Electro-mechanical effects in liquid crystals

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INVITED ARTICLE

Electro-mechanical effects in liquid crystals

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Linear and quadratic electromechanical effects of liquid crystals are reviewed. Among the linear effects the piezoelectric and flexoelectric effects and their analogues in low molecular weight fluid, nematic, smectic and columnar liquid crystals, in polymeric and elastomer liquid crystals, are discussed and compared with the piezo-electricity of conventional solid piezoelectrics. As the most important quadratic electromechanical effect, an overview is given of the electrostriction effects in fluid, polymeric and rubber-like liquid-crystalline systems. These topics are rarely discussed in the liquid crystal literature, although they are becoming increasingly important for future energy conversion and micro-energy-generating devices.

Keywords: electromechanical effects; liquid crystals; piezoelectricity; flexoelectricity

1. Preface

The first time I met Professor Alfred Saupe was in the summer of 1989, when I joined his group at the Liquid Crystal Institute at Kent State University, as a new post-doctoral fellow. My assignment was to study the viscosity of liquid crystal-polymer solutions. It was definitely an interesting project, but after solving all of the computer programming tasks, it did not occupy my whole time. At this point I asked him if, in my

Alfred Saupe, when he was 2 years old. (Picture from his wonderful wife, Brigitte Saupe.)

spare time, I could work more on my PhD project, which was the study of linear electromechanical effects in ferroelectric liquid crystals. After demonstrating the effect and explaining why I thought it was interesting, he had many questions (later I learned that if he asked a question, he really was interested and listened to the answer), and gave me two weeks to write the theory that I thought I had. After two weeks I gave him at least 10 pages of calculations, but at the second equation he found a major problem, so we decided to work it out together. This process then took a few years and gave us lots of ideas for new experiments that I carried out in two years and we published, finally, in the third year of my post-doctoral period. During this process, whilst also working on other tasks, I gained a clear impression that he was not only a genius in theory, but also in experi-mental work. Fortunately I was able to work with him on electromechanical effects in Halle, Germany after he became the Director of the Max Planck Working Group on Liquid Crystals. After I moved to Hungary and then back to Kent State, USA, where I worked on bent-core liquid crystals, I talked to him regularly. Each time, he quickly found out any problems I might be facing, and gave very good suggestions for the solution. During this process I think that I not only learned a great deal of physics, but he also became my second father who gave good advice, even in private matters. I wish he could still advise me today.

In this paper I would like to explain what we understood together about electromechanical effects, which was basically neglected at that time, but which grew to become a major area in liquid crystals of

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biological importance, and especially in liquid crystal gels and elastomers.

2.   Introduction

Electromechanical coupling in uniform dielectric media includes piezoelectricity, electrostriction and flexoelectricity. In this paper electrohydrodynamic instabilities and electrorotation effects, such as the rotation of a flat chiral nematic drop normal to an applied DC electric field [1], electro-pumping [2, 3], electrospinning [4] and electrotranslation [5–7] effects, will not be covered because they require non-zero thresholds.

Piezoelectricity, a linear coupling between stress and electric polarisation, was discovered in 1880 by Pierre and Jacques Curie [8]. One year later Lippmann [9] proposed, on the basis of thermodynamic principles, that the inverse effect (electrically induced pressure) must also exist. The Curie brothers also verified experimentally this converse piezoelectric effect.

Mathematically, the stress $\hat{T}$ is a second rank tensor, and the polarisation $\vec{P}$ is a vector, so the term coupling them, is a third rank tensor. For materials, in the absence of a spontaneous polarisation $\vec{P}_o$ or spontaneous strain $\hat{S}_o$, we can write for the direct and converse effect, respectively, that:

and
$$\begin{aligned} \vec{P}_i &= d_{ijk} T_{jk} \\ S_{ij} &= d_{kij} E_k. \end{aligned} \tag{1}$$

In these equations *i, j, k* are the coordinate axis, S_{ij} are the elements of the strain tensor and the elements $d_{i,jk}$ of the third rank tensor are the piezoelectric coefficients. For piezoelectricity to exist the material should be non-centrosymmetric, and such properties are restricted to 20 out of the 32 classes of crystal point symmetry groups [10]. Experiments show that present-day piezo sensors and actuators have piezoelectric constants in the range 10^{-10}–10^{-9} CN^{-1}, which renders them useful in a wide range of applications starting from the well-known ultrasonics and hydroacoustics [11], frequency standards [12] and ferroelectric ceramics [13–15] used in sensors, transducers, vibration dampeners and energy harvesters.

Electrostriction [16] is a quadratic mechanical deformation of a dielectric material under the forces exerted by an electrostatic field. Mechanical equilibrium of an electrostrictive material is described by $\nabla \cdot (\boldsymbol{T}^{elast} + \boldsymbol{T}^{visc} + \boldsymbol{T}^M) = 0$, where $\boldsymbol{T}^{elast}$ and $\boldsymbol{T}^{visc}$ are the elastic and viscous stress tensors, respectively, and $\boldsymbol{T}^M$ is the electrostatic (Maxwell stress) tensor. The electrostatic force per unit area (Maxwell stress) written by Landau [10] as $T_{ij}^M = -E_i D_j + \frac{1}{2} \delta_{ij} D_k E_k$, where $\delta_{ij} = 1$ only if i=j, otherwise it is zero (Kronecker delta

symbol), $\vec{E}$ and $\vec{D} = \hat{\boldsymbol{\varepsilon}} \cdot \vec{E}$ are the electric field and displacement (surface charge density). The resulting strain is, therefore, proportional to the square of the electric field, so no inverse of the effect exists because a strain would not define the polarity of the electric field. Unlike piezoelectricity, electrostriction can provide electrically-induced actuation without any hysteresis and applies to all crystal symmetries. It has numerous applications such as actuators and artificial muscles [17], or even as scanning Maxwell stress microscopy [18].

Flexoelectricity is also a linear effect, with both direct and converse components, but it does not require the lack of inversion symmetry, but a gradient of the strain tensor is needed to provide a polarisation. Formally the direct and converse flexoelectric coupling constants, e_{ijkl}, can be described with the same fourth rank tensor as:

$$\begin{aligned} P_i^{flexo} &= e_{ijkl} \frac{\partial S_{jk}}{\partial x_l}, \\ A \frac{\partial T_{ij}}{\partial x_k} &= e_{ijkl} E_k, \end{aligned} \tag{2}$$

where *A* is the surface area. Flexoelectricity in crystals was discussed first in 1964 [19] but soon after Meyer [20] showed that in liquid crystals with bent or pear-shaped molecules that director bend or splay, respectively, can result in an electric polarisation. The liquid crystal analogue of the direct flexoelectric effect (top of Equation (2)) can be written as $\vec{P}_f = e_1 \vec{n}(\text{div} \, \vec{n}) + e_3 (\text{curl} \, \vec{n}) \times \vec{n}$ [20]. In liquid crystals the theory was first verified experimentally as early as 1971 [21] and the flexoelectric coefficients found to be in the range of $e \sim 10^{-12}$–10^{-11} C m^{-1}. In solid crystals the developments were slower and the first experiments in 1988 [22] gave $e \sim 10^{-11}$–10^{-10} C m^{-1}.

The aim of this paper is to review the development of electromechanical studies in liquid crystals in all their existing forms (i.e. fluid, polymer, gel and elastomer). During these descriptions we will compare the results with those for solid crystals, where the studies proceeded independently.

3.   Piezoelectric effects of liquid crystals

The definition of piezoelectricity extended considerably over time. Originally it was used only for crystals in connection with compressions, but later it was generalised to polymers and other materials for any strains and stresses, including shear.

By symmetry not only solids, but also liquid crystals and other organised fluids, can represent linear coupling between electric (polarisation, field) and

Table 1. The most important liquid crystal phases with their symmetry and non-vanishing piezoelectric coupling constants.

Phase	Molecular shape	Symmetry	Non-zero piezoelectric constants
N, SmA, L_α	Cylinder	$D_{\infty h}$	N/O
N*, SmA*	Chiral cylinder	D_∞	$d_{1,23} = -d_{2,13}$
SmAP,	Bent shape	$C_{2\nu}$	$d_{3,11}; d_{3,22}; d_{3,33}, d_{1,13}; d_{2,23}$
SmC	Cylinder	C_{2h}	N/O
SmC*	Chiral cylinder	C_2	$d_{3,11}; d_{3,22}; d_{3,33}; d_{1,13}; d_{2,23}; d_{1,23}; d_{2,13}; d_{3,12}$
SmCP	Bent shape	C_2	$d_{3,11}; d_{3,22}; d_{3,33}; d_{1,13}; d_{2,23}; d_{1,23}; d_{2,13}; d_{3,12}$
SmC_G	Bent shape	C_1	all $d_{i,jk}$
Col_h; H_1, H_2	Cylinder	D_{6h}	N/A
Col*$_{tilt}$	Chiral cylinder	C_2	$d_{3,11}; d_{3,22}; d_{3,33}; d_{1,13}; d_{2,23}; d_{1,23}; d_{2,13}; d_{3,12}$
P_h	Bowl shape	$C_{\infty\nu}$	$d_{3,33}; d_{3,11}=d_{3,22}$
P^*_h	Chiral bowl	C_∞	$d_{3,33}; d_{3,11}; d_{3,22}$
P_{tilt}	Tilted bowl	C_2	$d_{3,11}; d_{3,22}; d_{3,33}, d_{1,13}; d_{2,23}; d_{1,23}; d_{2,13}; d_{3,12}$

mechanical (stress, strain) quantities. Structured fluids have a low symmetry and a rich variety of piezoelectric-type coupling constants may exist. Lack of inversion symmetry can be due to the chirality of rod-shaped molecules containing carbon stereo-centres or particular molecular shapes such as bent and asymmetric packing [23]. Chiral liquid crystal phases are the chiral nematics, chiral smectics (SmC* of rod-shaped molecules [24], or SmCP of bent-core molecules [25]) and chiral columnar phases.

Table 1 shows, following symmetry considerations, that a number of liquid crystal phases can have linear coupling between an electric field and mechanical strain. The non-vanishing piezoelectric coefficients are determined by the Curie principle, which states that the tensor coefficients characterising material properties should be invariant under the symmetry transformations of the substance [26]. From the definitions of Equation (1), it follows that $d_{i,jk}$ will transform as the product of x_i, x_j, x_k. Accordingly, in a system with inversion symmetry, transformations like $x \rightarrow -x$, $y \rightarrow -y$ and $z \rightarrow -z$, would require that $d_{-i,-j-k} = (-1)^3 d_{i,jk}$ for any i,j,k, which is equivalent to the statement that systems with inversion symmetry cannot be piezoelectric. At the other end of the symmetry range the materials with C_1 symmetry allow the presence of all piezoelectric constants. Since $d_{i,jk}=d_{i,kj}$, it means $3 \times 6 = 18$ constants. The number of possible non-zero components can be determined for each of the 20 out of the 32 crystallographic groups [27] and three of the continuous point groups belong to this category.

It can be seen from Table 1 that a number of liquid crystal phases, SmC* of chiral rod shapes, the tilted columnar phase of chiral disc-shaped molecules, the SmCP of achiral bent-core molecules and the tilted bowl-shaped molecules, have C_2 symmetry with eight independent piezoelectric coefficients.

On the other hand, liquid crystals are fluid, at least in some directions, so they cannot typically maintain elastic restoring forces. Accordingly, without

generalisation of the definition of strain, linear electromechanical effects can be regarded as piezoelectric only in directions where the material is of an elastic type (e.g. in the direction normal to the layers in smectics and in the plane normal to the columns in columnar liquid crystals). The borderline between elastic and viscous behaviour, however, is washed out in soft materials like liquid crystals. For example, we can ask if the hexatic phases (SmB, SmI, etc.) with quasi long-range order are elastic, or not. It is definitely very important to generalise the definition of piezoelectricity to fluid, or partially fluid directions. The mathematical definition given for solids can be formally maintained in the fluid directions by generalising the definition of the strain tensor $\vec{S} = \vec{\nabla} \cdot \vec{s}$ to hold even for displacements caused by viscous flows. This obviously can be done only for periodic motions, when $\vec{s}$ can be regarded as the amplitude of the vibration. For static cases the displacement, and the piezoelectric coupling constant determined in this way, would increase in time, and even for periodic situations, the piezoelectric constant could show abnormal frequency behaviour due to the viscous nature of the stress. For these reasons other expressions, such as 'linear electromechanical effect' for fluid-like motions may be preferred. The real piezoelectric behaviour of liquid crystals may be observed, for example, when their structure is frozen-in a glassy state, or the molecules are cross-linked, as in elastomers. Bearing in mind however, that the structure and symmetry of a frozen-in state is the same as that of a partially fluid one, the word 'piezoelectricity' may be used even in the fluid directions.

In Table 1 we also see that the SmA* and chiral nematic phases may possess a piezoelectric response in a geometry where electric polarisation is induced normal to the shear plane. This is illustrated in Figure 1. The smectic A* materials are composed of chiral molecules (illustrated as a helix). Owing to the molecular chirality they do not have mirror symmetry (this would invert the handedness), but they have two
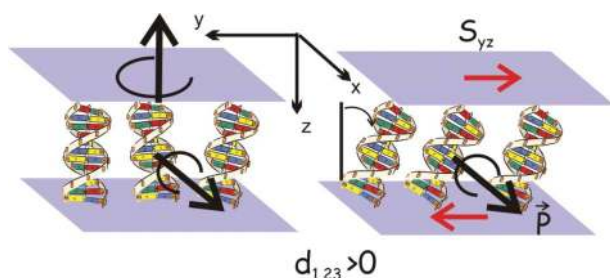
Figure 1. Explanation of the piezoelectric response in SmA* materials. Note: the double helices do not correspond to the actual molecular shape; they only illustrate the chirality of the molecules.

Figure 2. Illustration of the shear deformation of the director structure and the induction of net polarisation in the SmC* phase. The smectic layers are parallel to the xy plane. The tilt plane rotates from one layer to the other. (a) Undisturbed helical structure where the macroscopic polarisation is averaged to zero. (b) Due to the action of the shear along y, the axial symmetry of the configuration is broken and a non-zero polarisation component appears along x [34]. Arrows indicate the spontaneous polarisation $\vec{P}$, which is normal to the tilt plane (the plane determined by the layer normal and the projection of the tilt direction (the so-called c-director). Figure reproduced with permission of Taylor and Francis.

two-fold symmetry axes: one is in plane of the layers, x, the other one is parallel to the layer normal, z. When a shear is applied in the yz plane, a small tilt of the molecules is induced. When this happens, the material will not be symmetric with respect to a 180° rotation along the layer normal. It means that the x component of any vector, such as molecular dipole moments, will not be averaged to zero but would result in a net polarisation. The polarisation is sensitive to the sign of the strain and changes sign when the shear is reversed. This, therefore, is a piezoelectric effect given by the coupling constant $d_{x,yz} = P_x/S_{yz}$. We emphasise that in the piezoelectricity of the SmA* the chirality and tilt are needed for the electricity polarisation. This concept has enormous importance in explaining piezoelectric and ferroelectric phenomena in structured fluids. The converse effect, that is, the electroclinic, is another representation of the chirality–tilt–polarity triangle. In that case the molecular chirality and the field-induced polarity leads to the tilt.

The inverse of the effect, that is, an electric field along x would result in a shear strain, which would also lead to a tilt of the director. The optical consequence of this effect, rotation of the optic axis (the director) proportional to the electric field, is known as the electroclinic effect [28–30]. It is especially strong near to a transition to the spontaneously tilted SmC* phase and provides very fast (around 1–10 μs) thresholdless switching.

The tilt does not necessarily require a layer structure and the same concept can be employed to explain the piezoelectricity of the chiral nematic liquid crystal. In this case the shear along the helical axis leads to a tilt of the director towards the helical axis and a polarisation normal to the shear plane. This shear electricity was predicted by Prost [31], and was verified experimentally for chiral nematic elastomers, where the molecules are weakly cross-linked and so can sustain elastic strains [32, 33].
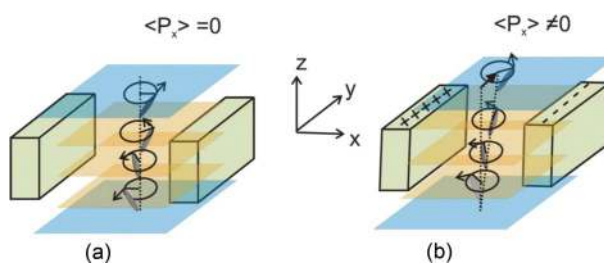
Direct [34, 35] and converse [36, 37] piezoelectric effects have been studied mostly in low molecular weight fluid SmC* liquid crystals.

The direct piezoelectric (or mechanoelectrical) effect in SmC* materials is due to the shear-induced polarisation [34], resulting from the distortion of the helix as illustrated in Figure 2. In the ground state (no-shear) the director is tilted with respect to the layer normal with an angle θ and forms a helix with a pitch, p. The spontaneous polarisation that due to the chirality is normal to the tilt plane was illustrated by Meyer *et al.* [24]. The shear in the yz plane aligns the c-director parallel to the shear and consequently the polarisation normal to the shear plane, which due to chirality leads to an accumulation of opposite charges on the electrodes placed normal to the helical axis and to the smectic layer normal as seen in Figure 2(b).

Direct piezoelectric-type signals were also studied in ferroelectric columnar liquid crystals [38], which have the same C_2 symmetries as the SmC* materials [39]. In spite of the same symmetry the piezoelectric constant is relatively low because the cross-section of the column is not circular, but slightly elliptical, which suppresses greatly the rotation of the polarisation by the elastic nature of the two-dimensional lattice structure. The piezoelectric response of SmC* elastomers [40, 41] and glasses [42] have also been observed. In the latter case a fluid liquid crystal was cooled to a glassy state in the presence of an electric field, so that the glass became poled. It is remarkable that the magnitude of the piezoelectric constants (50 pCN^{-1}) were found to be comparable to the poled piezoelectric polymer polyvinylidene fluoride [43].

Direct piezoelectrical effects were also observed on various biological systems and in lyotropic liquid crystals and membranes [44]. Since aqueous lyotropics suffer from high electric conductivity, it is important in experiments to reduce the conductivity. For this, water needs to be replaced with another hydrophilic solvent, such as ethylene glycol [45–47]. The first piezoelectric measurements of non-aqueous, cholesterol-containing lyotropic phases were performed by Petrov [48, 49] in 1988 using an oscillation drop method. Subsequently, these measurements were also carried out with hydrated lecithin gel phases without [50] and with cholesterol [51].

Recently, it was pointed out [52] that chiral lipid membranes in their L_α (lipid molecules on average are normal to the bilayers) phase have the same symmetry as chiral thermotropic smectic A materials, which is piezoelectric (see Table 1). Accordingly, a tilt of the lipids with respect to the bilayers results in an electric polarisation normal to the tilt plane as illustrated in Figure 1. Motivated by this notion, studying stacks of chiral lipids in their hydrated form was used to investigate amphotropic (both lyotropic and thermotropic) smectic materials [53]. By periodically shearing and compressing films of hydrated egg-yolk L-α-phosphatidylcholine, a uniform tilt of the director with respect to the bilayer's normal was induced, which produced an electric current perpendicular to the tilt plane and along the bilayers. The illustration of this effect together with the molecular structure of the major component of egg-yolk lecithin is shown in Figure 3(a). A representative experimental result of the mechanical vibration-induced electric polarisation is illustrated in Figure 3(b). Analysis of the results shows that the role of the horizontal shear is only to direct this buckling resulting in a uniform director tilt. It was found that the tilt-induced polarisation increases with temperature and reaches as high as $P = 300$ nC cm^{-2} at 70°C. These values are comparable to those in thermotropic SmC* materials [54].

In Figure 3(c) we have plotted the tilt angle dependence of the induced polarisation measured at room temperature. It shows a hysteresis, probably related to the effect of vertical vibration on the alignment. At increasing vibrational amplitudes the alignment becomes more and more uniform corresponding to an increasing slope. At decreasing amplitude the slope is almost constant below 3° showing that the homeotropic alignment basically remains constant. By periodically shearing and compressing non-aqueous lamellar phases of left (L-alpha-phosphatidylcholine), right (D-alpha-phosphatidylcholine) and racemic (DL-alpha-phosphatidylcholine) lipids, it was verified that the shear produced an electric current perpendicular
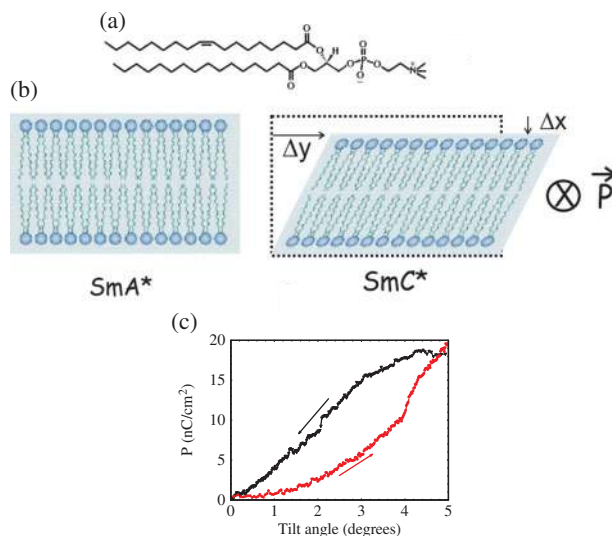

Figure 3. (a) Illustration of the molecular structure of phospholipid L-α-phosphatidylcholine. (b) Illustration of the pietzoelectricity. (c) The induced polarisation at the function of the tilt angle.

to the tilt plane only with chiral lipids, where the phase of the vibration had the opposite sign for the D and L enantiomers. This excludes any mechanism other than the piezoelectric origin of the effect [55].

It is important to note that the symmetry argument illustrated in Figures 1 and 3 is valid for any number of layers, including single or double lipid layers, which are the major components of cellular membranes. As most living cell membranes contain chiral lipids, we hypothesise that piezoelectricity may have a role in the function of cell membranes. For example, this coupling may allow for a wide variety of sensory possibilities of cell membranes such as mechano-reception, magneto-sensitivity. To verify the latter example electric currents induced by less than a 10^{-2} T alternating magnetic field in phospholipids doped with 0.5 wt% of ferrofluid of magnetite (Fe_3O_4) nanoparticles were also measured [53]. Indeed a response an order of magnitude larger than the background was detected. This observation can be explained by the magnetic particle-induced director tilt that induces the electric current by the same piezoelectric mechanism illustrated in Figure 3 These measurements suggest that piezoelectricity might have a role in magneto-reception where animals use magnetite particles to sense local changes in magnetic fields [56].

Chiral SmC elastomers are also ferroelectric. So far experiments have mainly concerned only converse piezoelectric effects and the direct piezoelectric measurements were only considered theoretically by

Adams and Warner [57], who described how the polarisation can be mechanically reversed by large, hard or soft strains of the rubber, depending upon sample geometry.

The converse piezoelectric effect (electric field-induced mechanical deformation) also influences the electro-optical responses. They are mainly unwanted since eventually they may lead to misalignment, but with clever design can also be used to re-heal alignment [58]. It is interesting to note that in the audio-frequency ranges the vibrations result in audible acoustic effects implying their possible use in electro-mechanical transducers [59–61]. A systematic study [62] with accurate control of the alignment revealed that the vibrations parallel to the smectic layers and the film surface are generally the strongest, especially if the polarisation is also parallel to the plates. The schematics of the experimental setup and the first application in the form of a home-made SmC* head-phone are illustrated in Figure 4.

The vibration normal to the film substrates (see Figure 5(a)) is due to the variation in the layer spacing. In contrast to the SmA* phase, in a tilted phase the resulting displacement is proportional to the field. Transversal vibrations involving variation of the sample thickness are strongest when the alignment favours spontaneous polarisation normal to the plates. The vertical vibration is due to the electroclinic effect and the mechanical coupling between the director tilt and smectic layer spacing as illustrated in Figure 5(a).

The vibration along the film surfaces (shear strain) (see Figure 5(b)) is due to backflow, that is, the coupling between the gradient of the director rotation z about the layer normal (Goldstone mode) and the viscous flow [62]. This mode is excited by the electric field via the torque $E \times P_o = EP_o \sin\phi$. The magnitudes

of small oscillations are accordingly proportional to $\sin\phi$, and are largest when the polarisation is parallel to the plates. Using a nematic-like description for the flow processes inside the smectic layers and taking into account the relevant constraints (the director rotates around a cone, the electric field couples linearly to the polarisation, which is always perpendicular to the director), the mechanical stress induced by the electric field was found to be parallel to the smectic layers, which for the unwound helix, results in a uniform stress:

$$\sigma_{xy} = \frac{\gamma_2 \cos 2\phi - \gamma_1}{2\gamma_1} EP_o \sin\phi, \tag{3}$$

where in the situation shown in Figure 5, the angle between the polarisation and electric field is $\varphi \sim 90°$, and γ_1 is the rotational viscosity, $\gamma_2 = \eta_b - \eta_c$ and η_b and η_c are the shear viscosities with the director in the direction of the flow gradient and parallel to the flow, respectively.

Very recently the first converse piezoelectric measurements in a new adamantane bent-core liquid crystal exhibiting a metastable ferroelectric phase with a large (9 mC m^{-2}) polarisation were published [63]. The material shows a reversible switching between a birefringent (opaque) and optically isotropic (clear) state. The clear state can be stabilised after poling with fields of about $20 \text{ V } \mu\text{m}^{-2}$. In this state the observed piezoelectric constant is about 100 nCN^{-1}, that is, comparable to commercial solid-state piezo transducers.

Converse piezoelectric-type (linear electromechanical) effects of free-standing ferroelectric SmC* films were studied by light scattering when AC electric fields were applied along the film surface [64–67]. The sketch of the experimental setup
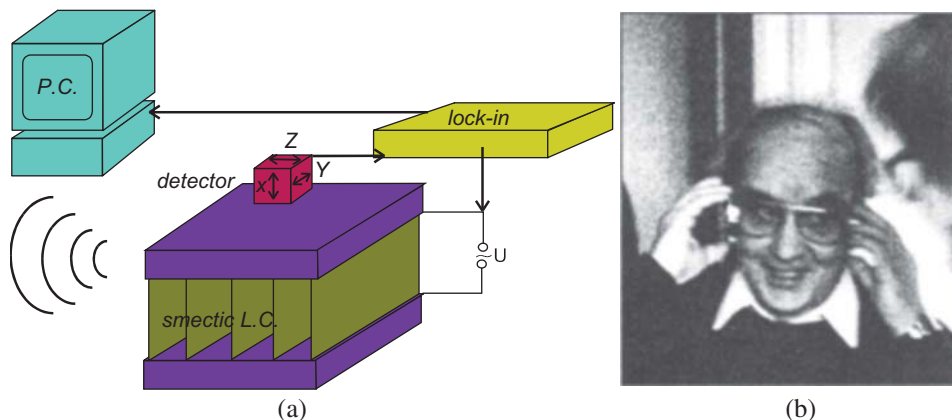

Figure 4.   (a) Illustration of the experimental technique to measure the linear electromechanical effect in SmC* ferroelectric liquid crystals. (b) The present author gives the world's first FLC headphone to Alfred Saupe on his 70th birthday. His first verbal reaction during the test was: 'needs more work'.
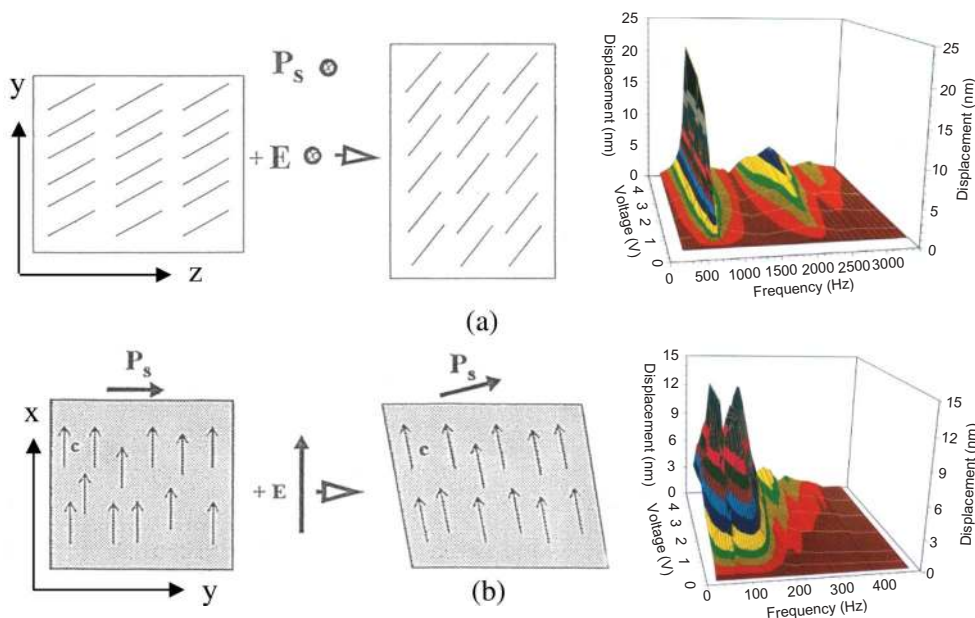
Figure 5. Illustration of the linear electromechanical effect of SmC* materials. (a) Effect due to the electroclinic mode that results in mechanical vibrations normal to the film. (b) The coupling of the gradient of the director rotation around the tilt cone (Goldstone mode) and macroscopic flow along the layer planes.

and the shape of the film under excitation are illustrated in Figure 6.

The role of converse piezoelectricity was also invoked [68] to explain the swelling of membranes in their response to voltage changes [69].

Experimental studies of the piezoelectric effects in SmC* elastomers, mainly restricted to the converse (linear electromechanical) investigations, was summarised recently by Hiraoka [70]. It is generally observed that the piezoelectric coupling constants in the SmC* phase are in the order of 30 pCN^{-1}, which is quite typical for other piezoelectric materials. Very recently Spillmann *et al.* [71] studied SmA* elastomers and found an electric field-induced twist where the twist

Figure 6. Illustration of the experimental technique and a schematic of the field-induced flow profile in ferroelectric SmC* free-standing films (after Yablonskii *et al.* [67]). Reprinted with permission from Yablonskii, S.V.; Oue, T.; Nambu, H.; Mikhailov, A.S.; Ozaki, M.; Yoshino, K. *Appl. Phys. Lett.* **1999**, *75*, 64–66. Copyright 1999 by the American Institute of Physics.

direction changes sign with that of the electric field. This effect seems to be due to electroclinic effects, that is, the sense of the twist is controlled by the chirality, such as that of the tilt in electroclinic SmA* materials [72].

4. Electrostriction

Quadratic electromechanical effects are observable in liquid crystals of any type of symmetry, yet the first and strongest effects are mainly observed in ferroelectric materials partially because they are characterised by large dielectric constants, or due to an indirect coupling between the electric field and macroscopic mechanical deformation. These two effects for fluid SmC* liquid crystals are illustrated in Figure 7. In Figure 7(a) we represent the effect of the Goldstone mode (the rotation of the director around a cone) on the periodic variation of the film thickness. This effect can lead to a change of film thickness by a maximum of $l \times \sin \theta \sim 1$ nm.

In Figure 7(b) the effect of the electroclinic onlayer spacing, and indirectly on film thickness, is shown. This is due to the decrease in the layer spacing upon the director tilt. Since the number of layers cannot vary rapidly, the change in layer spacing will result in a variation in the film thickness. This results in a force normal to the cover plate. This effect is strongest when the polarisation is parallel to the electric field. Although the induced tilt angle changes sign with the electric field, the resulting layer contraction is the same independently of the sign of the field. In this case
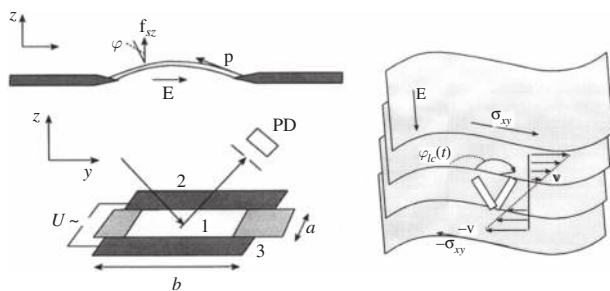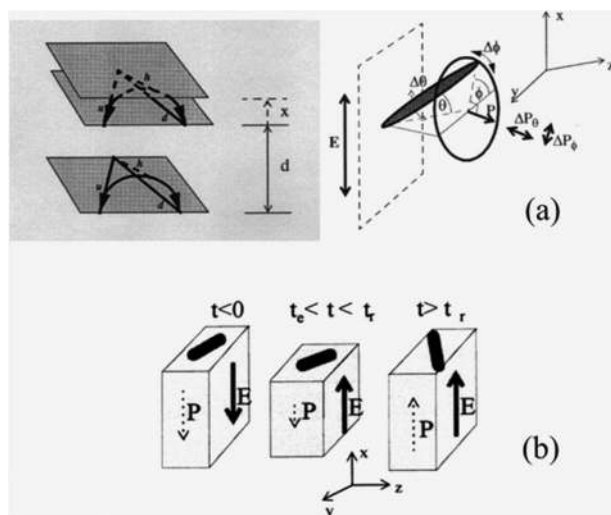
Figure 7. Illustration of the Goldstone mode (a) and the electroclinic mode (b) on film thickness, which appear as quadratic electromechanical effects.

whenever the layer spacing parallel to the electric field is decreased, the layer spacing should increase, since the volume of the material has to be unchanged [73]. We note that this latter effect is unwanted in ferroelectric liquid crystal displays: addressing the pixels sequentially can lead to pumping the material in some direction,

depending on the addressing scheme. On the other hand, nano-positioning devices can be designed based on the same effects, and also actuators.

Recently, considerable attention has been devoted to the quadratic electromechanical effects in liquid-crystalline polymers [74] and elastomers [75–80] due to their elastic responses associated with their large molecular shape and dielectric anisotropy, which are essential for high efficiency in the energy conversion between the electric and mechanical forms. In the case of ferroelectric polymeric and elastomeric materials the mechanism of the actuation is basically the same as illustrated in Figure 7(b).

Examples of non-ferroelectric materials include nematic elastomers with aligned nanotubes [81], swollen elastomers [82] and nematic gels [83, 84]. The electric field-induced strain in the nematic gels is illustrated in Figure 8. In this system a liquid crystal diacrylate C6M together with the 4-pentyl-4-cyanobiphenyl (5CB) molecules not containing reactive end groups, were photopolymerised *in situ* in cells with an anti-parallel homogeneous alignment and in a homeotropically oriented nematic state. It can be seen that more than 2% field-induced strains can be achieved under an electric field of 25 MV m^{-1} in nematic gel possessing an elastic modulus of 100 MPa along the actuation direction. Therefore, they could provide an intelligent
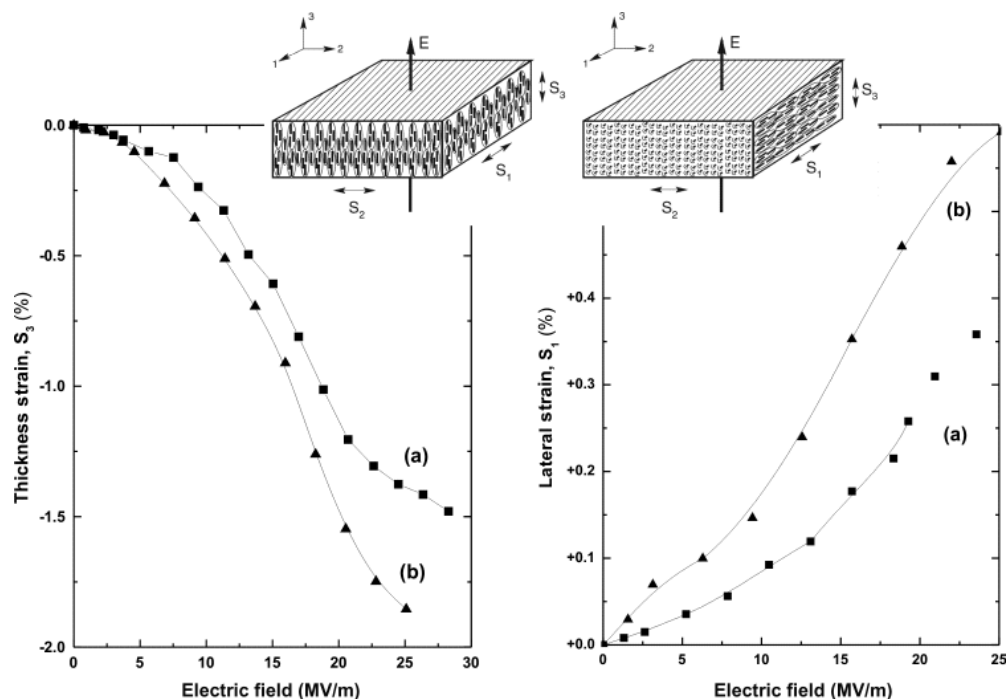

Figure 8. The electric field dependence of the thickness and strain of anisotropic liquid crystal gels in decreasing and increasing fields and their corresponding director structures shown in the insets. The applied field dependence of the amplitude of the thickness and strain S_3 in (a) homogeneous alignment and (b) homeotropic alignment. The inset shows schematically the coordinate system and the strains S_1, S_2 and S_3 for a homeotropic-aligned liquid crystal gel film under electric field **E** along the network chain direction **S** (after Huang *et al.* [83], taken with permission).

system for practical applications such as artificial muscle mimics and micro-electromechanical devices.

5. Flexoelectricity

A closely related phenomenon to the piezoelectricity in liquid crystals is the flexoelectricity introduced by Meyer [85]. His model assumes dipolar molecules with asymmetric shapes, such as pear-shape or bent-core molecules, as seen in Figure 9. The constituent molecules of the nematic liquid crystals are free to rotate around their axes, and in the absence of electric fields, their dipoles average out, so the net polarisation of the material is zero. However, when the liquid crystals, made up of polar pear- or banana-shaped molecules, are subjected to splay or bend deformations, respectively, they can become macroscopically polar because the polar structures correspond to a more efficient packing of the molecules.

As shown above, for weak deformations corresponding to the continuum limit, the induced flexoelectric polarisation $\vec{P}_f$ is proportional to the gradient of the strain, which in liquid crystals with director $\vec{n}$ corresponds to one of the possible director deformations: splay $[\vec{n}(\mathrm{div}\,\vec{n})]$, twist $[(\vec{n} \cdot \vec{\nabla} \times \vec{n})]$ or bend $[(\mathrm{curl}\,\vec{n}) \times \vec{n}]$. Higher order derivatives are negligible in the continuum limit, that is, when $a/l << 1$ (a, molecular dimension; l, periodicity of deformation).
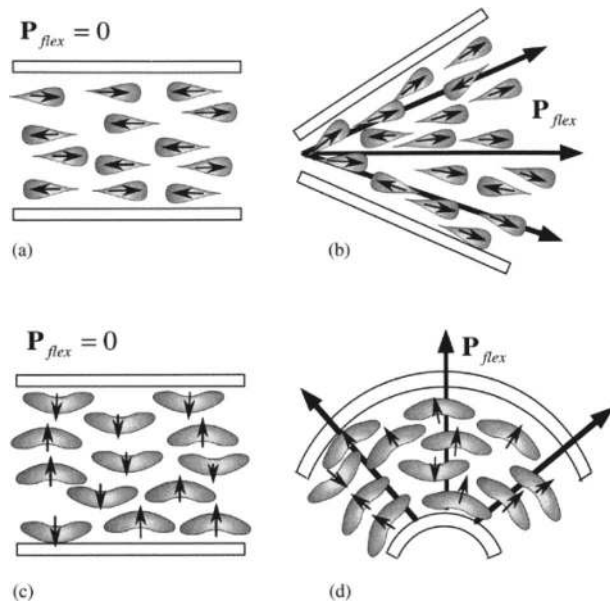

Figure 9. Illustration of flexoelectricity assuming polar non-centrosymmetric molecules. Upper row: pear-shaped molecules; lower row: banana-shaped molecules (after Meyer [85]). Reprinted with permission from Meyer, R.B. *Phys. Rev. Lett.* **1969**, *22*, 918. Copyright 1969 by the American Physical Society[1].

Taking into account the $D_{\infty h}$ symmetry of the system and the head-tail symmetry ($\vec{n} \Leftrightarrow -\vec{n}$), the twist term does not lead to a polarisation across the electrodes, and the flexoelectric polarisation can be given by only two coupling constants:

$$\vec{P}_f = e_1\vec{n}(\mathrm{div}\,\vec{n}) + e_3(\mathrm{curl}\,\vec{n}) \times \vec{n}, \qquad (4)$$

where e_1 (e_3) is the splay (bend) flexoelectric coefficient.

The molecular statistical approach to calculating the flexoelectric coefficients was developed independently by Helfrich [86] and Derzhanski and Petrov [87]. The calculation is based on the requirement to ensure the maximum packing condition. The excess number ($\Delta N = N_+ - N_-$) of the molecules with dipole moment, μ, determines the electric polarisation: $P = \Delta N\mu$. Dividing this by the distortion we get the flexoelectric coefficient (Figure 10). Without going into details we give just the results of Helfrich's [86] calculation. Accordingly:

(i) pear-shaped molecules:

$$e_1 = \frac{2\mu_\parallel K_{11}}{k_B T}\theta_o\left(\frac{a}{b}\right)^{1/3} N^{1/3}, \qquad (5)$$

with the estimates: $\mu_\parallel = 4 \times 10^{-30}$ Cm ($\approx 1D$), $K_{11} \sim 10^{-11}$ N, $k_B T \sim 5 \times 10^{-21}$ J, $\theta_o \sim 0.1$ rad, $a/b = 1$, $N = 10^{21}$ m^{-3} we get $e_1 = 2 \times 10^{-12}$ C m^{-1}, which is close to the experimental values.

(ii) banana-shaped molecules:

$$e_3 = \frac{\mu_\perp K_{33}}{2k_B T}\theta_o\left(\frac{b}{a}\right)^{2/3} N^{1/3}. \qquad (6)$$

By dimensional considerations an upper limit for molecules with very asymmetric shapes can be placed as e_1, $e_3 \leq \frac{\mu_e}{a^2}$, where the molecular dipole μ_e is in the range of 1–5 Debye (1D = 3.3 × 10^{-30} C m) and a around 2–4 × 10^{-9} m the typical molecular dimensions for low molecular weight liquid crystals. This gives $e_{1,3}$
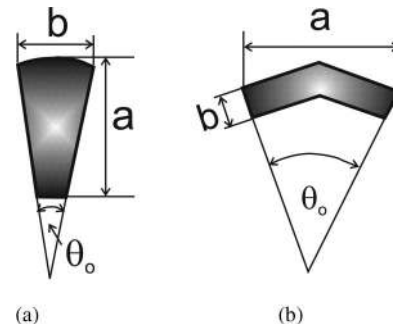

Figure 10. Molecular models used for the calculation of flexoelectric coefficients: (a) pear-shaped molecules; (b) banana-shaped molecules.
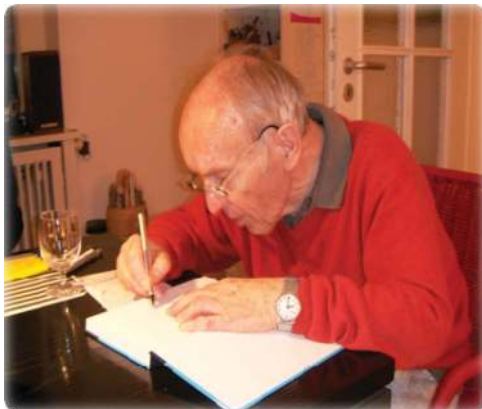
Figure 11.   My last picture of Alfred, shown signing one of his last works, the textbook '*One and Two-dimensional Fluids*' in December 2006 at his home in Badenweiler.

$<10^{-12}$ Cm^{-1}. Measurements of the distortion due to an electric field in a dielectrically stable configuration (e.g. a homeotropic cell with $\varepsilon_a <0$ and with weak surface anchoring) gives e_3 around 1.2×10^{-12} C m^{-1} [21]. This is as great as the upper limit of the theoretical value, indicating that not only the dipolar mechanism contributes to flexoelectricity. Indeed it turns out that flexoelectricity can exist even in materials with non-polar and axially symmetric molecules. In this case it is caused by the interaction between the electric field gradient and the molecular quadrupolar moments (quadrupolar mechanism) [88]. This actually became more evident later when the majority of experiments on calamitic (consisting of rod-shaped molecules) liquid crystals found e [89–95] to be larger than predicted theoretically from the dipole mechanism. The flexoelectric coefficients of calamitic liquid crystals with quadrupolar mechanism are actually typically in the range where non-liquid-crystalline elastomers were subjected to a deformation gradient realised in a truncated pyramid cut from elastomers via axial pressure [22]. In either case, however, although these effects are very fundamental and interesting, the flexoelectric coefficients are too small for practical applications.

Black lipid membranes are also flexoelectric, that is, they can generate an electric current, as observed first in 1973 [96], and called 'a peculiar kind of piezo-electric effect'. Later Petrov *et al.* [97, 98] studied this effect in detail and found that the molecular basis of the flexoelectricity of the lipid bilayers is provided by the asymmetric redistribution of charges, dipoles and the splayed uniaxial orientation of their quadrupoles [99]. Converse flexoelectric measurements [100] found that the splay flexoelectric coefficients are about $e_1\sim100$ pC m^{-1}, which is an order of magnitude larger than typically found for calamitic thermotropic liquid crystals. Converse flexoelectric studies of lyotropic liquid crystals, such as vesicles, is still an active subject [101]. Notably, the sensory mechanism of outer hair cell composite membranes [102, 103] can be understood by the flexoelectric properties of the lipid bilayer [104]. The converse of this effect, that is, voltage-generated curvature has also been observed and discussed by Todorov *et al.* [105]. Another related phenomenon is the ferroelectricity that results from tilted layered structures of chiral molecules, which has also been discussed extensively since the 1980s [20, 37, 106–108]. Ferroelectric phases are called either L$_\beta$* or SmC* phases where L or Sm stand for lamellar or smectic; β or C mean that the director is tilted with respect to the layers, and * indicates that the constituent molecules are chiral.

The latest developments in perovskite-type ferroelectrics and relaxor ferroelectric ceramics [109, 110] and in bent-core liquid crystals [111–114] show so-called giant flexoelectricity, which is three to four orders of magnitude larger than in normal dielectric crystals and liquid crystals (for ferroelectrics $e \geq 4 \times 10\mu$C m^{-1} and for the bent-core liquid crystals $e_3 \leq 80n$C m^{-1}). In addition, both measurements were made in special dynamic methods using a nanoscale cantilever beam [109, 110] or direct flexing by Skotch-yoke techniques [112] in the perovskite-type ferroelectrics and the bent-core nematic materials, respectively. Although for ferroelectric ceramics it is evident that the piezoelectric origin of the constituent ferroelectric domains is responsible for the giant flexoelectric effect, in bent-core nematic liquid crystals it is not clear because the phase is not ferroelectric. On the other hand, recent experiments on bent-core nematic liquid crystals indicate the presence of tilted smectic clusters [115, 116], which appear to be ferroelectric [117, 118]. Consequently the piezoelectric behaviour of these clusters may also be responsible for the giant flexoelectrcity in bent-core nematics, as well.

Independent of the exact nature of the giant flexoelectric effects, for properly engineered forms they hold promise for future applications. To compare the potentials of these two different systems, realistic achievable flexoelectric polarisation values and other mechanical constraints were calculated. For example, in barium strontium titanate, a polarisation of about 1 μC m^{-2} can be induced for a 1.8 mm thick slab with a strain gradient of 0.01 m^{-1} [119]; while with the bent-core nematic-liquid crystal composite, Harden *et al.* [113] generated a 2 nA cm^{-2} current density at 3 Hz with a 0.1 m^{-1} strain gradient, which corresponds to a 1 μC m^{-2} polarisation, that is, the same charge per area at a 10 times larger strain gradient but four times smaller film thickness. Thinner flexoelectric ceramic composites have been also fabricated, but they are both fragile and difficult to stress [120], whereas in principle we can easily make both fluid and

elastomeric bent-core liquid crystals at least an order of magnitude thinner, which would increase the induced current per unit volume by another factor of 10. Furthermore, flexoelectric crystals must have a suitable shape [121], which makes the fabrication process for crystalline or ceramic solid materials much more difficult. Of course, the future will tell if ferroelectric ceramics, or bent-core liquid-crystalline elastomers, will be more useful, and in which areas.

6.   Summary

The purpose of this brief review of electromechanical effects in liquid crystals was twofold. First, to give a short overview of the state of the art of this subject, which was first considered in fluid liquid crystals as early as 30 years ago. At this time these effects have not received much attention for multiple reasons. (i) After the 1980s, liquid crystal research was driven by the display industry; (ii) the magnitude of the effects was not apparent for applications; or (iii) when they appeared important, they were simply unwanted effects, as in SmC* displays, where the coupling between an electric field and a mechanical deformation often leads to misalignment.

In the last decade with the success of liquid crystal displays, and with the developments in liquid crystal gels and elastomers, much greater interest was devoted to electromechanical couplings rather than electro-optics. These were in line with the growing importance of efficient and green energy conversions and electricity generation. Combined with this growing demand and the lately observed increase in the magnitude and efficiency of electromechanical signals (see, for example, the giant-flexoelectric effects in bent-core nematic liquid crystals), we expect a rapid development in this field.

As in so many other areas in liquid crystals, Professor Alfred Saupe (see my last picture of him in Figure 11) also played a major role in understanding the basics of these effects.

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