\lambda}} = \begin{pmatrix} \lambda & 0 & \lambda_{\rm xz} \\ 0 & \lambda_{\rm yy} & 0 \\ \lambda_{\rm zx} & 0 & \lambda_{\rm zz} \end{pmatrix}.$$
(4.74)

The director in this case is given by

$$\mathbf{n} = (-\lambda_{yy}\lambda_{zx}, 0, \lambda_{yy}\lambda) \tag{4.75}$$

Note that to move the director in the xz plane the component  $\lambda_{zx}$  must be included. A  $\lambda_{xz}$  alone is not enough. The constraints of constant volume and layer spacing are given by

$$1 = \lambda \lambda_{\rm vv} \lambda_{\rm zz} - \lambda_{\rm vv} \lambda_{\rm zx} \lambda_{\rm xz} \tag{4.76}$$

$$1 = \lambda_{yy}^2 (\lambda_{zx}^2 + \lambda^2). \tag{4.77}$$

The free energy is given by the following expression

$$f = \frac{1}{2}\mu \frac{1}{\lambda_{zx}^2 + \lambda^2} \left( \lambda_{zx}^2 \left( \lambda_{yy}^2 + r\lambda_{zz}^2 + \lambda_{zx}^2 + \lambda_{xz}^2 \right) + 2(r-1)\lambda_{zz}\lambda_{zx}\lambda_{xz}\lambda + \left( \lambda_{yy}^2 + \lambda_{zz}^2 + 2\lambda_{zx}^2 + r\lambda_{xz}^2 \right)\lambda^2 + \lambda^4 \right).$$

$$(4.78)$$

The two constraints can be used to eliminate two of the variables. The choice of which variables to eliminate must be make with care so that the resulting deformation matrix still incorporates the constraints. The variables  $\lambda_{yy}$  and  $\lambda_{zz}$  are eliminated here.

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On elimination the free energy density is given by

$$f = \frac{1}{2}\mu \left\{ 1 + r\lambda_{xz}^2 + \lambda^2 + \lambda_{zx}^2 + \frac{1}{\lambda_{zx}^2 + \lambda^2} + \frac{2r\lambda_{xz}\lambda_{zx}}{\lambda^2}\sqrt{\lambda_{zx}^2 + \lambda^2} + \frac{\lambda_{zx}^2 r \left(1 + \lambda_{xz}^2\right)}{\lambda^2} \right\}.$$

$$(4.79)$$

This can be minimized w.r.t  $\lambda_{xz}$  and  $\lambda_{zx}$ . The first of these yields the expression

$$\lambda_{\rm xz} = -\frac{\lambda_{\rm zx}}{\sqrt{\lambda_{\rm zx}^2 + \lambda^2}}.\tag{4.80}$$

On substituting this into the expression obtained after minimisation w.r.t  $\lambda_{zx}$  we obtain the following equation

$$\lambda^2 \lambda_{\text{zx}} \left( \left( -1 + \lambda_{\text{zx}}^2 + \lambda^2 \right) \sqrt{\lambda_{\text{zx}}^2 + \lambda^2} \left( 1 + \lambda_{\text{zx}}^2 + \lambda^2 \right) = 0.$$
 (4.81)

From this equation it is clear that the following real solutions for  $\lambda_{zx}$  are obtained

$$\lambda_{\rm zx} = \pm \sqrt{1 - \lambda^2}, 0 \tag{4.82}$$

The first of these solutions is only valid for  $\lambda < 1$  and gives  $\lambda_{xz} = -\lambda_{zx}$ ,  $\lambda_{yy} = 1$ ,  $\lambda_{zz} = \lambda$ . In this solution  $\underline{\lambda}$  corresponds to a rotation about the y axis. This solution is disregarded here and the second,  $\lambda_{zx} = 0$ , is examined. From this result it follows that the director does not rotate when a stretch in the plane of the layers is applied. The remaining components in this case, and the free energy density are given by

$$\lambda_{yy} = \frac{1}{\lambda} \tag{4.83}$$

$$\lambda_{zz} = 1 \tag{4.84}$$

$$f = \frac{1}{2}\mu \left\{ \lambda^2 + \frac{1}{\lambda^2} + 1 \right\}.$$
 (4.85)

The Poisson ratios of the material in this configuration are of interest experimentally. In this case the Poisson ratios are (1,0) in the (y,z) directions respectively. Note that since the material is incompressible the sum of the Poisson ratios must be 1.

### Imposed $\lambda_{xz}$

For an imposed  $\lambda_{xz}$ , as shown in Fig. 4.9 c), it is not immediately clear how general a deformation matrix is required. Initially an upper triangular deformation matrix is considered here, and followed by a more general type of deformation matrix

$$\underline{\underline{\lambda}} = \begin{pmatrix} \lambda_{\rm xx} & 0 & \lambda \\ 0 & \lambda_{\rm yy} & 0 \\ 0 & 0 & \lambda_{\rm zz} \end{pmatrix}.$$
(4.86)

### 4.3. FINITE DEFORMATION EXAMPLES

The constraints of volume conservation and constant layer spacing are then

$$1 = \lambda_{xx}\lambda_{yy}\lambda_{zz}$$
(4.87)  

$$1 = \lambda_{xy}^{2}\lambda_{yy}^{2}.$$
(4.88)

$$l = \lambda_{xx}^2 \lambda_{yy}^2. \tag{4.88}$$

In this case the director remains parallel to the z axis throughout the deformation, and the free energy density is

$$f = \frac{1}{2}\mu \left\{ 1 + \frac{1}{\lambda_{xx}^2} + \lambda_{xx}^2 + r\lambda^2 \right\}.$$
 (4.89)

On minimising w.r.t.  $\lambda_{xx}$  it follows that  $\lambda_{xx}^2 = 1$ . Substituting this back into the free energy density

$$f = \frac{1}{2}\mu \left\{ 3 + r\lambda^2 \right\}.$$
 (4.90)

This has a minimum at  $\lambda = 0$  as expected for a shear deformation.

Note that for the slightly more general deformation

$$\underline{\underline{\lambda}} = \begin{pmatrix} \lambda_{\mathrm{xx}} & 0 & \lambda \\ 0 & \lambda_{\mathrm{yy}} & 0 \\ \lambda_{\mathrm{zx}} & 0 & \lambda_{\mathrm{zz}} \end{pmatrix} \quad ; \quad \mathbf{n} = (-\lambda_{\mathrm{zx}}\lambda_{\mathrm{yy}}, 0, \lambda_{\mathrm{xx}}\lambda_{\mathrm{yy}}) \,. \tag{4.91}$$

then the minimum energy solution corresponds to a rotation of the elastomer by 90°.

## Imposed $\lambda_{zx}$

This deformation is illustrated in Fig. 4.9 d). Whilst it is possible to use a very general deformation tensor, here a lower triangular form is used [Allowing a  $\lambda_{xz}$ component results in the elastomer rotating by  $90^{\circ}$  so that it is experiencing an effective pure  $\lambda_{xz}$  deformation].

$$\underline{\underline{\lambda}} = \begin{pmatrix} \lambda_{\rm xx} & 0 & 0\\ 0 & \lambda_{\rm yy} & 0\\ \lambda & 0 & \lambda_{\rm zz} \end{pmatrix}$$
(4.92)

The director is given by

$$\mathbf{n} = (-\lambda \lambda_{yy}, 0, \lambda_{xx} \lambda_{yy}).$$
(4.93)

The volume conservation and layer spacing constraints are now given by

$$1 = \lambda_{\rm xx} \lambda_{\rm yy} \lambda_{\rm zz} \tag{4.94}$$

$$1 = \lambda_{yy}^2 (\lambda_{xx}^2 + \lambda^2). \tag{4.95}$$

These two constraints can be used to eliminate  $\lambda_{yy}$  and  $\lambda_{zz}$  from the free energy density. The resulting expression for the free energy density is

$$f = \frac{1}{2}\mu \left\{ 1 + \lambda_{\rm xx}^2 + \lambda^2 + \frac{r\lambda^2}{\lambda_{\rm xx}^2} + \frac{1}{\lambda_{\rm xx}^2 + \lambda^2} \right\}.$$
 (4.96)

Whilst the equation resulting from minimising this equation w.r.t.  $\lambda_{xx}$  can be solved analytically, it is a quartic in  $\lambda_{xx}^2$  so the solution is algebraically complicated. For illustrative purposes a particular numerical solution is calculated here, using the simplex method available in the NAG library (E04ccF). From



Figure 4.11: The figure shows the three relaxed components of the deformation tensor, and the cosine of the angle that the director makes with the z axis as a function of imposed shear  $\lambda = \lambda_{zx}$ , for the case of a side chain system with anisotropy r = 2.3.

Fig. 4.11 it is clear that on shearing the system it contracts in the y direction and extends in both the z and x directions to accommodate the rigid smectic planes. An illustration of this is shown in Fig. 4.12.



Figure 4.12: The figure illustrates the different stages of shear of a sample with r = 2.0 for  $\lambda_{zx}$  taking the values: a) 0.1, b) 0.2, c) 0.3, d) 0.4, e) 0.5, and f) 0.6.

## 4.3.2 Fundamental deformations for infinite B

Of the deformations considered above only two are fundamental to the elasticity of a smectic elastomer: the  $\lambda_{xx}$  and the  $\lambda_{xz}$  deformation. To illustrate this point the above deformation, imposed  $\lambda_{zx}$ , is now decomposed into these two deformations plus a rotation.

$$\underline{\lambda} = \underline{W} \cdot \underline{D} \tag{4.97}$$

where

$$\underline{\underline{W}} = \begin{pmatrix} \cos\gamma & 0 & \sin\gamma \\ 0 & 1 & 0 \\ -\sin\gamma & 0 & \cos\gamma \end{pmatrix} \quad ; \quad \underline{\underline{D}} = \begin{pmatrix} 1 & 0 & \lambda_{xz} \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \lambda_{xx} & 0 & 0 \\ 0 & \frac{1}{\lambda_{xx}} & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

With these definitions it is found that the director orientation is given by

$$\mathbf{n} = (\sin\gamma, 0, \cos\gamma),\tag{4.98}$$

and the free energy density is

$$f = \frac{1}{2}\mu \left( 1 + \lambda_{\rm xx}^2 + \frac{1}{\lambda_{\rm xx}^2} + r\lambda_{\rm xz}^2 \right).$$
(4.99)

To compare this system with the imposed  $\lambda_{zx}$  deformation considered above, set  $\tan \gamma = -\lambda_{xz}$  which results in the deformation tensor

$$\underline{\lambda} = \begin{pmatrix} \frac{\lambda_{\text{xx}}}{\sqrt{1+\lambda_{\text{xz}}^2}} & 0 & 0\\ 0 & \frac{1}{\lambda_{\text{xx}}} & 0\\ \frac{\lambda_{\text{xx}}\lambda_{\text{xz}}}{\sqrt{1+\lambda_{\text{xz}}^2}} & 0 & \sqrt{1+\lambda_{\text{xz}}^2} \end{pmatrix}.$$
(4.100)

Since  $\lambda_{zx}$  is imposed in the reference frame, then  $\lambda$  obeys the relation

$$\lambda = \frac{\lambda_{\rm xx} \lambda_{\rm xz}}{\sqrt{1 + \lambda_{\rm xz}^2}}.\tag{4.101}$$

We can use this relation to eliminate  $\lambda_{xz}$  and obtain the following deformation tensor

$$\underline{\underline{\lambda}} = \begin{pmatrix} \sqrt{\lambda_{xx}^2 - \lambda^2} & 0 & 0\\ 0 & \frac{1}{\lambda_{xx}} & 0\\ \lambda & 0 & \frac{\lambda_{xx}}{\sqrt{\lambda_{xx}^2 - \lambda^2}} \end{pmatrix}.$$
(4.102)

An effective  $\lambda_{xx}$  is now defined  $\alpha = \sqrt{\lambda_{xx}^2 - \lambda^2}$  so as to compare with the deformation of  $\lambda_{zx}$  imposed in the reference frame. The same form for the free energy density is obtained, just as in Eq. (4.96)

$$f = \frac{1}{2}\mu \left( 1 + \alpha^2 + \lambda^2 + \frac{1}{\alpha^2 + \lambda^2} + \frac{\lambda^2 r}{\alpha^2} \right).$$
(4.103)

This shows that when  $B \to \infty$  there are only two fundamental deformations namely a stretch perpendicular to the layer normal and a simple shear perpendicular to the layer normal.

#### 4.3.3 $B < \infty$

The same uniform deformations as §4.3.1 are now considered but this time allowing for a finite layer modulus. The finite layer modulus results in a threshold behaviour as when the elastomer is stretched parallel to the layer normal, because a cross over from stretching the layer spacing to rotation of the layers. In this section the microstructure associated with layer rotation will not be considered. However, its effect on the elastic properties of the material are small because of the low energy cost of the interfaces between domains. The rotation of the layers combined with the microstructure (similar to that observed in nematic elastomers) provides an explanation of the Helfrich-Hurault effect observed in smectic LSCEs. Note that this is a different physical reason for the Helfrich-Hurault effect than in liquid smectics. In liquid smectics the undulations in the layers occur because of a competition between bending the layers, penalised by the Frank elastic constants, and keeping their spacing fixed. In liquid crystal elastomers the threshold is controlled by the competition between the energy cost of stretching the layers and shearing the elastomer – a rubber elastic effect. In the following subsections the ratio of the layer modulus to the rubber modulus is denoted as:  $b = \frac{B}{\mu}$ .

### Imposed $\lambda_{zz}$

For the case of finite layer modulus, it is assumed that the deformation matrix has the same form as for the infinite layer modulus case

$$\underline{\underline{\lambda}} = \begin{pmatrix} \lambda_{\rm xx} & 0 & 0\\ 0 & \lambda_{\rm yy} & 0\\ \lambda_{\rm zx} & 0 & \lambda \end{pmatrix}.$$
(4.104)

For a finite layer modulus the constraints are that of volume conservation

$$\det(\underline{\lambda}) = 1 = \lambda_{xx}\lambda_{yy}\lambda, \qquad (4.105)$$

and of no rotation of the layers with respect to the matrix

$$\mathbf{q} = \underline{\lambda}^{-T} \cdot \mathbf{q}_0. \tag{4.106}$$

More care is required than in §4.3.1 when calculating the director as can no longer simply write down the components from the cofactors. The director must be normalised explicitly

$$\mathbf{n} = \left(-\frac{\lambda_{\text{zx}}}{\sqrt{\lambda_{\text{xx}}^2 + \lambda_{\text{zx}}^2}}, 0, \frac{\lambda_{\text{xx}}}{\sqrt{\lambda_{\text{xx}}^2 + \lambda_{\text{zx}}^2}}\right). \tag{4.107}$$

The free energy density for the system can now be written down, including the new contribution from the finite layer modulus using the expression from Eq. (4.63) for  $d/d_0$ .

$$f = \frac{1}{2}\mu \left\{ \lambda_{\mathrm{xx}}^2 + \frac{1}{\lambda_{\mathrm{xx}}^2 \lambda^2} + \lambda_{\mathrm{zx}}^2 + \frac{(\lambda_{\mathrm{xx}}^2 + r\lambda_{\mathrm{zx}}^2)\lambda^2}{\lambda_{\mathrm{xx}}^2 + \lambda_{\mathrm{zx}}^2} + b\left(\frac{\lambda\lambda_{\mathrm{xx}}}{\sqrt{\lambda_{\mathrm{xx}}^2 + \lambda_{\mathrm{zx}}^2}} - 1\right)^2 \right\},$$

where the volume conservation constraint has been used to eliminate  $\lambda_{yy}$ . This expression can be minimized numerically, using the simplex algorithm, for different values of b. The solution for the different components of the deformation tensor for a particular b value is shown in Fig. 4.13. The figure



Figure 4.13: An illustration of values of the deformation tensor components for an imposed  $\lambda_{zz}$  for the case when b = 5 and r = 2. The  $\lambda_{zx}$  component has an asymptote of  $\frac{1}{\sqrt{\lambda_{cr}}}$  for large  $\lambda_{zz}$ .

(with a small b value for clarity) shows that there is a critical, threshold value of the elongation  $\lambda = \lambda_{\rm cr}$  when the layer rotation starts to occur. Shear  $\lambda_{\rm zx}$  starts with a singular edge and the transverse contraction  $\lambda_{\rm yy}$  remains constant. It is possible to guess an analytic solution to this model based on the  $B \to \infty$  solution and the numerics above. The solution splits into two parts: before and after the discontinuity. Before the layers start to rotate,  $\lambda_{\rm zx} = 0$ . The free energy density is given by

$$f = \frac{1}{2}\mu \left\{ \lambda_{\rm xx}^2 + \frac{1}{\lambda_{\rm xx}^2 \lambda^2} + \lambda^2 + b(\lambda - 1)^2 \right\}.$$
 (4.108)

This free energy density has a minimum when  $\lambda_{xx}^2 = \frac{1}{\lambda}$ . Thus before the layers start to rotate the material has Poisson ratios  $(\frac{1}{2}, \frac{1}{2})$  in the (x, y) directions. The free energy density and the nominal stress for this minimum

energy solution are given by

$$f = \frac{1}{2}\mu \left\{ \frac{2}{\lambda} + \lambda^2 + b(\lambda - 1)^2 \right\}$$
 (4.109)

$$\sigma_{\text{nom}} = \mu \left( \lambda - \frac{1}{\lambda^2} \right) + B(\lambda - 1).$$
(4.110)

When layer rotation starts at  $\lambda_{\rm cr}$ , numerically it is clear that  $\lambda_{\rm yy} = \frac{1}{\sqrt{\lambda_{\rm cr}}}$  is a constant. Starting from this assumption avoids having to minimise over  $\lambda_{\rm yy}$ and thereby simplifies the problem. After the transition occurs it follows that  $\lambda_{\rm xx} = \frac{\sqrt{\lambda_{\rm cr}}}{\lambda}$  so that the material now has Poisson ratios (0, 1). Minimising the free energy density w.r.t.  $\lambda_{\rm zx}^2$  yields, after some simplification

$$0 = 1 + \frac{(r-1)\lambda^4 \lambda_{\rm cr}}{(\lambda_{\rm cr} + \lambda_{\rm zx}^2 \lambda^2)^2} + b \left[ \frac{\lambda^3 \sqrt{\lambda_{\rm cr}}}{(\lambda_{\rm cr} + \lambda_{\rm zx}^2 \lambda^2)^{3/2}} - \frac{\lambda_{\rm cr} \lambda^4}{(\lambda_{\rm cr} + \lambda_{\rm zx}^2 \lambda^2)^2} \right].$$
(4.111)

Solution of this equation for  $\lambda_{zx}$  at first sight is complicated, however  $\lambda_{zx}$  only appears in the following combination

$$p^2 = \lambda_{\rm zx}^2 + \frac{\lambda_{\rm cr}}{\lambda^2}.$$
(4.112)

The combination p is a function only of r - 1, b and  $\lambda_{cr}$ , that is  $f(r, b, \lambda_{cr})$ , and obeys the equation

$$0 = p^4 + (r-1)\lambda_{\rm cr} + b\left(p\sqrt{\lambda_{\rm cr}} - \lambda_{\rm cr}\right).$$
(4.113)

This is because Eq. (4.111) is a polynomial in p. At the critical value,  $\lambda_{\rm cr}$ , using the fact that  $\lambda_{\rm zx} = 0$  it follows that  $p = \frac{1}{\sqrt{\lambda_{\rm cr}}}$ . From Eq. (4.113) the following equation for the critical value of  $\lambda_{\rm cr}$  can be obtained

$$\lambda_{\rm cr}^3(r-b-1) + b\lambda_{\rm cr}^2 + 1 = 0.$$
(4.114)

This equation can be solved analytically by the general formula for cubic equations. However it is more useful to analyse its limits. The first few terms in the expansion for large b yield

$$\lambda_{\rm cr} = 1 + \frac{r}{b} + r(r-3)\frac{1}{b^2} + O\left(\frac{1}{b^3}\right). \tag{4.115}$$

To obtain a threshold at all, the condition b > r - 1 must be obeyed. Below this layer modulus there is no instability. From  $p^2 = \frac{1}{\lambda_{cr}}$  in Eq. (4.112) the induced shear is

$$\lambda_{\rm zx} = \pm \sqrt{\frac{1}{\lambda_{\rm cr}} - \frac{\lambda_{\rm cr}}{\lambda^2}}.$$
(4.116)

#### 4.3. FINITE DEFORMATION EXAMPLES

Note that there are two solutions here corresponding to the two directions that the director can rotate. On substituting the form of  $\lambda_{zx}$  back into the free energy density the following expression is obtained

$$f = \frac{1}{2}\mu \left\{ \frac{2}{\lambda_{\rm cr}} + \lambda_{\rm cr}^2 + r(\lambda^2 - \lambda_{\rm cr}^2) + b(\lambda_{\rm cr} - 1)^2 \right\}.$$
 (4.117)

From Eq. (4.109) and Eq. (4.117) the nominal stress can be calculated using the equation:  $\sigma_{\text{nom}} = \frac{\partial f}{\partial \lambda}$ . The results for the nominal stress are thus

$$\sigma_{\rm nom} = \begin{cases} \mu \left(\lambda - \frac{1}{\lambda^2}\right) + B(\lambda - 1) & \lambda < \lambda_{\rm cr} \\ \mu r \lambda & \lambda > \lambda_{\rm cr} \end{cases}$$
(4.118)

Note that the continuity of the nominal stress with  $\lambda$  can be used to derive Eq. (4.114). From this result it is clear that the ratio of the two slopes is related to  $\lambda_{\rm cr}$ , which provides a convenient experimental check of the threshold stretch. Thus for large *B* the ratio of the two slopes can be calculated, and their ratio taken to obtain

$$\frac{r\mu}{B} \approx \lambda_{\rm cr} - 1. \tag{4.119}$$

Experimentally  $\mu$  can be obtained from stretching the rubber in the layers, yielding a modulus of  $E_{\perp} = 4\mu$ , and thus obtain the anisotropy of the polymers, r by combining these two results. An illustration of Eq. (4.118) is shown in Fig. 4.14, again for the same small value of b.



Figure 4.14: The figure illustrates the nominal stress for a smectic elastomer stretched parallel to the layer normal, with r = 2 and b = 5.

It is interesting to calculate the layer spacing of the system as a function of the imposed stretch. The layer spacing is given by

$$\frac{d}{d_0} = \frac{1}{\lambda_{yy}\sqrt{\lambda_{xx}^2 + \lambda_{zx}^2}} = \frac{\lambda\lambda_{xx}}{\sqrt{\lambda_{xx}^2 + \lambda_{zx}^2}}.$$
(4.120)

Before layer rotation starts  $\lambda_{zx} = 0$  and so the layer spacing increases as  $d/d_0 = \lambda$ . After layer rotation starts we have from the same expression  $d/d_0 = \lambda_{cr}$ . Thus after rotation of the layers starts their spacing remains fixed, and the only cost in deforming the system is that of shearing the rubber. This is because, as the layers rotate, the component of the force along the layers remains constant.

The threshold behaviour shown here occurs even for very small values of B. This is because the way in which the director deforms with the matrix has been imposed. Physically this is correct for large B. As B is reduced this constraint will become less rigidly enforced and the cross-links will be able to move through one layer to the next. Thus the threshold behaviour predicted for small B values ( $\sim \mu$ ) is unlikely to be correct in practise.

To check the trial solution outlined above and to ensure there are no other solutions, all the solutions to the minimisation of the free energy are now calculated. To factorise the free energy, a change of variables is employed: the variables  $\lambda_{xx}$  and  $\tan \phi = -\frac{\lambda_{zx}}{\lambda_{xx}}$  are used to express the free energy. The expression for the free energy density is then given by

$$f = \frac{1}{2}\mu \left\{ \lambda_{xx}^2 + \frac{1}{\lambda_{xx}^2 \lambda^2} + \lambda_{xx}^2 \tan^2 \phi + (\cos^2 \phi + r \sin^2 \phi) \lambda^2 + b(\lambda \cos \phi - 1)^2 \right\}.$$

Minimising this equation w.r.t.  $\lambda_{xx}$  yields

$$0 = 2\lambda_{\rm xx} \left( 1 - \frac{1}{\lambda^2 \lambda_{\rm xx}^4} + \tan^2 \phi \right). \tag{4.121}$$

This equation has the solutions  $\lambda_{xx}^2 = 0, \pm \frac{\cos \phi}{\lambda}$ . The only physical solution is  $\lambda_{xx}^2 = \frac{\cos \phi}{\lambda}$ . Minimising the free energy w.r.t.  $\phi$  and substituting for  $\lambda_{xx}$  yields

$$0 = \frac{\sin \phi}{\lambda \cos^2 \phi} + \lambda^2 (r - 1) \sin \phi \cos \phi - b\lambda (\lambda \sin \phi \cos \phi - \sin \phi)$$
(4.122)

This equation can be factorised using the solutions previously calculated as follows

$$\lambda \sin \phi \left( \cos \phi - \frac{\lambda_{\rm cr}}{\lambda} \right) \left( \lambda^2 (r - 1 - b) \cos^2 \phi - \frac{\lambda}{\lambda_{\rm cr}^2} \cos \phi - \frac{1}{\lambda_{\rm cr}} \right) = 0 \quad (4.123)$$

provided that Eq. (4.114) is obeyed. Thus the previous solution (a combination of the first and second factors) is a minimum. The third factor can be shown to be real only if  $\lambda_{\rm cr}^2 b < -3/4$ , and thus is never a relevant solution in this case. The first solution is thus a minimum in the free energy and the only solution.

#### Imposed $\lambda_{xx}$

A deformation matrix of the form

$$\underline{\underline{\lambda}} = \begin{pmatrix} \lambda & 0 & \lambda_{\rm xz} \\ 0 & \lambda_{\rm yy} & 0 \\ 0 & 0 & \lambda_{\rm zz} \end{pmatrix}$$
(4.124)

will be used here. A  $\lambda_{zx}$  element is not included here because it creates additional, but physically uninteresting rotating solutions. The rotation about the y axis would take the layers into the stretch direction (the x direction) and would be energetically unfavourable. A  $\lambda_{xz}$  component is included here because from the the equivalent experiment with a nematic elastomer it is expected to be non-zero. However since it does not facilitate layer rotation this element will turn out to be zero. This deformation tensor can be substituted into the free energy expression and the volume conservation constraint used to eliminate  $\lambda_{zz}$ . The resulting free energy density expression is given by

$$f = \frac{1}{2}\mu \left\{ \lambda_{\rm yy}^2 + r\lambda_{\rm xz}^2 + \lambda^2 + \frac{1}{\lambda_{\rm yy}^2\lambda^2} + b\left(\frac{1}{\lambda_{\rm yy}\lambda} - 1\right)^2 \right\},\tag{4.125}$$

This free energy density has only a few occurrences of  $\lambda_{xz}$  so it can be easily minimized w.r.t.  $\lambda_{xz}$  yielding  $\lambda_{xz} = 0$ 

For this deformation, it is instructive to calculate the Poisson ratios in the (y, z) directions for different values of b. Starting from Eq. (4.125) we make the substitutions  $\lambda_{zx} = 0$  and  $\lambda_{xz} = 0$ . The resulting free energy density is given by

$$f = \frac{1}{2}\mu \left\{ \lambda_{yy}^2 + \lambda^2 + \frac{1}{\lambda_{yy}^2 \lambda^2} + b \left( \frac{1}{\lambda_{yy} \lambda} - 1 \right)^2 \right\}$$
(4.126)

Minimisation of this free energy w.r.t.  $\lambda_{yy}$  results in the equation

$$\lambda^2 \lambda_{\rm yy}^4 - 1 = b(1 - \lambda \lambda_{\rm yy}) \tag{4.127}$$

From this equation it is clear that there are two limits of small and large b corresponding to  $\lambda_{yy} = \frac{1}{\lambda}$  for large b and  $\lambda_{yy} = \frac{1}{\sqrt{\lambda}}$  for small b. The material with a small b value is still a smectic in the sense that the director is constrained to lie along the layer normal. To calculate the Poisson ratios from this expression a small strain expansion is used

$$\lambda_{\rm yy} = 1 + \epsilon \tag{4.128}$$

$$\lambda = 1 + \omega. \tag{4.129}$$

The resulting expression to first order in  $\omega$  and  $\epsilon$  is given by

$$4\epsilon + 2\omega + b(\epsilon + \omega) = 0. \tag{4.130}$$

The Poisson ratio in the y direction,  $\nu$ , can then be identified as  $\nu = -\frac{\epsilon}{\omega}$ . In terms of b the Poisson ratio is

$$\nu = \frac{2+b}{4+b}.$$
 (4.131)

The cross over from Poisson ratios (z, y) = (0, 1) to (1/2, 1/2) is thus relatively slow. However, it is clear that for  $b \sim 60$ , as found in some experimental samples, the material is firmly in the (0, 1) class.

#### Imposed $\lambda_{xz}$

Again, the deformation tensor given in Eq. (4.86) is considered. The  $\lambda_{yy}$  component can be eliminated by using the volume conservation constraint. The resulting free energy density expression is

$$f = \frac{1}{2}\mu \left\{ \lambda_{\rm xx}^2 + \frac{1}{\lambda_{\rm xx}^2 \lambda_{\rm zz}^2} + \lambda_{\rm zz}^2 + r\lambda^2 + b\left(\lambda_{\rm zz} - 1\right)^2 \right\}$$
(4.132)

This free energy density does not couple  $\lambda$  and  $\lambda_{zz}$  and so the imposed shear cannot affect  $\lambda_{zz}$ . When this is minimized over  $\lambda_{xx}$  and  $\lambda_{zz}$  the solution  $\lambda_{zz} = \lambda_{xx} = 1$  is obtained, as in the more constrained case.

## Imposed $\lambda_{zx}$

In this case the deformation tensor given in Eq. (4.92) used. This deformation matrix does not permit body rotation of the rubber and is an experimentally reasonable deformation. Eliminating the component  $\lambda_{yy}$  using the volume conservation constraint ( $\lambda_{xx}\lambda_{yy}\lambda_{zz} = 1$ ) results in the following free energy density

$$f = \frac{1}{2}\mu \left\{ \lambda_{xx}^2 + \frac{1}{\lambda_{xx}^2 \lambda_{zz}^2} + \lambda^2 + r\lambda_{zz}^2 + \frac{\lambda_{zz}^2 (\lambda_{xx}^2 + r\lambda^2)}{\lambda_{xx}^2 + \lambda^2} + b \left( \frac{\lambda_{xx} \lambda_{zz}}{\sqrt{\lambda_{xx}^2 + \lambda^2}} - 1 \right)^2 \right\}.$$

$$(4.133)$$

This minimisation can be solved numerically using the simplex algorithm. A typical solution is illustrated in Fig. 4.15, together with the layer spacing for the same solution.

In this deformation the layer spacing is being strongly compressed. This is borne out by the layer spacing plot above. Even for very large b the layer spacing eventually yields and begins to decrease.



Figure 4.15: An example of the minimisation of the free energy in the case of imposed  $\lambda_{zx}$ . a) The deformation tensor components, b) the layer spacing. The example is for the case b = 5, r = 3.

## 4.3.4 Fundamental deformations for finite B

Note that where as in §4.3.2 the deformation could be broken up into two deformations, an imposed  $\lambda_{xx}$  and an imposed  $\lambda_{xz}$  plus a rotation, this is not possible here. In this case we require a third deformation: a stretch along the layer normal ( $\lambda_{zz}$ ). The decomposition is now illustrated by the imposed  $\lambda_{zx}$  case as considered above.

$$\underline{\lambda} = \underline{W} \cdot \underline{D} \tag{4.134}$$

where we define

$$\underline{\underline{W}} = \begin{pmatrix} \cos\gamma & 0 & \sin\gamma \\ 0 & 1 & 0 \\ -\sin\gamma & 0 & \cos\gamma \end{pmatrix}; \underline{\underline{D}} = \begin{pmatrix} 1 & 0 & \lambda_{\rm XZ} \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \lambda_{\rm XX} & 0 & 0 \\ 0 & \frac{1}{\lambda_{\rm ZZ}\lambda_{\rm XX}} & 0 \\ 0 & 0 & \frac{1}{\lambda_{\rm ZZ}} \end{pmatrix}.$$

The deformation matrix is thus

$$\underline{\underline{\lambda}} = \begin{pmatrix} \lambda_{\rm xx} \cos \gamma & 0 & \lambda_{\rm zz} (\lambda_{\rm xz} \cos \gamma + \sin \gamma) \\ 0 & \frac{1}{\lambda_{\rm xx} \lambda_{\rm zz}} & 0 \\ -\lambda_{\rm xx} \sin \gamma & 0 & \lambda_{\rm zz} (\cos \gamma - \lambda_{\rm xz} \sin \gamma) \end{pmatrix}.$$
(4.135)

From this deformation matrix we can calculate the director

$$\underline{\underline{\lambda}}^{-T} \cdot \mathbf{n}_0 = \left(\frac{\sin\gamma}{\lambda_{\rm zz}}, 0, \frac{\cos\gamma}{\lambda_{\rm zz}}\right) \tag{4.136}$$

Note that in this case care must be taken to normalise the director. The rotation required to reduce this deformation to the form of an imposed  $\lambda_{zx}$ 

deformation is  $\tan \gamma = -\lambda_{xz}$ . The following deformation matrix is then obtained

$$\underline{\underline{\lambda}} = \begin{pmatrix} \alpha & 0 & 0\\ 0 & \frac{1}{\alpha\beta} & 0\\ \lambda & 0 & \beta \end{pmatrix}$$
(4.137)

where

$$\alpha = \sqrt{\lambda_{\rm xx}^2 - \lambda^2} \quad ; \quad \beta = \frac{\lambda_{\rm xx}\lambda_{\rm zz}}{\sqrt{\lambda_{\rm xx}^2 - \lambda^2}} \quad ; \quad \lambda = \frac{\lambda_{\rm xx}\lambda_{\rm xz}}{\sqrt{1 + \lambda_{\rm xz}^2}}. \tag{4.138}$$

The free energy is then of the same form as Eq. (4.133) and we have the decomposition of the mode.

A decomposition can be performed on the imposed  $\lambda_{zz}$  deformation. The starting point is again Eq. (4.135), but this time setting  $\tan \gamma = -\lambda_{xz}$ . The resulting matrix is then compared to that of imposed  $\lambda_{zz}$  so that the identification  $\lambda = \lambda_{zz} \sqrt{1 + \lambda_{xz}^2}$  can be made. This decomposition gives a geometric reason for the threshold observed when  $\lambda_{zz}$  is imposed. Suppose that the elastomer deforms with only the  $\lambda_{zz}$  component. The free energy density is then

$$f_{\rm zz} = \frac{1}{2}B(\lambda - 1)^2. \tag{4.139}$$

Alternatively the sample could deform by a shear  $\lambda_{xz}$ , which leaves the layer spacing unchanged, and then rotate to accomplish the same  $\lambda_{zz}$  value. In this case the free energy density is

$$f_{\rm xz} = \frac{1}{2}\mu r \lambda_{\rm xz}^2 = \frac{1}{2}\mu r (\lambda^2 - 1) . \qquad (4.140)$$

Comparing these two energy densities for small  $\epsilon$  where  $\lambda = 1 + \epsilon$ , it is clear that that  $f_{zz} \sim \frac{1}{2}B\epsilon^2 < f_{xz} \sim \mu r\epsilon$ , provided that  $\epsilon < 2\mu r/B$ . The latter energy is first order rather than second order in the strain and explains why it is so costly and unphysical (it is second order finally where it intercedes after  $\lambda_{cr}$ ). This decomposition also shows that an imposed  $\lambda_{zz}$  is equivalent to an imposed  $\lambda_{xz}$  deformation plus a rotation and a fixed stretch along the layer normal such that  $d/d_0 = \lambda_{cr}$ . The decomposition explains why the modulus of the sample after the threshold is the same as that for an imposed  $\lambda_{xz}$  deformation.

## 4.4 Comparison with experiment

The model outlined in §4.2 can be compared with numerous pieces of experimental data. Here the Poisson ratios, the elastic moduli and the x-ray scattering are considered.

#### 4.4.1 Experimentally measured elastic properties

Firstly consider the Poisson ratios. When stretched in plane, the model considered here produces, for large b, Poisson ratios (0,1) which are observed experimentally in [63]. When stretched parallel to the layer normal the observed Poisson ratios are (1/2, 1/2). The model is consistent with this before the threshold occurs, and layer rotation begins. After threshold the model predicts Poisson ratios of (1,0) which are not the same as those observed experimentally. This is because the sample, which is cylindrically symmetric about the stretch axis, maintains its cylindrical symmetry by forming microstructure consisting of many small domains. This point is crucial in the analysis of the x-ray data.

In the experimental study of Nishikawa and Finkelmann [66] the elastic moduli of a smectic elastomer were measured. The sample used in their experiments was found to have an anisotropy of  $r \approx 1.6$  from swelling anisotropy measurements. The threshold strain was found to be  $\epsilon_c \approx 3\%$  with a corresponding stress of  $\sigma_N \approx 1.12 \times 10^5$ Pa. The modulus before threshold was  $E_{\text{before}} = 3.2 \times 10^6$  Pa, and the modulus after threshold was  $E_{\text{after}} = 1.1 \times 10^5$ Pa. Although they comment that after threshold the modulus is similar to the in-plane modulus they do not give a value for the in-plane modulus. According to the theory outlined above from the reported moduli we expect  $\epsilon_c \approx \frac{E_{\text{after}}}{E_{\text{before}}} \approx 3.4\%$  which is extremely close to their reported threshold strain given that the transition is not totally sharp when observed experimentally. From the values of r and  $E_{\text{after}}$  we would expect an in plane modulus of  $4\frac{E_{\text{after}}}{r} \approx 2.75 \times 10^5$ Pa. Fig. 4.16 shows a fit of this theory to the elastic data of [66].

The fit to the experimental data is good given the small number of parameters in the model for such a complicated material.

## 4.4.2 X-ray scattering

Reference [66] also contains x-ray data for a smectic elastomer as it is being stretched along the layer normal. It is observed that the x-ray peaks corresponding to the layers rotate as the sample is stretched. There is also a sharp drop in the intensity of these peaks which was attributed to melting of the smectic phase to the nematic or isotropic phase by Nishikawa and Finkelmann.

Fig. 4.17 below compares the calculated orientation of the director with the experiment of [66]. As is clear from the figure the rotation of the smectic layers is in good agreement with the model discussed here.

The above theory does not predict that the smectic phase melts on stretching. The energy cost to perform this melting can be calculated as follows: the entropy change found in [66] for the smectic-isotropic phase transition was  $\Delta S = 2.4 \times 10^{-2} \text{JK}^{-1} \text{g}^{-1}$ . Thus the cost for melting at 300K for a sample with density  $\rho \sim 1 \text{g cm}^{-3}$  is  $T\Delta S\rho \sim 7.2 \times 10^6 \text{ J m}^{-3}$ . To pay the cost of



Figure 4.16: The figure shows a fit of the theory to the data of [66]. The values used for the fit were:  $B = 3.2 \times 10^{6}$ Pa and  $r\mu = 1.1 \times 10^{5}$ Pa.



Figure 4.17: Comparison of the calculated orientation of the director (dotted line) with the experimental points of [66] (circular points).

melting, an energy density of  $\frac{1}{2}B(\lambda_{\rm cr}-1)^2 \sim 8 \times 10^4 {\rm J/m^3}$  is available from the input elastic energy and is clearly rather little.

An alternative explanation that is consistent with the above proposed model of the smectic elastomer is the formation of microstructure. The break up of the sample into regions of tilted domains is cylindrically symmetric around the stretch axis. The regions that are tilted toward the x-ray beam no longer meet the Bragg condition for diffraction, and as a result do not contribute intensity to the scattered beam. This loss of intensity is inversely proportional to  $\sin \phi$  where  $\phi$  is the angle through which the smectic layers have tilted (Fig. 4.18).



Figure 4.18: The figure illustrates the incident beam of xrays, wavevector **k**, impinging on a stretched smectic elastomer sample. The layer normal in the sample is distributed on the ring shown. Only a small range of layer normals that are distributed around the Bragg condition can contribute to the scattering. This contribution is inversely proportional to the circumference of the ring i.e. to  $\frac{1}{\sin \phi}$ .

The fit of this prediction to the experimental data given in [66] for the ratio of the small angle scattering to the large angle scattering is given in Fig. 4.19. The finite intensity at small angles is recovered because the finite resolution of the detector means that at small  $\phi$  all the layer normals are detected.

The formation of microstructure is also consistent with the observed broadening of the wide angle scattering, and also with the the opacity of the sample after the critical strain, and the elastic moduli of the sample. The formation of microstructure and the break up of the sample into domains on stretching is analogous to the formation of stripes in the nematic case [75, 76]. This problem is analogous to the formation of microstructure in the phase transi-



Figure 4.19: The figure shows the experimental data of [66] ( $\circ$ ) with two fitting curves. The solid curve corresponds to  $\frac{0.3}{\sin\phi}$  which does not take into account the resolution of the detector, and the dashed curve corresponds to  $\frac{9}{\pi} \sin^{-1} \left(\frac{0.1045}{\sin\phi}\right)$  which attempts to account for this.

tion from austenite to martensite, and has been studied using more advanced techniques which should be applicable to the smectic elastomer [77–80].

## 4.5 Conclusions

A large deformation model of a smectic elastomer can be formulated, founded on a microscopic model of the chains that comprise the elastomer. Deep in the smectic phase the cross-link points are confined to sit between the smectic layers. This restriction on where the cross-link points can lie results in a rigid coupling between the affine deformations of the matrix and the smectic layer normal.

The threshold behaviour observed when the smectic elastomer is stretched parallel to the layer normal can be explained in terms of this model. The cloudiness of the sample is due to microstructure formation in the bulk which parallels the formation of stripes in nematic elastomers. In the case of the nematic elastomer, the sample clears once the director is fully rotated. This is not possible for a smectic elastomer. The experimental data fits well with this model, including the loss of x-ray intensity as a result of the microstructure

## 4.5. CONCLUSIONS

formation in the smectic, and the opacity of the sample observed after the critical strain.

## •Chapter Five•

## Soft elasticity of smectic elastomers

The subject of this chapter is soft modes in smectic elastomers. First a discussion of some of the aspects of soft modes in nematic elastomers is undertaken to provide an introduction and some background. The soft modes of two types of smectic elastomers — biaxial smectic A (SmA) and smectic C (SmC) — are then analysed using a Gaussian model, with an added constraint ensuring that the spacing between the layers remains fixed (see chapter 4). The geometries under which smectic elastomers can exhibit a soft elastic response are explored, both in general terms and by giving specific examples.

## 5.1 Introduction

## 5.1.1 Biaxial liquid crystals

The mesogens that make up biaxial liquid crystalline materials do not have continuous rotational symmetry; they are analogous to books rather than rods. Consequently they can show uniaxial order and biaxial order; like books stacked together. Although biaxial nematic phases are rare, examples of several lyotropic biaxial nematic liquid crystalline phases have been observed [81, 82]. It was only recently that thermotropic phases were reported in bentcore molecules [83] after x-ray diffraction confirmed that the phase was a biaxial nematic. This conclusion has now been confirmed by observations from conoscopy and texture [84]. It is thought that biaxial phases will be of technological importance, in displays for example, because of the faster switching time offered by the secondary alignment axis.

## 5.1.2 Smectic C liquid crystals

The SmC phase of a liquid crystal can be described as a two-dimensional liquid in each layer, but with the molecules in the layer tilted with respect to the layer normal (Fig. 5.1). As a consequence these materials are electrically, magnetically and optically biaxial. For optically inactive molecules, the alignment in each layer is the same. However, if the molecules are optically active then the direction of tilt precesses around the z-axis from one layer to the next and a helical configuration results, called smectic C<sup>\*</sup> (SmC<sup>\*</sup>). R. B. Meyer pointed out that whilst the SmC phase has an inversion centre, the SmC<sup>\*</sup> phase does not, and consequently can be ferroelectric [85].



Figure 5.1: An illustration of the SmC phase, together with a diagram indicating the relationship between the director,  $\mathbf{n}$ , the layer normal,  $\mathbf{k}$  and the tilt angle  $\theta$ . The vector  $\mathbf{c}$  is the component of  $\mathbf{n}$  perpendicular to  $\mathbf{k}$ .

## 5.1.3 Soft elasticity in nematic elastomers

Nematic elastomers exhibit a range of unusual properties. Perhaps the most striking is that of soft elasticity i.e. deformation at no elastic cost. These soft elastic modes can be understood from several different view points; from general symmetry arguments [86], from continuum models, and from particular microscopic models based on anisotropic chain conformations [32]. The occurrence of soft modes is independent of the particular description used, since they occur in any model with the same symmetries as a nematic elastomer [87].

The polymer chains that make up the nematic elastomer can be modelled using an anisotropic Gaussian distribution provided that the chains are long enough. The initial probability distribution of the end-to-end spans is then given by

$$P_0(\mathbf{R}_0, \underline{\ell}_0) = \left(\frac{2\pi L}{3\det[\underline{\ell}_0]}\right)^{-1/2} \exp\left\{\frac{-3}{2L}\mathbf{R}_0 \cdot \underline{\ell}_0^{-1} \cdot \mathbf{R}_0\right\},\tag{5.1}$$

where  $\mathbf{R}^0$  is the end-to-end span and L the arc length. The tensor  $\underline{\ell}_0$  defines the effective step lengths of the polymer at the moment of cross-linking

$$\langle R_{0\alpha}R_{0\beta}\rangle_{P_0} = \frac{1}{3}L\ell_{0\alpha\beta}.$$
(5.2)

The step anisotropy,  $\underline{\ell}_0$ , is a function of the nematic order parameter,  $\underline{Q}_0$ . The form of this function depends on the model of the polymer chain used and the coupling between the side groups and the polymer backbone. The particular model of this coupling is unimportant for obtaining qualitative features of the elastomer.

On cross-linking the elastomer consists of strands between cross-links all of arc length L, with end-to-end vectors drawn from the distribution  $P_0(\mathbf{R}_0, \underline{\ell}_0)$ . The elastic properties can then be found by calculating the average properties of the strands, with the assumption that the cross-link points deform affinely

$$\mathbf{R} = \underline{\lambda} \cdot \mathbf{R}_0. \tag{5.3}$$

This is approximately true for individual chains. It is correct on average and is exact in the limit of infinite cross-link point functionality [1]. For deformations such that  $|\lambda| < (L/\ell_0)^{1/2}$  the molecular configurations are still anisotropic Gaussians, described by a new step anisotropy  $\underline{\ell}$ . The elastic free energy per strand of a distorted state when quench averaged over  $\mathbf{R}_0$  is

$$-\langle \ln P(\mathbf{R},\underline{\ell})\rangle_{P_0} = \frac{1}{2} \left[ \operatorname{Tr}\left(\underline{\underline{\lambda}} \cdot \underline{\ell}_0 \cdot \underline{\underline{\lambda}}^T \cdot \underline{\ell}^{-1}\right) - \ln\left(\det[\underline{\ell}_0 \cdot \underline{\ell}^{-1}]\right) \right].$$
(5.4)

Minimising the free energy expression obtained in Eq. (5.4) w.r.t.  $\underline{\lambda}$  with the constraint det $[\underline{\lambda}] = 1$  yields the following expression

$$\underline{\lambda} \cdot \underline{\ell}_0 \cdot \underline{\lambda}^T = \underline{\ell}. \tag{5.5}$$

A general solution to Eq. (5.5) is given by

$$\underline{\lambda} = \underline{\ell}^{1/2} \cdot \underline{W} \cdot \underline{\ell}_0^{-1/2}, \tag{5.6}$$

where  $\underline{W}$  is a general rotation matrix. It can be shown that these modes comprise the long-wavelength limits of the Goldstone modes for this system, i.e. they are the analogs of spin wave excitations in ferromagnetic systems, or director waves in a nematic liquid crystal [87]. These zero energy, long wavelength deformations arise because of the broken-symmetry of the nematic elastomer. This expression also describes the soft modes for biaxial nematic elastomers [88].

For the case of a uniaxial nematic elastomer Eq. (5.6) can be rearranged into the form

$$\underline{\lambda} = \underline{\underline{W}} \cdot \underline{\underline{\ell}}_{\mathbf{n}'}^{1/2} \cdot \underline{\underline{\ell}}_{0}^{-1/2} \tag{5.7}$$

where  $\mathbf{n}'$  is a unit vector on the surface of a sphere and  $\mathbf{n} = \underline{W} \cdot \mathbf{n}'$ . In this form it is clear that the soft modes available to a nematic elastomer can be found by selecting  $\mathbf{n}'$  from the surface of a sphere, and then carrying out a general rotation,  $\underline{W}$  (i.e.  $\mathbf{n}'$  defines the shape of the body which can then be rotated).

For the case of a biaxial nematic elastomer the same rearrangement can be carried out, but this time after the choice of  $\mathbf{n}'$  has been made, the position of the secondary axis can be selected from any point on a specified great circle.

## Soft modes in biaxial nematics

As pointed out in §5.1.1 biaxial liquid crystalline phases are rare. However biaxial nematic phases [89] biaxial smectic A phases [90] have been found in liquid crystalline polymers and in principle it should be possible to make a biaxial nematic or biaxial SmA liquid crystal elastomer. The properties of a biaxial phase must necessarily be described by biaxial tensors, and the case of the shape tensor of a biaxial polymer is no different. Suppose that the shape tensor has principal axes  $\mathbf{l}$ ,  $\mathbf{n}$  and  $\mathbf{m}$  which are orthogonal and normalised. The shape tensor can be expressed as

$$\underline{\ell} = \ell_{\parallel} \mathbf{n} \mathbf{n}^{T} + \ell_{1} \mathbf{m} \mathbf{m}^{T} + \ell_{2} \mathbf{l} \mathbf{l}^{T}$$
(5.8)

$$= \underline{\delta} + (r-1)\mathbf{n}\mathbf{n}^{T} + \frac{p}{2}\mathbf{m}\mathbf{m}^{T} - \frac{p}{2}\mathbf{l}\mathbf{l}^{T}, \qquad (5.9)$$

where  $p = (\ell_1 - \ell_2)/\ell_{\perp}$  and  $\ell_{\perp} = \frac{1}{2}(\ell_1 + \ell_2)$ . In biaxial nematics rotations of the shape tensor about the principal director, **n** are significant, whereas in a uniaxial nematic they are not. An explicit example of a soft mode arising from this sort of rotation is presented in [88]. This mode is given here as it will prove useful in our discussion of soft modes in smectic A elastomers. For a soft mode with angle of rotation  $\phi$  about  $\mathbf{n}_0 \equiv \mathbf{n} = \mathbf{z}$  of the form  $\underline{\ell}_{\phi}^{1/2} \cdot \underline{\ell}_0^{-1/2}$ the following deformation tensor is obtained

$$\underline{\lambda} = \begin{pmatrix} 1 - (1 - 1/\sqrt{r_{\perp}})\sin^2\phi & (1 - \sqrt{r_{\perp}})\sin\phi\cos\phi & 0\\ (1/\sqrt{r_{\perp}} - 1)\sin\phi\cos\phi & 1 + (\sqrt{r_{\perp}} - 1)\sin^2\phi & 0\\ 0 & 0 & 1 \end{pmatrix}$$
(5.10)

where  $r_{\perp} = \ell_1/\ell_2$  is a material parameter expressing the degree of biaxiality.

In SmA elastomers the layers break the rotational symmetry of the state so that only rotations of the matrix points about the layer normal leaves the free energy unchanged. It will be shown that since the director has no component in the layers there can be no soft modes in SmA elastomers, except for the case of a biaxial order parameter.

## 5.1.4 Experimental literature on smectic C elastomers

Several investigations on the preparation of monodomains from SmC elastomers have been performed. The principles of aligning the SmC elastomer are the same as those of a nematic elastomer, i.e. cross-linking under a load. However, aligning smectic elastomers, and particularly SmC elastomers, is more involved because both the director and the layers must be aligned.

An investigation by Semmler and Finkelmann [91] into aligning SmC elastomers by found some success by adopting a two stage process of non-collinear stretches. On straining a polydomain chiral SmC sample by  $\lambda = 1.6$  the sample remains opaque, indicating that there is no director alignment. X-ray scattering shows a small degree of alignment, which does not improve on annealing. A new approach was adopted whereby the SmC sample was first loaded a small amount and then swollen with toluene, until it reached an isotropic state. It was then gradually deswollen and reformed into the smectic state whilst under load. The sample shows good director alignment, but the layers can have any orientation on the surface of a cone. The resulting sample was centrosymmetric. A second stretch is then applied at an angle of  $90^{\circ} - \theta$  where  $\theta$  is the tilt angle. As a result the layers rotate around so that the stretch direction is contained within the layer. The result is a non-centrosymmetric monodomain. This alignment can be locked in by another cross-linking stage.

An alternative approach of Hiraoka and Finkelmann [92, 93] was to use a mechanical shear field. The same procedure as described above was used to obtain a uniaxially aligned director field. The sample was then sheared through an angle equal to the tilt angle of the director w.r.t. the layers in the SmC phase. Again a well aligned monodomain, with aligned layers is obtained. This technique of making monodomains has recently made it possible to observe spontaneous deformations in the SmC phase [94].

SmC<sup>\*</sup> elastomers may also prove to be of great technological significance, for example they possess the correct phase symmetry to exhibit second harmonic generation, that is generate light at a frequency of twice that of the incident light. This has been the subject of experimental research [95]. Their piezoelectric properties have also been studied experimentally [96, 97]. This may prove to be significant because whilst conventional piezoelectric materials can only achieve small strains, rubbery materials could achieve much larger strains. The ferroelectric properties of these materials have also been intensively studied [98–102]. As a result of these ferroelectric properties SmC elastomers show giant electristriction effects (analogous to piezoelectricity but with strain proportional to the square of the applied electric field) [103]. Polydomain SmC elastomers have also been shown to exhibit shape memory which may also prove to be important technologically [104].

## 5.2 Soft modes of biaxial smectic A elastomers

## 5.2.1 Model biaxial smectic A elastomer

The model of a biaxial SmA used here is an extension of the model presented in chapter 4. It is assumed that there is no interaction between the formation of the layers and the secondary alignment axis of the mesogens. As a result the required free energy density is given by

$$f = \frac{1}{2}\mu \operatorname{Tr}\left[\underline{\lambda} \cdot \underline{\ell}_0 \cdot \underline{\lambda}^T \cdot \underline{\ell}^{-1}\right] + \frac{1}{2}B\left(d/d_0 - 1\right)^2$$
(5.11)

where both  $\underline{\ell}_0$  and  $\underline{\ell}$  are now biaxial, with principal axes **n**, **m** and **l**. The primary alignment axes of the mesogens, **n** is identified with the smectic layer normal, but the secondary alignment axis is free to rotate in the plane of the layer to rotate in the plane of the layers. Consequently, the soft modes of this biaxial SmA arise because of the freedom of the secondary alignment axis. If we assume that the layers move affinely with the matrix, then it follows that the layer spacing is given by

$$\frac{d}{d_0} = \frac{1}{|\underline{\lambda}^{-T} \cdot \mathbf{n}_0|},\tag{5.12}$$

where  $\mathbf{n}_0$  is the initial direction of the primary axis of alignment.

## 5.2.2 General form of soft modes in biaxial SmA elastomers

Since the model of biaxial SmA elastomer considered here is based on that of a nematic elastomer, the starting point used is the general form of soft modes in nematic elastomers

$$\underline{\lambda} = \underline{\ell}^{1/2} \cdot \underline{W} \cdot \underline{\ell}_0^{-1/2}, \qquad (5.13)$$

where  $\underline{W}$  is a general rotation matrix,  $\underline{\ell}_0$  is the initial biaxial anisotropy tensor and  $\underline{\ell}$  is the current anisotropy tensor of the polymer. A general deformation could in principle change the layer spacing. However for soft modes the layer spacing must remain fixed. This constraint can be expressed via Eq. (5.12) as

$$\mathbf{n}_{0}^{T} \cdot \underline{\lambda}^{-1} \cdot \underline{\lambda}^{-T} \cdot \mathbf{n}_{0} = 1.$$
(5.14)

Inserting the general form of a soft mode Eq. (5.13) into the layer spacing constraint Eq. (5.14) yields the following equation

$$\frac{1}{r} = \mathbf{n}_0^T \cdot \underline{W}^T \cdot \underline{\ell}^{-1} \cdot \underline{W} \cdot \mathbf{n}_0.$$
(5.15)

For uniaxial SmA, the only solution to this equation is  $\mathbf{n} = \underline{W} \cdot \mathbf{n}_0$  because the quadric surface associated with  $\underline{\ell}^{-1}$  only has the correct width at one point. Thus there is no freedom for the director and no soft modes in uniaxial SmA elastomers except for pure rotations. This is because if the layer normal  $\mathbf{n}$  is moved by any deformation other than a rotation then the layer spacing will be changed and the resulting state will be higher in energy. However, in biaxial SmA elastomers the secondary alignment axis means that there is still enough freedom for a soft mode to exist.

The soft modes can be decomposed into their component rotations to gain a better understanding of them as follows. First we write the general deformation matrix as

$$\underline{\underline{W}} = \underline{\underline{W}}_{\mathbf{R}} \cdot \underline{\underline{W}}_{\mathbf{n}_0}, \tag{5.16}$$

where  $\underline{W}_{\mathbf{n}_0}$  is a rotation about  $\mathbf{n}_0$  and  $\mathbf{n} = \underline{W}_{\mathbf{R}} \cdot \mathbf{n}_0$ . Using this in Eq. (5.13) results in the following expression for the soft mode:

$$\underline{\lambda} = \underline{\ell}^{1/2} \cdot \underline{W}_{\mathbf{R}} \cdot \underline{W}_{\mathbf{n}_0} \cdot \underline{\ell}_0^{-1/2}$$
(5.17)

$$= \underline{\underline{W}}_{\mathbf{R}} \cdot \underline{\underline{W}}_{\mathbf{n}_{0}} \cdot \left[\underline{\underline{\ell}}_{\mathbf{n}_{0},\mathbf{m}',\mathbf{l}'}^{1/2} \cdot \underline{\underline{\ell}}_{0}^{-1/2}\right].$$
(5.18)

The factor in square brackets here is a familiar soft mode from the example given in  $\S5.1.3$ . Thus all soft modes in biaxial SmA elastomers can be decomposed into a rotation of the soft mode that has the primary alignment axis (i.e. **n**) fixed and a secondary rotation axis displaced from its initial position.

## 5.2.3 Particular example of a soft mode in a SmA elastomer

For later comparison with the soft modes of an SmC elastomer, the soft mode associated with an imposed  $\lambda_{xx}$  component is now presented. This mode will have a fixed primary alignment direction,  $\mathbf{n}_0$ , but will have a mobile secondary alignment direction,  $\mathbf{m}$ . Fig. 5.2 shows an illustration of this mode. In the centre of the diagram the secondary alignment axis,  $\mathbf{m}$  is depicted. Along the outside of the diagram the shape of the biaxial SmA elastomer is illustrated as viewed from above.

## 5.3 Soft modes of smectic C elastomers

## 5.3.1 Model smectic C elastomer free energy

The model of an SmC elastomer described here is again an extension of the SmA elastomer model presented in chapter 4. It is based on a constrained version of the nematic elastomer. Whilst it is a specific microscopic model of the SmC elastomer phase, its features are more general and the soft modes explored here are also present in other, continuum, approaches [105].



Figure 5.2: An illustration of the soft mode of a biaxial smectic A elastomer. In this case the layer normal is out of the page and the secondary director,  $\mathbf{m}$ , is shown in the centre of the diagram. The  $\mathbf{m}$  axis rotates by  $\phi = 30^{\circ}$  from one image to the next and an anisotropy of  $r_{\perp} = 2$  was chosen.

Note that on undergoing a phase change from the nematic to the smectic state, the degree of anisotropy of the polymer, r, may be changed because of the additional penalty of the polymer chains for crossing the smectic layers. Whilst in the SmA this effect can be roughly modelled by decreasing the value of r for prolate chains on transition to the smectic phase, its effect for SmC elastomers is not quite so simple. The uniaxial tensor representing the polymer shape in the nematic state is compressed along the layer normal, which is not along one of the principal axes. The shape anisotropy tensor is thus biaxial. However, here it is modelled as uniaxial for simplicity. The novel soft elasticity arises because of the biaxial arrangement of  $\underline{\ell}$  about the layer normal. The same qualitative behaviour is expected for a truly biaxial  $\underline{\ell}$  as that generated by a uniaxial  $\underline{\ell}$  constrained to be tilted at a fixed angle to the layer normal.

The elastic free energy terms and the smectic layer modulus terms result in the following free energy expression

$$f = \frac{1}{2}\mu \operatorname{Tr}\left[\underline{\underline{\lambda}} \cdot \underline{\underline{\ell}}_0 \cdot \underline{\underline{\lambda}}^T \cdot \underline{\underline{\ell}}^{-1}\right] + \frac{1}{2}B\left(\frac{d}{d_0} - 1\right)^2.$$
(5.19)

where B is the modulus associated with stretching the layers, d is the current layer spacing and  $d_0$  is the initial layer spacing. The expression for the layer spacing is given by

$$\frac{d}{d_0} = \frac{1}{|\underline{\lambda}^{-T} \cdot \mathbf{k}_0|},\tag{5.20}$$

where  $\mathbf{k}_0$  is the initial position of the layer normal in the solid (since it is no longer identical to  $\mathbf{n}_0$ ) and  $\underline{\lambda}^{-T}$  denotes the inverse transpose of the deformation matrix.

The director is made up of two parts, **k** parallel to the layer normal, and **c** perpendicular to the layer normal ( $\mathbf{k} \cdot \mathbf{c} = 0$ ). Since the director is tilted at an angle  $\theta$  to the layer normal (see Fig. 5.1) the following expression holds

$$\mathbf{n} = \mathbf{k}\cos\theta + \mathbf{c}\sin\theta. \tag{5.21}$$

Another term in this model penalising the tilt of the director away from making angle  $\theta$  with the layer normal could be included. However, since the main concern here is soft modes, deviation from tilt  $\theta$  with any energy cost would remove softness during deformation. Consequently, this term is not included here, and the tilt angle simply regarded as being fixed. In any event, away from the SmA  $\rightarrow$  SmC transition it is expected that the associated modulus is very high.

## 5.3.2 The general form of soft modes

Since the model of SmC elastomers used here is based on that of a nematic elastomer, the starting point used is the general form of soft modes in nematic elastomers Eq. (5.13), but must also obey the layer constraint Eq. (5.20). The deformation tensor must obey

$$\mathbf{k}_{0}^{T} \cdot \underline{\lambda}^{-1} \cdot \underline{\lambda}^{-T} \cdot \mathbf{k}_{0} = 1, \qquad (5.22)$$

i.e. constancy of layer spacing must be rigidly obeyed.

It is convenient to introduce a new auxiliary vector,  $\mathbf{w}_0 = \underline{\underline{\ell}}_0^{1/2} \cdot \mathbf{k}_0$ . The vectors  $\mathbf{w}_0$ ,  $\mathbf{n}_0$  and  $\mathbf{k}_0$  all lie in the same plane with  $\mathbf{w}_0$  between  $\mathbf{n}_0$  and  $\mathbf{k}_0$ . This is clear from the expression

$$\mathbf{w}_0 = \underline{\ell}_0^{1/2} \cdot \mathbf{k}_0 = \mathbf{k}_0 + (\sqrt{r} - 1) \cos \theta \mathbf{n}_0 , \qquad (5.23)$$

which can be obtained by using  $\underline{\ell}_0^{1/2} = (\sqrt{r} - 1)\mathbf{n}_0\mathbf{n}_0^T + \underline{\delta}$ . Note that the modulus of  $\mathbf{w}_0$  is not unity but rather  $w_0^2 = 1 + (r-1)\cos^2\theta > 1$  for r > 1.

Substituting the general soft mode Eq. (5.13) into the layer spacing constraint, Eq. (5.22), and using  $\mathbf{w}_0$ , one obtains

$$\mathbf{w}_0^T \cdot \underline{W}^T \cdot \underline{\ell}_{\mathbf{n}}^{-1} \cdot \underline{W} \cdot \mathbf{w}_0 = 1$$
(5.24)

Substituting in the tensor  $\underline{\ell}_{\mathbf{n}}^{-1} = (\frac{1}{r} - 1)\mathbf{n}\mathbf{n}^T + \underline{\delta}$  reduces the above equation to

$$(\underline{W} \cdot \mathbf{w}_0)^T \cdot \mathbf{n} = \pm \sqrt{r} \cos \theta.$$
 (5.25)

That is, Eq. (5.25) is the equation of two planes that the tip of the director **n** sits on. They are a distance  $\pm 1/(1 + \frac{1}{r}\tan^2\theta)^{1/2}$  from the origin, and with normal vector along the  $\underline{W} \cdot \mathbf{w}_0$  direction. Additionally the director is a unit vector and thus the allowed directors **n** after distortion sit on the intersection of the planes with the unit sphere  $\mathbf{n} \cdot \mathbf{n} = 1$ . These circles of intersection are always guaranteed since the distance of the planes from the origin is less than unity.

The orientation of the layer normal can also be calculated. Since it deforms affinely with the matrix then it is given by

$$\mathbf{k} = \frac{\underline{\lambda}^{-T} \cdot \mathbf{k}_0}{|\underline{\lambda}^{-T} \cdot \mathbf{k}_0|} \to \underline{\lambda}^{-T} \cdot \mathbf{k}_0, \qquad (5.26)$$

the simplification occurring because the layer spacing is fixed, that is  $d/d_0 = 1$ which follows from the fixed layer spacing of Eq. (5.25). When considering a particular soft deformation constructed by choosing a particular  $\underline{W}$  in Eq. (5.13), the above determines the choice of  $\underline{W}$  to achieve a desired **n** and **k**. Proceed by inserting a soft  $\underline{\lambda}^{-T}$  into Eq. (5.26) to determine the new **k**. It is  $\underline{\lambda}^{-T} = \underline{\ell}_{\mathbf{n}}^{-1/2} \cdot \underline{W} \cdot \underline{\ell}_{0}^{1/2}$ , on inverting and transposing. The normal then becomes  $\mathbf{k} = \underline{\ell}_{\mathbf{n}}^{-1/2} \cdot \underline{W} \cdot \mathbf{w}_{0}$ . Multiplying both sides from the left by  $\underline{\ell}_{\mathbf{n}}^{1/2}$ , and using the explicit form for  $\underline{\ell}_{\mathbf{n}}^{1/2}$  and recalling  $\mathbf{n} \cdot \mathbf{k} = \cos \theta$ , one obtains

$$\underline{W} \cdot \mathbf{w}_0 = \mathbf{k} + (\sqrt{r} - 1) \cos \theta \mathbf{n}, \qquad (5.27)$$

Thus the three vectors  $\underline{W} \cdot \mathbf{w}_0$ , **k** and **n** obey a the relation of the same form as Eq. (5.23). This motivates the definition of a new auxiliary vector  $\underline{W} \cdot \mathbf{w}_0 = \mathbf{w}$ .

The allowed soft modes correspond to the points where the two planes defined in Eq. (5.25) intersect a unit sphere. To analyse the soft modes first the case without  $\underline{W}$  is studied, followed by the more general case of those modes including a matrix  $\underline{W}$ .

## Geometrical interpretation of soft modes of the form $\underline{\ell}_n^{1/2} \cdot \underline{\ell}_0^{-1/2}$

The algebraically simplest (but certainly not physically simplest) soft modes in an SmC elastomer are those without a  $\underline{W}$  matrix. In this case the final director must lie on the intersection of the unit sphere and the planes of Eq. (5.25)). An illustration of this is shown in Fig. 5.3. The figure shows the initial director  $\mathbf{n}_0$  and the initial layer normal  $\mathbf{k}_0$  and two circles on the surface of the sphere, corresponding to the final orientation of the director  $\mathbf{n}$  and layer normal  $\mathbf{k}$ , that obey the layer constraint. Note that not all final



Figure 5.3: An illustration of the director orientations that satisfy the layer constraint.

positions of the director are possible with soft modes of this form. For **n** not on the circle of Fig. 5.3, an appropriate  $\underline{W}$  must be included such that the required final director position still obeys the layer constraint.

# Geometrical interpretation of general soft modes of the form $\underline{\ell}_n^{1/2}\cdot\underline{W}\cdot\underline{\ell}_0^{-1/2}$

To construct a soft mode that obeys the layer constraint with the director in the final position **n** requires the inclusion of an additional matrix  $\underline{W}$ . The general soft mode can be re-expressed just as in Eq. (5.7) and Eq. (5.18)  $\underline{\lambda} = \underline{W} \cdot \underline{\ell}_{\mathbf{n}'}^{1/2} \cdot \underline{\ell}_{\mathbf{0}}^{-1/2}$ . A fictitious director **n**' defined by  $\underline{W}^T \cdot \mathbf{n} = \mathbf{n}'$  plays the role of **n** in the simple soft mode of Fig. 5.3. The rotation matrix can then be broken down into two successive rotations,  $\underline{W} = \underline{W}_{\mathbf{R}} \cdot \underline{W}_{\mathbf{w}_0}(\xi)$  where the latter is a rotation by  $\xi$  about  $\mathbf{w}_0$  and takes  $\mathbf{n}'$  to  $\mathbf{n}_0$ , and  $\underline{W}_{\mathbf{R}}$  takes  $\mathbf{n}_0$ to **n**. Specifically  $\underline{W}_{\mathbf{R}}^T \cdot \mathbf{n} = \mathbf{n}_0$  and  $\underline{W}_{\mathbf{w}_0}^T \cdot \mathbf{n}_0 = \mathbf{n}'$  and one explicitly sees  $\underline{\ell}_{\mathbf{n}'}^{1/2} = \underline{W}_{\mathbf{w}_0}^T \cdot \underline{W}_{\mathbf{R}} \cdot \underline{\ell}_{\mathbf{n}}^{1/2} \cdot \underline{W}_{\mathbf{w}_0}$ . The power of the method is that  $\underline{\lambda}$  is now

$$\underline{\underline{\lambda}} = \underline{\underline{W}}_{\mathbf{R}} \cdot \underline{\underline{W}}_{\mathbf{w}_0}\left(\xi\right) \cdot \underline{\underline{\ell}}_{\mathbf{n}'}^{1/2} \cdot \underline{\underline{\ell}}_{0}^{-1/2}.$$
(5.28)

where the soft mode  $\underline{\ell}_{\mathbf{n}'}^{-1/2} \cdot \underline{\ell}_{0}^{1/2}$  is parametrised by the angle  $\xi$  and is independent of  $\underline{W}_{\mathbf{R}}$  which can freely be set in order to obtain whatever final director is desired, that is  $\mathbf{n} = \underline{W}_{\mathbf{R}} \cdot \mathbf{n}_{0}$ . This general, final director is not confined to the circle about  $\mathbf{w}_{0}$ , see Fig. 5.4 a) and b) for an illustration of the procedure. Having decided where the final director is to point, one then applies



Figure 5.4: a) shows the first stage of the process: a rotation about  $\mathbf{w}_0$ , b) shows the second stage: a general rotation about the axis  $\mathbf{R}$ .

the body rotation  $\underline{W}_{\mathbf{R}} \cdot \underline{W}_{\mathbf{w}_0}(\xi)$  to the softly deformed sample to complete the deformation Eq. (5.28).

All of the rotations can be separated out of the soft mode leaving just a symmetric deformation by using the polar decomposition theorem

$$\underline{\lambda} = \underline{\ell}_{\mathbf{n}'}^{1/2} \cdot \underline{\ell}_0^{-1/2} = \underline{U} \cdot \underline{S}, \tag{5.29}$$

where  $\underline{U}$  is a rotation matrix and  $\underline{S}$  is a symmetric matrix. The rotation axis for this decomposition must be in the  $\mathbf{n}' \wedge \mathbf{n}_0$  direction. This information can be used to construct  $\underline{U}^T \cdot \underline{\lambda}$  and demand that it is symmetric to find  $\underline{S}$ . The resulting rotation angle is given by

$$\tan \alpha = \frac{(1 - \sqrt{r})^2 \mathbf{n}_0 \cdot \mathbf{n}' \sqrt{1 - (\mathbf{n}_0 \cdot \mathbf{n}')^2}}{(1 + r) - (\mathbf{n}_0 \cdot \mathbf{n}')^2 (1 - \sqrt{r})^2}$$
(5.30)

Now a particular example of Eq. (5.28) is considered. Here rigid clamping constraints are not included so there is no formation of microstructure.

## 5.3.3 Example: Imposed $\lambda_{yy}$

To illustrate the soft modes an elongation in any direction could be imposed, provided the director has scope to rotate into that direction and thereby to extend the sample. This excludes stretches parallel to  $\mathbf{n}_0$ . An elongation perpendicular to the layer normal is particularly simple because it does not induce the layer normal to rotate.

An extension in the **y** direction is imposed on an elastomer with its layer normal in the **z** direction and the in-plane component of the director in the **x** direction, i.e.  $\mathbf{c} = \mathbf{x}$  initially. The deformation matrix will be of the form

$$\underline{\underline{\lambda}} = \begin{pmatrix} \lambda_{\rm xx} & 0 & \lambda_{\rm xz} \\ \lambda_{\rm yx} & \lambda_{\rm yy} & \lambda_{\rm yz} \\ 0 & 0 & \lambda_{\rm zz} \end{pmatrix}, \tag{5.31}$$

where the components  $\lambda_{xy}$  and  $\lambda_{zy}$  are not included. This is because these components deform the sample by translating the y faces of the sample in the  $\pm \mathbf{x}$  and  $\pm \mathbf{z}$  directions. Any small y forces associated with the yy elongation would generate counter torques and quickly eliminate the components in question. The  $\lambda_{zx}$  component is excluded because without compensating elongation in the  $\mathbf{z}$  direction it would compress the layers, see the analogous problem when a SmA is stretched along the layer normal in chapter 4. It would also rotate a component of the director perpendicular to the stretch direction.

The initial orientation of the layer normal and the director are given by

$$\mathbf{n}_0 = (\sin\theta, 0, \cos\theta) \tag{5.32}$$

$$\mathbf{k}_0 = (0, 0, 1) \tag{5.33}$$

where  $\theta$  is the tilt angle of the director (typically around 20°). The current orientation of the director is assumed to be

$$\mathbf{n} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta), \qquad (5.34)$$

and the layer normal, **k** unmoved. The layer normal ( $\mathbf{k}_0 = \mathbf{z}$ ) cannot be moved by deformation tensors of the form Eq. (5.31) since it must be derived from the expression  $\mathbf{k} = \underline{\lambda}^{-T} \cdot \mathbf{k}_0$  (i.e. the elements of  $k_i$  are derived from the cofactors of the elements  $\lambda_{iz}$ , all of which vanish except for the cofactor of  $\lambda_{zz}$ , as can be seen by inspection of Eq. (5.31)). In addition, the only consistent rotation matrices  $\underline{W}_{\mathbf{R}}$  that leave the layer normal unmoved, must have their rotation axis, **R**, parallel to  $\mathbf{k}_0$ . This rotation must take  $\mathbf{n}_0 \to \mathbf{n}$ . Thus  $\underline{W}_{\mathbf{R}}$  can be identified as a rotation of angle  $\phi$  around an axis parallel to  $\mathbf{k}_0$ , and could be written more concretely as  $\underline{W}_{\mathbf{k}_0}(\phi)$ . Bearing this in mind, one constructs the tensor  $\underline{\lambda} = \underline{W}_{\mathbf{k}_0}(\phi) \cdot \underline{W}_{\mathbf{w}_0}(\xi) \cdot \underline{\ell}_{\mathbf{n}'}^{1/2} \cdot \underline{\ell}_{\mathbf{0}}^{-1/2}$  (for the details of this see §5.A). The only remaining variable is  $\xi$ , and this can be determined by demanding that  $\lambda_{xy} = 0$  in the appendix expression for  $\underline{\lambda}$ . Writing  $\rho = \sin^2 \theta + r \cos^2 \theta \equiv w_0^2$ , this yields the following equation for  $\xi$ 

$$0 = \cos\xi\sin\phi + \sqrt{\frac{r}{\rho}}\cos\phi\sin\xi.$$
 (5.35)

Using this expression for  $\xi$  all the components of the deformation tensor can be obtained. Defining  $a(\phi) = \sqrt{\cos^2 \phi + \frac{\rho}{r} \sin^2 \phi}$  produces the following matrix for  $\underline{\lambda}$ 

$$\begin{pmatrix} a(\phi) & 0 & \frac{(r-1)\sin 2\theta}{2\rho}(-a(\phi) + \cos \phi) \\ \left(1 - \frac{\rho}{r}\right)\frac{\sin 2\phi}{2a(\phi)} & \frac{1}{a(\phi)} & \frac{(r-1)\sin 2\theta}{2\rho}\left(\sin \phi - \left(1 - \frac{\rho}{r}\right)\frac{\sin 2\phi}{2a(\phi)}\right) \\ 0 & 0 & 1 \end{pmatrix}$$

This tensor is explicitly constructed to be a soft mode and evidently has  $det[\underline{\lambda}] = 1$ . To illustrate this mode Fig. 5.5 shows how this sample deforms for various different azimuthal angles,  $\phi$ . The figure gives a view of a block of SmC rubber down the layer normal and should be compared with Fig. 5.2. Note that even after a rotation of the director of  $\phi = \pi$  the rubber does not



Figure 5.5: An illustration of the soft mode of a SmC elastomer. In this case the layer normal remains out of the page and the **c** direction together with  $\phi$  is shown in the centre of the diagram. A tilt angle of  $\theta = 30^{\circ}$  and an anisotropy of r = 8 were chosen.

return to its original configuration. Because of the tilt of the director w.r.t. the layer normal a strain  $\lambda_{xz} < 0$  is generated after  $\phi \to \pi$  and this component has a  $\cos \phi$  term. By contrast  $\lambda_{yx} = \lambda_{yz} = 0$  and  $\lambda_{yy} = 1$  at  $\phi = \pi$ ; indeed  $\lambda_{yz}$  depends on  $2\phi$ . At the intermediate value of  $\phi = \pi/2$  the elastomer has contracted along the direction of the original anisotropy tensor and so has developed both a  $\lambda_{xz}$  and  $\lambda_{yz}$  components of shear, that is with displacements in both the **x** and **y** directions. The maximum extension in the **y** direction occurs at  $\phi = \pi/2$ , when the  $\lambda_{yy}$  component takes the value  $\sqrt{r/\rho}$ . For the case with  $\theta = 30^{\circ}$  and r = 2 this gives a maximum extension of roughly 7%.

## 5.4. CONCLUSIONS

Alternatively, one can think of imposing the  $\lambda_{yy}$  extension to induce the rotation  $\phi$  of **c**, Fig. 5.6, and the sympathetic shears  $\lambda_{xz}$ ,  $\lambda_{yz}$  and  $\lambda_{yx}$ , Fig. 5.7. These plots of the explicit forms given for the elements of  $\underline{\lambda}$  reveal singular edges to the rotation  $\phi$  at  $0, \pi$  and  $2\pi$  analogously to those seen in nematic soft elasticity. Although for r = 2 and  $\theta = 30^{\circ}$  the extend of soft extension is only 7%.



Figure 5.6: Director rotation  $\phi$  about the layer normal against elongation,  $\lambda_{yy}$ , perpendicular to its initial direction  $(r = 2, \theta = 30^{\circ})$ .

It should be noted that the sample can develop very large shears softly; at  $\phi = \pi$ ,  $\lambda_{xz} \sim -\frac{1}{2}$ , see Fig. 5.7.

## 5.4 Conclusions

A geometrical interpretation of the soft modes in two phases of smectic elastomers has been presented. It was found that there is only one soft trajectory for the director, excluding body rotations, as a consequence of the restrictions imposed upon the elastomer by the fixed layer constraint. Specific examples of this mode were presented for a monodomains of biaxial SmA or SmC. They can respond softly to a single imposed component of the deformation tensor. An illustration of imposed  $\lambda_{yy}$  was given but in principle we could impose any other component, including  $\lambda_{zz}$ , through a combination of the single soft trajectory and a body rotation. The experimental boundary conditions of



Figure 5.7: Sympathetic shears  $\lambda_{yx}$ ,  $\lambda_{yz}$  and  $\lambda_{xz}$  in response to an imposed  $\lambda_{yy}$ . Again r = 2 and  $\theta = 30^{\circ}$ .

fixed ends near the clamps mean that any soft mode will be accompanied by microstructure, as is frequently the case in nematic elastomers.
## **5.A** Details of the deformation matrix

Here details of the calculation of the deformation tensor required for a soft mode when the  $\lambda_{yy}$  component is imposed are given. The following vectors are required

$$\mathbf{k}_0 = (0, 0, 1) \tag{5.36}$$

$$\mathbf{k}_{0} = (0, 0, 1)$$
(5.36)  

$$\mathbf{c}_{0} = (0, 1, 0)$$
(5.37)

$$\mathbf{w}_0 = \underline{\ell}_0^{1/2} \cdot \mathbf{k}_0 \tag{5.38}$$

$$\mathbf{c} = (\cos\phi, \sin\phi, 0) \tag{5.39}$$

$$\mathbf{k} = \mathbf{k}_0 = \mathbf{R} \tag{5.40}$$

From these vectors we can calculate the rotation matrices

$$\underline{W}_{\mathbf{k}_{0}}(\phi) = \underline{\delta}\cos\phi + (1 - \cos\phi)\mathbf{k}_{0}\mathbf{k}_{0}^{T} + (\sin\phi)\mathbf{k}_{0} \wedge$$
(5.41)

$$\underline{W}_{\mathbf{w}_0}(\xi) = \underline{\delta} \cos \xi + \frac{(1 - \cos \xi)}{w_0^2} \mathbf{w}_0 \mathbf{w}_0^T + \frac{\sin \xi}{w_0} \mathbf{w}_0 \wedge \quad . \tag{5.42}$$

Using the expression

$$\underline{\lambda} = \underline{\ell}_{\mathbf{n}}^{1/2} \cdot \underline{W}_{\mathbf{k}_0}(\phi) \cdot \underline{W}_{\mathbf{w}_0}(\xi) \cdot \underline{\ell}_0^{-1/2},$$

results in the following

$$\begin{pmatrix} \cos\xi\cos\phi - \sqrt{\frac{\rho}{r}}\sin\xi\sin\phi & -\sqrt{\frac{r}{\rho}}\cos\phi\sin\xi - \cos\xi\sin\phi & \cdots \\ \sqrt{\frac{\rho}{r}}\cos\phi\sin\xi + \cos\xi\sin\phi & \cos\xi\cos\phi - \sqrt{\frac{r}{\rho}}\sin\xi\sin\phi & \cdots \\ 0 & 0 & \cdots \\ \cdots & \frac{(r-1)\sin2\theta}{2\rho}\left(\cos\phi(1-\cos\xi) + \sqrt{\frac{\rho}{r}}\sin\xi\sin\phi\right) \\ \cdots & \frac{(r-1)\sin2\theta}{2\rho}\left(-\sqrt{\frac{\rho}{r}}\sin\xi\cos\phi + (1-\cos\xi)\sin\phi\right) \\ \cdots & 1 \end{pmatrix}$$

To determine  $\xi$  simply demand that the  $\lambda_{xy}$  component is zero and obtain the matrix given in the text.

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