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Liquid Crystal Elastomers

M. WARNER
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PREFACE

Liquid crystals are unusual materials. As their name suggests, they inhabit the grey area between liquids and solids. They have long range orientational order, typically of the unique axes of their component rod-like or plate molecules. Spatial variations of this average direction of molecular orientation are resisted by so-called curvature (Frank) elasticity. On the other hand liquid crystals can flow, albeit as anisotropic liquids.

Polymers too are unusual materials. Above the glass transition, the physics is mostly dominated by the high entropy inherent in the disorder of their component long chain molecules. Resistance to molecular shape change arises mostly from the imperative to maintain high entropy. Viscoelastic flow and rubber elasticity are macroscopic manifestations of this principle. Thus rubber, where the long molecules are linked together, also inhabits the grey region between liquids and solids. Though nominally a solid, rubber is capable of very high deformations, greater than any other type of solid. Its internal molecular motion is rapid, as in a liquid, with the resulting amorphous solid being highly extensible rather than glassy. If it were not for the few crosslinks holding the chains into a percolating network, rubber would flow under stress, as ordinary polymers and other liquids do. The bulk (compression) modulus of typical rubber is of the same order as that of all liquids, and solids, but the shear modulus is about $10^{-4} - 10^{-5}$ times smaller. Thus rubber essentially deforms as a liquid, that is by shearing at constant volume. It is a weak solid and therein lies its enormous technological importance.

This book is concerned about the phenomena arising when these two marginal materials, liquid crystals and polymers, are combined into one even more mysterious material – polymer liquid crystals. For two compelling reasons we shall concentrate on such polymers crosslinked into networks, that is, on elastomers and gels made from polymer liquid crystals:

1. Liquid crystal elastomers exhibit many entirely new effects that are not simply enhancements of native liquid crystals or polymers. We shall see their thermal phase transformations giving rise to spontaneous shape changes of many hundreds of per cents, transitions and instabilities induced by applied mechanical stress or strain, and some unusual dynamical effects. Strangest of all, we shall see elastomers under some conditions behaving entirely softly, deforming as true liquids do without the application of stress. All these new forms of elasticity have their genesis in the ambiguities between liquid and solid that are present in liquid crystals and polymers, but are only brought to light in a crosslinked rubbery network.
2. A molecular picture of rubber elasticity is now well established. Since the late 1930s its entropic basis has been understood and turns out to be as universal as, say, the ideal gas laws. The rubber shear modulus, μ, is simply $n_s k_B T$ where n_s counts the number of network strands per unit volume, and temperature T enters for the same entropic reason it does in the gas laws. There is no mention of the

chemistry of chains or other molecular details and the picture is thus of great generality. We call this the classical theory, to which various complexities such as crosslink fluctuations, entanglements and nematic interactions have later been added.

By contrast to simple polymers, which change shape only in response to external forces, liquid crystal polymers do so *spontaneously* when they orientationally order their monomer segments. Can one nevertheless create a picture of their rubber elasticity of the same generality as that of classical rubber? It turns out that one can, with the sole extra ingredient of chain shape anisotropy (a single number directly measurable by experiment). We shall treat this anisotropy phenomenologically and find we can explore it at great length. One could go into many theoretical complexities, taking into account effects of finite chain extensibility, entanglements and fluctuations – however, in all cases, the underlying symmetry of spontaneously anisotropic network strands enters these approaches in the same way and the new physical phenomena are not thereby radically influenced.

Alternatively, one could try to calculate the polymer chain anisotropy that appears in the molecular picture of rubber elasticity. There is, however, no universal agreement about which way to do this. A further complication is that polymer liquid crystals can be either main chain or side chain variants, where the rod-like elements are found respectively in, or pendant to, the polymer backbone. Nematic and smectic phases of considerable complexity and differing symmetry arise according to the molecular geometry. For instance side chain fluids can exist in 3 possible uniaxial nematic phases, $N_{\rm I}$, $N_{\rm II}$ and $N_{\rm III}$, with still further biaxial possibilities.

In this book, by concentrating on *Liquid Crystal Elastomers*, rather than polymer liquid crystals *per se*, we relegate these theoretical uncertainties in the understanding of polymer liquid crystals to a subsidiary role. Key physical properties of crosslinked elastomers and gels are established without any detailed knowledge of *how* chains become spontaneously elongated or flattened. When more molecular knowledge is required, an adequate qualitative understanding of nematic and smectic networks can be obtained by adopting the simplest molecular models of polymer liquid crystals. In contrast, a treatise on polymer liquid crystals would have to address these issues rather more directly.

These two reasons, the existence of novel physical phenomena and their relative independence from the details of molecular interactions and ordering, explain the sequence of arguments followed by this book. We introduce liquid crystals, polymers and rubber elasticity at the rather basic level required for the universal description of the main topic – Liquid Crystal Elastomers. Then we look at the new phenomena displayed by these materials and, finally, concentrate on the analysis of key features of nematic, cholesteric and then smectic rubbery networks.

Rubber is capable of very large extensions. Many important new phenomena of nematic origin only occur at extensions of many tens of percents and are themselves highly non-linear. Linear continuum theory is utterly incapable of describing such a regime and this inadequacy is a motivation for our molecular picture of nematic rubber elasticity. However, it is clear that in liquid crystal elastomers we have not only the Lamé elasticity of ordinary solids and the Frank curvature elasticity of liquid crystals, but also novel contributions arising from the coupling of the two. The richness and complexity of this new elasticity are such that it is worthwhile also analysing it using the powerful and general methods of continuum theory. There is a second motivation for studying continuum theory – for smectic elastomers there is not yet any underlying molecular theory and phenomenological theory is the best we can do. Because of their important technological applications, for instance in piezo- and ferroelectricity, an understanding of smectic elastomers is a vital priority. The latter chapters of our book are devoted to this, addressing the linear continuum approaches to elastomers with more complicated structure than simple uniaxial nematics. We also build a bridge between the elasticity methods of rubber and the application of continuum theory into the non-linear regime. At this point we revisit the symmetry arguments which explain why 'soft elasticity' is possible and why it cannot be found in classical elastic systems.

We were tempted to take 'Solid Liquid Crystals' as our title. This would have been apt but obscure. We hope that this book will illuminate the peculiar materials that merit this description.

Mark Warner and Eugene Terentjev
26 February 2003

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From the initial speculations of the late 60s to the ideas of artificial muscles in the late 1990s, the presence of Pierre-Gilles de Gennes can be felt in the field and in this book. We are grateful for his personal encouragement over many years in many different areas. In 1981 Heino Finkelmann discovered all three elastomer phases and subsequently in the 1990s found routes to nematic, cholesteric and smectic monodomains. We have been inspired by both his pioneering chemistry and deep physical insights into the processes underlying liquid crystal elastomers, and also benefited enormously from his advice and help with techniques of sample preparation. Sam Edwards, one of the founders of modern polymer physics, introduced us to polymer networks. He has been a constant source of advice and motivation in our work on liquid crystal elastomers and in the writing of this book. His philosophy of the necessity of molecular models of polymers when one is confronted with non-linear effects, as is the case throughout this book, will be evident to the reader.

Over the years, we have enjoyed fruitful scientific collaboration and exchange of ideas with F. Kremer, G.R. Mitchell, W. Stille, R.V. Talroze, R. Zentel and many others. Geoffrey Allen and Ed Samulski first introduced us to the idea of nematic effects in elastomers generally and have encouraged our work over many years. Several people have influenced us in a particularly crucial way: Robert Meyer shared his penetrating insight into many new effects in elastomers, including but not limited to Freedericks transitions, stripes and field deformations of cholesterics. We drew much from contact with Tom Lubensky on soft elasticity and non-linear continuum theory. Our work on the continuum description of smectics was in part in collaboration with him. Peter Olmsted's clear and concise formulation of soft elasticity in molecular theory, and his symmetry arguments for its existence, is an approach adopted in large measure in our book and also helped us formulate our current understanding of the whole subject. We also thank Stuart Clarke and Yong Mao for guidance, advice and criticism over their years of collaboration with us. Richard James exposed us to the concept of quasi-convexification and the mechanisms of macroscopic, inhomogeneous soft deformation. He and Antonio DeSimone convinced us that nematic elastomers were an outstanding example of where this process can occur.

The first chapter of Tom Faber's remarkable book on fluid mechanics inspired our Birds Eye View of the material of this book. A. DeSimone and S. Conti, generously gave advice and also material for the relevant sections of Chapter 8. Samuel Kutter provided many figures from his own work. He, James Adams and Daniel Corbett commented critically on the book, much improving it, though its shortcomings have to remain ours. David Green helped us overcome technical difficulties of LaTeX.

Finally, we thank our wives Adele and Helen for their endurance and patience over the period when this book was written, which was far too long by any measure.

CONTENTS

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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.

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 suffices. Also one needs to understand the resolution of large deformations into their component pure shears and rotations, the latter also being important in these unusual solids. Hopefully 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 ordering is nematic – where the mean ordering direction of the rods, the director $\boldsymbol{n}$, is uniform. The rod-like character of the molecules changes little when they orient to form a nematic phase. Long polymer chains, with incorporated rigid anisotropic units can also order nematically and thus form liquid crystalline polymers. Now, by contrast, these molecules elongate when their component rods orient. A change of average molecular shape has thus been introduced, from spherical to spheroidal as the isotropic polymers become nematic. In the prolate spheroidal case, the long axis of the spheroid points along the nematic director $\boldsymbol{n}$, Fig. 1.1.

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. It will turn out that radical properties can now arise from this new ability to change molecular shape while in the solid state. To understand the consequences 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

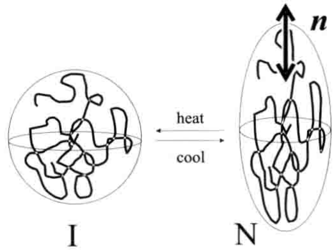

FIG. 1.1. Polymers are on average spherical in the isotropic (I) state and elongate when they are cooled to the nematic (N) state. The director $\boldsymbol{n}$ points along the long axis of the shape spheroid. (The mesogenic rods incorporated into the polymer chain are not shown in this sketch, only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

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 opto-mechanical effects and rotatory-mechanical coupling. We give a preview below of these effects in the form a sketch – details and rigour 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

[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.

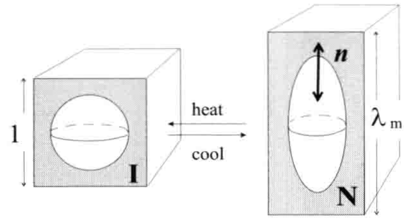

FIG. 1.2. A unit cube of rubber in the isotropic (I) state. Embedded in it is shown the average of the chain distribution (spherical). The block elongates by a factor λ_m on cooling to the nematic (N) state, accommodating the now elongated chains.

driven by molecular shape change, explains why polymers are sometimes thought of as 'entropic springs'. Macroscopic changes in shape are coupled to molecular changes. In conventional rubber it is always the macroscopic that drives the molecular; the molecular conformational entropy offers the elastic resistance.

Nematic polymers suffer spontaneous shape changes associated with changing levels of nematic (orientational) order, Fig. 1.1. In monodomain nematic elastomers 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 $\lambda_m > 1$ on cooling or $1/\lambda_m < 1$ on heating. This process is perfectly reversible. Starting in the nematic state, chains become spherical on heating and lose memory of their nematic genesis. 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

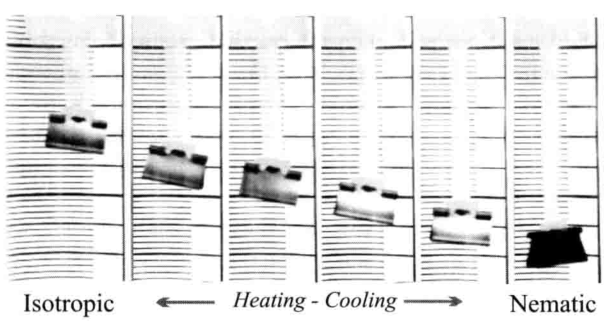

FIG. 1.3. A strip of nematic rubber extends and contracts according to its temperature. Note the scale behind the strip and the weight that is lifted!

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