What Is Flexoelectricity and How Does It Differ From Piezoelectricity?

A uniform mechanical strain electrically polarizes a piezoelectric material. There is extensive literature on the formal development of the phenomenological theory of piezoelectricity; however, simply put, this phenomenon may be described by the following linearized relation between the components of the polarization vector (P) and the strain tensor (ε):

\[ P_i = d_{ijkl} \epsilon_{jk} \]

The piezoelectric property tensor (d) is third order. Group theory states that only noncentrosymmetric crystals may exhibit properties dictated by third-order tensors [1], and accordingly, common insulators which possess a centrosymmetric crystal structure, such as Si and NaCl, are nonpiezoelectric.

However, as schematically alluded to in Fig. 1, a nonuniform strain may break the mirror symmetry even in otherwise centrosymmetric crystals. The relation of the polarization to the extent of the nonuniformity of the strain field, or strain gradient, is known as flexoelectricity: \( P_i \sim d_{ijkl} \epsilon_{jk} + f_{ijkl}(\partial \epsilon_{jk}/\partial x_l) \), where \( f_{ijkl} \) are the components of the so-called flexoelectric tensor. While the piezoelectric property is nonzero only for selected materials, the strain gradient-polarization coupling (i.e., flexoelectricity tensor) exists but not how important it will be in a given material. Flexoelectricity becomes important when one or more of the following (sometimes overlapping) situations occur:

1. The material’s flexoelectricity coefficients are unusually large: This is usually the case for high dielectric constant materials like ferroelectrics and complex oxide ceramics, cf. Refs. [4] and [17–21].
2. The more traditional form of electromechanical coupling, e.g., piezoelectricity, is absent: In such a case, flexoelectricity then provides perhaps the only significant route to couple mechanical deformation and electrical stimuli. For example, biological membranes have no crystalline symmetry that would permit piezoelectricity. Accordingly, flexoelectricity—which relates changes in curvature to the development of polarization—becomes quite important.
3. The feature size in the structure of interest is “small”: Large strain gradients can induce a strong flexoelectric response even if the magnitude of flexoelectric coefficients is not large. For a given strain field, large strain \( f_{ijkl} \) are generated easily only at the nanoscale. Here we mention that the precise scale at which this effect becomes

How “Significant” Is the Flexoelectric Effect?—Is It Just an “Exotic” Phenomenon or Something That May Have Some Compelling Implications?

The jury is still out on how important flexoelectricity may turn out to be. Even though all dielectrics are flexoelectric, the effect may be negligibly small and is dictated by the strength of the flexoelectricity tensor (f). In other words, symmetry considerations guarantee that flexoelectricity exists but not how important it will be in a given material. Flexoelectricity becomes important when one or more of the following (sometimes overlapping) situations occur:

1. The material’s flexoelectricity coefficients are unusually large: This is usually the case for high dielectric constant materials like ferroelectrics and complex oxide ceramics, cf. Refs. [4] and [17–21].
2. The more traditional form of electromechanical coupling, e.g., piezoelectricity, is absent: In such a case, flexoelectricity then provides perhaps the only significant route to couple mechanical deformation and electrical stimuli. For example, biological membranes have no crystalline symmetry that would permit piezoelectricity. Accordingly, flexoelectricity—which relates changes in curvature to the development of polarization—becomes quite important.
3. The feature size in the structure of interest is “small”: Large strain gradients can induce a strong flexoelectric response even if the magnitude of flexoelectric coefficients is not large. For a given strain field, large strain \( f_{ijkl} \) are generated easily only at the nanoscale. Here we mention that the precise scale at which this effect becomes
prominent depends (largely) on the relative strength of the elastic properties, dielectric coefficients, and flexoelectric coefficients. Usually, sub-10 nm characteristic length scales are required, cf. Refs. [8,9,25]; albeit in some contexts (e.g., soft materials or ferroelectrics), this effect can also manifest with feature sizes of several hundreds of nanometers [18,26].

(4) Soft materials: Strain gradients scale inversely with the elastic stiffness. Experiments appear to indicate that the flexoelectric coefficients of soft materials (such as polymers) are at least the same order of magnitude as hard crystalline materials, if not stronger [22–24]. However, the elastic stiffness of soft materials can be several orders of magnitude smaller than hard ceramics. Accordingly, there is an expectation that flexoelectricity will be important for soft materials. Preliminary analysis of Deng et al. [26,27] appears to confirm this where flexoelectricity was shown to create artificial piezoelectric materials whose apparent piezoelectric strength is nearly 20 times larger than the hard ferroelectrics like barium titanate.

What Is the Connection Between Nanotechnology and Flexoelectricity?

As alluded to in the response to the previous question, strain gradients are most easily achievable at the nanoscale, and accordingly, for appreciable flexoelectricity, nanostructures and nanomaterials are highly relevant. For example, Ref. [28] provides a study of how the dynamic and energy harvesting response of a flexoelectric beam changes with size—nontrivial results are usually obtained only at nanoscale dimensions.

Fig. 3 The first figure depicts a nonpiezoelectric 2D sheet with circular pores. Under uniform stretching, strain gradients develop in the vicinity of the holes, and therefore, the local polarization due to flexoelectricity is nonzero; however, the net or average polarization remains zero, and thus, overall there is no emergent piezoelectric response. The second figure shows the same sheet with triangular pores. In this case, again, locally, in the vicinity of the triangular holes, polarization develops. Unlike the previous case, however, there also exists now a net nonzero polarization, and thus, this hypothetical material with triangular holes exhibits an apparent piezoelectricity even though the native material itself is nonpiezoelectric. (Reproduced from Ahmadpoor and Sharma [9] with permission from the National Center for Nanoscience and Technology (NCNST) and The Royal Society of Chemistry.)


Arguably, one of the most interesting applications of flexoelectricity is to create apparently piezoelectric materials without using piezoelectric materials [29]. The central idea underpinning this is quite simple: Consider a material consisting of two or more different nonpiezoelectric dielectrics—as a concrete example that has been studied in the past we may think of a (dielectric) graphene nanoribbon impregnated with holes (Fig. 3) [11]. Upon the application of uniform stress, differences in material properties at the interfaces of the materials will result in the presence of strain gradients. Those gradients will induce polarization due to the flexoelectric effect. As long as certain symmetry rules are followed, the net average polarization will be nonzero. Thus, the artificially structured material will exhibit an electrical response under uniform stress behaving, therefore like a piezoelectric material. Regarding symmetry, topologies of only certain symmetries can realize the aforementioned concept. For example, circular holes distributed in a material will not yield apparently piezoelectric behavior even though the flexoelectric effect will cause local polarization fields. Due to circular symmetry, the overall average polarization is zero (Fig. 3(a)). A similar material but containing triangular shaped holes (or inclusions), for example, and aligned in the same direction, will exhibit the required apparent piezoelectricity. In a similar vein, a finite bilayer or multilayer configuration may also be used (Fig. 3(b)—see the discussion in Ref. [25]). Zelisko et al. [13] characterized graphene nitride nanosheets (g-C3N4) both experimentally and via ab initio simulations. Intrinsically, pristine graphene nitride nanosheets are nonpiezoelectric; however, in one of its stable form, the sheets are riddled with triangular holes, as shown in Fig. 4. In their work, it was confirmed that indeed flexoelectricity, together with triangular defects, causes graphene nitride to exhibit an apparent piezoelectricity.

What Are Some Possible Implications and Applications of Flexoelectricity?

The idea of designing artificial piezoelectric materials has already been explained in the response to the preceding questions. Here are some other implications and applications of flexoelectricity:
(1) Energy harvesting: To date, research on energy harvesting is centered around piezoelectric materials, e.g., Ref. [30]. Several recent works have appeared that have illustrated the potential for the use of flexoelectricity in energy harvesting [28,31–33]. More recently, Deng et al. [28] have developed a complete theoretical continuum model for flexoelectric nanoscale energy harvesting (Fig. 5). When a cantilever beam, covered by conductive electrodes on its top and bottom surfaces, undergoes bending vibrations, an alternating potential difference is generated across the electrodes. Many conventional piezoelectrics (which are often ferroelectrics) lose their piezoelectricity above the so-called Curie temperature. Flexoelectricity, in contrast, can persist to fairly high temperatures and can be fruitfully exploited to circumvent this limitation of conventional piezoelectrics [34]. In that context, flexoelectricity is a possible solution in situations where piezoelectric materials cannot be used.

(2) Material behavior: Flexoelectricity has been found to play a prominent role in a range of phenomena exhibited by ferroelectric nanostructures or bulk specimens with nanoscale features. Some examples are: polarization rotation in thin films [35], indentation size effect [36], fracture toughness [37], and defects [38], among others.

(3) Sensors and actuators: Very few works have actually exploited the concept of flexoelectricity to create sensors and actuators—a natural application of any multifunctional coupling. Some examples are: Bhaskar et al. [39] who have created the so-called electromechanical strain diode as well as an MEMS device on silicon [40] and Wang et al. [41] who fabricated a ferroelectric micromachined diaphragm.

What Is the Role of Flexoelectricity in Biology?
Two representative examples of nonuniform strain modes are bending and torsion. Relatively, little energy is required to induce curvature in soft biomembranes whose bending modulus is only slightly higher (10–20 kGPa) than the thermal energy scale. In the context of biomembranes, flexoelectricity takes the following form: \( P = f \vec{n} \), where \( \vec{n} \) is the normal vector to the membrane midplane. Given the absence of any plausible micromechanism for piezoelectricity, flexoelectricity is most likely the key mechanism underpinning the electromechanical coupling in biomembranes. It has been found to be relevant for studying ion channels, thermal fluctuations, equilibrium shape of the vesicle, and electromotility [26,42–47]. Based on several hypotheses and experiments [48–55], the mammalian hearing mechanism appears to be one of the most exciting implications of flexoelectricity in biology. Hair cells are the primary sensory receptors in the auditory system that transform the mechanical vibrations of sound into sensible electrical action potential. Though the corresponding mechanism is still not fully understood, one possible explanation is that flexoelectricity is the electromechanical coupling mechanism in the outer hair cells of the mammalian ears (Fig. 6).

What Are Some Open Areas of Research in Flexoelectricity?
Despite the emergence of active interest in this area in both the mechanics and physics community, the topic of flexoelectricity is wide open. We mention here just a few topics that may be of interest to the mechanics community.

The connection of flexoelectricity to traditional mechanics topics such as defects and fracture is only just being touched upon. Likewise, while a few works (cited elsewhere in this article) have exploited flexoelectricity to design novel forms of multifunctional materials, this path has hardly been exhausted.

A tantalizing future direction in the case of flexoelectricity is in the realm of soft materials. As indicated previously, larger strain gradients are easily possible in soft materials, and thus, the prospects of a stronger flexoelectric response along with the possibility of large deformations are attractive. While flexoelectricity, both from a quantum view point (cf. Ref. [56]) as well as classical (cf. Ref. [7]), appears to now be well-understood, a clear microscopic picture underpinning flexoelectricity in soft materials is still lacking. Perplexingly, experiments appear to indicate flexoelectricity to be both large and small in a variety of polymers [22–24]. Currently, the Maxwell stress effect is exploited for electromechanical actuation in soft materials. However, the latter suffers from some disadvantages: the Maxwell stress effect is a one-way coupling, i.e., mechanical deformation does not produce an electric field, large electric fields are required for actuation, and finally, reversal of electric field does not reverse the direction of the deformation. In contrast, appropriately used flexoelectric response will not suffer from any of these disadvantages.
Fig. 6 Hair bundles consist of several stereocilia that are connected by thin fibers called tip links and organized in rows of decreasing height. The axes of hair bundles point away from the center of the cochlea. Mechanosensitive ion channels are located within the wall of the stereocilia near the top and tethered to adjacent stereocilia by tip link tension. Bending of the hair bundle toward the tallest row imposes tip link tension on channels in the shorter neighbor causing them to open and make the cellular inner environment more electrically positive. Similarly, bending the bundle in the opposite direction closes the channel, causing the cell to become more negative. During these processes, a voltage difference emerges across the thickness of the stereocilia membrane, and due to the flexoelectric response of the cellular membrane, the radius of the stereocilia changes. Accordingly, the height of the stereocilia increases (or decreases) to maintain the fixed volume. Caption quoted from the text of Ahmadpoor and Sharma [9].

Perhaps the biggest need currently is in the development of flexoelectricity-based applications and careful materials characterization experiments. In general, theoretical and computational work has far outpaced experimental efforts in this direction. Having said that, even from a computational viewpoint, atomistic calculations of flexoelectric constants are nontrivial due to the fact that periodic boundary conditions make the imposition of strain gradients rather difficult.

With the exception of graphene, boron nitride and (to some degree) graphene nitride [12–14], a characterization of the flexoelectricity in other 2D materials is still missing. In particular, we note that to date, flexoelectricity has not been experimentally evaluated for any of the 2D inorganic materials—however, as described in the main text, considerably more progress has been made in the case of lipid bilayers [57–61].

Finally, the connection of flexoelectricity to other multifunctional materials, such as magnetoelectrics and liquid crystal elastomers, is wide open.

Acknowledgment
Financed support from NSF CMMI Grant No. 1463339 and the M.D. Anderson Professorship was gratefully acknowledged.

References