

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_I , N_{II} and N_{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.

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