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Wider Impact Statement

A mechanical stress induced electric polarization is called direct piezoelectricity, and an electric field induced mechanical stress is called converse piezoelectricity.

The history of piezoelectricity (pressure electricity) started over 130 years ago by the discovery of the Curie Brothers in a ferroelectric crystal, Rochelle Salt. As effects analogous to the piezoelectricity have been observed in various crystals, polymers and biomaterials with lack of inversion symmetry, so the definition of the piezoelectricity has been evolved to describe a linear coupling between mechanical stress and electric polarization.

Soon after the discovery of ferroelectricity in chiral liquid crystals with two- and one-dimensional fluid order, owing to the lack of their inversion symmetry, linear electromechanical effects analogous to the direct and converse piezoelectricity have also been observed in these materials that can still sustain static stress in certain directions.

On the other hand, the newest liquid crystal phase, the ferroelectric nematic liquid crystal (N_F) phase is truly three-dimensional fluid, and a steady stress can only be sustained by surface tension. It is therefore of principal interest to study and compare piezoelectricity of the liquid N_F materials with solid and partially solid piezoelectric materials. In this review we also discuss the challenges and possible future applications of liquid piezoelectricity.



Data availability Statement

Data is available from the corresponding authors by reasonable requests.



From Solid to Liquid Piezoelectric Materials

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Abstract:

The history and evolution of the piezoelectricity is reviewed starting from the discovery of pressure (“piezo” in Greek) electricity by the Curie Brothers in a ferroelectric crystal, up today when liquid piezoelectricity was observed in polar anisotropic fluids, the ferroelectric nematic liquid crystal (N_F) materials. As effects analogous to the piezoelectricity have been observed in various crystals, polymers and biomaterials with lack of inversion symmetry, so the definition of the piezoelectricity has been evolved to describe a linear coupling between mechanical stress and electric polarization. A mechanical stress induced electric polarization is called direct piezoelectricity, and an electric field induced mechanical stress is called converse piezoelectricity. Soon after the discovery of ferroelectricity in chiral liquid crystals with two- and one-dimensional fluid order, owing to the lack of their inversion symmetry, linear electromechanical effects analogous to the direct and converse piezoelectricity have also been observed in those materials. While these materials in certain directions can sustain static stress, the N_F phase is truly three-dimensional fluid, and a steady stress can only be sustained by surface tension. The review is concluded by a summary and analysis of direct and converse piezoelectric measurements on several N_F materials, and by recapping the challenges and possible future applications of liquid piezoelectricity.



I. Introduction

In 1880 Pierre and Jacques Curie¹ detected electric charge on some (sodium chlorate, boracite, tourmaline, quartz, calamine, topaz, tartaric acid, sugar and Rochelle salt) crystals when compressed in certain directions. The charge observed was found to be proportional to the pressure and disappeared when the pressure was removed. These observations mark the birth of “piezoelectricity”; “piezo” is the Greek word for “pressure”. Only one year later, Lippmann proposed^{2,3} that the converse effect (i.e., strain induced by electric charges) must, owing to thermodynamics, also exist. This prediction was also verified by the Curie brothers⁴. The early history of piezoelectricity⁵ was complete with Voigt’s first rigorous formulation of piezoelectricity⁶ in 1894.

The next stage of this story led to the birth of the ultrasonic technology during the Great War in 1918. It was Langevin who applied both the converse and direct piezoelectric effects to both emit and detect sound waves underwater utilizing large plates of quartz^{7,8}. Soon thereafter Cady demonstrated that the frequency can be stabilized if a quartz crystal is used in resonance with an electrical oscillator⁹. Such quartz crystal oscillators were first used by the US National Bureau of Standards as frequency standards and later they became critical in the development of broadcasting radio waves.¹⁰

The third wave of the studies of piezoelectricity begin in the 1940s with the observation of new strong piezoelectric materials, especially barium titanate^{11–13}. The field developed quickly with the subsequent discovery of piezoelectricity in certain polymers, both synthetic and biological, beginning in the 1970s^{14–19}. The native effects in polymers and biomaterials¹⁶ are generally small but can be increased by poling by strong DC electric fields, typically at elevated temperatures. Owing to their flexibility and ease of fabrication, piezoelectric polymers opened up a whole new vista of applications and/or device concepts that would not have been possible using conventional crystalline piezoelectrics. One particularly well-known and commercially attractive example is the poly (vinylidene fluoride) (PVDF)²⁰; PVDF has been used in diverse applications ranging from infrared detector technology to audio speakers. More recently, certain cellular polymers (ferroelectrets) have been also found to behave like soft, sensitive piezoelectrics^{21–24}. Fiber mats constructed of polylactic acid (PLA) dispersed with ferroelectric barium titanate (BT)



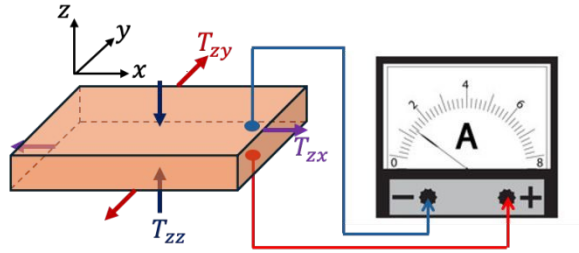
nanoparticles were also found to be highly piezoelectric, having 100x larger piezoelectric response per weight than of single crystal BT and of pure piezoelectric ceramic fibers^{25,26}. At present solid piezoelectric materials are used in energy harvesting²⁷, various sensors²⁸ and even in transistors (piezotronics)²⁹.

The mathematical description of piezoelectricity was originally developed for crystals subject to reversible compression and extension. This later was generalized to arbitrary strain/stress, including shear. Both stress $\hat{T}$ and strain $\hat{S}$ are represented by tensors of second rank. T_{ij} describes the i th component of a reversible force per unit area (i.e., stress) acting in a surface element pointing in direction j . Tensor formulation is necessary because when one considers materials that are not fully isotropic. In this case, it is possible (for example) that a force in one direction can lead to a displacement in a perpendicular direction. Tensor formulation is the precise and compact methodology to account for all possible combinations of material response to external forces. An individual component of reversible strain is given by $S_{ij} = \partial s_i / \partial x_j$, where s_i is i th component of the displacement of a volume element from the equilibrium position. When we consider the case of a substance having equilibrium position subject to reversible displacement, we infer that the material displaces elastically, which is the case for crystals, ceramics and solid polymers when subject to sufficiently small stress/strain. With this in mind, the piezoelectric effects are illustrated in described as follows.



(a) Direct piezoelectric effectInput: Mechanical stress (T_{zx} , T_{zy} and T_{zz})

Output: Electric current

**(b) Converse piezoelectric effect**

Input: Voltage

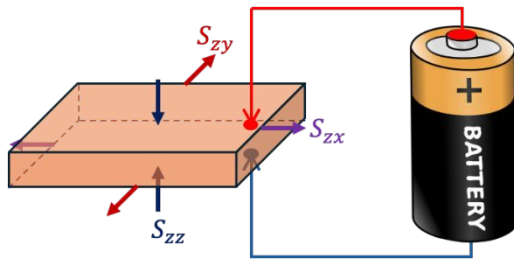
Output: Mechanical strain (S_{zx} , S_{zy} and S_{zz})

Figure 1: Illustration of the direct and converse piezoelectric effects. Note: In (a) the output 'current' will only be induced when the stress is changing. For a constant stress it will be an induction of charge.

The *direct piezoelectric effect* when a macroscopic electric polarization vector $\vec{P}$ is produced by mechanical stress $\hat{T}$, can be expressed by the equation:

$$P_i = \sum_{jk} \gamma_{ijk} T_{jk}, \quad (1)$$

where the coefficients of the third rank tensor γ_{ijk} are known as the piezoelectric charge coefficients.

In the *converse* (or "inverse") *effect* the material becomes strained when an external electric field $\vec{E}$ is applied. This is expressed via:

$$S_{jk} = \sum_i \gamma_{ijk} E_i, \quad (2)$$

where S_{jk} is the jk component of the strain tensor.



As pointed out by Lippmann³, both the direct and converse effects are manifestations of the same fundamental property of the substance: a linear coupling between a second-rank tensor (like strain or stress) and a first-rank tensor (such as the polarization or electric field vector). This is emphasized by the fact that the same coefficients γ_{ijk} are found in both equations above.

Of critical importance are the symmetries of the material in question. This is the reason most substances do *not* exhibit piezoelectricity. Underlying this entire phenomenon is the Curie principle, which states that the tensor coefficients characterizing material properties should be invariant under the symmetry transformations of the substance³⁰. Therefore, any material that possesses inversion symmetry transformations, i.e., is unchanged by the transformation $(x,y,z) \rightarrow (-x, -y, -z)$, would require that $\gamma_{ijk} = (-1)^3 \gamma_{ijk}$, which can only be true if $\gamma_{ijk} \equiv 0$. This means that materials with inversion symmetry cannot be piezoelectric. In other words, piezoelectricity is only observable in materials that lack inversion symmetry. Furthermore, it is possible to identify which components of γ_{ijk} must vanish based solely on the symmetry group of any given material. As was pointed out by Woldemar Voigt⁶ in 1894, 20 out of the 32 crystallographic groups and 3 of the continuous point groups³¹ lack inversion symmetry and so *may* exhibit piezoelectricity. The least symmetric materials with C_1 symmetry permit all γ_{ijk} to be non-zero. Since $\gamma_{ijk} = \gamma_{ikj}$, there can be at most $3 \times 6 = 18$ independent tensor elements.

Due to the technological importance of piezoelectric materials for transducers, frequency standards, ultrasonics etc., the third-rank tensor representation of the piezoelectric coupling constant are often replaced (for simplicity) by a 2nd rank tensor following the convention below. Directions are identified using the three axes, labeled 1, 2 and 3, where 3 is chosen parallel to the direction of polarization. Since the 2nd rank stress and strain tensors are symmetric, then have 6 independent elements and can be expressed as 6x1 tensors (6 element vectors) : T_λ and S_λ , where $\lambda = \frac{(i+j)}{2}\delta_{ij} + [9 - (i+j)](1 - \delta_{ij})$, i.e., 11→1; 22→2; 33→3; 23 = 32→4; 13 = 31→5; 12 = 21→6 transformations are used³². In this case the piezoelectric charge constants are formally expressed as 3 x 6 element 2nd rank tensors and denoted as d_{ij} . These are defined, along with several other piezoelectric constants and their definitions, in Table 1. These piezoelectric constants are various partial derivatives with respect to one independent parameter evaluated while another is held constant, as is typical in formulations



of thermodynamics. These conditions can be regarded as “mechanically free,” “short circuit,” “open circuit,” and “mechanically clamped,” respectively.³³

Symbol	Name	Definition
d	Piezoelectric charge coefficient or piezoelectric strain coefficient	$d_{ij} = \left(\frac{\partial D_i}{\partial T_j} \right)_E = \left(\frac{\partial S_j}{\partial E_i} \right)_T$
g	Piezoelectric voltage coefficient (voltage output constant)	$g_{ij} = - \left(\frac{\partial E_i}{\partial T_j} \right)_D = \left(\frac{\partial S_j}{\partial D_i} \right)_T$
e	Piezoelectric stress coefficient	$e_{ij} = - \left(\frac{\partial T_j}{\partial E_i} \right)_S = \left(\frac{\partial D_i}{\partial S_j} \right)_E$
h	Piezoelectric stiffness coefficient	$h_{ij} = - \left(\frac{\partial E_i}{\partial S_j} \right)_D - \left(\frac{\partial T_j}{\partial D_i} \right)_S$

Table 1: Various piezoelectric constants used in literature with their definitions.³³

While these notations are simpler, they are also less transparent than the third-rank tensor notation. For this reason, where possible, in this paper we will retain the third-rank tensor formulation.

Additionally, there is another coupling constant called electromechanical coupling coefficient k , which is defined as the ratio of the mechanical energy accumulated in response to an electrical input or vice versa. It also corresponds to the fraction of electrical energy that can be converted into mechanical energy and vice versa.

Everything discussed above is related to solid piezoelectric materials. But is this strictly restricted to solid materials, or can this phenomenon occur in fluids? Can liquids be piezoelectric? Isotropic liquids such as water, methanol, acetone, etc. have inversion symmetry, so piezoelectricity is forbidden. Recently a “fluid piezoelectric” effect was reported for an ionic liquid³⁴, whereby upon compression an electric signal proportional to the compression was observed. By definition it cannot be considered piezoelectric, since that fluid is isotropic with centrosymmetry, while genuine piezoelectricity requires the lack of inversion symmetry. In fact, it was subsequently determined that the effect is due to a reversible pressure induced liquid to crystalline solid transition.³⁵ Such an effect results in an effective $d_{33} < 0.5 \text{ pC/N}$ piezoelectric coupling constant.



There are states of matter intermediate between crystalline solids and isotropic liquids. These are liquid crystals that possess less than three-dimensional solid behavior. “Nematic (N)” liquid crystals are three-dimensional liquids but anisotropic, i.e., have long-range orientational and short-range positional order. “Smectic (Sm)” liquid crystals have layered structure with one-dimensional positional order. Accordingly, they are one-dimensional solids and two-dimensional liquids. Finally, “columnar (Col)” liquid crystals have two-dimensional positional order, so they are two-dimensional solids and one-dimensional liquids. Along their liquid directions where there is no positional order, liquid crystals are also unable to support shear stress.³⁶ However, they also have some degree of density periodicity in the smectic and columnar phases, so they have the ability to sustain some elastic strain along their positional order (solid direction).

Significantly, several categories of liquid crystal materials lack inversion symmetry, therefore they allow the existence of non-zero, piezoelectric-type third-rank tensors. The origin of this symmetry property may arise, e.g., because of molecular chirality and/or polar molecular packing as studied extensively^{37–49} and will be discussed in section III for chiral nematic (N*), ferroelectric tilted smectic (SmC*)^{50,51} of chiral rod-shaped molecules, tilted columnar⁵² phase of chiral disc-shaped molecules, and tilted polar smectic (SmCP)⁵³ phases of bent-core liquid crystal phases. Their symmetry, allow the existence of piezoelectric charge coupling constant that may involve stress either along their solid or liquid directions. The question is whether we can call a linear coupling between electrical and mechanical fields as piezoelectric if they involve fluid direction or should we just talk about linear electromechanical effects. Certainly nothing is wrong to talk only about linear electromechanical effects as piezoelectricity belongs to that category as well. On the other hand, it is also possible to generalize the definition of the piezoelectricity to liquids if their symmetry allows it. The advantage of this approach is that it would group together phenomena in materials with the same underlying symmetry. In this review we are following this approach: generalize strain for liquid directions and compare the same symmetry enabled linear electromechanical effects among solid and fluid materials.

The definition of strain tensor $\hat{S} = \vec{\nabla} \cdot \vec{s}$ to be valid in liquids can be done only for periodic motions where the displacement vector is $\vec{s}(t) = \vec{s}_0 \cdot e^{i\omega t}$, where ω is the angular frequency of the vibration. For static cases, the displacement and the calculated piezoelectric coupling constant



determined by this way would increase in time, and even for periodic situations, the piezoelectric constant could show abnormal frequency behavior due to the viscous nature of the stress. The static displacement in liquids would be limited by the size of the fluid sample. Microscopic size liquid objects have elastic response due to the dominance of the surface tension, thus providing an additional argument for talking about piezoelectric effects in those fluids.

The justification for such treatment is provided by the recent discovery of ferroelectric nematic liquid crystals that are polar orientationally ordered three-dimensional fluids.^{54–60} In spite of their genuine 3D fluidity, in electric fields they often behave as solid particles or microrobots⁶¹, they can also form metastable freestanding filaments^{62,63} that can be stabilized in small electric fields⁶³.

The main motivation of this paper is to review and compare the piezoelectric phenomena observed in wide range of materials from crystalline solids to 3D liquids. We will overview the main properties of solid piezoelectric materials such as of crystals, ceramics and polymers, and compare their behavior with polar nematic, smectic and columnar liquid crystals that can be regarded as three-, two-, and one-dimensional solids. Special emphasis will be devoted to recent measurements of converse⁶⁴ and direct⁶⁵ piezoelectric responses of ferroelectric nematic liquid crystals, for which we will present new results as well. Finally, the paper will be concluded by a comprehensive analysis of the results and by a future outlook.

II. Measurement techniques

II.A. Solid piezoelectric materials

Measuring piezoelectric effects in solid materials is well-established.^{66–68} Here we review some basics as well as important milestones. It is instructive to recall that at its most elemental, piezoelectricity means an electrical response resulting from the application of pressure. In that regard, and its simplest form, one applies pressure to a material and detects an electrical change, be it the appearance of charge separation, an electric current or a potential difference. Of course, these are all related to one another. Thus, measuring piezoelectricity is, at least conceptually, rather simple: apply stress to a material and measure the resulting electrical signal (see Figure 1a), as was done by the Curies. While conceptually simple, it is rather unspecific. One could easily use



two different material specimens, perhaps having different shape or growth conditions, put them in the same apparatus and measure two different electrical responses.⁶⁹

The much more specific measurement is not only the manifestation of “piezoelectricity”, but the measurement of the piezoelectric coefficient(s), that is individual elements of the $\hat{\gamma}$ tensor in Eq. 1. However, accompanying more specificity is a substantially more complicated measurement. More complex because such a measurement necessitates controlling the application of stress as well as the symmetry axes of the material to be studied. Implicit in this requirement is that the sample of material should have well-defined axes, i.e., a single crystal specimen.⁷⁰ Moreover, the individual axes need to be identifiable, either through prior crystallographic study of the specimen, or, in some cases, knowledge of the characteristic shapes formed by single crystal specimens. For example, quartz crystals frequently exhibit recognizable facets that accurately represent various symmetry axes. Having this knowledge, and the ability to apply stress in a particular and known direction with respect to these axes allows determination of individual elements of the piezoelectric charge tensor $\hat{\gamma}$, or alternatively the piezoelectric charge (or voltage) coefficient(s).

Very similar considerations apply when attempting to measure the inverse piezoelectric effect. That is, to apply an electrical potential difference and measure the resulting strain (see Figure 1b). As in the direct, if the goal is to measure the inverse piezoelectric “response”, it is conceptually simple. How much strain results from an applied potential difference? If the goal is to examine inverse piezoelectric coefficients, the same issues apply, but in a different sense. For an inverse measurement, one must apply an electric field in a specific (and known) direction with respect to crystallographic axes. Then the resulting strain (again, determining how specific strain elements occur compared to crystallographic axes). Measuring inverse piezoelectricity in crystalline materials, however, implies an additional complication in addition to the issues of orientation described above. Most crystalline materials have moduli exceeding 10 GPa; that means the induced strains are in general rather small and not straightforward to measure directly. Different approaches to that problem are noted below.



II.A.1. Measurement examples

Perhaps the first choice one must make in measuring piezoelectricity concerns time dependence. With a few exceptions, the choice is usually between ac and dc. The Berlincourt technique⁷¹ (see Figure 2) is standard for measurements at low frequencies, below 10 kHz or so. This is sometimes termed “quasistatic” piezoelectricity.

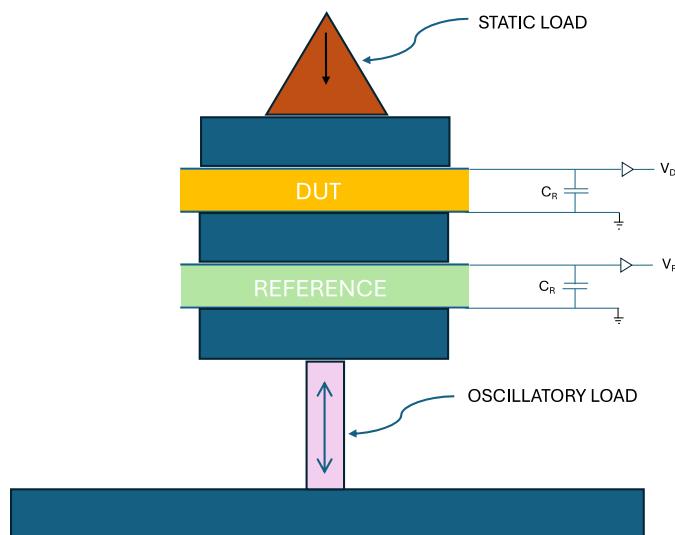


Figure 2: Schematic of the Berlincourt technique.

True dc (i.e., zero frequency) measurements are particularly difficult because of slow charge drift, finite electrical conductivity, etc. The quasistatic method is perhaps the simplest to implement, and there exists a handful of commercial instruments which are useful for determining d_{33} . This method has the advantage that it directly compares the piezoelectric response of an unknown material (“DUT” in Figure 2) to a reference material (usually lead zirconium titanate). Typically, one also employs a static force as a pre-load to prevent motion of the apparatus. The oscillatory load is usually sinusoidal, so that sensitive, phase-locked measurement techniques can be used to measure the piezoelectric charge induced. However, studies have been performed which question the reproducibility and accuracy of this method from material to material and laboratory to laboratory. It is perhaps most valuable for comparison between different materials or specimens that can be measured using one specific instrument and measurement protocol.

Techniques to determine multiple piezoelectric tensor coefficients at high frequency are better controlled, but unquestionably more difficult to implement. These techniques rely on the known



resonant and anti-resonant frequencies of specifically shaped crystal samples as well as measurements over a wide frequency range. Such measurements, along with an ingenious formulation⁷² allows simultaneous measurement of four elements of the piezoelectric tensor and six components of the elastic tensor. The drawback is that it requires highly precise preparation of single crystal specimens that have been cut to exact shapes along specific crystalline axes. Such a technique does not lend itself to either high throughput analysis.

As noted above, the direct measurement of converse piezoelectricity in crystals is made difficult because the induced strain is small. Two approaches have been fruitful, however. *In situ* measurements, in which an electric field is applied to a specimen that is housed within an atomic scattering device, such as an x-ray or neutron diffraction apparatus do allow direct measurement of strain, but only the strain within a small scattering volume of the apparatus.⁷³ A popular alternative is the laser interferometric method.⁷⁴ This technique permits measurement displacements in the nanometer range, which is sufficient to observe converse piezoelectricity. The drawback of both of these techniques is that they are neither simple nor inexpensive.

The above methods are applicable when a single crystalline specimen is available. This is not always practical or even achievable. Two notable examples would be thin-film and powdered (or sintered) materials. In both of these the challenge for measuring piezoelectricity is that the crystalline axis of the specimen is either unknown or highly randomized in space. In this case, even though stress may be applied, the relationship between the stress tensor and the crystalline axes is undetermined. In these situations, it is necessary to *pole* the piezoelectric before measurement. Poling involves subjecting the material to a sufficiently high electric field for an extended time. That is, field strong enough to, for example, rotate microcrystalline particles (in a sinter) along the poling direction. In a polycrystalline sample, poling can enlarge grains having dipole moment along the poling field at the expense of those in competing direction. The poling field should exceed the coercive field. In this process, both time and temperature are important, and poling close to (but less than the) Curie temperature is more efficient.

II.B. Soft piezoelectric materials

Investigating the piezoelectric properties of soft materials and fluids is, conceptually at least, the same process as for solids. Specifically, to study direct piezoelectricity one measures electrical



signal(s) generated in response to mechanical excitation (strain or stress). In case of inverse piezoelectricity, we measure mechanical response (deformation, vibration, or stress) induced by electric field. From the point of view of basic understanding of the electromechanical phenomena observed in a specific soft or fluid material, it is important to determine the distinct components of the piezoelectric coupling tensor, which can be more challenging compared to crystalline solids, in that the axes of symmetry of the material may not be static because the materials are soft.

As in the case of solid crystals, the symmetry axes, crystallographic directions must be determined and appropriately configured with respect to the direction of deformation (for direct) or to the electric field (for converse). This is necessary to discern specific information about the given component of the piezoelectric coupling tensor in any material. For liquid crystals, a well-developed technique to achieve “liquid single crystals” is based on controlling the boundary conditions of the local average molecular direction (the “director”) by surface orienting layers. Alternatively, the use of other external fields, e.g., magnetic, is also possible.

Almost all liquid crystal display technology, and very frequently diverse research endeavors as well, liquid crystals are introduced between two parallel, glass plates separated by a fixed distance usually much smaller than the plate size. This geometry is usually referred to as a “sandwich cell”. Generally, the glass surfaces have been treated to control the boundary value(s) of the liquid crystal’s optic axis (the director). In this manner, and under static conditions, the internal structure of the liquid crystal held between the plates becomes a boundary value problem to minimize the free energy density. There are two main types of surface alignments, respectively known as homeotropic and planar. In homeotropic, the director boundary condition is perpendicular to the glass plates, and in planar, it is parallel and in a common direction. Usually both types are based on anisotropic interaction between the LC and a polymer thin layer. Different polymer coatings are used for homeotropic and planar alignments⁷⁵.

To achieve planar orientation, the polymer chains are usually aligned by rubbing along the favorable direction. Commonly, planar alignment is considered to establish strong anchoring. In most cases, the director does not lie perfectly in the plane of the substrate at a planarly treated surface. It is tilted by a small angle (1° - 5°) called pretilt in the plane that is perpendicular to the substrate and parallel with the rubbing direction. The pretilt is uniform and it depends on the



materials used. Rubbing breaks the symmetry and provides a tool for polar alignment of the spontaneous polarization in ferroelectric nematic liquid crystals which are of special interest from the point of view of piezoelectricity⁶⁴. In such polar materials, uniform structure is achieved with parallel rubbing direction on the opposite boundaries, while antiparallel rubbing leads to a twisted structure. Besides rubbed polymers, obliquely evaporated SiO thin layers forming anisotropic periodic surface structures can also be used to achieve planar orienting layers. An emerging technique is the so-called photo-alignment^{76,77} that uses light sensitive materials and linearly polarized light to align the molecules or polymer chains properly.

Homeotropic alignment can be achieved by coating of polymers that have amphiphilic parts preferring perpendicular orientation with respect to the substrate. Alternatively, silane-based monolayers are also often used to achieve homeotropic alignment example for such compound are: dimethyloctadecyl[3-(trimethoxysilyl)propyl] ammonium chloride (DMOAP) and octadecyltrichlorosilane (OTS). With given boundary conditions, different kinds of liquid crystals will adopt varying static configuration. Depending on the plate separation and the helical pitch, chiral phases may exhibit twisted structures instead of a uniform one.

In contrast to solid piezoelectric crystals, soft or fluidic materials are much easier to deform, therefore preserving the symmetry axes with respect to the deformation or to the direction of the electric field may be much more difficult, even impossible. While surface alignment can be useful to maintain a liquid single crystal structure effectively up to a few micrometers thickness, at larger sizes liquid crystals tend to suffer from faults in the orientational field by forming defects structures and domains of different orientations separated by domain walls. Upon dynamic deformation, material flow is induced in fluids, which can affect the structure and distort the original liquid single crystal. This phenomenon is called flow alignment, and it is due to the coupling between director rotation and material flow.⁷⁵ Reorientation of the spontaneous polarization by a strong electric field (poling) may be possible in soft or fluidic materials as well. Nevertheless, such poling may not have long lasting effect because of the back relaxation of the spontaneous polarization into its original, equilibrium state.

Measurement of direct piezoelectricity in fluids or soft materials requires the following components: mechanical actuator, deformation analyzer, sample holder, electrical signal detector



as seen in Figure 3. To investigate the inverse effect, the components are similar but instead of a mechanical actuator and an electrical signal detector, a voltage source is needed, while the same deformation analyzer can be applied to determine the mechanical response of the material. In the following paragraphs, we overview the details of the apparatuses mentioned above.

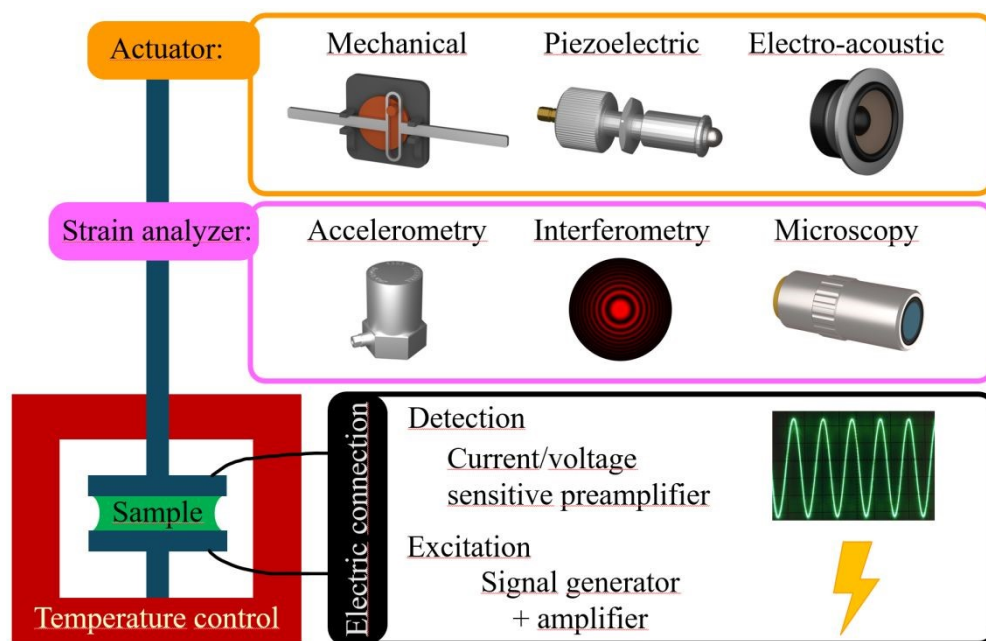


Figure 3: Main components of electromechanical experiments for soft materials.

The role of the mechanical actuator is to generate a linear periodic movement (vibration) that is used to create deformation in the studied material. The two basic parameters of the vibration are the amplitude A and frequency f . Mechanical actuators such as the Scotch yoke are used for low frequency ($f \lesssim 10$ Hz), and large amplitude ($A \gtrsim 1$ mm).⁷⁸ At intermediate frequencies ($10 \text{ Hz} \lesssim f \lesssim 20 \text{ kHz}$) loudspeakers are commonly applied⁴³, while at higher frequencies ($f \lesssim 100 \text{ kHz}$) and small amplitudes piezoelectric actuators are available.

The electrical response of the system can be characterized by measuring electrical current using a current sensitive preamplifier or by measuring the voltage drop on a relatively low, known resistance. Also, the response with the open circuit, or high impedance load can be characterized by measuring the induced voltage by the deformation.



To characterize both the direct and inverse piezoelectric effect, the deformation amplitude must be precisely determined. At higher amplitudes, a straightforward technique is optical microscopy. At lower amplitudes than the optical resolution interferometric methods can be applied. Except at low frequencies, a convenient option is to use accelerometers combined with the lock-in technique, which allows an easy and precise evaluation of deformation amplitudes even as low as the nanometer range.⁴⁸

III. Comparisons between piezoelectric materials

A. 3-D solid piezoelectric materials

In contrast to naturally occurring materials such as quartz, or serendipitously discovered Rochelle salt, new piezoelectric materials with a perovskite structure, such as barium titanate (BT) and lead zirconate titanate (PZT), were prepared. These piezoelectric ceramics display significantly higher piezoelectric constants compared to the first piezoelectrics (see Table 2) However, to exhibit piezoelectric behavior, these materials must first undergo a process known as poling.⁷⁹ Due to their excellent piezoelectric properties, stability, and cost-effectiveness, ceramic materials have become the most widely used class of piezoelectric materials.⁸⁰

Since its discovery in 1950, PZT has become one of the most widely used piezoelectric materials in technologies such as sensors or actuators.⁸¹ However, it has a large Young's modulus that limits the extent to which it can deform.⁸² Additionally, it contains the toxin lead, which makes it unsuitable for many applications because of health/environmental concerns. Smolensky et al. discovered one of the most important lead-free piezoelectric materials, $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT), in 1960.⁸³ BNT has piezoelectric constant of 75 pC N^{-1} which can be enhanced to 173 pC N^{-1} by adding specific dopants.⁸⁴ These compounds exhibit exceptionally high strain, making them highly desirable for actuator applications.⁸⁵ However, as high driving electric field is required to trigger a large strain and the large strain hysteresis⁸⁶, it is difficult to use them in many applications. These challenges were resolved by introducing another environmentally friendly lead-free $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (KNN) ceramics where it provides relatively high unipolar strain with reduced strain hysteresis in a low strength driving electric field.⁸⁷ Undoped KNN has piezoelectric constant between $80\text{-}160 \text{ pC N}^{-1}$ which can be increased up to 700 pC N^{-1} by fabricating the highly textured



form of KNN-based ceramics.^{88–91} In addition to its use in high-temperature applications, KNN is also valuable in energy harvesting and biomedical devices.⁹²

	d_{33} (pC N ⁻¹)	g_{33} (VmN ⁻¹)	k	Y (GPa)	T _C (°C)	Advantages	Limitations
<i>Lead zirconate titanate (PZT)</i>	360	0.025	0.6–0.7	65	350	Stable, strong, degradation-resistant, high resonant frequency. Used in micro-sensors for energy harvesting and AFM.	Rigid, high impedance, limited energy harvesting and applications. Lead content makes it unsuitable for body-implanted devices.
<i>Potassium sodium niobate (KNN)</i>	pure: 80–180 ⁹³ modified : < 700	0.047	0.51	104	400	High Curie temperature, lead-free, safe for medical implants and energy harvesting.	KNN properties are inferior to PZT, and difficult processing limits its applications. ⁹⁴
<i>Barium titanate (BT)</i>	Pure: 191 Modified < 620	0.011	0.49	67	130	High capacitance, used in sonar detection, phonograph needles, and actuators.	low Curie temperature, poor temperature stability ⁹⁵
<i>Bismuth sodium titanate (BNT)</i>	Pure: 75 Doped: 173	-	~0.21	93.3	<290 With dopant: >300	Lead-free, ideal for actuators due to high strain response.	High electric field needed for large strain, the large strain hysteresis ⁸⁶
<i>Aluminum nitride (AlN)</i>	5	0.1	0.23	344.83	>2000	Used in MEMS, AlN thin films are ideal for resonators and sensors.	Low piezoelectric coefficient, difficult fabrication. ^{96,97}
<i>Lithium niobate</i>	6	0.023	0.23	202	1150	MEMS resonators	
<i>ZnO nano generators</i>	9.2,12.4	0.13	-	40		Used in self-powered nano-devices and field-effect transistors.	
<i>Lead magnesium niobate-lead zirconate titanate (PMN-PZT) (S-crystal)</i>	1530	0.036	0.93	65.9–99.6 ⁹⁸	211	Actuators, ultrasonic transducers and transformers due to high dielectric permittivity and high piezoelectric coefficients ⁹⁹	
<i>Lead magnesium niobate-lead titanate (PMN-30%PT) (Single crystal)</i>	2000	0.040	0.93	~117 ¹⁰⁰	137	Large displacement actuators, medical ultrasonic imaging transducers with superior broadband characteristics	Low Curie temperature, not good for flexible and wearable electronics due to rigidity and fragility.
Sm-PMN-PT	4100	0.037	0.95	-	121	Good uniformity, room temperature applications, e.g., for high-frequency medical imaging and low field-driven actuators.	Low curie temperature limits high temperature applications
Nd-PMN-PT	3090	0.028	0.95	-	138	Strong candidates for high-performance piezoelectric transducer.	

Table 2: Properties of Ceramic piezoelectric materials.



Barium titanate (BT)-based ceramics are another promising high-strain piezo-materials, first discovered during World War II^{11–13} It was the first perovskite-structured ferroelectric material and was widely used in sonar applications and phonograph needles^{101,102}. As an alternative to PZT, BT has gained significance in actuator applications.¹⁰³ Aluminum nitride (AlN) and lithium niobate are lead-free piezoelectric ceramics with the advantage of a high Curie temperature exceeding 1000°C¹⁰⁴, although they have low piezoelectric constants of 5 pC N⁻¹ and 6 pC N⁻¹, respectively.^{96,105} AlN thin films are ideal for resonators and sensors due to their high thermal conductivity and low dielectric and acoustic losses.¹⁰⁶ They are also commonly used in microelectromechanical systems (MEMS) because of their high temperature and humidity stability, as well as their compatibility with CMOS processing.¹⁰⁴ Lithium niobate, with its excellent electromechanical coupling and very high quality factor, is a favored material for MEMS resonators.^{107–109}

The application of piezoelectric materials is primarily confined to actuators and sensors, largely due to their low energy conversion efficiency. In contrast, nanostructured piezoelectric materials have higher energy conversion efficiency, as they can endure greater strain. Moreover, nanostructured materials have higher surface-to-volume ratios which further enhance their performance.¹¹⁰ For example, pressure trigger was developed using a zinc oxide (ZnO) piezoelectric fine-wire (PFW), such as a microwire or nanowire, which activates when subject to an external impact force.¹¹¹ By synthesizing ZnO nanorods on conductive textiles, textile-based PEDOT:PSS/CuSCN/ZnO wearable nanogenerators have been fabricated successfully. This has substantial promise for self-powered, soft, electronic devices.¹¹² In contrast, despite excellent piezoelectric properties, piezoelectric ceramics are typically brittle; this limits their use in energy harvesting applications like transducers because of their inability to absorb large strains without sustaining damage.¹¹³

In addition to pure PZT, there are several other piezoelectric materials, such as relaxor ferroelectrics (e.g., PMN-PZT, PMN-PT, PNN-PZT), that exhibit significantly high piezoelectric properties. The piezoelectric constant (d_{33}) reaches approximately 1530 pC/N for $\langle 001 \rangle$ single crystal (S-crystal) and 1100 pC/N for $\langle 001 \rangle$ textured ceramic (T-ceramic) in the 0.4Pb(Mg_{1/3}Nb_{2/3})O₃–0.25PbZrO₃–0.35PbTiO₃ (PMN-PZT) composition synthesized via conventional solid-state reaction method.¹¹⁴



Lead magnesium niobate-lead titanate (PMN-PT) $[0.70\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.30\text{PbTiO}_3]$ is another well-known relaxor ferroelectric exhibits exceptionally high electromechanical performance with piezoelectric coupling constant, $d_{33} \approx 2000 \text{ pC/N}$ and electromechanical coupling factor, $k_{33} \approx 0.93$ in single crystal form.¹¹⁵ These values are nearly 30 times higher than those of BaTiO_3 and about four times higher than those of bulk PZT.¹¹⁶ Furthermore, top-down fabrication method has been used to develop a PMN-PT single crystal nanobelt functioning as nanogenerator with an output voltage of 1.2 V.¹¹⁷

Rare-earth doping, particularly at the A-site of the perovskite structure, has proven effective in enhancing piezoelectric properties of relaxor ferroelectric crystals by introducing local structural heterogeneity. For example, Sm-doped $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (Sm-PMN-PT) single crystals with the composition $\text{Sm}_{0.01}\text{Pb}_{0.985}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.70}\text{Ti}_{0.30}]\text{O}_3$ grown using a modified vertical Bridgman method exhibit d_{33} values between 3400 and 4100 pC/N showing good uniformity.¹¹⁵ However, their relatively low Curie temperature limit their use in high-temperature applications. To address this, Nd^{3+} were introduced to replace Pb^{2+} with the composition $\text{Nd}_{0.002}\text{Pb}_{0.997}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.68}\text{Ti}_{0.32}]\text{O}_3$. The resulting Nd-doped PMN-PT crystals showed piezoelectric coefficients above 3000 pC N^{-1} making them strong candidates for high-performance piezoelectric transducer.¹¹⁸

Another notable example is the $[001]_C$ -textured relaxor ferroelectric composition PNN-PZT $[0.55\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.15\text{PbZrO}_3-0.3\text{PbTiO}_3]$, which exhibits excellent piezoelectric properties ($d_{33} = 1210 \text{ pC} \cdot \text{N}^{-1}$, $d_{33}^* = 1773 \text{ pm} \cdot \text{V}^{-1}$ at $5 \text{ kV} \cdot \text{cm}^{-1}$). These values were achieved using 2 vol% BaTiO_3 platelet templates.¹¹⁹

One of the first piezoelectric polymer materials (see Table 3), semi-crystalline polyvinylidene fluoride (PVDF) was discovered by Kawai in 1969.¹⁹ In semi-crystalline materials, microscopic crystals are randomly oriented and dispersed within an amorphous matrix. These materials will exhibit piezoelectric properties when the micro-crystals reorient after poling.¹²⁰ At present, PVDF is the most widely used piezopolymer, given that poled PVDF demonstrates the highest yet observed piezoelectric coupling, ranging from 24 to 34 pC N^{-1} in β -phase. Due to its flexibility, low acoustic impedance, excellent electromechanical response, biocompatibility, and chemical stability, PVDF is used in a wide range of applications.¹²¹ Examples include wearable piezoelectric energy harvesters and biomedical engineering applications.^{122,123}



Material	d_{33} (pC/N)	g_{33} (Vm/N)	k	Y (GPa)	T _c (°C)	Advantages	Limitations
PVDF (Semi-crystalline)	24 to 34 ¹²⁴	0.34 ¹²¹	0.20	4.18	75-80	Flexible, stable, low acoustic impedance, excellent response. Used in wearable energy harvesters and biomedical devices.	Lack of β phase limits its applications. ¹²⁵ Narrow operating temperature. ¹²⁶
PVDF-TrFE (Semi-crystalline)	-25 to -40	-0.542	~0.29	~1.5	~110	Advantages over PVDF in fabrication and piezoelectric applications; used in sensors and power harvesters.	high processing temperature, limited long-term stability, high cost. ¹²⁷
Nylon-11 (polyamide) (Semi-crystalline)	7.2 ¹²⁸	-	-	-	-	Harvest energy from movement, used in apparel, health monitoring, sportswear, and portable energy generation. ¹²⁹	Conventional fabrication does yield piezo nylon; polyamides are hydrophilic.
Polyimide (Amorphous)	-2.7	0.087	-	-	225	High glass transition temperature, use in MEMS devices	Low piezo constant, time decaying response.
Parylene-C (Amorphous)	-2 ¹²⁴	-	0.02 ¹²⁰	2.8 ¹²⁰	-	Biocompatibility, stability, low acoustic and mechanical impedance, MEMS.	Low piezo constant, Low Energy Harvesting Efficiency.

Table 3: Properties of piezoelectric polymers.

Unlike pure PVDF, the copolymer PVDF-TrFE (trifluoroethylene) does not require poling to exhibit piezoelectric properties. Although the TrFE units reduce the dipole moment of the PVDF chain due to the addition of a third fluorine atom¹²¹, the piezoelectric constant of PVDF-TrFE was found to be in the range of 25 to 40 pC N⁻¹.¹³⁰ Various methods have been utilized to prepare PVDF-TrFE sheets and films, and to also enhance piezoelectric properties. These have been developed for applications, such as power harvesters, flexible tactile sensors, capacitor-based sensors, touch sensors and actuators.^{131–135} However, the induced strain in both PVDF and its copolymers with TrFE is highly dependent on a strong electric field, which significantly compromises their reliability and restricts their practical use in wearable devices.¹³⁶

In addition to PVDF and its various copolymers, piezoelectric effects have also been observed in other semi-crystalline materials, such as polyamides, for example in odd-numbered nylons, such as nylon-11, that exhibits a piezoelectric constant of 7.2 pC N⁻¹ in the δ' -phase.¹³⁷ This material

can play a crucial role in energy harvesting, as well as in smart and wearable electronic textile applications. However, traditional fiber production methods such as melt extrusion and melt spinning produce non-piezoelectric polycrystalline α -phase nylon fibers, limiting the potential applications of piezoelectric nylon-11 in E-textiles.¹²⁹

Polyimides are one of the most important amorphous polymers; their glass transition temperature makes them ideal for high-temperature applications.¹³⁸ Although they have a lower piezoelectric constant (-2.7 pC N^{-1}) compared to PVDF, they are usable over a larger temperature range. While the piezoelectric properties of PVDF can deteriorate when exposed to temperatures above 70°C , polyamides maintain their piezoelectricity up to 150°C , making them ideal for high-temperature MEMS sensor applications. The first study on Parylene-C (PA-C) as a piezoelectric material was conducted in 2011 and the d_{33} value was found to range from -0.01 to -2.00 pC/N .¹²⁴ Due to its biocompatibility and chemical stability, Parylene-C (PA-C) is highly suitable for integration into MEMS devices, including sensors and cantilevers. Although piezoelectric polymers are cost-effective, lightweight, flexible, and offer a simple solution for numerous applications, they do have drawbacks. These include limited mechanical strength, poor thermal stability, low piezoelectric coefficients and low electromechanical coupling coefficient. The combination of all of these leads to poor energy harvesting capabilities.

Alternatively, piezoelectric composite materials (Table 4) combine the desirable properties of ceramics with the flexibility of polymers offering the advantages of both materials. The concept of piezoelectric ceramics/polymer composites was first introduced in the 1970s by Newnham.¹²¹ Piezocomposites have the higher coupling properties and dielectric constant of ceramics, along with the mechanical flexibility and low acoustic impedance of polymers. The polymer in the composites can be either piezoelectric or non-piezoelectric.¹⁰² For instance, poly dimethyl sulfide (PDMS) lacks intrinsic piezoelectric properties, but it can still be used as a polymer matrix in composites because of its flexibility, thermal stability, and chemical durability.

One of the most widely used piezocomposites is PVDF-PZT. Pure PZT exhibits high impedance, rigidity, brittleness, and inflexibility¹³⁹, while PVDF has low piezoelectric coefficient and low stiffness. Individually, these attributes limit possible applications. However, by combining PVDF and PZT in a composite, the electromechanical and mechanical properties can be significantly enhanced. Using a 3/7 fraction ratio, PVDF-PZT composite has $d_{33} = 35.8 \text{ pC/N}$, greater than



that of pure PVDF (18.3 pC/N). Such composite films are suitable for small force sensor applications.¹⁴⁰ Remarkably, a self-powered PZT/PVDF piezoelectric sensor has been developed for real-time monitoring of table tennis training.¹⁴¹

A lead-free piezocomposite has been developed by dispersing BT ceramic grains into a PVDF matrix. The piezoelectric constant for the 0.6BaTiO₃/0.4PVDF composite was found to be 28 pC/N which was increased to 61pC/N when BaTiO₃ nanowires with 50 vol% of BaTiO₃ were dispersed into 5.5 wt% of a PVDF polymer matrix.¹⁴² Due to mechanical flexibility and relatively high dielectric constants, this composite has significant potential for use in wearable electronics.^{143–145} Additionally, BCZT/PDMS piezocomposites have achieved $g_{33} = 0.6 \text{ Vm/N}$, the highest value recorded so far in piezocomposites. This promises significant potential applications for wearable electro-mechanical technologies.¹⁴⁶

Other composites have been developed by loading cellulose nanofibers (CNF) with ZnO to form CNF/ZnO composites, which exhibit a piezoelectric constant of 9.5 pm/V. This value can be further increased to 25 pm/V (with $d_{33} \approx 31 \text{ pC/N}$) by incorporating PVDF into the composite, resulting in the PVDF/CNF@ZnO (E-PVDF/CZ) composite. A flexible piezoelectric sensor was developed for applications in energy harvesting and environmental monitoring.¹²⁵

Material	d_{33} (pC N ⁻¹)	g_{33} (V × mN ⁻¹)	Y (GPa)	Advantages	Limitations
PVDF-PZT (30-70)	35.8 ¹⁴⁰	-	0.894-1.725 ¹⁴⁰	Softer than PZT, used in force sensor, self-powered sensor for real-time monitoring of sport activity.	Uneven mixing of fillers in the matrix, small mechanical force transmission to the piezoelectric particles, and low polarization efficiency.
BaTiO ₃ /PVDF (60-40)	28	0.16 ¹⁴²	35 ¹⁴³ (with 50 vol% of BaTiO ₃)	Self-powered wearable electronics, Actuators and Energy Harvesting.	
BCZT with PDMS	31 ¹⁴⁶	0.6 ¹⁴⁶		Low-power wearable and portable electronic devices. Energy supplies for implantable biomedical devices	
ZnO-CNF	9.49 ¹²⁵			Energy harvesting and environmental monitoring.	
ZnO-CNF-PVDF	31±2.07 ¹²⁵			Excellent flexibility, Self-powered wearable electronic devices.	

Table 4: Properties of composite piezoelectric materials.

Traditional polymer-ceramic piezocomposites often suffer from poor stress transfer between the polymer matrix and ceramic fillers, thereby limiting their energy harvesting capabilities. To

overcome this, biofibril template method was used to develop 3D Sm-doped PMN-PT ceramic skeleton, which was then embedded in a flexible polymer matrix. The resulting piezocomposite exhibits significantly enhanced performance, achieving an open-circuit voltage of approximately 60 V and a short-circuit current density of $\sim 850 \text{ nA} \cdot \text{cm}^{-2}$, with a peak instantaneous power density of $\sim 11.5 \mu\text{W} \cdot \text{cm}^{-2}$ which is about 16 times greater than that of traditional nanoparticle-based composites.¹⁴⁷

Piezoelectricity can also be observed in porous charged polymers, commonly referred to as ferroelectrets, discovered in 1990's by Kirjavainen.¹⁴⁸ Different polymers, such as polypropylene (PP), poly(ethylene terephthalate) (PET), poly(ethylene naphthalate) (PEN), poly(tetrafluoro ethylene) (PTFE), cross-linked PP (XPP), and some cyclo-olefines, have been considered for different cellular films, see Table 5. Ferroelectrets has wide range of applications due to their high piezoelectric constants, low cost, flexibility and low specific weight.¹⁴⁹ Cellular polypropylene (PP) is a significant ferroelectrets exhibiting $d_{33} = 1.2 \text{ nC/N}$ for a single layer. This response can be further multiplied by using multilayer films. The material performs well in fatigue resistance, stiffness and charge-trapping properties.¹⁵⁰ Cellular PP has been used in pressure sensing applications such as touch pads, accelerometers, long-term respiration monitoring due to their good sensitivity and capability for self-power.^{151,152} Cross-linked PP ferroelectret films exhibit d_{33} as large as 230 pC/N. These films can be utilized to harvest sound energy by being applied to the inner walls of cavities in Helmholtz resonators, making them ideal for applications in road transport and high-speed railways.¹⁵³ Polyester ferroelectrets, such as polyethylene terephthalate (PET) foams and polyethylene naphthalate (PEN), demonstrate piezoelectric coefficients of 500 and 140 pC/N, respectively, while maintaining stable sensitivity up to 80 °C.¹⁴⁹ Ferroelectrets have emerged as promising materials for a broad spectrum of applications, including tactile sensors, accelerometers, gaming, robotics and force myography (FMG) which detects body motion. This is attributed to their exceptional piezoelectric coefficients, low elastic moduli, high flexibility, and notable stretchability.^{124,154–156} Despite their advantages, ferroelectrets face several challenges, primarily related to limited long-term and thermal stability. Overcoming these limitations could significantly enhance their performance and broaden their scope of application in various fields.

Material	d_{33}	g_{33}	Y(GPa)	Advantages	Limitations
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	(pC N ⁻¹)	(V × mN ⁻¹)			
Semi-crystalline Cellular Polypropylene (Ferroelectrets)	130–2100	30	0.002	Low cost, good fatigue resistance, Used in microphones, transducers and accelerometers.	Limited long-term and thermal stability, electrets tend to gradually lose polarization at higher temperatures.
PDMS with polar nanoparticles.	37(<i>d</i> ₃₁) ^{157,158}		1.5 ¹⁵⁹	Stretchable sensors, energy harvesting, soft robotics, and flexible electronics	
Soft composite fiber mats (BT+PLA) ^{160,161}	□1000		□0.0001	Lightweight, biocompatible, application in active implants, artificial muscles, sensors, textiles	

Table 5: Properties of Cellular piezoelectric materials.

Highly piezoelectric biocompatible soft fibers were created by dispersing BT ceramic particles into electrospun poly lactic acid (PLA). The strongest converse piezo response was observed when the BT particles were uniformly aligned and poled within the fiber, resembling ferroelectret polymer foams. This response was an order of magnitude greater than that seen in single-crystal BT films. These mats, due to the PLA’s biocompatibility, have potential applications in biological fields such as biosensors, artificial muscles, and energy harvesting devices.^{160,161}

Piezoelectricity has also been explored in various biomaterials (Table 6), including collagen, DNA, bone, cellulose, and amino acids.^{14,162,163} The piezoelectric constant of bone was measured to be 0.2 pC/N.¹⁶⁴ It was found that piezoelectricity in collagen contributes to the piezoelectric effect observed in bone.^{164,165} The piezoelectric constant for type I collagen fibrils in both murine and bovine Achilles tendons was found to range between 1 – 2 pm/V^{166,167}, while for D-periodic reconstituted collagen fibrils, the value was 1.6 pm/V.¹⁶⁸

The piezoelectric effect in DNA films, particularly due to shear and hydration effects, has also been studied, though the origin remains unclear and the quantitative values poorly determined.¹⁶⁹ Non-chiral amino acid glycine demonstrates a piezoelectric response, with β-glycine and γ-glycine with piezoelectric coefficients of 6 pm/V and 10 pm/V, respectively.¹⁶⁹ In cellulose nanofibers (CNF) piezoelectric force microscopy (PFM)¹²⁵ provided *d*₃₃ = 5.9 pm/V, while *d*₃₃ = 0.4 pm/V for pure wood cellulose. In spite of this, cellulose can be incorporated into piezoelectric composites as a functional filler to enhance performance.¹⁷⁰ Beyond natural materials, the piezoelectric properties of the M13 bacteriophage have also been studied, showing a response of up to 7.8 pm/V. A phage-based piezoelectric generator has been developed, capable



of generating up to 6 nA of current and 400 mV potential, which can be used to power liquid crystal displays (LCDs). These viral particles, along with other biomaterials, show significant potential for applications in energy storage, generation, and tissue regeneration.¹⁷¹

Materials	$d_{33}(\text{pC N}^{-1})$	Young's Modulus (MPa)	$g_{33}(\text{V} \times \text{mN}^{-1})$	Advantages	Limitations
Collagen fibres ¹⁶⁸	~1-2			Important for tissue engineering applications.	Low piezoelectric coefficients limit technological applications
M13 bacteriophage ¹⁷¹	7.8				
DNA ¹⁷²	Not known				
Bone ¹⁷³	0.2				
β -glycine (amino acids) ¹⁶⁹	6	15	8.13		
γ -glycine ¹⁶⁹	10	28	0.46		
Cellulose	0.4 ¹⁷⁰				
Cellulose nanofibers (CNF)	5.85 ¹²⁵				

Table 6: Piezoelectric properties of biomaterials.

B. *Smectic and Columnar liquid crystals (1-D and 2-D solids)*

Smectic liquid crystals have a one-dimensional layered structure, while columnar liquid crystals form a structure ordered in two directions and fluid in the third. These can be described as one-, or two - dimensional solids respectively. Such symmetries, in some cases, permit linear couplings between electric field and mechanical strain, i.e. piezoelectricity. A schematic of possible molecular packing, their respective symmetry groups (using Schönflies notations), and the non-vanishing piezoelectric coefficients for known smectic liquid crystals is shown in Figure 4.

The SmA^* phase (see Figure 4(a)) has D_∞ symmetry, i.e., complete rotation symmetry along the long molecular axis but without a mirror plane (due to the molecular chirality). In this phase shear along the smectic layers (indicated by light magenta planes) by stresses T_{12} or T_{13} result in an electric polarization along axis 3 or 2, respectively. This yields non-zero $\gamma_{3,12} (= -\gamma_{2,13})$ piezoelectric coupling coefficients. Such an effect was tested and measured in the $\text{SmA}^* (L_\alpha)$ phase of phospholipid L- α -phosphatidylcholine, which is often considered as a model for bilayer cellular membranes.¹⁷⁴ The underlying physical mechanism was postulated to be mechanical shear



(T_{12} or T_{13}) induced tilt of the average molecular orientation (director) with respect to the layer normal, that leads to a shear-induced SmC^* configuration (see Figure 4(b)) with polarization normal to the tilt (shear) plane.^{50,175} The induced polarization was found to be proportional to the induced tilt angle with a coefficient of $\sim 60 \text{ nC}/(\text{cm}^2 \cdot \text{degree})$. Cell membranes made up from lipid bilayers, also have SmA^* structure, suggesting that cell membranes should also be piezoelectric. The piezoelectric origin of the effect was confirmed by studies comparing non-aqueous lamellar phases of left-handed (L_α -phosphatidylcholine), right-handed (D_α -phosphatidylcholine) and racemic (DL- α -phosphatidylcholine) lipids.¹⁷⁶

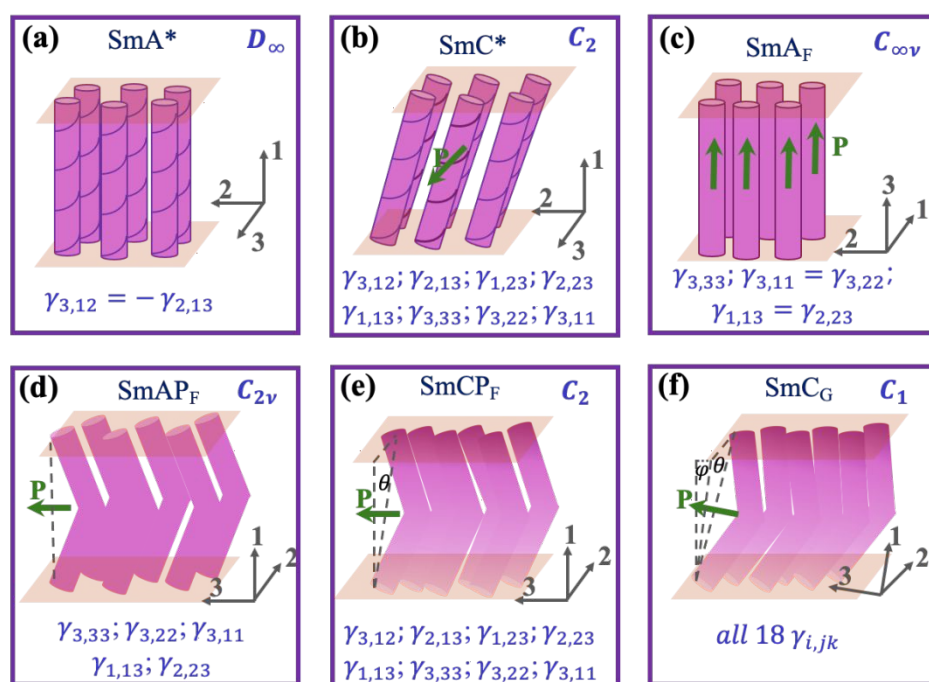


Figure 4: The sketch of the molecular packing, their symmetry using Schönflies notations, and the non-vanishing piezoelectric coefficients determined by the Curie-principle for known non-centrosymmetric smectic liquid crystals.

It was further hypothesized that electric charge separation can be induced along membranes when the lipids become tilted as a result of mechanical stimuli. Importantly, the tilt-induced polarization occurs within the insulating chains of the bilayers and therefore cannot be screened by free ions of the surrounding aqueous plasma. It has been suggested that cell membrane piezoelectricity may be utilized in mechanoreceptors; and can even explain some species (e.g. pigeons turtles) can



navigate without visual reference. In some cases, animal cells contain magnetite (Fe_3O_4) nanoparticles that form chains and act as compass needle to sense local changes in magnetic field^{177,178}. Although magnetoreception of migratory animals is well established experimentally, its biophysical mechanism is not yet clear. The chains of these magnetite nanoparticles are connected to the cell membranes via nanofibers, thus exerting shear stress on the cell membrane when the compass needle moves. Piezoelectric coupling of cell membranes, as explained above, suggests that shear-induced electric signal may open ion-channels embedded in the cell membrane and thus trigger much larger electric signals that depends on the position of the ion channel and on the shear induced polarization. This may provide both orientational and positional information necessary for navigation.

The converse piezoelectric effect in SmA^* leads to a shear strain in 1 – 2 plane due to an electric field applied in the perpendicular direction. Such shear strain is expected to 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 has been indeed observed and is known as electro-clinic effect.¹⁷⁹ Spillmann *et al* studied SmA^* elastomers and found electric field-induced twist whose direction changes sign with that of the electric field.¹⁸⁰ The sense of the twist is controlled by the chirality, just as the direction of the tilt in the electro-clinic SmA^* materials.

Piezoelectric effects have been studied experimentally largely in the SmC^* phase (see Figure 4(b)). SmC^* is the first liquid crystal phase that was found to be ferroelectric.^{50,51} As argued by Meyer, the ferroelectric polarization is along the smectic layers perpendicular to the tilt plane due to the combined effect of the director tilt and chirality. Without director tilt the material would be SmA^* , where an electric polarization along the layers would be canceled due to continuous symmetry axis normal to the layers. This symmetry would allow for a 180° rotation along the director that would cancel any vector response within the layer, as illustrated in Figure 4a). As we discussed above, in spite of the lack of ferroelectricity, this phase is piezoelectric. A director tilt without molecular chirality also would not allow for a polarization within the smectic layers as illustrated in Figure 4(b). This phase has a C_{2v} symmetry, i.e., a two-fold rotation normal to the tilt plane, as such rotation would not change the structure. This 180° rotation would allow for the existence of a vector normal to the tilt plane. On the other hand, the SmC phase also has a mirror symmetry in the tilt plane (this is expressed by the v in the subscript), which would negate a vector normal to the tilt plane. The SmC^* phase lacks both rotation symmetry along the director and the mirror



plane along the tilt plane, thus allowing a non-zero polar vector, such as the electric polarization normal to the tilt plane (see Figure 4c)). Such a situation is often expressed as *tilt + chirality* $\rightarrow$ *polarity*. As can be seen in Figure 4(b), there are 8 piezoelectric constants in SmC^* with C_2 symmetry that can be non-zero. Those are the terms where the coordinates (1 and 2) normal to the electric polarization vector (3) appear either twice or together.¹⁸¹ This is because an inversion of coordinates 1 and 2 (which is allowed by symmetry) will change the sign of the coupling constant, so two of them must be done simultaneously.

Figure 4(c) shows the structure of a polar smectic A (SmA_F) phase with polarization direction along the director of achiral rod-shape molecules with high molecular dipole moments. Such phase just has been observed recently among materials that also form the 3D fluid ferroelectric nematic (N_F) liquid crystal phase.^{182,183} The symmetry and the possible piezoelectric couplings of this phase is the same as of the N_F phase and is discussed subsequently. Due to the very recent observation of this phase, no experimental confirmation of its piezoelectric response is yet available.

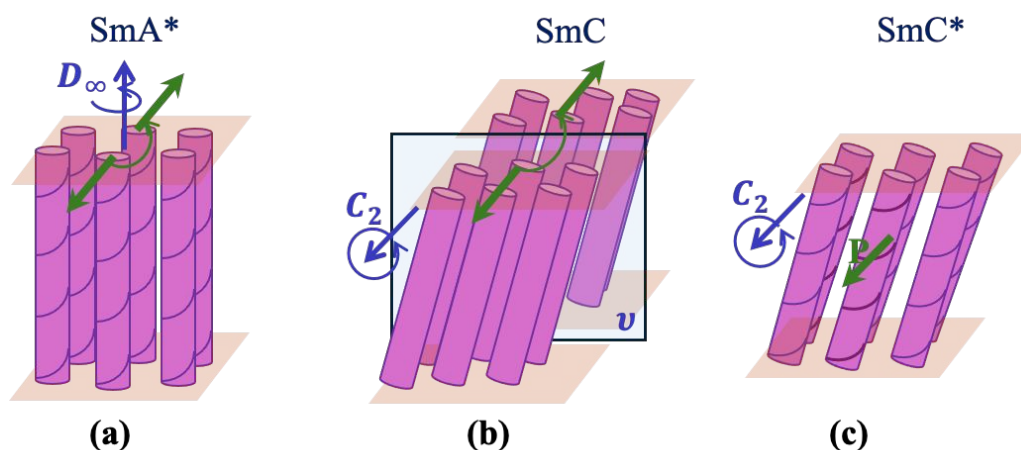


Figure 5: Illustration of Meyer's arguments to explain the existence of polarization in chiral smectic C^* liquid crystals. (a): SmA^* has D_∞ symmetry: an infinite fold rotation along the director (smectic layer normal) that includes a 180° rotation which would turn any vector along the smectic layer to opposite direction. (b): a non-chiral SmC phase with C_{2v} symmetry including a 2-fold rotation normal to the tilt plane and a mirror plane along the tilt plane that rotates a vector normal to the tilt plane into opposite direction. (c): a chiral smectic C^* (SmC^*) phase that has only a two-fold rotation (C_2) symmetry axis normal to the tilt plane, which allows the existence of a non-zero vector (such as spontaneous polarization) normal to the tilt plane.



Figure 4(d-f) show structures, symmetries and possible piezoelectric coupling constants of achiral bent shape molecules forming smectic phases.^{53,182,184–187} It is noteworthy that the SmCP_F phase has the same C_2 symmetry and the same 8 possible piezoelectric coupling constants as of the SmC^* phase. Furthermore, the double tilted SmC_G phase is the least symmetric 2-dimensional fluid phase^{184,187,188}, which has only C_1 symmetry that allows for all 18 possible piezoelectric coupling constants.

Experimentally the first observation was a direct piezoelectric response, i.e., shear-induced polarization^{189,190}. It arises from the distortion of the helix as illustrated in *Figure 6*. In the ground state (no-shear, *Figure 6a*) the director, which is tilted with respect to the layer normal by an angle θ , forms a helix having chiral pitch, p ; p is typically in the micron range. Consequently, the spontaneous polarization is rotated in subsequent layers⁵⁰ but will average to zero over distances greater than p .

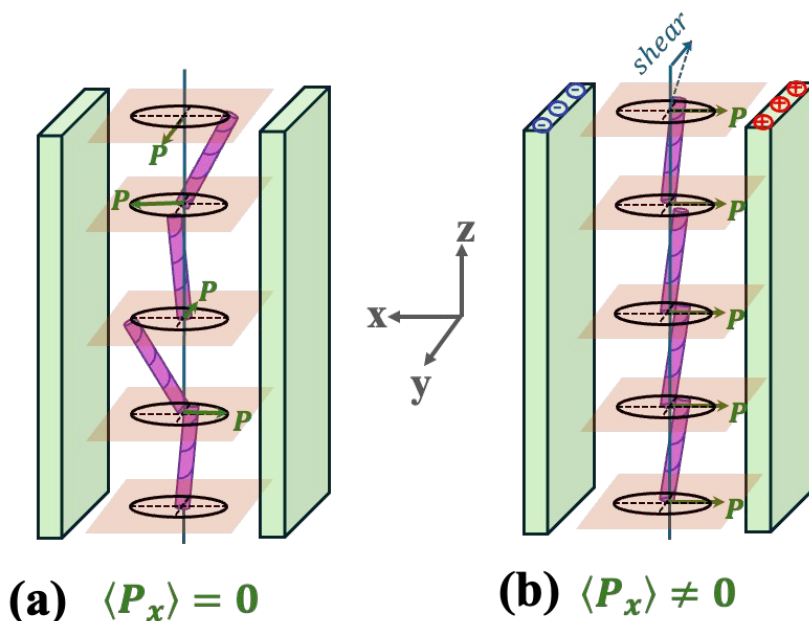


Figure 6: Illustration of the shear deformation of the director structure and the induction of net polarization in the SmC^ phase. The smectic layers are parallel to the x-y plane. The tilt plane rotates from one layer to the other. (a) Undisturbed helical structure where the macroscopic polarization is averaged out. (b) Due to the action of the shear along y, the axial symmetry of the configuration is broken, and a non-zero polarization component appears along x. Arrows indicate the spontaneous polarization $\vec{P}$, 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)).*



The shear in the yz plane aligns the projection of the c -director (the projection of $\hat{n}$) onto the layer plane parallel (and consequently the polarization normal) to the shear plane, leading to $\langle P_x \rangle \neq 0$, as seen in *Figure 6(b)*. Ferroelectric chiral SmC^* elastomers can be also ferroelectric. However, so far their direct piezoelectricity was only considered theoretically by Adams and Warner.¹⁹¹ Direct piezoelectric effects were also observed in lyotropic liquid crystals and in membranes with C_2 symmetry.¹⁹²

Converse piezoelectric responses in SmC^* materials have been also studied since 1985.⁴⁹ A systematic study with accurate control of the alignment revealed that induced motion parallel to the smectic layers (and the film surface) is generally the strongest, especially if the polarization is also parallel to the plates.⁴² Motion normal to the film substrates is due to the electro-clinic effect that causes a field-induced variation of the tilt angle that results in a change of the layer spacing. When the polarization is parallel to the field, the tilt angle (consequently the value of the polarization) increases and the layer spacing decreases. When the polarization is opposite to the field, the tilt angle decreases and the layer spacing increases. Since the number of layers cannot change in short time, the variation of the layer spacing results in a force normal to the cover plate, and a variation of the film thickness (see *Figure 7(a)*).

Motion along the film surfaces (shear strain) is related to “backflow”¹⁹³, i.e., to the coupling between the gradient of the director rotation about the layer normal (Goldstone mode¹⁹⁴) and the flow field. This mode is excited by the electric field via the torque $\vec{E} \times \vec{P} = E \cdot P \cdot \sin\Phi$, where Φ is the angle between the electric field and the spontaneous polarization. The magnitudes of piezoelectric oscillations are therefore largest when the polarization is parallel to the film surface and perpendicular to the applied electric field (see *Figure 7(b)*). Typically, piezoelectric coupling constants in the SmC^* phase are in the order of 50 pC/N, which is comparable to solid piezoelectric materials.



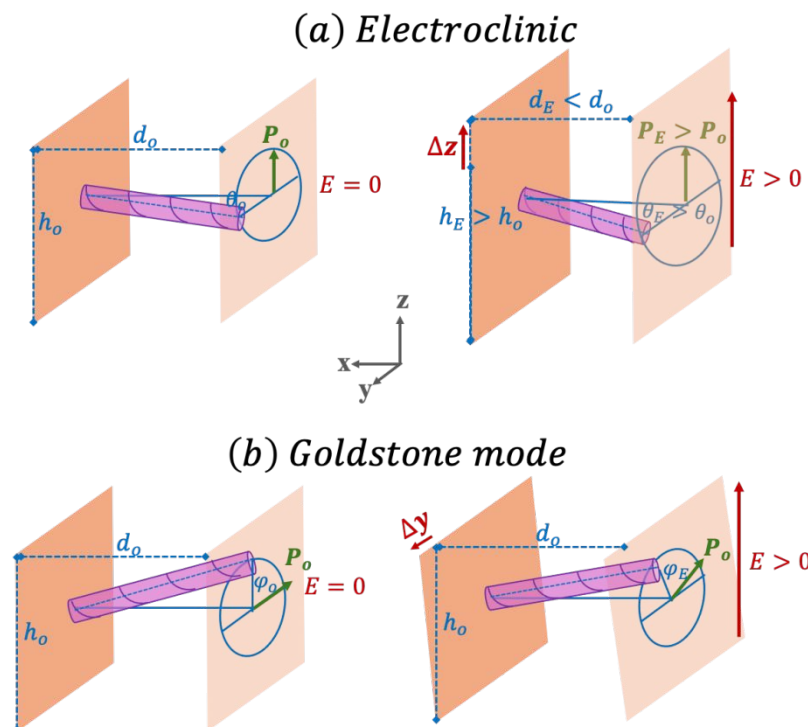


Figure 7: Illustration of the linear electromechanical effect of SmC^* materials due to the electroclinic effect (a) and the backflow related to the Goldstone mode director rotation (b).

In addition to bulk thermotropic SmC^* materials confined between glass plates, converse piezoelectric-type responses were also observed in free-standing ferroelectric SmC^* films subject to AC electric fields applied along the film surface.^{195–197} Additionally, this was also observed in lyotropic liquid crystal.¹⁹² Finally, the converse piezoelectric effect has also been reported in SmC^* glasses¹⁹⁸ and elastomers¹⁹⁹ that can sustain strain in all three directions.

Experimentally only one piezoelectric coupling constant has been determined in the synclinic tilted polar ferroelectric SmC_sP_F phase (molecules are tilted in the same direction in subsequent layers) with $P_o \approx 5 \text{ mC/m}^2$ polarization by testing the converse piezoelectric responses in two directions. It was found that $\gamma_{3,33} \approx 2\gamma_{3,22} \approx 100 \text{ nC/N}$.²⁰⁰

Candidate molecular structures, symmetries and allowed non-zero piezoelectric constants of columnar liquid crystals (2-D solid materials) are shown in Figure 8. Figure 8(a) shows the tilted chiral columnar (Col_t^*) phase⁵² with C_2 symmetry and 8 possible piezoelectric coupling constants. Figure 8(b) illustrates the hexagonal pyramidal (P_h) phase of achiral bowl (pyramidal)-shaped



molecules with C_{6v} symmetry and 3 possible (2 independent) non-zero piezoelectric constants. Figure 8(c) represents the chiral hexagonal pyramidal shape (P_h^*) phase with C_6 symmetry and 3 independent possible non-zero piezoelectric constants. Finally, Figure 8(d) shows the tilted pyramidal (P_t) phase of achiral bowl (pyramidal)-shaped molecules with C_{1v} symmetry and 3 possible (2 independent) non-zero piezoelectric constants.

The ferroelectric Col_t^* columnar liquid crystal 1,2,5,6,8,9,12,13-octakis[(S)-2-heptyloxy]dibenzo[*e,l*]pyrene ($D8m^*10$)²⁰¹ has demonstrated converse piezoelectric effect.⁴⁰ A piezoelectric coupling constant $\gamma_{3,33} \sim 1 \text{ pC/N}$, is reported; this is 1000x less than is typical in SmC* materials.

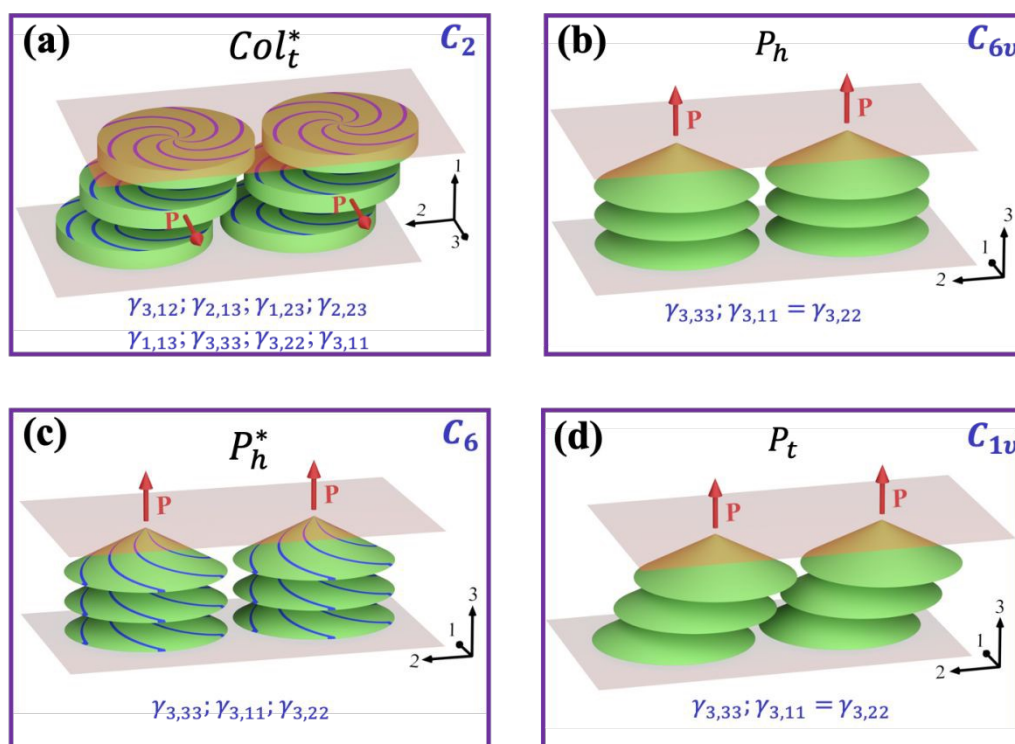


Figure 8: Molecular structures, symmetries and Possible non-zero piezoelectric constants of columnar liquid crystals (2-D solid materials). (a): Tilted chiral columnar (Col_t^*) phase with C_2 symmetry and 8 possible piezoelectric coupling constants; (b): Hexagonal pyramidal (P_h) phase of achiral bowl (pyramidal)-shaped molecules with C_{6v} symmetry and 3 possible (2 independent) non-zero piezoelectric constants; (c): Chiral hexagonal pyramidal shape (P_h^*) phase with C_6 symmetry and 3 independent possible non-zero piezoelectric constants; (d) Tilted pyramidal (P_t) phase of achiral bowl (pyramidal)-shaped molecules with C_{1v} symmetry and 3 possible (2 independent) non-zero piezoelectric constants.



C. *Liquid crystals lacking spatial order (3-D liquids)*

Nematic (N) and chiral nematic (or cholesteric; N*) liquid crystals are fluid in three directions, i.e., their long-range order is purely orientational (no positional order). The N phase has inversion symmetry and as such does not allow piezoelectricity. The N* has the same D_{∞} symmetry along the director as does SmA*, so only the $\gamma_{1,23} = -\gamma_{2,13}$ piezoelectric coefficients (see Figure 4(a)) may be non-zero. However, the optical axis of N* follows a helix so that all piezoelectric coefficients average to zero over distance greater than the helix pitch, which typically is $0.1 \mu\text{m} < p < 100 \mu\text{m}$.⁷⁵ To date the only reports of piezoelectricity in N* are in polymerizable materials where crosslinked chiral molecules produce an unwound N* elastomer.^{202,203} In this case, while there is no long-range positional order, cross-linking severely restricts molecular motion, resulting in the ability to sustain elastic strain.

Fluid liquid crystals with ferroelectric nematic (N_F) phase^{54–59,204} represent materials combining true 3D fluidity with polar order. That is, true fluid materials lacking inversion symmetry; this permits several piezoelectric couplings. The N_F phase has $C_{\infty v}$ symmetry, i.e., continuous rotational symmetry about the polar axis and mirror symmetry through any plane containing the polar axis. This means that any reflection through the 1 – 3 (or 2 – 3) plane changes the sign of 2 (or 1), therefore, components of $\gamma_{i,jk}$ containing an odd number of either 1 or 2, must be zero. Thus, the non-vanishing piezoelectric tensor elements are $\gamma_{3,33}, \gamma_{3,11} (= \gamma_{3,22})$ and $\gamma_{1,13} (= \gamma_{2,23} = \gamma_{1,31} = \gamma_{2,32})$. The depictions of non-zero coupling constants in converse piezoelectric effects are shown in Figure 9.



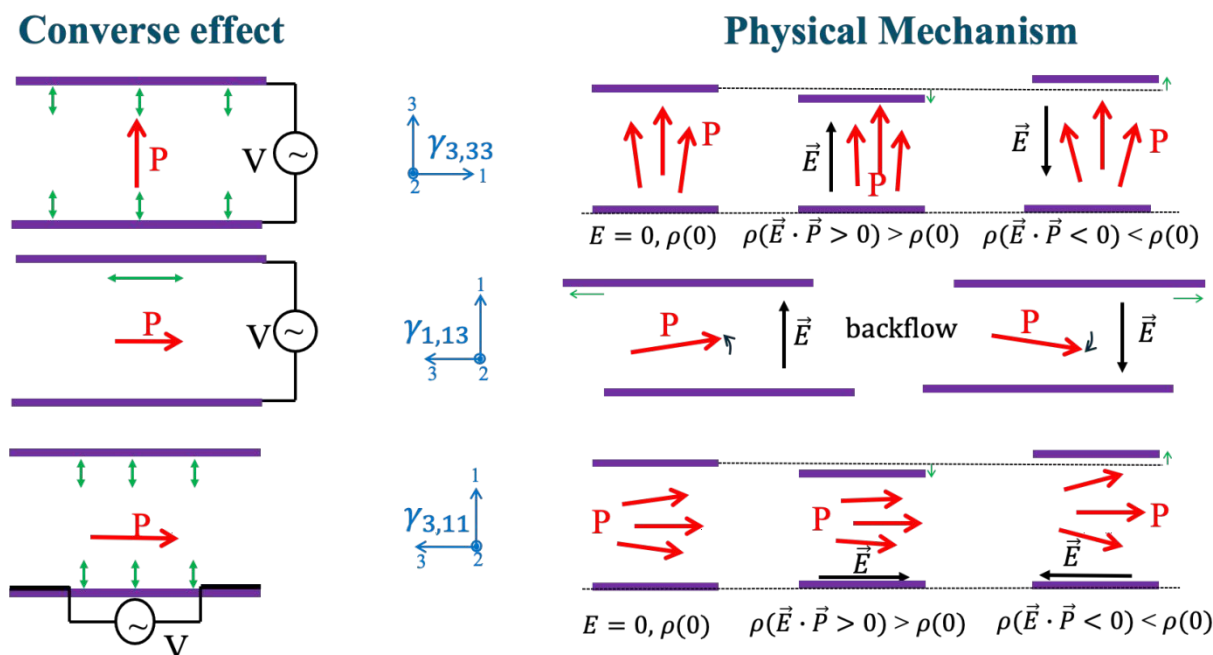


Figure 9: Depictions of non-zero coupling constants (left) in converse piezoelectric effects and the proposed physical mechanisms (right) corresponding to those coefficients. In each illustration black arrows and circuit elements represent the stimulus (electric field or applied voltage); green double headed arrows show the response (mechanical vibration, and red arrows show the direction of the spontaneous polarization.

By controlling the geometry, i.e., the alignment direction in the N_F phase, the direction of the applied electric field one can determine various components of γ . For example, with electrodes on top and bottom of a thin film (parallel plate capacitor geometry) and the director aligned perpendicular to these plates, one can measure $\gamma_{3,33}$ by detecting film thickness variations induced by the electric field. In order to discriminate between converse piezoelectricity and other non-linear (higher harmonic) electromechanical effects, one typically uses a sinusoidal electric potential and phase-sensitive detection to assure that only motion having the same frequency is sampled.

In contrast to $\gamma_{3,33}$, $\gamma_{1,13}$ can be measured with voltage applied between the electrodes when the material in N_F phase is aligned parallel to the substrate. For the measurements the motion detector (which usually is an accelerometer as described in II/B) should detect the vibration of the top plate parallel to the rubbing direction of the alignment layer.



The third non-zero coupling constant, $\gamma_{3,11}$, can be measured with the director aligned parallel to the substrate, and using an in-plane electric field in the same direction; in this case motion normal to the substrate must be determined.

The physical mechanisms leading to the mechanical displacements allowed by the non-zero coupling coefficients, are illustrated on the right side of Figure 9. Specifically, when the ferroelectric nematic material is subject to an electric field parallel to the polarization, fluctuations of the polar order are suppressed, leading to both an increased polarization and closer intermolecular packing resulting in a greater mass density: $\rho(E) > \rho(0)$. Since the ferroelectric nematic materials are incompressible, greater density implies a lesser total volume so that the boundary surfaces experience a force towards each other. Reversing the sign of the applied electric field will result in a decreased polar order and decreased mass density $\rho(-E) < \rho(0)$, which will cause the thickness to increase. This effect is limited to applied electric fields below the coercive threshold. Thus, by measuring vertical boundary plate motion at the frequency of the applied electric field, we can determine the value of $\gamma_{3,33}$.¹⁹³

The vertical vibration of a planar aligned N_F material upon in-plane electric field corresponding to $\gamma_{3,11}$ has the same field-induced density variation mechanism as of $\gamma_{3,33}$ (see right-bottom part of Figure 9). It is important to emphasize that in all converse piezoelectric measurements in the N_F phase the applied small electric field should not cause significant rotation and realignment of the director. The horizontal vibration of the boundary plate in the $\gamma_{1,13}$ geometry might be due to the backflow¹⁹³, i.e., the coupling of the flow to the inhomogeneous director rotation as illustrated in the right - middle part of Figure 9.

Máthé *et al*⁶⁴ explored converse piezoelectricity in N_F materials by measuring vertical vibration of room temperature ferroelectric nematic mixtures from Merck, FNLC 1571 and FNLC 919. The coupling constant calculated from the measured displacements was found to exceed 1 nC/N at frequencies below 6 kHz, which is comparable to values found in both cellular polymers (ferroelectrets)^{21–24}, and soft, composite fiber mats^{160,161}. We note that in these measurements the alignment was not homeotropic but actually pre-tilted, i.e., closer to planar. As explained in Figure 9, a strictly planar alignment should yield zero displacement. Therefore, it was surmised that the



effect measured is in fact due to the small alignment component along the homeotropic direction. This implies that the actual value of $\gamma_{3,33}$ is substantially greater than the quantity measured. To measure the real $\gamma_{3,33}$ coupling constant, one needs to achieve and maintain homeotropic alignment. Unfortunately, the depolarization field²⁰⁵ present in any N_F material renders perfect homeotropic alignment rather difficult to achieve in practice.

Here we report the first measurement of $\gamma_{1,13}$. This requires uniform planar alignment, electric field perpendicular to this alignment, and measurement of the motion along the alignment direction (see Figure 9). Additionally, we have also measured the motion in the other two orthogonal directions: normal to the substrates (z-axis) and along the substrate perpendicular to the rubbing direction (y-axis).

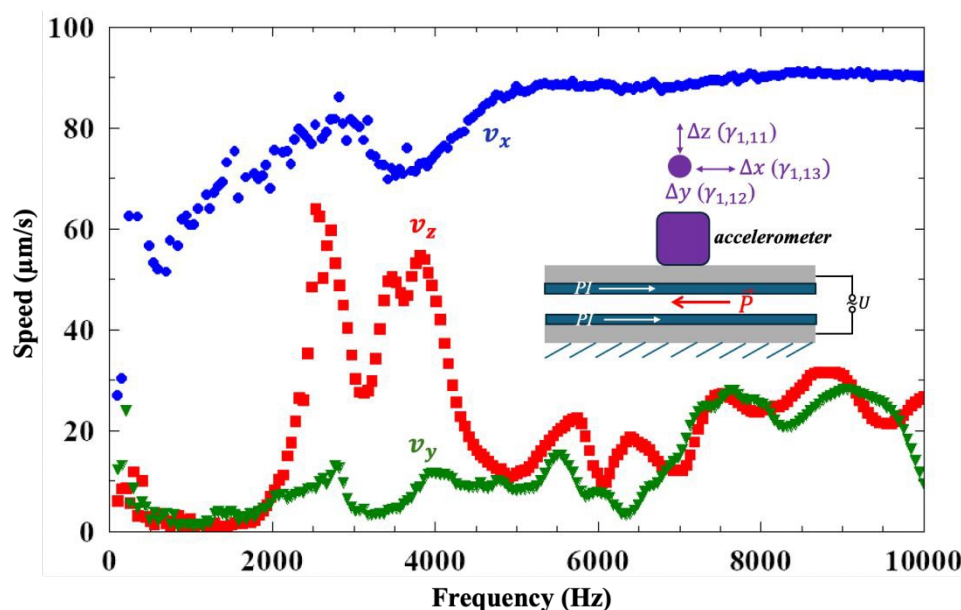


Figure 10: Frequency dependence of the speed of the top movable plate of a 50 μm cell filled with a ferroelectric nematic mixture KPA-02 at room temperature. The inset shows the geometry and the choice of coordinate system in the measurements.

According to the symmetry considerations and the proposed physical mechanism shown in Figure 9, motion in these two directions should be forbidden. We use a sinusoidal electric excitation having frequency f and measure the induced accelerations at the same frequency. Thus, the speed of the induced motion will be $v(f) = \frac{a(f)}{2\pi f}$. This is shown in Figure 10 for a 50 μm cell



filled with a room temperature ferroelectric nematic mixture KPA-02.²⁰⁶ On cooling KPA-02 has an isotropic to N_F phase transition at 47 °C, whereas in heating becomes isotropic at 56 °C. The N_F phase is stable below room temperature and its polarization is $P_o \approx 0.045 \text{ C/m}^2$ at room temperature.

One can see that the largest response is indeed found along the x -axis, where the frequency dependence of the speed is relatively smooth. From the definition of the piezoelectric coupling constant, its magnitude can be expressed as $\gamma = \frac{S}{E}$, where $S = \Delta x / L$ is the strain, and $E \approx \frac{U}{L}$ is the applied electric field. This yields $\gamma_{1,13} = \frac{\Delta x}{U} = \frac{v_x}{2\pi f U}$. From Figure 10 we see that below $f \sim 1 \text{ kHz}$ $v_x \propto f$ and $\gamma_{1,13} \sim 3 \frac{\text{nm}}{\text{V}} = 3 \text{ nC/N}$ is nearly constant. At $f \sim 6 \text{ kHz}$ $\gamma_{1,13} \sim 0.8 \frac{\text{nm}}{\text{V}} = 0.8 \text{ nC/N}$, and roughly decreases in inversely proportion to the frequency. These values are larger than of the strongest piezoelectric crystals (see Table 2) and comparable to that of soft ferroelectrets.^{21–24} This is arguably due to the softness of the fluids with loss moduli $G'' = \eta \cdot \omega$, where $\eta \sim 0.1 - 1 \text{ Pa} \cdot \text{s}$ is the typical flow viscosity of the FNLC materials. At $f = 6 \text{ kHz}$ $G'' \sim 10^4 \text{ Pa}$, i.e., hundred thousand times smaller than typical crystalline moduli. This effect, combined with the 10x smaller polarization of ferroelectric nematic fluids than of crystalline ferroelectrics, provides a context for the larger effective piezoelectric constants of ferroelectric nematic liquids than of typical ferroelectric crystals. It also explains why at high frequencies we find $\gamma_{1,13} \propto \omega^{-1}$ for the N_F fluids. Finally, we note that the measured $\gamma_{1,13}$ values may be smaller than the real values, as in our analysis we assumed that the ferroelectric polarization is completely aligned, which maybe far from the case. Although experiments carried out in thin films show that the ferroelectric polarization aligns antiparallel to the rubbing direction^{207,208}, this alignment maybe less effective for thick films. In the 400–2000 Hz range the movement along the other two axes is vanishingly small. This is expected as the motion along z and y would involve $\gamma_{1,11}$ and $\gamma_{1,12}$ which are zero by symmetry. Nonetheless, we detect relatively large motion along z as seen by peaks around $\sim 2.6 \text{ kHz}$ and $\sim 3.8 \text{ kHz}$ frequencies. These peaks appear to be related to the bending mode of the top glass plate⁴². The higher frequency mode apparently is related to the bending with respect to the y direction of the glass plate, thus leading to a decrease of the motion in the x direction. Other smaller peaks at higher frequencies are either higher harmonics or are coupled to other elastic elements of the sample. The response in y direction includes smaller peaks mainly correlated with those in z direction. The responses in the z and y directions could be related



to the imperfect alignment, the fact that the top plate is not exactly parallel to the bottom one, therefore a motion in x direction is coupled to a vertical motion. Additionally, the accelerometer has up to 2% cross-talk, i.e., a small fraction of the horizontal motion is picked up by the accelerometer aligned in the other two directions.

As was found by Máthé *et al* for FNLC 1571 and FNLC 919⁶⁴, temperature dependent measurements show that the converse piezoelectric response exists only in the ferroelectric nematic phase. The temperature dependence (for both increasing and decreasing temperature) of the induced oscillation amplitude $A_x(f) = \frac{a(f)}{(2\pi f)^2}$ of KPA-02 is shown in the main panel of Figure 11 for a 50 μm thickness film subject to $3V_{\text{rms}}$, at frequency 3 kHz.

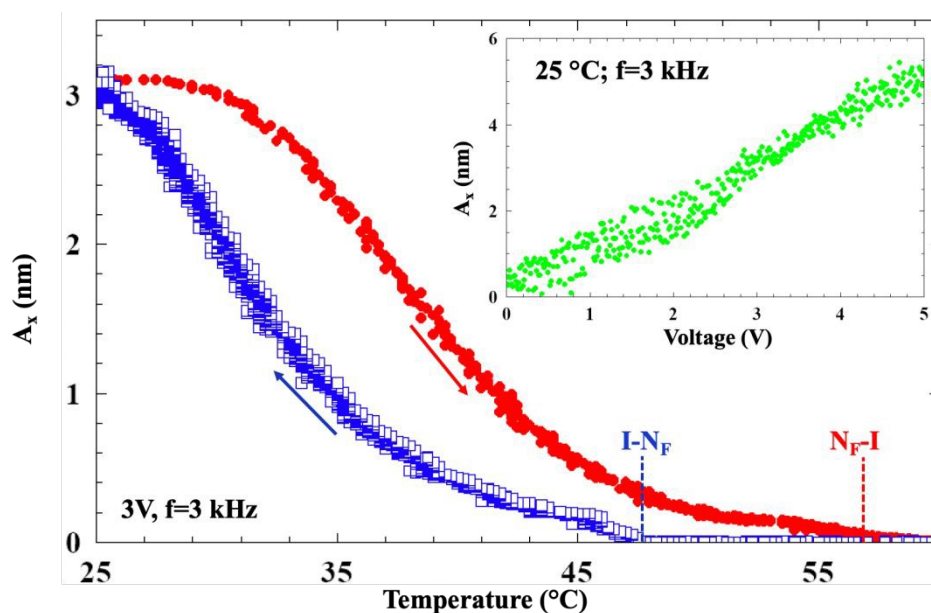


Figure 11: Temperature dependence of the amplitude of the periodic vibration along the director of a 50 μm KPA-02 film under 3V, 3 kHz electric voltages on heating and cooling. Inset: voltage dependence of A_x measured at 3 kHz at 25 $^{\circ}\text{C}$.

The inset shows the voltage dependence of $A_x(f)$ at 25 $^{\circ}\text{C}$ and 3kHz. Within measurement error, the voltage dependence is linear for electric potential below 5 V. This is expected for small fields ($E < E_l$) that do not cause large director rotation and realignment. The magnitude of E_l increases with frequency as discussed by Máthé *et al.*⁶⁴



A direct effect, related to piezoelectricity, called viscous mechano-electric response, was explored by Rupnik et al.⁶⁵ They employed a room-temperature, FNLC 1571 material in the 1-200 Hz frequency range using a simple demonstrator device. A mechano-electric response (mechanical deformation-induced electric signal) was observed when the ferroelectric nematic liquid was placed into a deformable container with electrodes, and the electric current induced by both periodic and irregular actuation of the container is examined. The experiments reveal several distinct viscous mechano-electric phenomena, where both shape deformations and material flow cause changes in the electric polarization structure of a ferroelectric nematic liquid. The results show that the mechano-electric features of the material promise a considerable applicative perspective spanning from sensitive tactile sensors to energy harvesting devices. Although the authors did not measure the piezoelectric coupling constant, they estimated the theoretical limits of the electric energy generation of ferroelectric nematic materials. They found that 100 Hz actuation frequency and 100 k Ω load resistance may generate $\sim 0.1 \text{ W/cm}^2$ power per unit area which is comparable to the specific power produced by solar photovoltaic panels at natural illumination conditions. Their experiments however achieved only 0.01% of the theoretically estimated current showing that there much optimization necessary to achieve practical ferroelectric nematic based mechano-electric transduction.

The piezoelectric effects observed experimentally so far in liquid crystals and liquid crystal elastomers with their typical values at given frequencies are summarized in Table 7.

LC Phase	Measured coupling constant in pC/N @ frequency in kHz	Characteristics
SmA* (phospholipids)	100 at 0.08 ³⁸	Director tilt induces polarization normal to the bilayers in cell membranes
SmC*	Elastomer: 30 @ <0.1; 2D Fluid: $\gamma_{1,23} \sim 5000$ @ <1; $\gamma_{3,33} \sim 3000$ @ 0.5 ⁴²	γ_{123} : related to rotation of the director on tilt cone; γ_{333} : due to tilt angle variation
Col_t^*	1 @ <5 ⁴⁰	
SmC _s P _F	$\gamma_{3,33} \approx 2\gamma_{3,22} \approx 100 \text{ nC/N}$. ²⁰⁰	Converse piezoelectric effect of a bent-core synclinic ferroelectric liquid crystal
N _F	$\gamma_{3,33} \sim 1000$ @ < 6 ⁶⁴ ; $\gamma_{1,13} \sim 3000$ @ < 1 [this paper]	Converse piezoelectric responses of ferroelectric nematic liquid crystals



Table 7: Piezoelectric effects observed experimentally in liquid crystals and liquid crystal elastomers with their typical values at given frequencies.

IV. Challenges and Outlook

A piezoelectric response is strongly linked to the symmetry axes of the material. These axes can be difficult to control for soft materials such as the ferroelectric nematic liquids. For example, to determine individual coupling constants requires a ferroelectric nematic specimen with known, controllable and homogenous polarization. As Figure 9 shows, the measurement of $\gamma_{3,33}$ in a thin-film sample requires uniform homeotropic alignment, but the internal depolarization field frustrates this alignment. Planar alignment, that is required to measure the other two piezoelectric constants, is more straightforward to achieve with appropriate surface alignment layer. However, even with a uniform polarization field at the outset, there is always the possibility of material flow resulting in non-uniform alignment. In fact, for relatively thick N_F films there are always defects that anneal only slowly thus leading to a varying alignment even at zero electric field applied.

An example is shown in Figure 12 for a 50 μm KPA-02 sample under zero electric field (Figure 12 (a,b)) and under 3V, 3 kHz voltage applied (Figure 12 (c,d)) at 0 min (Figure 12 (a,c)) and 60 min (Figure 12 (b,d)) after alignment (Figure 12 (a,b)) and after field applied (Figure 12(c,d)).

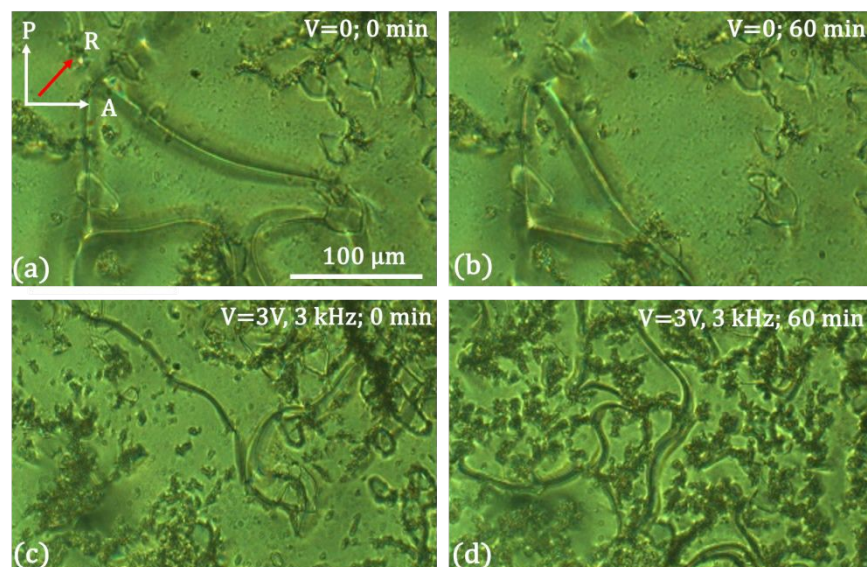


Figure 12: Textures of a 50 μm KPA-02 sample under zero electric field (a,b) and under 3V, 3 kHz voltage applied (c,d) at 0 min (a,c) and 60 min (b,d) after alignment (a,b) and after field applied (c,d).



One can see that the defects eventually shrink when no field is applied, while new defects are generated after as low as 3 V/50 μm field is applied at 3 kHz. These observations agree with recent papers that showed DC or AC voltages can induce realignment and formation of various patterns without a threshold^{209–211}.

Similar problem can occur during the investigation of the direct piezoelectric effect, where the sample is deformed. The deformation can induce flow in the sample which is also coupled to the orientation of the director field via the flow alignment.²¹² To decrease the reorientation effect of the electric field or the flow the applied voltage and the deformation should be small enough to minimize the effect of these phenomena.

An additional complication arises because of the mobility of any ionic species (and it is not possible to make ion-free preparations) is many orders of magnitude larger in fluids than in crystalline solids. Because of this, ionic motion and the resulting screening of electric fields is a factor that always must be considered; this of course is of particular importance at lower frequency. Another unexpected parameter that appears to affect the measured piezoelectric coupling constant is the thickness of the ferroelectric nematic film. This is illustrated in *Figure 13a*, where the amplitude of the converse piezoelectric vibration is shown for the prototypical ferroelectric nematic liquid crystal, RM734⁵⁴ as a function of applied voltage at $T=120\text{ }^{\circ}\text{C}$ under $f=4\text{ kHz}$ signal (*Figure 13(a)*) for different film thicknesses between 100 μm and 540 μm . The samples with $d > 300\text{ }\mu\text{m}$ thicknesses were filled with the liquid crystal at 300 μm film thickness and then the separation between plates was increased. This means that at $d \leq 300\text{ }\mu\text{m}$ we have films that fill the whole area, while at $d > 300\text{ }\mu\text{m}$ we have a bridge that does not fill the entire area (see inset in *Figure 13(a)*).

One can see that below 3 V the voltage dependences are linear for all film thicknesses, but the slope of the curves, i.e., the value of the piezoelectric constant ($\gamma = A_f/V$) strongly increases with the film thickness. Above 3V the voltage dependence is not linear anymore, which is likely due to the field-induced director realignment that leads to generation of quadratic (electrostriction effect) and other higher harmonics. The study the higher harmonic signals can be also done by the lock-in technique by simply choosing nf modes with $n = 2, 3, \dots$. This should also be one of the tasks of future studies.



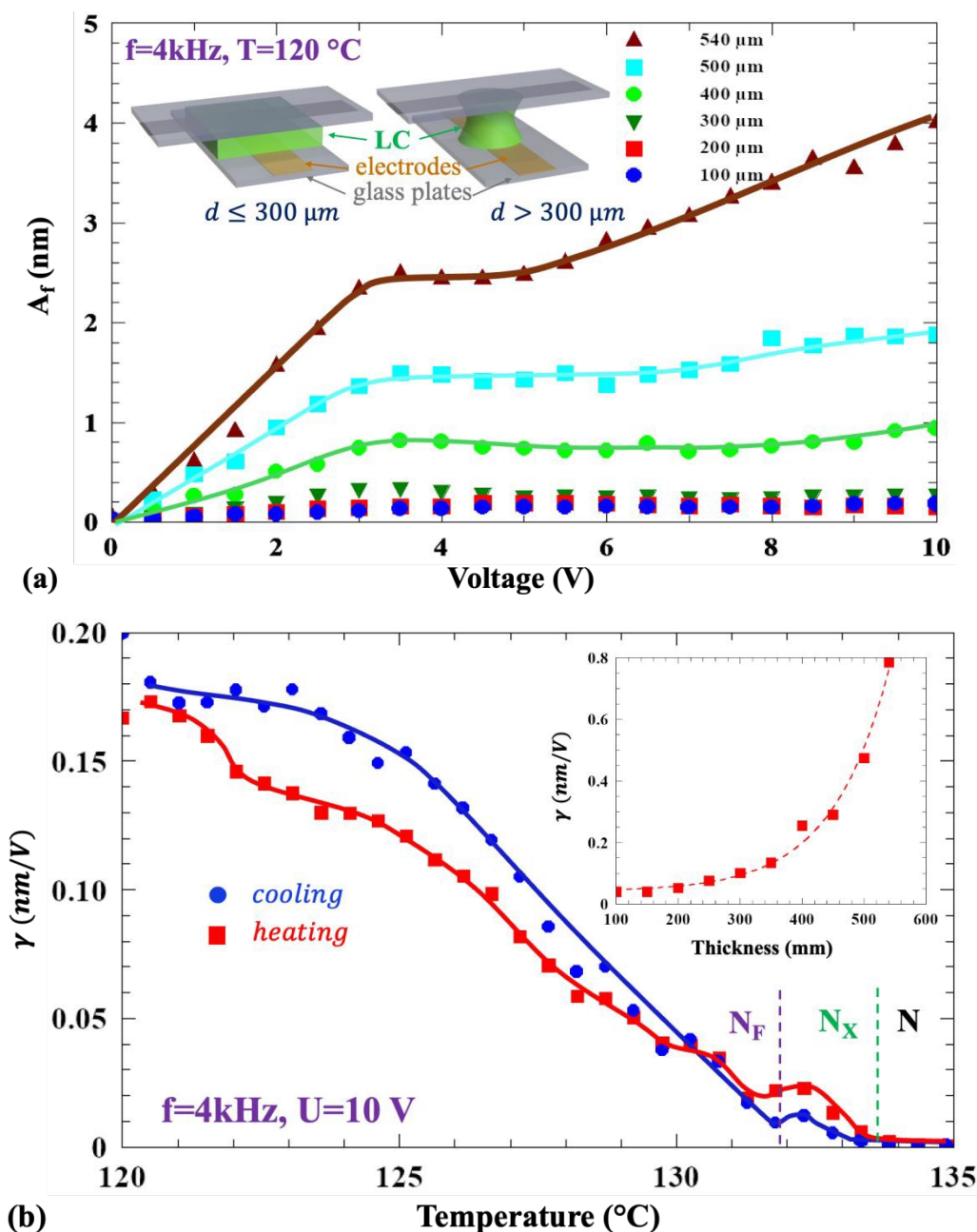


Figure 13: Measurement of the electric field induced vibration amplitude A_f of the cover glass normal to the film at the frequency ($f=4$ kHz) applied between the substrates of non-oriented RM734 films. (a) Voltage dependence at 120°C between 0 and 10 V for films with thicknesses between 0.1 mm and 0.54 mm. Inset shows the LC cell geometries for $d \leq 300 \mu\text{m}$ and $d > 300 \mu\text{m}$ thicknesses. (b) Temperature dependence of the vibration amplitude A_f under $U=10$ V, $f=4$ kHz applied voltage measured in $d=400 \mu\text{m}$ thick film in heating (red) and in cooling (blue) under $1^\circ\text{C}/\text{min}$ rate. Inset shows the film thickness dependence of the effective piezoelectric coupling constant.



In *Figure 13(b)* we show the temperature dependence of the converse piezoelectric signal for a $d = 450 \mu\text{m}$ thick film of RM734. As already shown by Máthé et al.⁶⁴, the piezoelectric signal vanishes in the conventional nematic phase as N has inversion symmetry. In the N_F phase it increases roughly proportionally to the value of the ferroelectric polarization measured by Chen et al.⁶⁰, indicating no significant realignment on cooling. On the other hand, the values in heating are slightly different from that of measured on cooling, indicating some alignment effects.

We also note that there is a narrow range at the top of the N_F phase with a slight increase of the effective piezoelectric constant. This range coincides with a modulated phase (N_X) range as shown recently by Thoen et al.²¹³, however it is not clear why that produces an increased piezoelectric response. That observation indicates the need for the study of the effect in the SmZ_A ^{214,215} and other modulated such as the splayed (N_S)⁵⁹ phase.

The film thickness dependence of the piezoelectric constant is shown in the inset to *Figure 13(b)*. The piezoelectric constant is almost constant below about $200 \mu\text{m}$ thickness, then increases exponentially. What can be the reason for this anomalous thickness dependence? One can think about the effect of surface tension (σ) that leads to a pressure $p = 2\sigma/R$, where $R = \frac{d}{2\sin(\alpha)}$ is the curvature radius, and d is the film and α is the contact angle between the glass and the liquid crystal. With typical the surface tension values of $\sigma \sim 0.03 \text{ N/m}$ and $\alpha < 90^\circ$, we get $p < \frac{0.12}{d} \text{ Pa}$. For $d \sim 100 \mu\text{m}$ this means $p \sim 10^3 \text{ Pa}$, which is much smaller than of the effective modulus $G = 2\pi\eta \cdot f$, which at $\eta \sim 1 \text{ Pa} \cdot \text{s}$ is $G \sim 2.4 \cdot 10^5 \text{ Pa}$. This means that we do not expect significant effect of the surface tension. Another, more likely possibility is an effective increase of the angle of the effective polarization with respect to the film surface at increasing film thickness. By increasing the gap between the glass plates, the morphology of the liquid changes significantly as the inset to *Figure 13(a)* illustrates for gap sizes that are smaller or close to the gap where the sample was filled and for gaps that are bigger, respectively. The reason for this film thickness dependence of the polarization direction is not clear and it will be one of the tasks of future work.

Finally, we note the need of the quantitative and systematic studies of the direct piezoelectric signals in the fluid N_F phase.



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