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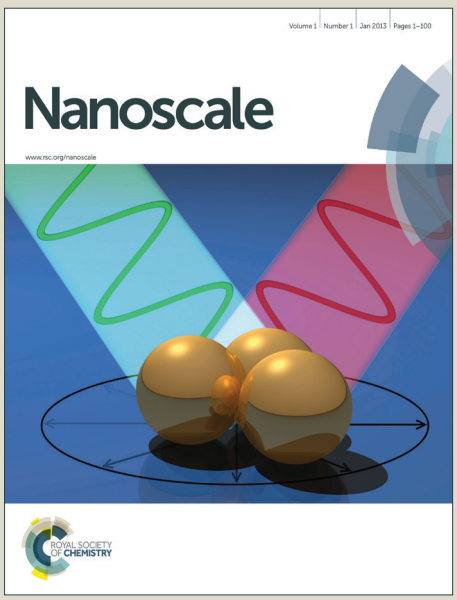

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Flexoelectricity in Two-dimensional Crystalline and Biological Membranes

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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 curvature and electric field. In this review, we highlight the recent advances made in our understanding of flexoelectricity in two-dimensional (2D) membranes—whether crystallines ones such as dielectric graphene nano ribbons 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.

1 Introduction

There are numerous types of electromechanical coupling mechanisms in dielectric materials. Piezoelectricity and the Maxwell stress effect* are fairly well-known and 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, 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 $\sim \varepsilon E^2/Y$ where ε is the dielectric constant, E is the electric field and Y represents the elastic modulus. As 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 crystals[6] and refers to the two-way *linear* coupling between the electric polarization and strain gradients. Experimental and theoretical works 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 sense and a converse effect *does* exist. Mathematically, piezoelectricity is often introduced through the following linear relation:

$$P_i \sim d_{ijk}\varepsilon_{jk} \tag{1}$$

In Equation (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 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 extent of the non-uniformity of the strain field or in other words, strain gradient[6–9,17]:

* 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.

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

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 (**d**) vanishes[18]. Indeed, flexoelectricity has been experimentally confirmed in both centrosymmetric materials like NaCl[10] 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 (–lets 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 **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 Equation (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 nano ribbons, MoS_2 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 tantalizing applications such as energy harvesting, sensors and actuators, biomedical devices among others. Several recent works 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.

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 Figure 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 a development of polarization.

  The ionic contribution to flexoelectricity was first described in detail by Tagantsev[8]. Later, using a lattice-dynamical approach, Maranganti and Sharma[23] 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 $BaTiO_3$ and $SrTiO_3$[24,25].

- Electronic Flexoelectricity: The discussion of ionic flexoelectricity is based on a classical picture and is

† 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 Vanderbilt[26] 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 Dayal[27] who provide an interesting insight into this issue from a purely classical viewpoint.

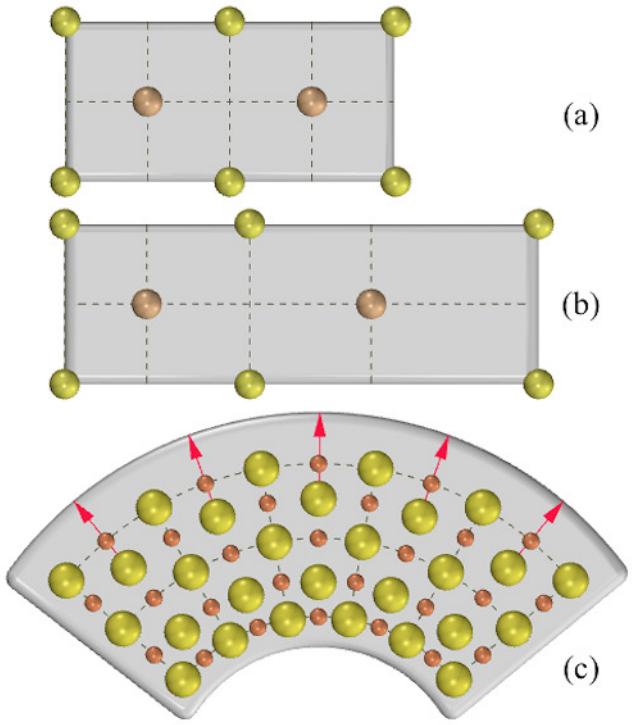

Fig. 1 (a): Deformed configurations of atoms in a centrosymmetric lattice under a uniform strain. (b): Deformed configuration of atoms in a centrosymmetric lattice under a non-uniform strain field. The atoms experience internal displacements in the presence of strain gradient that result in flexoelectric polarization. Adapted from reference [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.

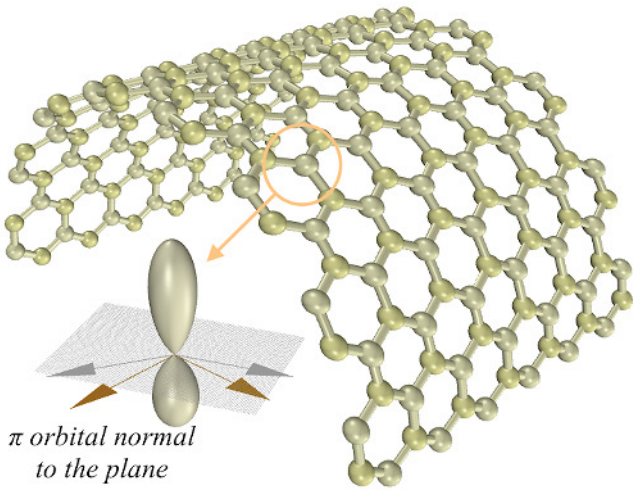

Fig. 2 Bending of graphene: upon bending, the symmetry of the electron distribution at each atomic site is broken, which leads to the polarization normal to the graphene ribbon; an infinite graphene sheet is semi-metallic; however, finite graphene nanoribbons can be dielectric depending upon surface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

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 therein [26]). For example, the ionic flexoelectricity mechanism outlined in the preceding paragraph would lead us to believe that a mono-atom material like graphene (dielectric) nano ribbon 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 shown in Figure. 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 nano ribbon is completely closed (to form a circular nanotube), the *net* dipole moment will vanish.

With specific emphasis on electronic flexoelectricity, several works have investigated flexoelectricity from a quantum viewpoint [26,28–31]. In a recent work, Hong and Vanderbilt [32] 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 flexoelectctricity. Resta [34], inspired by Martin [35], has theoretically discussed the effect of a free surface on flexoelectricity 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 Tagantsev [36] who showed that due to the non-zero contribution of the quadruple moment tensor, the surface flexoelectricty indeed exists. The surface flexoelectricity contribution has been elaborated further by Tagantsev in a recent review paper [22].

Also, Stengel[37], using a first principle approach, provided quantitative evidence of surface flexolelectricity and demonstrated that depending on the surface termination, a $SrTrO_3$ film can exhibit either positive or negative flexoelectric voltage.

2.2 Mathematical description and review of the modeling literature

Several recent works have mathematically studied flexoelectricity in 2D materials[38–43]. In general, as alluded to earlier in the context of Equation (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 works 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, Rey[40] 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-Yang[44] 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 displacement vector $\mathbf{w} : U \to \mathbb{R}^3$ and the polarization areal density vector $\mathbf{P} : U \to \mathbb{R}^3$. 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:

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

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 $(\varepsilon_0, \varepsilon)$ and the thickness of the membrane h as: $a = 1/(\varepsilon - \varepsilon_0)h$. 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:

$$\xi^{\text{self}}[\mathbf{w}, \mathbf{P}] = \int_{\mathbb{R}^3} \frac{\varepsilon_0}{2}|\nabla\zeta|^2, \qquad \text{div}[-\varepsilon_0\nabla\zeta + \mathbf{P}] = \rho_0 \tag{5}$$

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:

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

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

$$\begin{aligned} &\min \quad F[\mathbf{w}, \mathbf{P}] \\ &[\mathbf{w}, \mathbf{P}] \subset \mathscr{S} \end{aligned} \tag{7}$$

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 nano plates and nano beams have been studied by several authors[45–49].

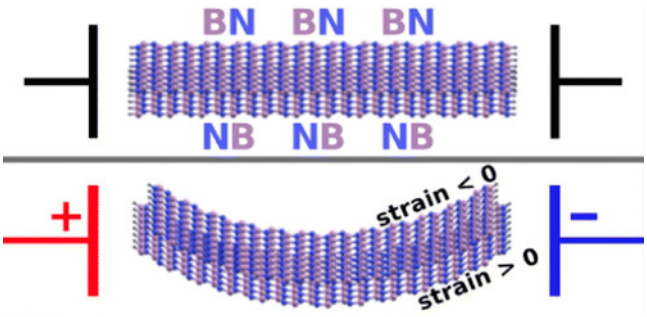

Fig. 3 Duerloo and Reed[53] found that a bilayer consisting of two BN monolayers exhibits a strong curvature induced electromechanical coupling. Using quantum mechanical calculations and a continuum model, they found that these bilayers (in response to an external electric field) amplify in-plane displacements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

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 MoS_2—which are piezoelectric to begin with. We note that BN and MoS_2 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 MoS_2 are expected to deviate from the simpler isotropic relation in Equation (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 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:

$$\begin{aligned} P_n &\sim f_n \kappa\, \mathbf{n} \\ P_t &\sim f_t \kappa\, \mathbf{t} \end{aligned} \tag{8}$$

It is also worthwhile to mention that a nonlinear flexoelectric response for 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 nano sheets 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 calculations[53], show that flexoelectric 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 a tantalizing avenue for future study.

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 pyramids 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 Sharma[57] showed, using first principle calculations, that merely by introducing triangular shaped holes in dielectric graphene nano ribbons, 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 (Figure 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, now imagine the case of non-centrosymmetric shaped holes such as the triangular ones shown in the bottom of Figure 4. In this case, under the action of uniform mechanical stretch or compression, a non-zero net polarization will emerge. While Chandratre and Sharma[57], using quantum calculations, were able to illustrate this notion for graphene nano ribbons, experimentally realizing small

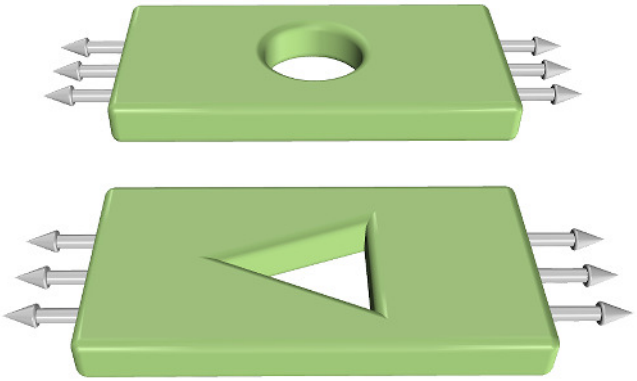

Fig. 4 The first figure schematically depicts a non-piezoelectric 2D sheet with circular pores. Under uniform stretching, strain gradients develop in the vicinity of the holes and therefore the local polarization due to flexoelectricity is non-zero, however the *net* or average polarization remains zero, 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 reference [58].

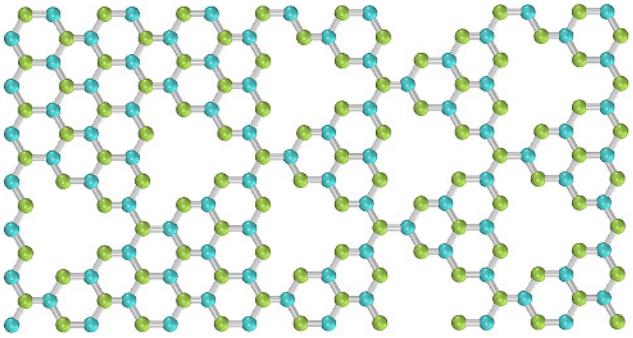

Fig. 5 Graphene nitride nano sheet, riddled by triangular holes, was experimentally and computationally shown to exhibit an apparent piezoelectric response. Adapted from reference [58].

Table 1 Comparison between the piezoelectric coefficient of g-C_3N_4 (induced due to flexoelectricity and defects, shown in Figure 5)[58] with some of common piezoelectric 2D structures.

Material	Piezoelectric coefficient (10^{-10}Cm^{-1})
g-C_3N_4	2.18
h-BN	1.38[60]
MoS_2	3.64[60]
WS_2	2.47[60]

triangular holes in graphene nano ribbons is impractical. Fortunately, a close "cousin" of graphene, 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-C_3N_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 Figure 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-C_3N_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 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 the 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-C_3N_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 the surface, breaks inversion symmetry and may generate strain gradient that lead to a flexoelectric response. This approach has been employed for graphene. In a 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) atoms 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/Å. Their finding of a linear relationship between strain and polarization appears to imply an emergent piezoelectric behavior. 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.

Composites of multi-layered systems is another alternative

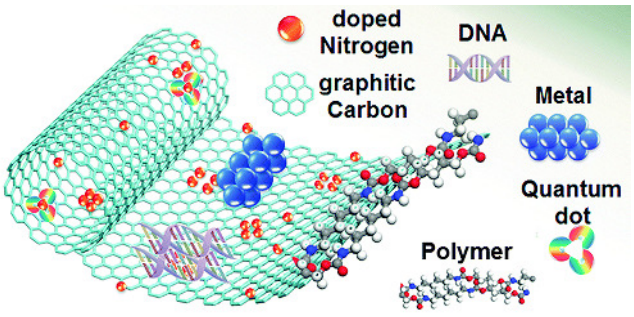

Fig. 6 Chemical doping of graphene surface with different components such as Nitrogen, polymers, and various metals can induce a piezoelectric response. Reproduced with permission from reference [64]

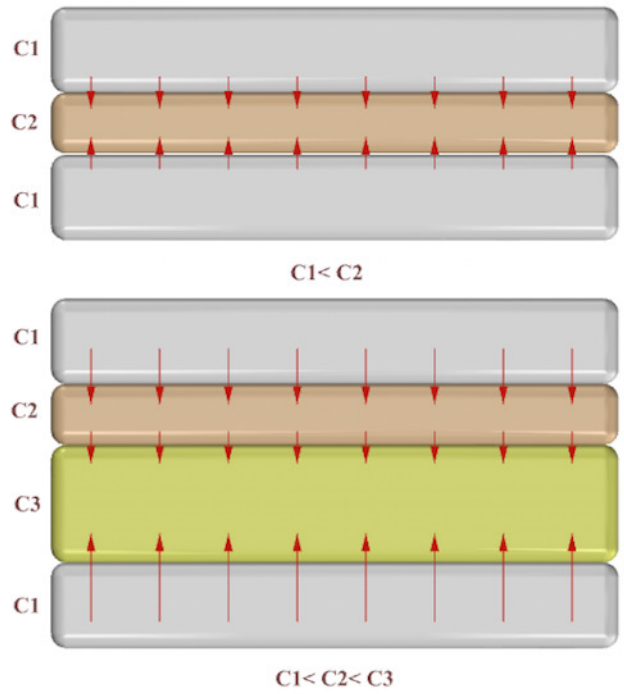

Fig. 7 Schematic of a comparison between periodic bilayer and trilayer superlattices. Red arrows indicate polarization. In a periodic bilayer, under uniform stretching or compression, the induced dipole moment in a layer cancels out the dipole moment induced in the other layer. Thus the overall average 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 reference [66]

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 feels 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 appeared 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.

A flexoelectric model of a multi-layered structure of barium strontium titanate(BST) was also proposed[67] 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 multilayer 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 tantalizing applications of flexoelectricity is in nano generators 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 a intensely researched topic. To date, research on this topic is centered around piezoelectric materials. Examples of exploiting piezoelectricity for energy harvesting range from shoe-mounted inserts[73,74] to unmanned aerial vehicles[75]. Due

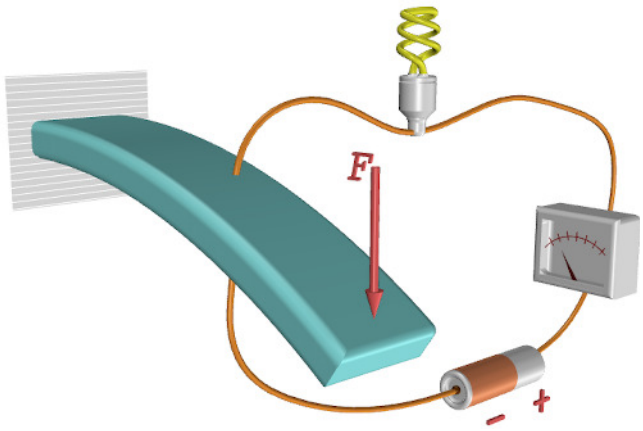

Fig. 8 Schematic of a centrosymmetric flexoelectric energy harvester under base excitation. The cantilever beam is covered by conductive electrodes on its top and bottom surfaces. Due to application of an external force or the movement of the base, the cantilever beam undergoes bending vibrations. Due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

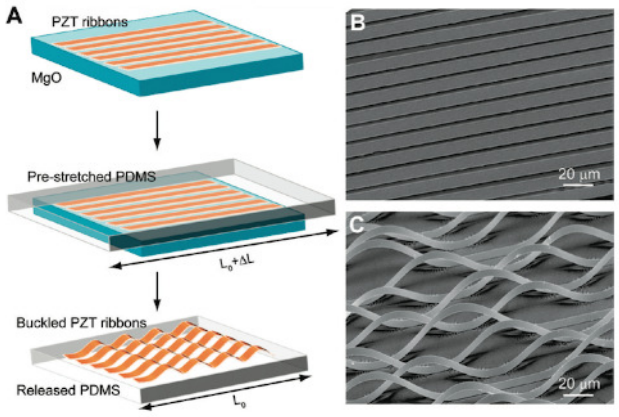

Fig. 9 Generating wavy piezoelectric ribbons on silicone rubber for application in flexible energy conversion. (a): From top to bottom: the ribbons are patterned on an MgO substrate; a slab of pre-strained PDMS is laminated against the PZT ribbons and peeled off quickly; PZT ribbons are transferred onto 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-strained conditions. The buckled ribbons exhibit enhanced piezoelectric performance compared to their flat counterparts. Reproduced from reference [81].

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 loose their piezoelectricity above a certain temperature due to phase transformations. Flexoelectricity, in contrast can persist to fairly high temperatures. In a 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 (Figure. 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 reduction of the beam's thickness from 3μm to 0.3μm, 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 nano scale 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 Figure 9 where the piezoelectric PZT ribbons on 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 flexoelectric curvature induced electric field to dramatically improve the sensitivity of the nano ribbons to small deformations. It has been also discussed[80] 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].

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— $10-20k_BT$— 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 biomembranes. 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 using classical electrostatics and continuum mechanics based arguments.‡ Mathematically, the flexoelectric behavior can be described by the same energy formulation as Equation (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 works 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 Equation(4). In the work of Petrov et. al., the flexoelectric constitutive law is expressed as follows:

$$P = f^e \kappa \tag{9}$$

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

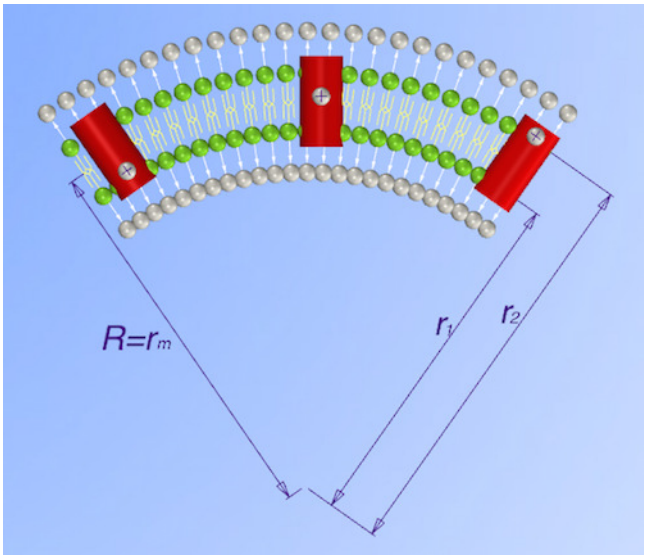

Fig. 10 A small part of a cylindrically deformed membrane is considered. Lipid molecules may carry charges and dipoles. The distribution of charges may vary due to ion transport. In this model it is assumed that the dipole and charge densities are functions of the radii and are uniformly distributed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

Use of the above equation conceals the inherent elastic coupling and it is best to use the complete model outlined in Equation (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 MoS_2. 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 postulate 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 naively linearized setting, external charges do not change the apparent

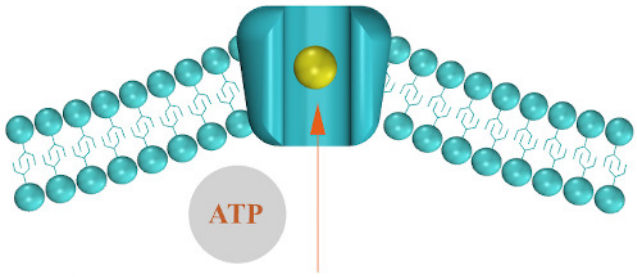

Fig. 11 This model of flexoelectricity driven ionic pump is proposed by Petrov[94]. Due to conformation transitions of the protein induced by ATP and ions, the phospholipid bilayer becomes curved. This curvature results in flexoelectric polarization and an electric field ensues which acts as the driving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

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 works in this direction were those due to Petrov[13–16] and Hristova et. al.[100]. In the latter, equations of Langmuir adsorption were used to evaluate the redistributed charge density (under bending) of the membrane electric double layers. In a similar vein, Derzhanski[101] presented a simple model of a spherically deformed membrane to describe the relation between the radius of curvature and the induced membrane voltage.

We briefly summarize the model put forth by Ahmadpoor et. al.[99]. For simplicity, here we consider a small part of a cylindrically deformed lipid membrane inside an electrolyte bath Figure 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 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 $P^e(r)$. Also let f_0, f_C and f_P be the intrinsic flexoelectric coefficient, that due to the presence of external charges and that due to the presence of external dipoles, respectively. Then the effective flexoelectric constant was derived to be:

$$f_{\text{eff}} = f_0 + f_C + f_P \tag{10}$$

wherein f_C and f_P are[99]:

$$\begin{aligned} f_C &= -\left(1 + \frac{h}{2r_m} + \frac{h^2}{6r_m^2} + \cdots\right) \\ &\quad \times a \int_{r_1}^{r_2} \frac{1}{r} \int_{r_1}^{r} r_1(r' - r_m)\rho^e(r')dr'dr \\ f_P &= \left(1 + \frac{h}{2r_m} + \frac{h^2}{6r_m^2} + \cdots\right) a \int_{r_1}^{r_2} \frac{r_1(r - r_m)}{r} P^e(r)dr \end{aligned} \tag{11}$$

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

3.2 Biological implications of flexoelectricity and literature review

As mentioned earlier, due to the fluidity of biological membranes and the fact that their bending stiffness is about 10-20k_BT, 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 repulsive force between two membranes in close vicinities. Helfrich[102] showed that this repulsive entropic force between two membranes is proportional to $1/d^3$ where d is the distance between the membranes. Petrov[109] investigated the effect of flexoelectricity on this repulsion and concluded that it leads to an attractive component, that at a certain distance cancels out the entropic repulsive force. In his model, such flexoelectric attraction becomes quite significant at shorter distances. Recently, using the formulation in Equation (4) Liu and Sharma[110], 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 Sharma[110] showed that flexoelectriciy enhances the softening effects of thermal fluctuations, while temperature appears to have a decreasing effect on the flexoelectric coefficient.

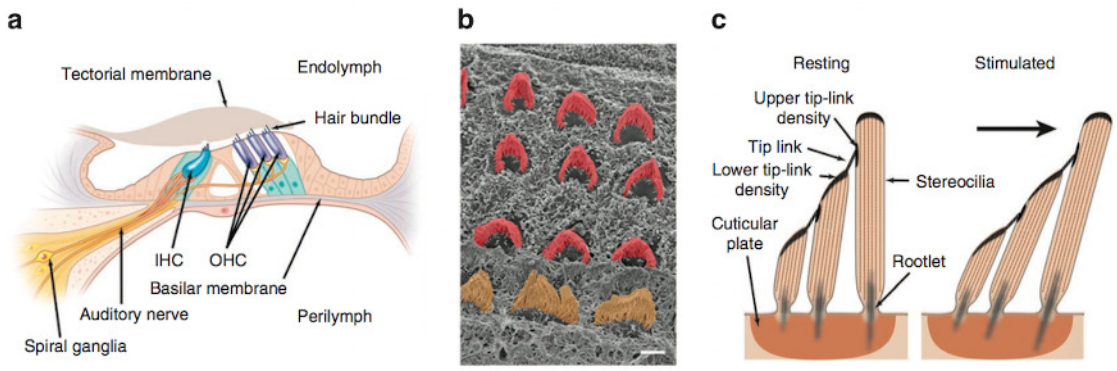

Fig. 12 (a) Cross-section of the organ of corti and hair bundles on the apical surface of inner hair cells (iHcs) and outer hair cells (oHcs). (b) Scanning electron microscopy image looking at the apical surface of hair cells with the tectorial membrane removed. iHc and oHc hair bundles are pseudo-colored 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 reference [119].

Both Mohammadi et. al.[42] and Deng et. al.[43] have presented a mathematical framework for flexoelectricity in biomembranes (summarized in section in 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 Rey[111] has also presented a theoretical framework that includes tension, bending, pressure, and flexoelectric effects to determine the equilibrium shape of the vesicle. Gao et. al.[112] established an electromechanical liquid crystal model of 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 Figure 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].

Electromotility[117] is the cell's movement in the presence of 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 Figure 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 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 hearing mechanism was first hypothesized by Hudspeth and Corey[120–124] and based on several interesting experiments, Brownell and co-workers[88–90,125,126] 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 bifurcation[127] 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 phosphorous[131,132], molybdenum disulfide[133,134], tungsten disulphide[135,136] and others. With the exception of graphene, BN and (to some degree) graphene nitride[28,30,58,60], a characterization of the flexoelectricity in these 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[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 works 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, works 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 works 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 mammalian 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[143–145].

Several other open questions remain regarding flexoelectricity in 2D materials. As an example, Duerloo and Reed[53] 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 gone into investigating this effect.

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