Introduction to Flexoelectricity: Its Discovery and Basic Concepts

Robert B. Meyer
The Martin Fisher School of Physics, Brandeis University
Waltham, MA, 02454, USA
e-mail: meyer@brandeis.edu

Flexoelectricity – what is it? How does it arise in liquid crystals? What are its consequences? What role does it play in liquid crystal phases, structures, and textures? How is it measured? What is its role, both realized and potential, in applications of liquid crystals? How was it discovered and what is its history in the context of the development of liquid crystal science and technology in the last 50 years? The name flexoelectricity clearly indicates the dual role of curvature distortions and electrical effects in liquid crystals, but just how are these two fundamental sets of concepts related by this phenomenon? This book attempts to lay out the answers to these questions, with a combination of broad reviews and focused insights into the role of flexoelectricity in the science and technology of liquid crystals. In this introduction there is first a little informal review of history along with some general comments on the fundamentals and the special challenges presented by this phenomenon, and then there is a brief sketch of the chapters of this book.

As a graduate student in the Division of Engineering and Applied Physics at Harvard University in the late 1960s, I was introduced to liquid crystals by David Turnbull, who suggested that I read Sir Frederick Charles Frank’s 1958 paper on the theory of symmetry, elasticity, and defects in liquid crystals. This paper introduced me to symmetry arguments as a powerful way of analyzing a system, and it made a deep impression on me. As I began working on liquid crystals, I soon came to realize that understanding molecular structure was crucial to understanding these systems, again an idea strongly suggested by Frank’s paper. I was soon fortunate enough to set up a collaboration with a young organic chemist at Harvard, Dave
Dolphin, who synthesized new liquid crystals, and I became deeply interested in the details of molecular structure, especially the shape, electrical polarity, and chirality of these molecules. My research focused on field effects in nematics and cholesterics, especially the unwinding of the cholesteric helix by the field interacting with the anisotropy of the susceptibility in the uniaxial liquid crystal. With this set of interests and ideas in mind, I returned to Frank’s paper,1 and reviewed again his symmetry arguments, especially his argument that if the molecular organization of the nematic phase were intrinsically polar, that is, if rod-like molecules with one end different from the other were arranged to be all oriented one way, then that element of macroscopic symmetry would imply both spontaneous electrical polarization and a term in the elastic free energy density linear in splay distortion. The presence of that linear splay term would lead to spontaneous splay distortion of the polar nematic in its ground state, rather than the simple uniaxial structure observed in known nematics. The lack of that spontaneous splay argued strongly against the polar organization of the molecules in the nematic phase. While Frank focused on the nature of the ground state symmetry and properties, it was a small step for me to apply the same argument to excitations from the ground state, and see that electrical polarization parallel to the molecular long axis (defined by a unit vector n called the director) would induce splay, and vice versa.

Looking again at Frank’s arguments for eliminating terms in the elastic free energy density linear in bend, I saw the connection between polarization perpendicular to the nematic director and bend distortions, which break the rotational symmetry about the director. Reviewing the theory of piezoelectric crystals, I realized that what I was studying was a kind of second-order piezoelectricity involving certain second-order strains of the liquid crystal structure, that is, curvatures, rather than the first-order shear strains of piezoelectric crystals, which of course could not be sustained in the fluid phase. It took Pierre-Gilles de Gennes to see that this coupling of curvatures and electrical polarization deserved a new name, and he coined the term flexoelectricity.

Looking back on this discovery, I am struck by several things. First, it seems to me that Frank should have discovered this effect! His deep insights into symmetry and structure focused on the ground state symmetry, and not on excitations from that state. I was in the fortunate situation of thinking about a number of topics concerning liquid crystals, especially the coupling between their molecular structure and their response to electric fields. The stunning development of liquid crystal science and technology
in the past 50 years has relied on the intimate interplay of knowledge and discovery in a wide range of sciences, including areas of physics, chemistry, biology, and engineering. The broader one’s knowledge and interests, the better prepared one is to make significant discoveries, especially in fields like materials science, which are intrinsically interdisciplinary. Second, it is clear that returning to basic symmetry arguments is always worthwhile, and insights based on symmetry will have the most significant impact, since they are not limited to the odd quirks of a single material, but apply to whole classes of materials. And third, it is always worthwhile to review the work, and to try to understand the thinking, of great scientists like F.C. Frank. Their insights, and the thought processes that led to them, are a powerful lesson on how to think creatively in science.

A second kind of hindsight about this discovery is that I made a basic mistake in defining the flexoelectric coefficients for splay and bend. Because the flexoelectric effect is linear in curvatures and fields, in any scheme of definitions, there is no preference for the coefficients to be positive or negative on the average; either sign is physically possible. However, there is a reasonable geometric argument for the relative signs of the two coefficients for splay and bend distortions. For a simple cylindrical curvature of the director field, with the nematic director either radial (pure splay) or tangential (pure bend), the flexoelectric coefficients should be defined so that the curvature-induced polarization is either radial outward or radial inward for both splay and bend cases. Unfortunately, I chose definitions of the bend and splay vectors that were intrinsically opposite to one another, in this geometric sense, so that the curvature-induced polarizations were opposite in sign, relative to the radial direction, for cylindrical splay and bend curvatures of the director field. Using the currently accepted coefficients $e_1$ and $e_3$ based on my original paper, this means that the mean flexoelectric coefficient is $\bar{e} = (e_1 - e_3)/2$. This is not wrong mathematically, but it is confusing, and one often sees the expression $(e_1 - e_3)/2$ referred to as the difference between the flexoelectric coefficients, rather than their mean, which is surely confusing. To alleviate this problem, first I would define the splay and bend vectors so that their polar properties are consistently oriented the same way with respect to curvature. The splay vector should be $S = n(\nabla \cdot n)$ and the bend vector should be $B = n \times (\nabla \times n)$, which is opposite in sign to the bend vector defined in my first paper. I would propose defining two new flexoelectric coefficients, $e_s$ and $e_b$ for the splay and bend cases, with $e_s = e_1$ and $e_b = -e_3$ of the previous definitions, related to the previously defined splay and bend vectors. The flexoelectric
polarization would now be defined as \( P_f = e_s n (\nabla \cdot n) + e_b n \times (\nabla \times n) \).

Thus the mean flexoelectric coefficient would now be \( \bar{e} = (e_s + e_b)/2 \).

Returning again to the value of considering fundamental symmetry arguments, I must point out one of the startling fundamental discoveries about flexoelectricity, made eight years after the publication of the discovery of the effect. My initial picture of the molecular origin of the effect was based on the idea that the steric polarity of the molecule and its electrical polarity are intimately coupled in the structure of the molecule, and that this coupling is the link that resulted in flexoelectricity. Thus a cone-shaped molecule must possess an electrical dipole moment oriented either parallel or antiparallel to the axis of the cone, and a banana-shaped molecule must possess a transverse dipole moment oriented either toward or away from the centre of curvature of the banana. A splay distortion would tend to orient the cone molecules preferentially, and this would produce a net polarization. Likewise a bend curvature would preferentially orient the bananas, again producing electrical polarization. One could likewise understand the inverse effects of polarization-induced curvature. The only question was the magnitude of the couplings, which required some model of the interaction of an individual molecule with the curvature-distorted director field. Symmetry demanded both the internal couplings of steric polarity and electrical polarity in the molecular structure and the coupling of the molecular shape to the curvature field, but by chance either of these couplings could be very large or very small in a particular material. Based on this picture, I believed that molecules that were not intrinsically polar, both electrically and sterically, would not exhibit flexoelectricity. Most liquid crystal molecules are polar, but highly symmetric molecules that entirely lack any net polarity also form liquid crystals, and it seemed clear to me that they would not exhibit flexoelectricity. However, in 1977, Prost and Marcerou published a paper that overturned this idea. They returned to the basic symmetry arguments about the structure of liquid crystals, relating to the most general description of the shape and charge distributions of molecules forming liquid crystals, and the structure of the distortion fields, splay and bend, which interact with the molecules. Highly symmetric molecules lacking a dipolar term in the description of their shape and charge distribution, but having a quadrupolar element to their structure, a natural requirement of any liquid crystal molecule, would interact with the curvature field to produce a spatial gradient of the quadrupole density, which is a dipole density! Thus even in these molecules curvature and electrical polarization are coupled to produce flexoelectricity. Again, the return to basic symmetry
arguments proved to be a powerful approach to understanding material structures and phenomena.

From the start, it was clear that flexoelectricity involved some special challenges both for theory and for experiments. I have spoken of the “discovery” of flexoelectricity\textsuperscript{2} in 1969 as an exercise in symmetry arguments and basic considerations of molecular structure and organization. But such “discoveries” in theory demand confirmation through observations of material properties and responses to applied fields, in this case, curvature fields and electric fields. Qualitatively, one must see that an applied electric field produces the expected curvatures, or conversely that curvatures produce the expected electrical polarizations, which must be detected in some way. Moreover, one wants to measure the strength of the effect, and relate it to the underlying structure of the molecules and their organization in the liquid crystal. This kind of quantitative knowledge is the basis for forming a solid understanding of any material and its properties, the kind of understanding that is necessary for progress, for instance in optimizing a material for a certain effect, or for designing an application of the effect to some practical purpose. Thus in the first paper, a rough estimate of the size of the effect was made, based on molecular properties, and two observations that might involve flexoelectricity were described. But these were only speculations to provide some initial guidance to possible experiments. They did not initially prove very useful, but they illustrated fundamental problems with the experimental aspects of flexoelectricity.

First, any electrical effect is immediately in competition with all other electrical effects, and must be carefully separated from them to be studied. For example, to study a curvature-induced polarization, one might consider producing a sample with a static curvature structure, say a layer of nematic confined between two cylindrical electrodes, with the director parallel or perpendicular to the electrodes. Flexoelectricity will produce space charges at the electrodes, but these would tend to be cancelled by free ionic charges in the material. Any fields produced by flexo-induced space charges would only propagate a distance of the order of the Debye screening length, so effects due to these fields would have to be detected on a microscopic scale in most materials.

Second, for observing curvature structures induced by an externally applied electric field, one must also consider the interaction of the field with the anisotropy of the polarizability of the medium, which tends to align the director either parallel or perpendicular to the applied field. This can suppress the flexoelectrically induced curvature in many geometries.
Third, because the flexoelectric terms in the free energy density are linear in the spatial derivatives, in a finite sample, they can often be integrated by parts as surface integrals rather than bulk integrals, so that the total flexoelectric energy in a sample is a function of the boundary conditions of the sample, and insensitive to continuous changes in the curvature structure within the sample. This means that the observation of a flexoelectrically induced structure often relies on weak anchoring of the director on the surfaces, or on the movement of topological defects into or through the sample, to change the topology of the interior of the sample contained by the strong anchoring boundary conditions. In the first case, it means that the observation of flexoelectric effects involves analysis combining knowledge of other effects, such as surface anchoring strength. In the second case, there is a threshold field to be crossed before the defects are generated or driven to new locations. Both of these restrictions make flexoelectricity difficult to study.

In general, flexoelectricity requires inhomogeneity in the sample being studied, and does not play a simply observed role in undistorted, single-domain samples in a homogeneous electric field, clearly the simplest sample geometry, and one commonly studied in liquid crystal experiments. It only plays a role when curvature distortions are involved or when there are inhomogeneous applied fields. This fundamental complication has been overcome in many clever experiments, so that there have now been many measurements of flexoelectricity in a range of materials.

For the development of engineering applications, flexoelectricity has some fundamental features to offer. Because it is linear in the applied electric field, it is fundamentally different from effects due to the anisotropy of the susceptibility in liquid crystals, which are quadratic in the field strength. Thus in a fixed geometry, the sign of the applied field matters, so positive and negative fields can produce quite different responses, either linear or non-linear in nature, depending on the geometry of the particular sample and electrodes. Moreover, the “difficulty” mentioned above, that certain flexoelectric responses require a change in sample topology, due to the motion of topological defects, can actually be more of a feature than a bug, leading to a sample response that locks in a change of topology after the external field is removed. This can be the basis of bistable or even multi-stable electrical switching phenomena, which are especially useful in display devices that retain information without continuing dissipation of electrical power.
Introduction to Flexoelectricity

The chapters of this book expand on the ideas mentioned here, as well as others that have arisen from the efforts of many talented scientists studying this rather unusual phenomenon over the past 40 years. To get the most out of this book, the reader should be familiar with the basics of liquid crystal phenomenology, including molecular structure, phases, textures, and typical sample geometries, as well as theoretical concepts, including curvature elasticity theory and some elements of the fluid dynamics of liquid crystals.

In the first chapter, Osipov presents a review of the molecular theory of the origins of the flexoelectric effect, with careful attention to how molecular shape and structural correlations determine the flexoelectric coefficients. In the second chapter, Madhusudana reviews the broad range of experimental methods that have been employed to measure the flexoelectric coefficients, discussing the many challenges this task has presented. Following these general reviews, in the third chapter, Jákli, Harden, and Eber discuss a particular measurement technique applied to an important new category of liquid crystal materials, the bent-core molecules, which can exhibit a giant flexoelectric effect. In the fourth chapter, Buka, Tóth-Katona, Eber, Krekhov, and Pesch discuss the role of flexoelectricity in pattern formation, especially addressing how this effect competes with other electro-dynamical effects leading to stripe patterns. Čepič, in Chapter 5, presents a clear argument for the role flexoelectricity plays in establishing the fundamental multi-layer ordering of the various polar smectic phases. In Chapter 6, Petrov traces the research on the role of flexoelectricity in the structure and molecular ordering of biological membranes, reviewing both theory and experimental results, including its role in nerve conduction and in the action of hair cells in hearing. In the final chapter, Rudquist and Lagerwall discuss in detail two important applications of flexoelectricity. The first is based on the flexoelectric response of a short-pitch cholesteric liquid crystal to a field applied perpendicular to the helix axis, which produces a fast linear electro-optical effect by rotating the average optical axis of the cholesteric. The second is based on the electric field-driven switching of a particular sample geometry between two topologically distinct states, by the field-induced motion of topological defects, an important feature of the non-linear flexoelectric response, as noted above. It is the basis of the first flexoelectric device to reach commercial production by the company ZBD, their acronym for “Zenithal Bistable Devices.” Based on the foundations of our current knowledge about flexoelectricity reviewed in this book, it will be interesting to see how the science and technology of flexoelectricity develop over the next 40 years.
References