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Flexoelectricity in two-dimensional crystalline and biological membranes

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The ability of a material to convert electrical stimuli into mechanical deformation, *i.e.* piezoelectricity, is a remarkable property of a rather small subset of insulating materials. The phenomenon of flexoelectricity, on the other hand, is universal. All dielectrics exhibit the flexoelectric effect whereby non-uniform strain (or strain gradients) can polarize the material and conversely non-uniform electric fields may cause mechanical deformation. The flexoelectric effect is strongly enhanced at the nanoscale and accordingly, all two-dimensional membranes of atomistic scale thickness exhibit a strong two-way coupling between the curvature and electric field. In this review, we highlight the recent advances made in our understanding of flexoelectricity in two-dimensional (2D) membranes—whether the crystalline ones such as dielectric graphene nanoribbons or the soft lipid bilayer membranes that are ubiquitous in biology. Aside from the fundamental mechanisms, phenomenology, and recent findings, we focus on rapidly emerging directions in this field and discuss applications such as energy harvesting, understanding of the mammalian hearing mechanism and ion transport among others.

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1. Introduction

There are numerous types of electromechanical coupling mechanisms in dielectric materials. Piezoelectricity and the Maxwell stress effect[†] are fairly well-known and have been extensively studied. The former, piezoelectricity, is a genuine two-way linear coupling that allows a material to convert a uniformly applied electric field into mechanical deformation and *vice versa*. Piezoelectricity is considered to be the dominant electromechanical transduction mechanism and has been exploited for a plethora of applications such as energy harvesting, sensing and actuation, advanced microscopes, artificial muscles, and minimally invasive surgery among others.^{1–4} Piezoelectricity is however restricted to dielectrics that possess a non-centrosymmetric crystalline structure and is usually found in hard brittle ceramics like barium titanate and lead zirconate titanate. Quartz is another common example. The so-called Maxwell stress and electrostriction are universally present in all dielectrics. However both represent a one-way electromechanical coupling. Due to either electrostriction or

the Maxwell stress effect, all dielectrics deform under the action of an electric field; however, in these phenomena, mechanical deformation does not lead to the development of an electric field. In fact, in both cases, the mechanical strain produced due to an imposed electric field scales as $\sim \epsilon E^2/Y$ where ϵ is the dielectric constant, E is the electric field and Y represents the elastic modulus. As is evident, reversal of the electric field will not lead to the reversal of mechanical strain. This peculiar nonlinear nature of the one-way coupling limits the applications of these two phenomena. Specifically, the effect is significant only for very soft materials such as dielectric elastomers.

The term “flexoelectricity” first originated in the context of liquid crystals⁶ and refers to the two-way linear coupling between the electric polarization and strain gradients. Experimental and theoretical studies have since then confirmed its presence in both crystalline and amorphous dielectrics.^{7–16} Like the Maxwell stress effect or electrostriction, flexoelectricity is also a universal phenomenon and is exhibited by all dielectrics. However, unlike them, the coupling occurs in a linearized manner and a converse effect does exist. Mathematically, piezoelectricity is often introduced through the following linear relation:

$$P_i \sim d_{ijk} \epsilon_{jk} \quad (1)$$

In eqn (1), the components of the polarization vector P_i are related to the components of the second order strain tensor ϵ_{jk} through the third order piezoelectric tensor components

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[†]Electrostriction is mathematically identical to the Maxwell stress effect although physically distinct. Since this subtlety is not germane to the present article, we avoid further discussion on this and simply refer the reader to Zhao *et al.*⁵ for further clarification.

d_{ijk} . Due to the tensor transformation properties, all odd-ranked tensors vanish under inversion-center symmetry. Thus, most of the common crystalline dielectrics, such as silicon and NaCl do not exhibit piezoelectric behavior whereas ZnO and GaAs do. Flexoelectricity, on the other hand relates polarization to the extent of the non-uniformity of the strain field or in other words, strain gradient:^{6–9,17}

$$P_i \sim d_{ijk}\epsilon_{jk} + f_{ijkl}\frac{\partial\epsilon_{jk}}{\partial x_l} \quad (2)$$

where f_{ijkl} are the components of the so called flexoelectric tensor. Two representative examples of non-uniform strain modes are bending and torsion. Group theory tells us that fourth order material property tensors are admissible in materials of any symmetry and accordingly, as alluded to before, flexoelectricity is indeed universal and is even present in centrosymmetric dielectrics where the piezoelectric tensor (\mathbf{d}) vanishes.¹⁸ Indeed, flexoelectricity has been experimentally confirmed in both centrosymmetric materials like NaCl¹⁰ as well as in ferroelectrics like barium titanate^{11,12} among others.

The focus of the present review article is on flexoelectricity in two-dimensional membranes that are (nearly) atomistically thin. This begs the question: what is special about flexoelectricity in 2D structures? Unlike piezoelectricity, flexoelectricity is strongly scale dependent.^{17,19} By and large, in most materials, the flexoelectric coefficients are of the magnitude such that significant strain gradients are required for an appreciable flexoelectric based electrical response. Two-dimensional crystalline membranes are atomistically thin and biological

membranes possess thicknesses on the order of just a few nanometers. In the context of membranes (let's say isotropic membranes for now), flexoelectricity just boils down to the following simple relation:

$$\mathbf{P} \sim f\kappa\mathbf{n} \quad (3)$$

Here κ is the mean curvature and \mathbf{n} is the normal vector to the membrane. As can be easily appreciated, it is relatively easy to bend or induce curvature in thin paper-like structures. Such structures, as per eqn (3), readily polarize and produce an electric field. In fact, with two-dimensional structures, a strain gradient in the form of bending is the easiest form of deformation. It is therefore not too far-fetched to claim that nearly all 2D thin (dielectric) structures are multifunctional in nature. Boron Nitride (BN) sheets, lipid bilayers, dielectric graphene nanoribbons, and MoS₂ sheets are but some of the examples of such structures. The unique feature of 2D materials to display flexible mechanical behavior and, due to flexoelectricity, a coupled electrical behavior, paves the way for fascinating applications such as energy harvesting, sensors and actuators, and biomedical devices among others. Several recent studies have already provided thorough reviews of flexoelectricity in three dimensional crystalline materials.^{20–22} In this article, we will focus primarily on the unique aspects of flexoelectricity in 2D materials with an emphasis on the review of mathematical and computational developments, recent experimental findings, applications and rapidly emerging areas.



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2. Flexoelectricity in crystalline membranes

2.1 Physical and microscopic mechanisms

The microscopic mechanism of flexoelectricity involves the redistribution of charges in the lattice structure when subjected to a non-uniform strain field. A full understanding of this necessarily requires a quantum viewpoint. Here, keeping in mind that we are primarily concerned with 2D materials, we present a simplified discussion.[‡] Broadly, two microscopic contributions to flexoelectricity may be identified: ionic and electronic.

- **Ionic flexoelectricity:** to explain this, we assume that crystalline dielectrics consist of well-defined point charges as shown in Fig. 1. In an undeformed centrosymmetric lattice structure, the centers of positive and negative charges coincide, and thus polarization is absent. Even if we were to strain it uniformly, the centers of positive and negative charges will continue to coincide and (consistent with our understanding of non-piezoelectric crystals) a polarization will not develop. However, upon application of a strain gradient like bending, the internal ions will shift in a non-affine manner. This non-affine shift of internal atoms in proportion to the imposed strain gradient leads to development of polarization.

The ionic contribution to flexoelectricity was first described in detail by Tagantsev.⁸ Later, using a lattice-dynamical approach, Maranganti and Sharma²³ evaluated the flexoelectric response of certain cubic crystalline ionic salts, perovskite dielectrics, III–V and II–VI semiconductors. Recently, focusing primarily on the ionic contribution, an effective Hamiltonian approach was developed and used to study the temperature dependence of flexoelectricity in ferroelectric thin films such as BaTiO₃ and SrTiO₃.^{24,25}

- **Electronic flexoelectricity:** the discussion of ionic flexoelectricity is based on a classical picture and is reasonable enough to explain flexoelectricity in ionic solids, however, it ignores the distinctly quantum nature of the flow of electronic charge under mechanical distortion and the modern theory of polarization developed over the last two decades (see Resta and Vanderbilt for a review on the modern theory of polarization and references therein²⁶). For example, the ionic flexoelectricity mechanism outlined in the preceding paragraph would lead us to believe that a mono-atom material like graphene (dielectric) nanoribbon will not polarize upon bending. However, explicit quantum calculations show that even a mono-atomic material like graphene will polarize under bending.^{28–31} Upon bending of such non-polar systems, as

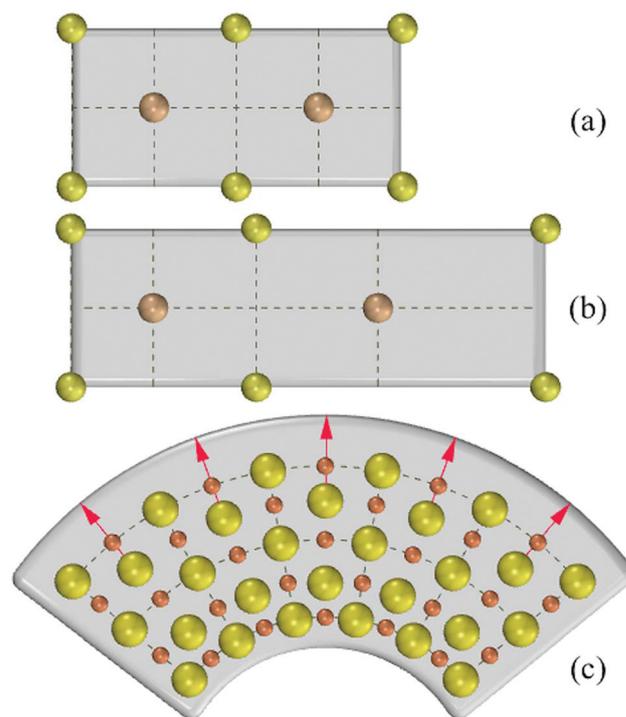


Fig. 1 (a) Deformed configurations of atoms in a centrosymmetric lattice under a uniform strain. (b) Deformed configuration of atoms in a centrosymmetric lattice under a non-uniform strain field. The atoms experience internal displacements in the presence of strain gradient that result in flexoelectric polarization. Adapted from ref. 20. (c) Flexoelectricity in the context of bending: when a part of a material is bent, the positions of the negative and positive charges transform in such a way that do not cancel out each other and lead to a strain gradient induced polarization.

shown in Fig. 2, the symmetry of the electron distributions in the out-of-plane direction is broken and a net dipole moment is induced at each atomic site. As a side note, it is worthwhile to mention that if the circularly bent graphene nanoribbon is completely closed (to form a circular nanotube), the net dipole moment will vanish.

With specific emphasis on electronic flexoelectricity, several studies have investigated flexoelectricity from a quantum viewpoint.^{26,28–31} In recent work, Hong and Vanderbilt³² developed a general density functional theory based formulation to compute piezoelectric and flexoelectric tensors and presented numerical values for various cubic insulators. Stengel,³³ using a density functional perturbation theory that includes both ionic and electronic effects, has derived the complete flexoelectric tensor of an arbitrary dielectric in terms of a linear response to atomic displacements. He further elaborates on some of the relevant topics such as electrical boundary conditions, static and dynamic flexoelectric responses and pure and mixed contributions of piezoelectricity and flexoelectricity. It is also worthwhile to mention that controversial perspectives exist in the literature on the surface and bulk contributions to material flexoelectricity. Resta,³⁴ inspired by Martin,³⁵ has theoretically discussed the effect of a free surface on flexo-

[‡] A well-known issue pertaining to the discussion of polarization in periodic crystalline materials is its dependence on the choice of the unit cell. The reader is referred to the paper by Resta and Vanderbilt²⁶ and references therein for a detailed discussion on this matter and how the concept of the so-called Berry phase has been used to resolve this controversy. We refer the reader to the work by Marshall and Dayal²⁷ who provide an interesting insight into this issue from a purely classical viewpoint.

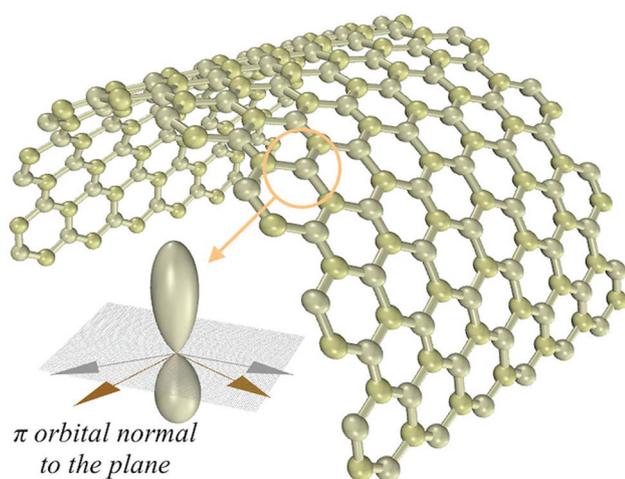


Fig. 2 Bending of graphene: upon bending, the symmetry of the electron distribution at each atomic site is broken, which leads to the polarization normal to the graphene ribbon; an infinite graphene sheet is semi-metallic; however, finite graphene nanoribbons can be dielectric depending upon surface termination. Adapted from ref. 29.

electricity and argued that it is indeed a bulk property and that there is no surface contribution to the flexoelectric response. This assertion is countered by Tagantsev³⁶ who showed that due to the non-zero contribution of the quadruple moment tensor, the surface flexoelectricity indeed exists. The surface flexoelectricity contribution has been elaborated further by Tagantsev in a recent review paper.²² Also, Stengel,³⁷ using a first principles approach, provided quantitative evidence of surface flexoelectricity and demonstrated that depending on the surface termination, a SrTrO₃ film can exhibit either positive or negative flexoelectric voltage.

2.2 Mathematical description and review of the modeling literature

Several recent studies have mathematically studied flexoelectricity in 2D materials.^{38–43} In general, as alluded to earlier in the context of eqn (3), flexoelectricity in 2D structures essentially refers to the interplay between curvature and electrical degrees of freedom. The modeling of coupled mechanical systems can superficially differ from one work to the other based on choice of independent variables *e.g.* displacement and polarization *vs.* displacement and electric field, or in the manner in which the derivations are carried out – *e.g.* using a true minimum variational principle or directly invoking the equations of motion. In some cases, this can cause confusion. We refer the reader to two studies of Liu which clarify much of these issues.^{38,39} Mohammadi *et al.*⁴² presented a simple (linearized) model of crystalline flexoelectric membranes and, using the developed framework, studied the effective properties of heterogeneous membranes. Starting from the viewpoint of a liquid crystal, Rey⁴⁰ developed the formulation of an isotropic (fluid) flexoelectric membrane under tension, bending and pressure and illustrated how flexoelectricity renormalizes

the membrane tension, shear and bending effects. Also Gao *et al.*⁴¹ using the framework given by Ou-Yang⁴⁴ studied the flexoelectric shape transformation of spherical and cylindrical vesicles in the presence of electric field. Here we briefly outline the formulation by Mohammadi *et al.*⁴² and Deng *et al.*⁴³

Let $U \subset \mathbb{R}^2$ be an open bounded domain in the xy -plane. Consider a thin dielectric membrane occupying $U \times (-h/2, h/2) \subset \mathbb{R}^3$, where h is the thickness of the membrane. If the thickness $h \ll 1$ the thin membrane may be idealized as a two-dimensional body; the thermodynamic state may be described by the displacement vector $\mathbf{w}: U \rightarrow \mathbb{R}^3$ and the polarization areal density vector $\mathbf{P}: U \rightarrow \mathbb{R}^3$. Thus the internal electromechanical energy density can be postulated as $W = W(\mathbf{w}, \mathbf{P})$. The membrane can experience a number of deformation modes, such as shearing, stretching or compression and bending. Moreover, these various modes of deformations can be coupled in cases such as graphene and uncoupled for many others such as lipid bilayers which are fluid membranes that cannot undergo shearing strains. A complete continuum model to account for the coupled deformations modes in anisotropic 2D structures has not yet been established in the literature. For the simpler case wherein the membrane's deformation is restricted to bending, the electromechanical energy density for an isotropic membrane may be expanded up to quadratic orders of curvature and polarizations as:

$$W[\mathbf{w}, \mathbf{P}] = \frac{1}{2} \kappa_b \kappa^2 + \frac{1}{2} a |\mathbf{P}|^2 + f \mathbf{P} \cdot \mathbf{n} \quad (4)$$

where κ is the mean curvature and \mathbf{n} is the normal vector of the surface. κ_b is the associated bending stiffness, a is the inverse dielectric susceptibility and can be expressed in terms of vacuum and dielectric permittivities (ϵ_0 , ϵ) and the thickness of the membrane h as: $a = 1/(\epsilon - \epsilon_0)h$. Also, f is the flexoelectric coefficient. Furthermore, the self-field energy associated with the electric field induced by polarization—constrained by Maxwell equation—can be written as:

$$\xi^{\text{self}}[\mathbf{w}, \mathbf{P}] = \int_{\mathbb{R}^3} \frac{\epsilon_0}{2} |\nabla \zeta|^2, \quad \text{div}[-\epsilon_0 \nabla \zeta + \mathbf{P}] = \rho_0 \quad (5)$$

in which ζ is the potential field and ρ_0 is the external charge density (if present). For the case of small deflections, using the so-called Monge gauge, the curvature in turn can be written as $\kappa = -\Delta w$. The total free energy is then the summation of the internal electromechanical and self-field contributions:

$$F[\mathbf{w}, \mathbf{P}] = \int_U (W[\mathbf{w}, \mathbf{P}] - \mathbf{P} \cdot \mathbf{E}^{\text{ext}}) + \xi^{\text{self}}[\mathbf{w}, \mathbf{P}] \quad (6)$$

where the second term is the work done by the external electric field \mathbf{E}^{ext} . The equilibrium state is such that the total free energy is minimized over all possible variations of state variables:

$$\min_{[\mathbf{w}, \mathbf{P}] \subset \mathcal{S}} F[\mathbf{w}, \mathbf{P}] \quad (7)$$

The variational procedure can be readily carried out and the reader is referred to Mohammadi *et al.*⁴² for the complete

description of the pertinent (Euler–Lagrange) partial differential equations and the associated boundary conditions governing isotropic flexoelectric membranes. In their work, to “custom-design” flexoelectric properties, the aforementioned mathematical model was solved to find the effect of shape, volume fraction and the electromechanical properties of the inhomogeneities on the apparent flexoelectric response of 2D crystalline heterogeneous membranes. Deng *et al.*⁴³ also have presented some illustrative examples such as the interaction of a charged particle with an isotropic flexoelectric membrane among others.

Using a model similar (but not identical) to what has been described above, bending induced flexoelectric effects on nanoplates and nanobeams have been studied by several authors.^{45–49}

2.3 Review of the literature and applications

The idea of employing strain gradients to induce polarization suggests a potential to enhance the electromechanical response in thin films such as atomically thin sheets of BN or MoS₂—which are piezoelectric to begin with. We note that BN and MoS₂ do not exhibit piezoelectric behavior in bulk crystalline form, however, the symmetry properties of their monolayers endows them with piezoelectric behavior. Moreover, the strength of piezoelectricity in these monolayers is either comparable to, or exceeds, that of several common 3D piezoelectric crystals such as quartz and AlN.⁶⁰ Unlike the case of an isotropic graphene, where bending does not lead to an in-plane polarization, 2D anisotropic materials like BN and MoS₂ are expected to deviate from the simpler isotropic relation in eqn (3). In other words, even under perfect circular bending, the resulting polarization response is likely to be at an angle to the normal direction of the membrane and therefore polarization is also likely to develop within the plane. Though flexoelectricity is typically referred to the interplay between the curvature and the out-of-plane polarization, for many cases of 2D anisotropic systems such as BN, the in-plane flexoelectric contribution may be of more interest.²⁸ Accordingly, for these anisotropic membranes, one may have to separately relate the in- and out-of-plane components of the polarization to the curvature using their corresponding flexoelectric coefficients:

$$\begin{aligned} P_n &\sim f_n \kappa \mathbf{n} \\ P_t &\sim f_t \kappa \mathbf{t} \end{aligned} \quad (8)$$

It is also worthwhile to mention that a nonlinear flexoelectric response in some cases of noncentrosymmetric crystals such as BN sheets has been observed, where the polarization is related to the square of curvature ($P_t \sim (1/R^2)$).^{50–52} An interesting discovery was made by Duerloo *et al.*⁵³ where they found that bilayer stacking nanosheets of BN, strongly enhanced the curvature induced (in plane) polarization.⁵³ One possible explanation for this observation is that in this bilayer stacking configuration, the sheets under bending, experience further strain gradient at the interface that lead to enhanced polarization. Quantum mechanical calculations⁵³ show that flexoelec-

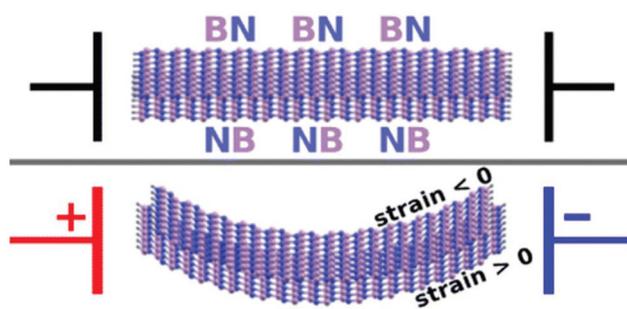


Fig. 3 Duerloo and Reed⁵³ found that a bilayer consisting of two BN monolayers exhibits a strong curvature induced electromechanical coupling. Using quantum mechanical calculations and a continuum model, they found that these bilayers (in response to an external electric field) amplify in-plane displacements by factors of as much as 10^3 – 10^4 —when compared with a single monolayer. Reproduced with permission from ref. 53.

tric response in bilayer BN is larger (by a factor of 10^3 – 10^4) than the corresponding value in single layer sheet. To the authors of this review article, the reasons for this large amplification in polarization response due to bilayer stacking are not clear and therefore represent an exciting avenue for future study (Fig. 3).

A rather intriguing application of flexoelectricity is to make apparent piezoelectric materials/structures without actually using piezoelectric materials. A simple example of this was proposed by Fousek *et al.*,⁵⁴ who argued that a truncated pyramid like structure will act like a piezoelectric material. Due to the varying cross-sectional area, a uniformly imposed stress or load will result in strain gradients in the interior of the structure and thus cause polarization. This was later experimentally observed in BST truncated pyramid arrays.^{55,56} The resulting apparent piezoelectric response is found to be size-dependent and, at sub-micro length scales, an effective piezoelectric response rivaling that of common piezoelectric ceramics may be achieved.

Pyramids are more of a “structure” rather than a “material” and an alternative approach to create apparently piezoelectric materials (in the more traditional sense) without using piezoelectric materials is *via* the use of defects and inclusions. This approach has been proposed for graphene—which is manifestly a non-piezoelectric material. Chandratre and Sharma⁵⁷ showed, using first principles calculations, that merely by introducing triangular shaped holes in dielectric graphene nanoribbons, the material behaves like a piezoelectric. A non-piezoelectric sheet without any defects does not show any piezoelectric response under uniform stretching. Now consider a non-piezoelectric sheet with circular holes (Fig. 4). A uniform stretch results in a non-uniform strain field around the boundary of the holes. However, due to the symmetry of the holes, the total net polarization will be zero. Finally, imagine the case of non-centrosymmetric shaped holes such as the triangular ones shown in the bottom of Fig. 4. In this case, under the action of uniform mechanical stretch or com-

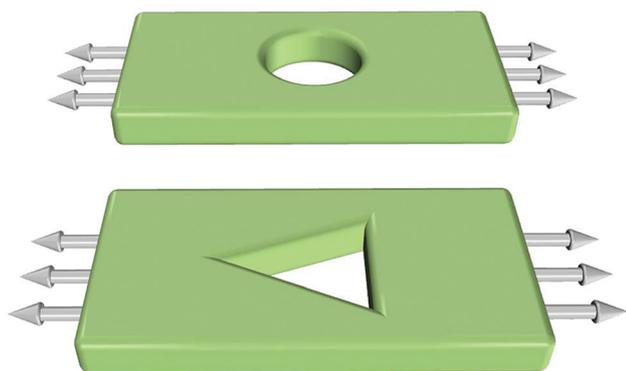


Fig. 4 The first figure schematically depicts a non-piezoelectric 2D sheet with circular pores. Under uniform stretching, strain gradients develop in the vicinity of the holes and therefore the local polarization due to flexoelectricity is non-zero, however the net or average polarization remains zero, and thus overall there is no apparent 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 non-zero polarization and thus this hypothetical material with triangular holes exhibits an apparent piezoelectricity even though the native material itself is non-piezoelectric. Adapted from ref. 58.

pression, a non-zero net polarization will emerge. While Chandratre and Sharma,⁵⁷ using quantum calculations, were able to illustrate this notion for graphene nanoribbons, experimentally realizing small triangular holes in graphene nanoribbons is impractical. Fortunately, a close “cousin” of graphene, the so-called graphene nitride nano-sheets naturally exhibit triangular holes in one of its phases. Zelisko *et al.*⁵⁸ characterized graphene nitride nano-sheets ($g\text{-C}_3\text{N}_4$) both experimentally and *via ab initio* simulations. Intrinsically, pristine graphene nitride nano-sheets are non-piezoelectric however, in one of its stable form, the sheets are riddled with triangular holes,⁵⁹ as shown in Fig. 5. In their work, it was confirmed that indeed flexoelectricity, together with triangular defects cause graphene nitride to exhibit an apparent piezoelectricity. A comparison between the corresponding piezoelectric coefficient of $g\text{-C}_3\text{N}_4$ (induced due to flexoelectricity and defects) is made with those of common piezoelectric 2D structures such as hexagonal boron nitride (h-BN), MoS_2 and WS_2 shown in Table 1. Graphitic carbon nitride sheets exhibit a greater piezoelectric response than hexagonal boron nitride (h-BN), but smaller than that of molybdenum disulphide (MoS_2) and tungsten disulphide (WS_2).⁶⁰ More importantly, when it comes to multi-layered structures of these piezoelectric materials, only graphene nitride exhibits piezoelectricity. Due to the antiparallel stacking sequence, h-BN, MoS_2 and WS_2 are centrosymmetric and hence non-piezoelectric. In contrast, sheets of $g\text{-C}_3\text{N}_4$ in their multi-layered form are not stacked in the same way and thus maintain their piezoelectricity.

In addition to mechanical defects described in the preceding paragraph, apparent piezoelectricity may also be induced through chemical doping.^{61–65} Adsorption of various atoms on

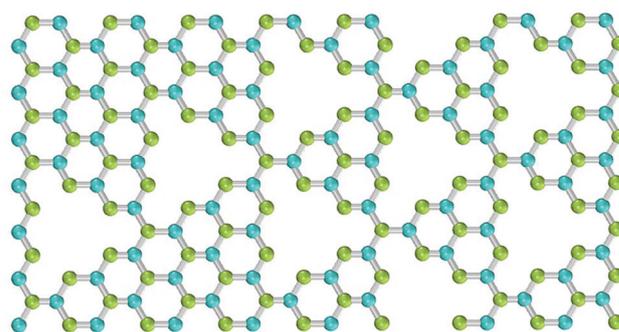


Fig. 5 Graphene nitride nanosheet, riddled by triangular holes, was experimentally and computationally shown to exhibit an apparent piezoelectric response. Adapted from ref. 58.

Table 1 Comparison between the piezoelectric coefficient of $g\text{-C}_3\text{N}_4$ (induced due to flexoelectricity and defects, shown in Fig. 5)⁵⁸ with some of common piezoelectric 2D structures

Material	Piezoelectric coefficient (10^{-10} cm^{-1})
$g\text{-C}_3\text{N}_4$	2.18
h-BN	1.38 ⁶⁰
MoS_2	3.64 ⁶⁰
WS_2	2.47 ⁶⁰

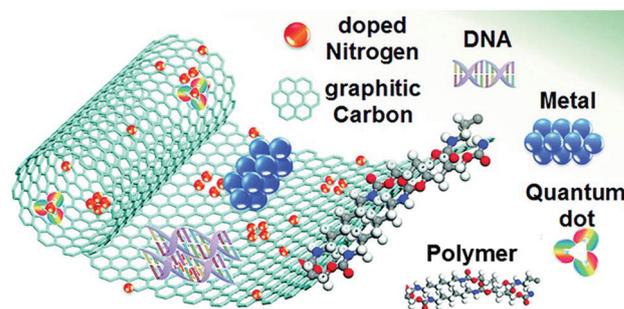


Fig. 6 Chemical doping of graphene surface with different components such as nitrogen, polymers, and various metals can induce a piezoelectric response. Reproduced with permission from ref. 64.

the surface breaks inversion symmetry and may generate strain gradient that leads to a flexoelectric response. This approach has been employed for graphene (Fig. 6). In recent work, Ong and Reed,⁶⁵ using density functional theory, studied the effect of doping on the electromechanical response of graphene. They considered various adatoms including lithium (Li), potassium (K), hydrogen (H), and fluorine (F) and calculated the in-plane deformation in response to an external out-of-plane electric field. They found an approximately linear relationship between the field and strain at field amplitudes between -0.5 to 0.5 V \AA^{-1} . Their finding of a linear relationship between strain and polarization appears to imply an emergent piezoelectric behav-

ior. Nevertheless, the mechanism cannot be uniquely attributed to pure piezoelectricity or flexoelectricity. A possible approach to check for the contribution of flexoelectricity is to calculate the in-plane strain gradient field. We speculate that in the vicinity of inhomogeneities (doping domains) there is a sharp strain gradient which leads to a flexoelectric contribution in the lines of the previously discussed cases of pore-riddled graphene and/or graphene nitride.

A composite of multi-layered systems is another alternative approach to create apparently piezoelectric materials without using piezoelectric materials. Sharma *et al.*⁶⁶ proposed a model of a superlattice of thin films stacked in an odd-ordered sequence to induce strain gradient under normal loading. To elucidate the corresponding physical mechanism, consider a periodic bilayer of thin films. Each layer in such a periodic bilayer experiences identical strain gradients but in opposite directions at each interface. Due to the inversion symmetry of the strain gradient, the resulting dipole moment in one bilayer is canceled out by the dipole moment appearing in the next bilayer, and hence the overall average polarization in the composite is zero. Nevertheless, careful choice of elastic properties and superlattice sequence can break the geometric centrosymmetry. If one inserts a third layer, the inversion symmetry is broken. This periodic tri-layered superlattice thus is capable of inducing a non-zero polarization in the system (Fig. 7).

A flexoelectric model of a multi-layered structure of barium strontium titanate (BST) was also proposed⁶⁷ to enhance electromechanical sensitivity. The proposed cantilever structure is composed of two active layers (piezoelectric or non-piezoelectric) and a supporting layer in between. Under a mechanical load at the end of the cantilever, the layers undergo bending and generate strain gradient along the normal direction and consequently induce electric polarization. The resulting response from theoretical calculations and experimental measurements was compared to that of a single layered model of BST. A remarkable enhancement in the flexoelectric response was found in the multilayered structure. A comparison between the piezoelectric response of a single layer BST with the flexoelectric response of the proposed multilayered structure shows that at small thicknesses, the proposed flexoelectric model is significantly stronger. When the thickness of the cantilever beam is large enough, the electromechanical response converges to that of what is expected from a pure piezoelectric mechanism. Furthermore, careful choice of material in the middle layer with regard to its mechanical properties allows the possibility of tailoring a desired electromechanical response.

One of the most exciting applications of flexoelectricity is in nanogenerators and harnessing energy from mechanical vibrations. The reader is referred to a recent review on some of the novel experimental attempts in this area by Jiang *et al.*⁶⁸ Energy harvesting from dynamical systems,^{69–72} primarily for applications in self-powered miniature sensors and electronic devices, has emerged as an intensely researched topic. To date, research on this topic is centered on piezoelectric materials. Examples of exploiting piezoelectricity for energy

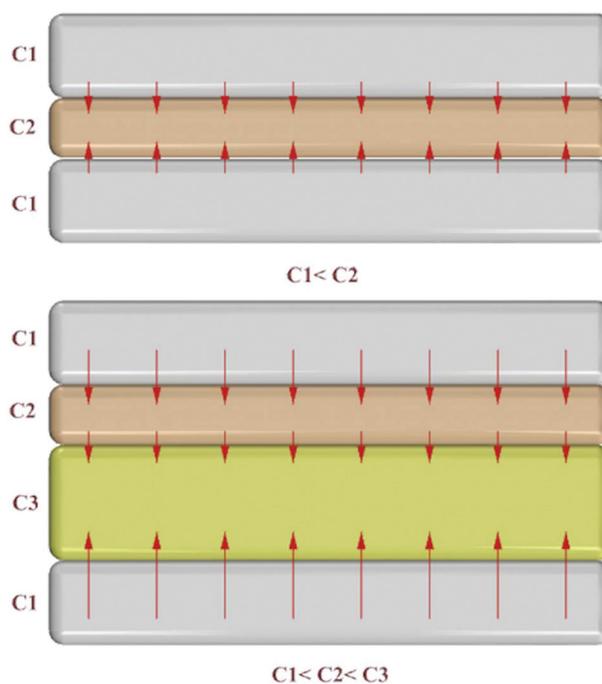


Fig. 7 Schematic of a comparison between periodic bilayer and trilayer superlattices. Red arrows indicate polarization. In a periodic bilayer, under uniform stretching or compression, the induced dipole moment in a layer cancels out the dipole moment induced in the other layer. Thus the overall average polarization in a periodic bilayer super-lattice is zero. In contrast, a periodic trilayer superlattice shows that careful choice of material properties and superlattice topology can break the geometric centrosymmetry. Averaged strain gradients and thus the averaged induced polarization over the unit cell of a periodic trilayer superlattice are nonzero. Adapted from ref. 66.

harvesting range from shoe-mounted inserts^{73,74} to unmanned aerial vehicles.⁷⁵ Due to the universal nature of flexoelectricity, we expect the latter to offer some advantages in situations where piezoelectric materials cannot be used or alternatively, to greatly enhance the energy harvesting capabilities of materials that are already piezoelectric. For example, many ferroelectrics lose their piezoelectricity above a certain temperature due to phase transformations. Flexoelectricity, in contrast can persist at fairly high temperatures. In recent work, Mbarki *et al.*⁷⁶ exploited flexoelectricity in functionally graded thin films to tunable high temperature piezoelectrics.

The basic idea of flexoelectricity based energy harvesting was proposed first by Majdoub *et al.*^{77,78} More recently Deng *et al.*⁷⁹ developed a theoretical continuum model for flexoelectric nanoscale energy harvesting (Fig. 8). The cantilever beam is covered by conductive electrodes on its top and bottom surfaces. Due to application of an external force or the movement of the base, the cantilever beam undergoes bending vibrations. As a result, an alternating potential difference is generated across the electrodes. Accordingly, the symmetric thin beam can be used as a good alternative for the flexoelectric energy harvester at sub-micron scales. A dramatic size effect in flexoelectric energy harvesting is observed in this model.⁷⁹ Upon

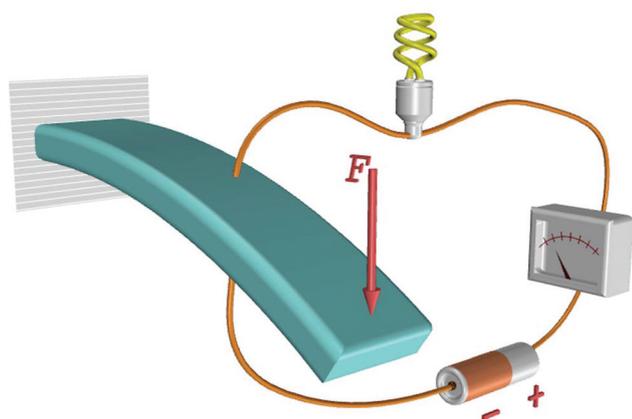


Fig. 8 Schematic of a centrosymmetric flexoelectric energy harvester under base excitation. The cantilever beam is covered by conductive electrodes on its top and bottom surfaces. Due to application of an external force or the movement of the base, the cantilever beam undergoes bending vibrations. Due to flexoelectric contribution, an alternating potential difference is generated across the electrodes. Adapted from ref. 79.

reduction of the beam's thickness from 3 μm to 0.3 μm , the mechanical-to-electrical energy conversion efficiency was found to increase by two orders of magnitude! Such a remarkable size effect in flexoelectric energy harvesters makes them quite favorable for micro and nanoscale systems.

However, notwithstanding the developments described in the preceding paragraphs, the exploitation of flexoelectricity for energy harvesting is still at its infancy and most recent advancements in this area have been towards enhancing piezoelectric behavior.^{80–82} One example is shown in Fig. 9 where the piezoelectric PZT ribbons on a rubber substrate are employed for flexible energy conversion^{80,81} where in ribbons of the piezoelectric ceramic PZT is rendered stretchable by printing onto a pre-stretched PDMS substrate to induce bending deformations. The resulting wavy shaped ribbons can undergo larger strains with enhanced piezoelectric response due to the presence of strain gradients and flexoelectric effect. The pre-existing curvature in the ribbons provides the possibility of using the flexoelectric curvature induced electric field to dramatically improve the sensitivity of the nanoribbons to small deformations. It has been also discussed⁸⁰ that the pre-existing curvature may be designed for a desired electromechanical response.

Flexoelectric effects are stronger, when the material experiences large deformations. Soft materials, due to their flexibility are good candidates to exploit flexoelectric effects. The model by Deng *et al.*⁷⁹ can also be used for soft materials—in the linearized regime. Inspired by flexoelectricity in biological membranes, Rey *et al.*⁸³ also proposed an energy harvesting consisting of a soft thin membrane subjected to harmonic forces due to contacting bulk fluid. It was shown that both bending modulus and bending viscosity have significant roles in the resulting electric field and efficiency.⁸³

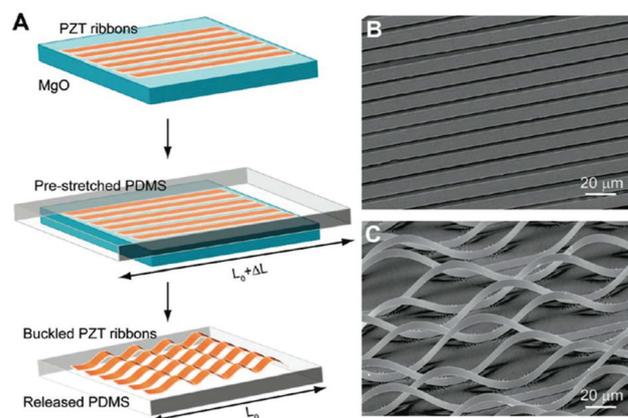


Fig. 9 Generating wavy piezoelectric ribbons on silicone rubber for application in flexible energy conversion. (A) From top to bottom: the ribbons are patterned on an MgO substrate; a slab of pre-stretched PDMS is laminated against the PZT ribbons and peeled off quickly; PZT ribbons are transferred onto PDMS and form wavy/buckled structures due to strain relaxation. (B) SEM image of PZT ribbons transfer printed to PDMS with zero pre-strain. (C) Buckling of PZT ribbons under pre-stretched conditions. The buckled ribbons exhibit enhanced piezoelectric performance compared to their flat counterparts. Reproduced from ref. 81.

3. Flexoelectricity in soft and biological membranes

Flexoelectric behavior has also been extensively studied in the context of soft condensed matter – specifically liquid crystals and biological membranes.^{13,14,84–87} The phospholipid molecules in most biomembranes consist of two components: hydrophilic heads and hydrophobic tails. Accordingly, when they are dispersed in an electrolyte, they arrange themselves into two sheets including charges and dipole moments on the surfaces. The resulting membrane is fluid-like within the plane but can sustain a variety of mechanical deformation modes including bending and compression in its thickness direction. The typical thickness of the ideal lipid bilayers and biological membranes is between 3–5 nm. Given that the bending moduli of bio-membranes are typically small— $10\text{--}20k_{\text{B}}T$ —these 2D structures undergo large thermal fluctuations even at room temperature. Needless to say, relatively little energy is required to induce curvature in these soft bio-membranes. During curvature deformation, the density of the charges and dipoles on the top and bottom of the surface alter and a non-zero net polarization is developed. In contrast to crystalline membranes, the microscopic mechanisms underpinning flexoelectricity in biomembranes can be explained purely by using classical electrostatics and continuum mechanics based arguments. § Mathematically, the flexoelectric be-

§ The relevant length scales for flexoelectricity in biological membranes are larger than in monolayered crystalline membranes and accordingly classical mechanics provide a reasonable description rendering quantum considerations unnecessary.

havior can be described by the same energy formulation as in eqn (4) which may be interpreted as an extension of Helfrich Hamiltonian that includes the flexoelectric electromechanical coupling and the dielectric energy. Most of the pioneering theoretical studies in this area have emerged from the physics of liquid crystals.^{13–16} We highlight that the notation of the flexoelectricity in most of the literature^{13–16} on biomembranes is different from what has been introduced in eqn (4). In the work of Petrov *et al.*, the flexoelectric constitutive law is expressed as follows:

$$P = f^e \kappa \quad (9)$$

Use of the above equation conceals the inherent elastic coupling and it is best to use the complete model outlined in eqn (4). The flexoelectric coefficient f that appears in (4) is related to f^e as $f^e = -f/a$. The typical values of f^e for biomembranes have been experimentally^{16,95–97} measured to be in the range of 10^{-21} – 10^{-18} C.

Flexoelectricity is likely to be the key electromechanical mechanism in biomembranes. This statement can be easily appreciated if we recognize that fluid membranes cannot (easily) have the low symmetry needed for a phenomenon like piezoelectricity to occur—as it does in some 2D crystalline membranes such as BN or MoS₂. Despite this, there has been relatively scant work on the topic of biological flexoelectricity and much of what exists has been pioneered by Petrov.^{13–16,95–98}

3.1. Physical and microscopic mechanisms

The detailed microscopic mechanism underlying flexoelectricity in biological membranes was recently clarified in the work by Ahmadpoor *et al.*⁹⁹ The central hypothesis of that work is that geometrical nonlinearity, in combination with the presence of external charges and/or dipolar distributions leads to the flexoelectric effect. They examined the effect of external charges and dipolar distributions on the apparent flexoelectricity of a lipid bilayer membrane. In a simple linearized setting, external charges do not change the apparent flexoelectricity. However, Ahmadpoor *et al.*⁹⁹ showed, using a rigorous mathematical model, that carefully accounting for geometric nonlinearity and the associated change in the polarization permits the observation of some nontrivial coupling effects. Prior insightful studies in this direction were those of Petrov^{13–16} and Hristova *et al.*¹⁰⁰ In the work of the latter, Langmuir adsorption equations were used to evaluate the redistributed charge density (under bending) of the membrane electric double layers. Similarly, Derzhanski¹⁰¹ presented a simple model of a spherically deformed membrane to describe the relationship between the radius of curvature and the induced membrane voltage.

We briefly summarize the model put forth by Ahmadpoor *et al.*⁹⁹ For simplicity, we consider here a small part of a cylindrically deformed lipid membrane inside an electrolyte bath (Fig. 10). The membrane thickness is h and let the radii of the inner, outer and mid surfaces be r_1 , r_2 and r_m . Lipid molecules

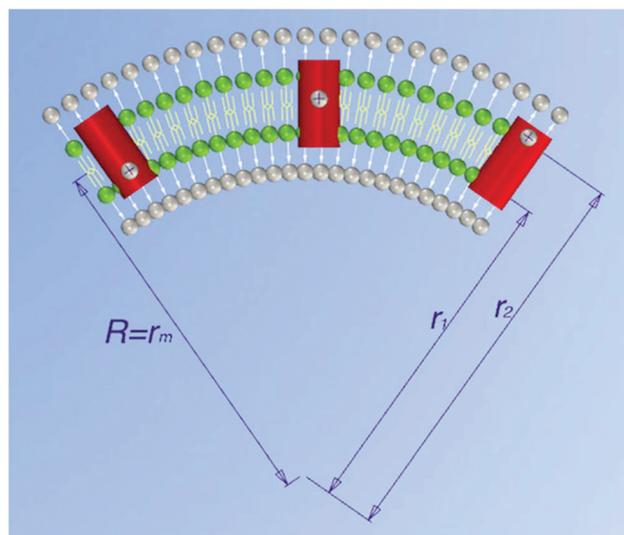


Fig. 10 A small part of a cylindrically deformed membrane is considered. Lipid molecules may carry charges and dipoles. The distribution of charges may vary due to ion transport. In this model it is assumed that the dipole and charge densities are functions of the radii and are uniformly distributed along the surface. Reproduced from ref. 99.

may carry dipoles or charges either along the thickness of the membrane or on the surfaces. These dipoles and charges might be “external” or the intrinsic properties of the lipid molecules. The former may be due to proteins and ion channels, for instance. In general, the charges and dipoles may be distributed in and around the membrane in a complex manner, however, to present the central results developed in ref. 99, we consider the simplest possible case, in which the distributions of the charges and dipoles are radial; neglecting any angular variation. The external charges and dipoles are uniformly distributed along the surface of the membrane with densities of $\rho^e(r)$ and $P^e(r)$. Let f_0 be the intrinsic flexoelectricity coefficient. Also let f_C and f_P be the flexoelectric contributions of the external charges and dipoles, respectively. Then the effective flexoelectric constant was derived to be:

$$f_{\text{eff}} = f_0 + f_C + f_P \quad (10)$$

wherein f_C and f_P are:⁹⁹

$$f_C = - \left(1 + \frac{h}{2r_m} + \frac{h^2}{6r_m^2} + \dots \right) \times a \int_{r_1}^{r_2} \frac{1}{r} \int_{r_1}^r r_1 (r' - r_m) \rho^e(r') dr' dr \quad (11)$$

$$f_P = \left(1 + \frac{h}{2r_m} + \frac{h^2}{6r_m^2} + \dots \right) a \int_{r_1}^{r_2} \frac{r_1 (r - r_m)}{r} P^e(r) dr$$

The expressions in eqn (11) exhibit the nonlinear and curvature-dependent nature of the flexoelectricity in highly curved membranes. Such nonlinear behavior has been also observed in experiments.⁸⁸

3.2 Biological implications of flexoelectricity and the literature review

As mentioned earlier, due to the fluidity of biological membranes and the fact that their bending stiffness is about $10\text{--}20k_{\text{B}}T$, they are likely to experience large thermal undulations. These thermal fluctuations are an important element of a variety of biophysical phenomena and a detailed discussion of this topic is certainly beyond the scope of the present article. It is sufficient to say here that statistical mechanics of biological membranes is a keenly studied subject and the reader is referred to the following literature for further information.^{102–109} One of outcomes of thermal fluctuations is that they generate a repulsive force between two membranes in close vicinity. Helfrich¹⁰² showed that this repulsive entropic force between two membranes is proportional to $1/d^3$ where d is the distance between the membranes. Petrov¹⁰⁹ investigated the effect of flexoelectricity on this repulsion and concluded that it leads to an attractive component, which at a certain distance cancels out the entropic repulsive force. In his model, such flexoelectric attraction becomes quite significant at shorter distances. Recently, using eqn (4) Liu and Sharma¹¹⁰ investigated the influence of flexoelectricity and thermal fluctuations on the mechanical and dielectric properties of biomembranes. It is well-known in the biomembrane literature that thermal fluctuations cause a softening of the membranes. Liu and Sharma¹¹⁰ showed that flexoelectricity enhances the softening effects of thermal fluctuations, while temperature appears to have a decreasing effect on the flexoelectric coefficient.

Both Mohammadi *et al.*⁴² and Deng *et al.*⁴³ have presented a mathematical framework of flexoelectricity in biomembranes (summarized in section 2.2). Deng *et al.*⁴³ specifically present some illustrative examples such as the deformation of a biomembrane due to the interaction with an ion. Recently Rey¹¹¹ has also presented a theoretical framework that includes tension, bending, pressure, and flexoelectric effects to determine the equilibrium shape of a vesicle. Gao *et al.*¹¹² established an electromechanical liquid crystal model of a cell's membrane based on Eringen's micropolar theory.¹¹³ They studied the shape deformation of spherical and cylindrical vesicles in response to an externally imposed electric field, incorporating the contributions of elastic bending, osmotic pressure, surface tension, flexoelectricity and Maxwell pressure into the free energy of the system. Finally, Loubet *et al.*¹¹⁴ derived the electrostatic contribution to membrane mechanical properties, such as bending stiffness, tension, spontaneous curvature and flexoelectric coefficient. In their model, they considered an infinite planar membrane with a uniform areal charge and dipole densities that vary along the thickness. They used the Poisson–Boltzmann approach—which is a mean-field approximation and does not take into account the ion correlations—and derived the equilibrium stress equations. Abou-Dakka *et al.*¹¹⁵ formulated a flexoelectric actuation model of a tethered circular membrane in the presence of an oscillating electric field. Their model can be

employed to explain how the outer hair cells in mammalian ears function.

Flexoelectricity has a number of implications in biology, including ion transport, electromotility and mammalian hearing mechanism. Voltage gated channels are transmembrane proteins that are activated in response to the change in local electric fields. The membrane, due to flexoelectricity undergoes conformational deformations in the presence of external fields which impose mechanical forces on the boundaries of the channel that make it activated. The usual sources of electric fields are ionic concentration gradients in the local environment of the cell. The ion pumps use flexoelectricity in a similar manner. As a result of the conformation transformations of the protein induced by ATP and ions, the membrane becomes curved. The resulting curvature as shown in Fig. 11 induces polarization and a so-called depolarizing electric field emerges that results in the generation of a driving force for ion pumping.^{94,116}

Electromotility¹¹⁷ is the cell's movement in the presence of an electric field across the cell membrane. As observed in experiments,¹¹⁸ the mammalian hearing mechanism critically relies on cell's electromotility. Hair cells are the primary sensory receptors in the auditory system that transform the mechanical vibrations of sound into sensible electrical action potential.¹¹⁹ Though, the corresponding mechanism is still not fully understood, one possible explanation is that the stereocilia in inner hair cells are flexoelectric. Hair bundles consist of several stereocilia (as shown in Fig. 12) 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

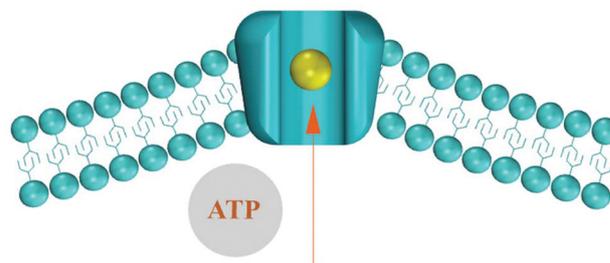


Fig. 11 This model of flexoelectricity driven ionic pump is proposed by Petrov.⁹⁴ Due to conformation transitions of the protein induced by ATP and ions, the phospholipid bilayer becomes curved. This curvature results in flexoelectric polarization and an electric field ensues which acts as the driving force for ion translocation. Adapted from ref. 94.

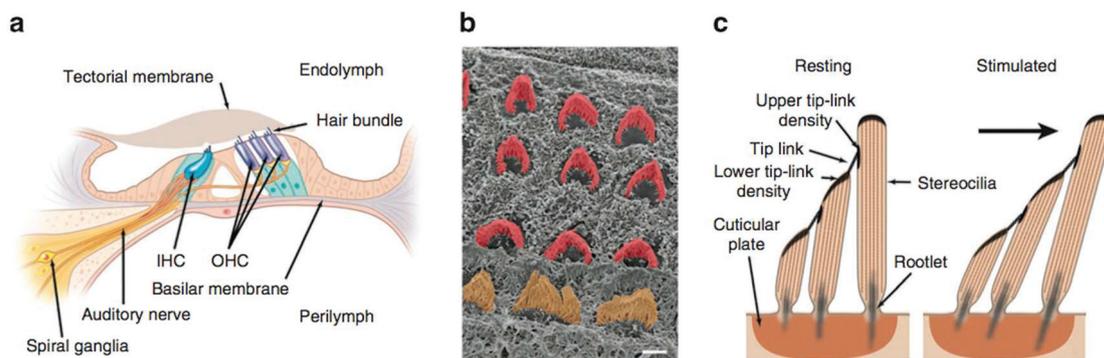


Fig. 12 (a) Cross-section of the organ of Corti and hair bundles on the apical surface of inner hair cells (iHcs) and outer hair cells (oHcs). (b) Scanning electron microscopy image looking at the apical surface of hair cells with the tectorial membrane removed. iHc and oHc hair bundles are pseudo-colored orange and red, respectively. (c) Elongation of a schematic of the hair bundle and hair cell apical surface. When hair bundles are stimulated, the stereocilia are tilted towards the tallest row of stereocilia. Reproduced with permission from ref. 119.

thickness of the stereocilia membrane and due to the flexoelectric properties of cellular membrane, the radius of the stereocilia changes. Accordingly, the height of the stereocilia increases (or decreases) to maintain the fixed volume. The contribution of electromechanical coupling in the hearing mechanism was first hypothesized by Hudspeth and Corey^{120–124} and based on several interesting experiments, Brownell and co-workers^{88–93,125,126} have argued that flexoelectricity is indeed the mechanism that serves to link mechanics and electricity in this context. Interestingly, the hair bundles not only transduce the mechanical signals into electric ones, but also amplify the weak mechanical stimuli. The corresponding mechanism involves the emergence of instability phenomenon, namely – Hopf bifurcation¹²⁷ a discussion of which is beyond the scope of this paper. For further details, the reader is referred to the recent review on hearing mechanism by Reichenbach and Hudspeth.¹²⁸

4. Concluding remarks and future directions

Flexoelectricity is a fascinating form of electromechanical coupling and is especially relevant to the easily curved 2D materials such as graphene and biological membranes. Despite a fair amount of recent activity, several open questions remain and there are numerous avenues for future research. First and foremost, the complete characterization of the flexoelectric properties of many of the 2D materials is still incomplete. Although the first 2D material, graphene, was synthesized just a short while ago, several novel material systems have emerged since then *e.g.* boron nitride,^{129,130} black phosphorus,^{131,132} molybdenum disulfide,^{133,134} tungsten disulfide^{135,136} and others. With the exception of graphene, BN and (to some extent) graphene nitride,^{28,30,58,60} characterization data of the flexoelectricity in these 2D materials are 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.^{15,16,95–97}

Simulating flexoelectricity 2D materials and their variants (*e.g.* layered or composite structures) from an atomistic viewpoint is quite challenging. The quantum mechanical approaches are computationally expensive since modeling of bending (or other nonuniform deformation modes such as torsion) necessarily precludes the use of periodic boundary conditions to simplify computations. Furthermore, even if quantum methods are cleverly used, they are limited in the sense that, practically speaking, only zero Kelvin information can be obtained. As an alternative, empirical force-field based molecular dynamics may be used, however developing potentials to model electromechanical behavior is notoriously difficult and that itself is an active area of research.¹³⁷ Recently, a piezoelectric molecular dynamics model for boron nitride nanotubes has been proposed by Yamakov *et al.*¹³⁸ Similar studies are also required for other 2D materials. Regarding quantum mechanical calculations, a promising recourse may be found in the recently developed Objective Structures based approach.^{139–141}

A theoretical framework for 2D membranes that properly accounts for large deformations and possible anisotropic effects is still absent. The former is important for biological membranes while the latter is of interest in the case of crystalline membranes. In particular, for crystalline membranes, in-plane elastic behavior is coupled with bending which makes the modeling of such membranes quite complex. As already alluded to earlier, studies on experimental characterization of flexoelectric response in 2D structures are rather scarce.

One of the applications of flexoelectricity is in energy harvesting. Existing theoretical and computational studies are based on the linear flexoelectricity effect^{79,83}—we expect much to be gained from examining nonlinear effects and is thus an open avenue for research. In particular, inspired by how mam-

malian hearing mechanism works, possible flexoelectricity based energy harvesting schemes may be created. On these lines we note that several bio-inspired applications of soft materials have been proposed in the literature e.g. liquid crystalline elastomer (LCE) soft actuators that are extensively used in artificial muscles, micro-robots and MEMS.^{142–145}

Several other open questions remain regarding flexoelectricity in 2D materials. As an example, Duerloo and Reed⁵³ found that the polarization-curvature in BN bilayers is amplified by 3–4 orders of magnitude compared to a single BN layer. We can only speculate about the mechanisms underpinning this observation and further investigation of this topic is an interesting avenue for future study. Likewise, Tagantsev^{22,36} presents a careful distinction between surface flexoelectricity and bulk flexoelectricity. What are the ramifications of this in the context of 2D materials?

Finally we point out the phenomenon of photoflexoelectricity – which is the coupling between light, mechanical strain gradients and electrical field. It was first observed in lipid membranes^{146,147} and later in liquid crystals.¹⁴⁸ Recent studies of the phenomenon include investigation of the use of photochromic elastomers^{149–152} as actuators and energy harvesting systems. Beyond the few cited references, hardly any work has been carried out to investigate this effect.

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