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A BIRD'S EYE VIEW OF LIQUID CRYSTAL ELASTOMERS

Liquid crystal elastomers bring together, as nowhere else, three important ideas: *orientational order* in amorphous soft materials, *responsive molecular shape* and *quenched topological constraints*. Acting together, they create many new physical phenomena that are the subject of this book. This bird's eye view sketches how these themes come together and thereby explains the approach of our book.

In the early chapters we introduce the reader to liquid crystals and to polymers since they are our building blocks. One could regard the first part of our book as a primer for an undergraduate or graduate student embarking on a study of polymer or liquid crystal physics, or on complex fluids and solids. Then elastomers are discussed both from the molecular point of view, and within continuum elasticity. We need to understand how materials respond at very large deformations for which only a molecular approach is suitable. Also one needs to understand the resolution of strains into their component pure shears and rotations, the latter also being important in these unusual solids. We also provide a primer for the basics of these two areas that are otherwise only found in difficult and advanced texts.

Classical liquid crystals are typically fluids of relatively stiff rod molecules with long range orientational order. The simplest case is nematic – where the average ordering direction of the rods, the director $\boldsymbol{n}$, is uniform. Long polymer chains, with incorporated rigid anisotropic units can also order nematically and thus form liquid crystalline polymers. By contrast with rigid rods, these flexible chains elongate when their component rods align. This results in a change of average molecular shape, from spherical to spheroidal as the isotropic polymers become nematic. In the prolate anisotropy case, the long axis of the spheroid points along the nematic director $\boldsymbol{n}$, Fig. 1.1.

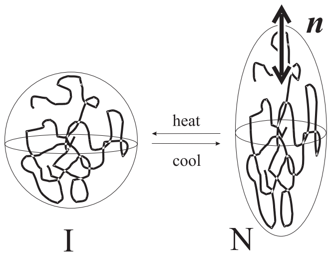

FIG. 1.1. Polymers are on average spherical in the isotropic (I) state and elongate when they are cooled to the nematic (N) state. The director $\boldsymbol{n}$ points along the principal axis of the shape spheroid. (The mesogenic rods incorporated into the polymer chain are not shown in this sketch, only the backbone is traced.)

So far we have no more than a sophisticated liquid crystal. Changes in average molecular shape induced by changes in orientational order do little to modify the properties of this new liquid crystal. Linking the polymer chains together into a gel network fixes their topology, and the melt becomes an elastic solid – a rubber. Radically new properties can now arise from this ability to change molecular shape while in the solid state. To understand this we have to consider rubber elasticity.

In rubber, monomers remain highly mobile and thus liquid-like. Thermal fluctuations move the chains as rapidly as in the melt, but only as far as their topological crosslinking constraints allow. These loose constraints make the polymeric liquid into a weak, highly extensible material. Nevertheless, rubber is a solid in that an energy input is required to change its macroscopic shape (in contrast to a liquid, which would flow in response). Equivalently, a rubber recovers its original state when external influences are removed. Systems where fluctuations are limited by constraints are known in statistical mechanics as 'quenched' - rigidity and memory of shape stem directly from this. It is a form of imprinting found in classical elastomers and also in chiral solids, as we shall see when thinking about cholesteric elastomers.

Can topology, frozen into a mobile fluid by constraints, act to imprint liquid crystalline order into the system? The expectation based on simple networks would be 'yes'. This question was posed, and qualitatively answered, by P-G. de Gennes in 1969. He actually asked a slightly more sophisticated question: Crosslink conventional polymers (not liquid crystalline polymers) into a network in the presence of a liquid crystalline solvent. On removal of the solvent, do the intrinsically isotropic chains remember the anisotropy pertaining at the moment of genesis of their topology?[1] The answer for ideal chains linked in a nematic solvent is 'no'! Intrinsically nematic polymers, linked in a nematic phase of their own making, can also elude their topological memory on heating. How this is done (and failure in the non-ideal case) is a major theme of this book.

Second, what effects follow from changing nematic order and thus molecular shape? The answer is new types of thermal- and light-induced shape changes.

The third question one can ask is: While in the liquid-crystal state, what connection between mechanical properties and nematic order does the crosslinking topology induce? The answer to this question is also remarkable and is discussed below. It leads to entirely new effects – shape change without energy cost, extreme mechanical effects and rotatory-mechanical coupling. We give a preview below of these effects in the form of a sketch – details have to await the later chapters of the book.

Rubber resists mechanical deformation because the network chains have maximal entropy in their natural, undeformed state. Crosslinking creates a topological relation between chains that in effect tethers them to the solid matrix they collectively make up. Macroscopic deformation then inflicts a change away from the naturally spherical average shape of each network strand, and the entropy, S, falls. The free energy then rises, $\Delta F = -T\Delta S > 0$. This free energy, dependent only on an entropy change itself driven by molecular shape change, explains why polymers are sometimes thought of as

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[1] G. Allen saw the similarity of this question to that of crosslinking in the presence of a mechanical field, a great insight considering how monodomain liquid crystal elastomers are made today.

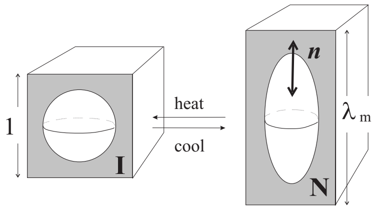

FIG. 1.2. A unit cube of rubber in the isotropic (I) state. Embedded in it is shown the average of the chain distribution (spherical). The block elongates by a factor λ_{m} on cooling to the nematic (N) state, accommodating the now elongated chains.

'entropic springs'. Macroscopic changes in shape are coupled to molecular changes. In conventional rubber it is always the macroscopic that drives the molecular; the induced conformational entropy of macromolecules offers the elastic resistance.

Nematic polymers suffer spontaneous shape changes associated with changing levels of nematic (orientational) order, Fig. 1.1. One now sees a reversal of influence: changes at the molecular level induce a corresponding change at the macroscopic level, that is induce mechanical strains, Fig. 1.2: a block of rubber elongates by a factor of $\lambda_{\mathrm{m}} > 1$ on cooling or $1/\lambda_{\mathrm{m}} < 1$ on heating. This process is perfectly reversible. Starting in the nematic state, chains become spherical on heating. But mechanical strain must now accompany the molecular readjustment. Very large deformations are not hard to achieve, see Fig. 1.3. Provided chains are in a broad sense ideal, it turns out that chain shape can reach isotropy both for the imprinted case of de Gennes (on removal of nematic solvent) and for the more common case of elastomers formed from liquid crystalline polymers (on heating). Chains experiencing entanglement between their crosslinking points also evade any permanent record of their genesis. Many real nematic elastomers and gels in practice closely conform to these ideal models. Others are non-ideal – they retain some nematic order at high temperatures as a result of their order and topology combining with other factors such as random pinning fields and compositional fluctuations. They still show the elongations of Fig. 1.3, but residues of non-ideality are seen in the elastic effects we review below.

This extreme thermomechanical effect, and the phenomena of Figs. 1.5 and 1.7, can only be seen in monodomain, well aligned samples. Without very special precautions

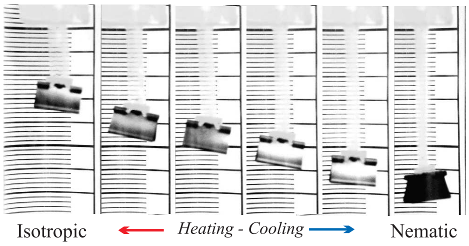

FIG. 1.3. A strip of nematic rubber extends and contracts according to its temperature. Note the scale behind the strip and the weight that is lifted!

during fabrication, liquid crystal elastomers are always found in polydomain form, with very fine texture of director orientations. The great breakthrough in this field, developing a first method of obtaining large, perfect monodomain nematic elastomers, was made by Küpfer and Finkelmann in 1991.

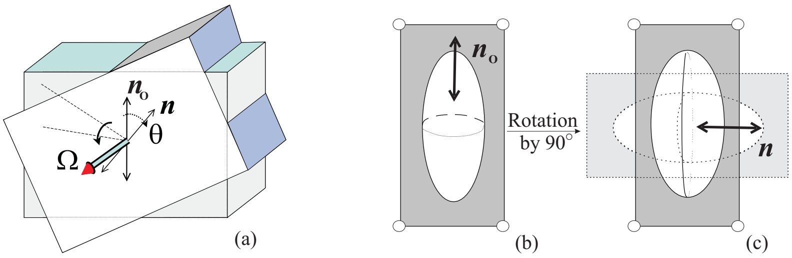

FIG. 1.4. (a) Rotations of the director and matrix by angles θ and Ω, respectively. From (b) to (c) the director, and thus chain shape distribution, is rotated by 90^o from $\boldsymbol{n}_o$ to $\boldsymbol{n}$. The rubber is mechanically clamped and hence the chains in (c) that would be naturally elongated along $\boldsymbol{n}$ must be compressed: the dotted spheroid in (c) is compressed to the actual solid spheroid.

Nematic-elastic coupling was the third question we posed and gives rise to new rotational phenomena ubiquitous in liquid crystal elastomers. It is possible to rotate the director and the rubber matrix independently, see Fig. 1.4 (a). Such relative rotations of the body and of its internal anisotropy axis show that nematic elastomers are not simply exotic, highly-extensible, uniaxial crystals. Such materials belong to a class displaying so-called Cosserat elasticity, but with the distinction that deformations and rotations can be large in elastomers. Imagine now rotating the director while clamping the body so its shape does not change, Figs. 1.4(b) and (c). The natural, prolate spheroidal distribution, when rotated by 90^o to be along $\boldsymbol{n}$, has a problem. Chains do not naturally fit, since the clamped body to which they are tethered is not correspondingly elongated along $\boldsymbol{n}$ to accommodate their long dimensions. Chains in fact must have been compressed to fit, at considerable entropy loss if they were very anisotropic. A rotation of 180^o recovers the initial state, so the free energy must be periodic, and turns out to be $F = \frac{1}{2}D_1 \sin^2(\theta - \Omega)$. The rotational modulus, D_1, was first given by de Gennes in the infinitesimal form $\frac{1}{2}D_1(\theta - \Omega)^2$. A rotation of the director in Fig. 1.4(b) would lead to a 'virtual' intermediate state depicted by dotted lines in Fig. 1.4(c). Subsequent squeezing to get back the actual body shape demanded by the clamp condition (full lines) of Fig. 1.4(c) costs an energy proportional to the rubber modulus, μ, and to the square of the order, Q, (since Q determines the average chain shape anisotropy). Thus $D_1 \sim \mu Q^2$. In contrast to ordinary nematics, it costs energy to uniformly rotate the director independently of the matrix.

In liquid nematics it is director gradients that suffer Frank elastic penalties, and thus long-wavelength spatial variations of the rotation angle cost vanishingly small energy. Thermal excitation of these rotations causes even monodomain nematic liquids to scatter light and to be turbid. Not so monodomain nematic elastomers which are optically clear because even long wavelength director rotations cost a finite rubber-elastic energy $\frac{1}{2}D_1\theta^2$ and cannot be excited, see Fig. 1.5. The excitations have acquired a mass, in the language of field theory.

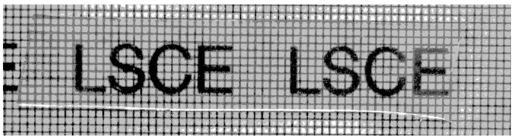

FIG. 1.5. A strip of monodomain 'single-crystal' nematic rubber. It is completely transparent and highly birefringent (image: H. Finkelmann).

Local rotations, so central to nematic elastomers, yield a subtle and spectacular new elastic phenomenon which we call 'soft elasticity'. Imagine rotating the director but now *not* clamping the embedding body, in contrast to Figs. 1.4(b) and (c). One simple response would be to rotate the body by the same angle as the director, and this would clearly cost no energy. However, contrary to intuition, there is an infinity of other ways by mechanical deformation to accommodate the anisotropic distribution of chains without its distortion as it rotates. Thus the entropy of the chains does not change, in spite of macroscopic deformations. Figure 1.6 illustrates the initial and final states of a 90^{o} director rotation. They are separated by a path of states, characterised by an intermediate rotation angle θ and by a corresponding shape of the body, one of which is shown. This θ-state is shown in the sketch (b) accommodating the spheroid without distorting it. A special combination of shears and elongations/compressions is required, but it turns out not very difficult to achieve in experiment!

One of the traditional ways to rotate the director in liquid crystals is by applying an electric (or magnetic) field and generating a local torque due to the dielectric anisotropy. Due to the nematic-elastic coupling, the director rotation is very difficult if an elastomer sample is mechanically constrained. Apart from a few exceptions (all characterised by a very low rubber-elastic modulus, such as in highly swollen gels) no electrooptical response can occur. However, if the elastomer is mechanically unconstrained, the situation changes remarkably. In a beautiful series of experiments, Urayama (2005,2006)

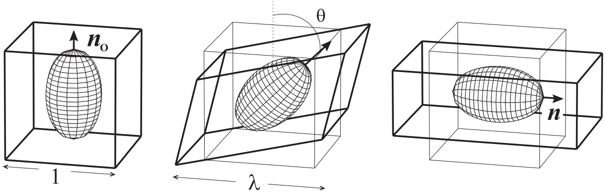

FIG. 1.6. Rotation of chain shape distribution, from $\boldsymbol{n}_{\mathrm{o}}$ to $\boldsymbol{n}$, with an intermediate state θ shown. The unconstrained rubber deforms to accommodate the rotating director without distorting the chain distribution.

has confirmed the prediction of soft elasticity: that the field-induced director rotation has no energy cost, can easily reach 90^{o} rotation angles and has associated mechanical strains that almost exactly follow the sketch in Fig. 1.6.

Practically, when dealing with rubbers, one might instead impose a mechanical distortion (say an elongation, λ, perpendicular to the original director) and have the other components of strain, and the director orientation, follow it. The result is the same – extension of a rubber costs no elastic energy and is accompanied by a characteristic director rotation. The mechanical confirmation of the cartoon is shown in stress-strain curves in Fig. 1.7(a) and the director rotation in Fig. 1.7(b).

We have made liquid crystals into solids, albeit rather weak solids, by crosslinking them. Like all rubbers, they remain locally fluid-like in their molecular freedom and mobility. Paradoxically, their liquid crystallinity allows these solid liquid crystals to change shape without energy cost, that is to behave for some deformations like a liquid. Non-ideality gives a response we call 'semi-soft'. There is now a small threshold before director rotation (seen in the electrooptical/mechanical experiments of Urayama (2005,2006), and to varying degrees in Fig. 1.7); thereafter deformation proceeds at little additional resistance until the internal rotation is complete. This stress plateau, the same singular form of the director rotation, and the relaxation of the other mechanical degrees of freedom are still qualitatively soft, in spite of a threshold.

There is a deep symmetry reason for this apparently mysterious softness that Fig. 1.6 rationalises in terms of the model of an egg-shaped chain distribution rotating in a solid that adopts new shapes to accommodate it. Ideally, nematic elastomers are rotationally invariant under separate rotations of both the reference state and of the target state into which it is deformed. If under some conditions, not necessarily the current ones, an

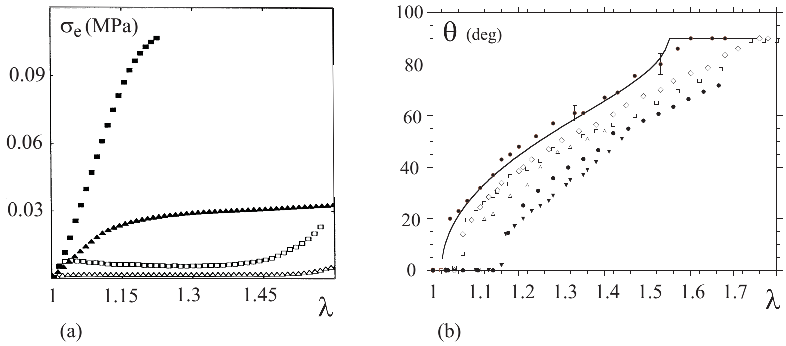

FIG. 1.7. (a) Stress-deformation data of Küpfer and Finkelmann (1994), for a series of rubbers with the same composition and crosslinking density, but differing in preparation history: some show a normal elastic response while others are remarkably soft. (b) The angle of director rotation on stretching nematic elastomer perpendicular to the director for a variety of different materials, from Finkelmann *et al.* (1997). The solid line from, theoretical modeling, accurately reproduces singular points and characteristic shape of data.

isotropic state can be attained, then a theorem of Golubović and Lubensky shows that in consequence soft elasticity must exist. It is a question of care with the fundamental tenet of elasticity theory, the principle of material frame indifference. We shall examine this theorem and its consequences many times in this book, including what happens when the conditions for it to hold are violated, that is when semi-softness prevails.

Elastic softness, or attempts to achieve it, pervade much of the elasticity of nematic elastomers. If clamps or boundary conditions frustrate uniform soft deformation trajectories, microstructures will evolve to allow softness with the cost of interfaces being a relatively smaller price to pay. There are similarities between this so-called 'quasi-convexification' and that seen in martensite and other shape-memory alloys.

Cholesteric liquid crystals have a helical director distribution. Locally they are very nearly conventional nematics since their director twist occurs typically over microns, a much longer length scale than that associated with nematic molecular ordering. They can be crosslinked to form elastomers which retain the cholesteric director distribution. Several phenomena unique to cholesterics emerge: Being locally nematic, cholesteric elastomers would like on heating and cooling to lose and recover orientational order as nematic elastomers do. However, they cannot resolve the requirement at neighbouring points to spontaneously distort by λ_{m}, but in different directions. Accordingly, their chains cannot forget their topologically imprinted past when they attempt to reach a totally isotropic reference state (the second de Gennes' prediction of 1969). Thus cholesteric rubbers also cannot deform softly in response to imposed strains. Their optical and mechanical responses to imposed stress are exceedingly rich as a result. They are brightly coloured due to selective reflection and change colour as they are stretched – their photonic band structure changes with strain. They can emit laser radiation with a colour shifted by mechanical effects. Further, the effect of topological imprinting can select and extract molecules of specific handedness from a mixed solvent. Such rubbers can act as a mechanical separator of chirality – a new slant on a problem that goes back to Pasteur.

We have sketched the essentials of nematic (and cholesteric) rubber elasticity. This survey leaves out many new phenomena dealt with in later chapters, for instance electromechanical Freedericks effects, photo-elastomers that drastically change shape on illumination, rheology and viscoelasticity that crosses between soft and conventional depending upon frequency and geometry, and so on.

Smectics are the other class of liquid crystal order. They have plane-like, lamellar modulation of density in one direction (SmA), or additionally a tilt of the director away from the layer normal (SmC). Many other more complex smectic phases exist and could also be made into elastomers. In many smectic elastomers, layers are constrained not to move relative to the rubber matrix. Deformations of a rubber along the layer normal are thus resisted by a layer spacing modulus, B, of the order of 10^2 times greater than the shear modulus of the matrix. Distortions in plane, either extensions or appropriate shears, are simply resisted by the rubber matrix. Thus SmA elastomers are rubbery in the two dimensions of their layer planes, but respond as hard conventional solids in their third dimension. Fig. 1.8 shows this behaviour. Such extreme mechanical anisotropy promises interesting applications.

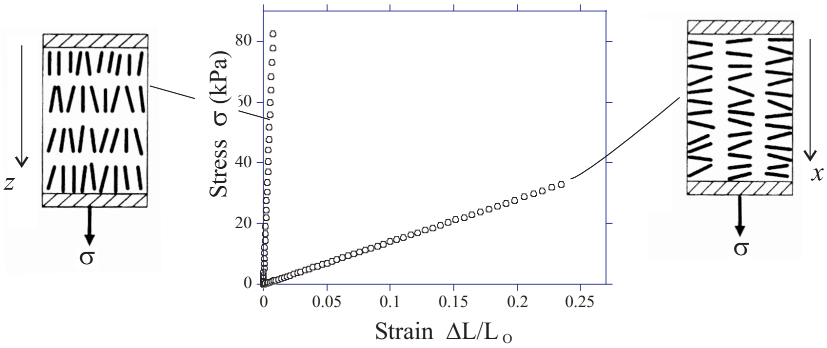

FIG. 1.8. In-plane fluidity and parallel rigidity in a smectic A elastomer (Nishikawa *et al.*, 1997). The Young modulus parallel and perpendicular to the layer normals differ very greatly - the rubber elasticity is two-dimensional.

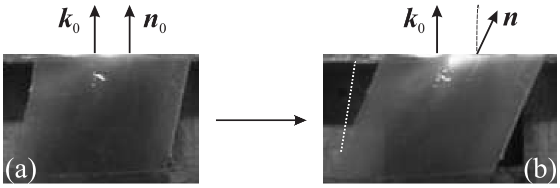

FIG. 1.9. (a) A SmA elastomer (Hiraoka *et al.*, 2005). (b) Spontaneous shear λ_{xz} in achieving the SmC state.

The director tilt associated with the transition from SmA to SmC induces distortion in the polymer chain shape distribution. Since chain shape is coupled to mechanical shape for an elastomer, one expects, and sees in Fig. 1.9, spontaneous distortion. This response to order change is analogous to the elongations associated with orientational order of chains on entering the nematic state, but here we instead have shear. The amplitude is also large, of the order of 0.4 in the figure. As in the nematic case, the broken symmetry suggests a mechanism for SmC solids richer still than that of SmA elastomers, including SmC soft elasticity equivalent to that of Fig. 1.6.

The tilted, SmC, liquids also exist in chiral forms which must, on symmetry grounds be ferroelectric. Their elastomers are too. Ferroelectric rubber is very special: mechanically it is soft, about 10^4 times lower in modulus than ferro- and piezoelectrics because, as sketched above, its molecules are spatially localised by topological rather than energetic constraints. Distortions give polarisation changes comparable to those in ordinary ferroelectrics. But the response in terms of stress must necessarily be 10^4 times larger than in conventional materials.

We end our preview as we started – solids created by topological constraints are soft and highly extensible. Liquid crystal elastomers share this character with their important cousins, the conventional elastomers. But their additional liquid crystalline order gives them entirely new kinds of elasticity and other unexpected phenomena.