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Flexoelectricity in soft materials and biological membranes

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ABSTRACT

Flexoelectricity and the concomitant emergence of electromechanical size-effects at the nanoscale have been recently exploited to propose tantalizing concepts such as the creation of "apparently piezoelectric" materials without piezoelectric materials, e.g. graphene, emergence of "giant" piezoelectricity at the nanoscale, enhanced energy harvesting, among others. The aforementioned developments pertain primarily to hard ceramic crystals. In this work, we develop a nonlinear theoretical framework for flexoelectricity in soft materials. Using the concept of soft electret materials, we illustrate an interesting nonlinear interplay between the so-called Maxwell stress effect and flexoelectricity, and propose the design of a novel class of apparently piezoelectric materials whose constituents are intrinsically non-piezoelectric. In particular, we show that the electret-Maxwell stress based mechanism can be combined with flexoelectricity to achieve unprecedentedly high values of electromechanical coupling. Flexoelectricity is also important for a special class of soft materials: biological membranes. In this context, flexoelectricity manifests itself as the development of polarization upon changes in curvature. Flexoelectricity is found to be important in a number of biological functions including hearing, ion transport and in some situations where mechanotransduction is necessary. In this work, we present a simple linearized theory of flexoelectricity in biological membranes and some illustrative examples.

1. Introduction

Piezoelectrics are an intriguing class of materials where a uniform mechanical strain can induce an electric field and conversely, a uniform electric field can cause mechanical actuation. This phenomenon has found wide applications: in energy harvesting, sensing and actuation, advanced microscopes, artificial muscles, minimally invasive surgery among others (Wang et al., 2010; Madden et al., 2004; Gautschi, 2002; Labanca et al., 2008). Both soft materials (e.g. polymers) and hard crystalline ceramics exhibit this phenomenon albeit the microscopic mechanisms underpinning piezoelectricity differ in these two classes of materials (Furukawa, 1989; Damjanovic, 1998).

Recently, a somewhat understudied electromechanical coupling, flexoelectricity, has attracted a fair amount of attention from both fundamental and applications points of view leading to intensive experimental (Cross, 2006; Ma and Cross, 2001, 2002, 2003, 2006; Catalan et al., 2004; Zubko et al., 2007; Fu et al., 2006, 2007) and theoretical activity in this topic (Sharma

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et al., 2007; Eliseev et al., 2009, 2011; Maranganti and Sharma, 2009; Majdoub et al., 2008a,b, 2009a,b; Sharma et al., 2010, 2012; Gharbi et al., 2011; Kalinin and Meunier, 2008; Dumitrica et al., 2002). The aforementioned works and nearly all the current literature on flexoelectricity focus on crystalline materials. Since several concepts pertaining to flexoelectricity in crystalline materials also carry over to soft matter, in the following, we provide some discussion of the former subject also.

To understand flexoelectricity better, it is best first to allude to the central mathematical relation that describes piezoelectricity:

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

In the above equation the polarization vector P_i is related to the second order strain tensor ε_{jk} through the third order piezoelectric material property tensor d_{ijk}. Tensor transformation properties require that under inversion-center symmetry, all odd-order tensors vanish. Thus, most common crystalline materials, e.g. Silicon, and NaCl are not piezoelectric whereas ZnO and GaAs are. Physically, however, it is possible to visualize how a non-uniform strain or the presence of strain gradients may potentially break the inversion symmetry and induce polarization even in centrosymmetric crystals (Tagantsev et al., 2009; Tagantsev, 1986; Maranganti et al., 2006). This is tantamount to extending relation (1) to include strain gradients:

$$P_i \sim d_{ijk}\varepsilon_{jk} + f_{ijkl}\frac{d\varepsilon_{jk}}{dx_l} \tag{2}$$

Here f_{ijkl} are the components of the so-called flexoelectric tensor. While the piezoelectric property is non-zero only for select materials, the strain gradient-polarization coupling (i.e., flexoelectricity tensor) is in principle non-zero for all (insulating) materials. This implies that under a non-uniform strain, all dielectric materials are capable of producing a polarization. The flexoelectric mechanism is well-illustrated by the non-uniform straining of a graphene nanoribbon—a manifestly non-piezoelectric material (Fig. 1(a)) (Dumitrica et al., 2002; Chandratre and Sharma, 2012). Flexoelectricity has been experimentally confirmed in several crystalline materials such as NaCl, ferroelectrics like Barium Titanate among others, e.g. Refs. (Fu et al., 2006, 2007). The mechanisms of flexoelectricity in polymers (while experimentally proven) still remain unclear (Baskaran et al., 2011, 2012; Chu and Salem, 2012) and atomistic modeling (being conducted by the authors) is expected to shed light on this issue in the near future. We speculate that the presence of frozen dipoles and their thermal fluctuations is the cause of flexoelectricity in soft materials, however, we cannot offer a more definitive explanation at this point and simply emphasize that this phenomenon has been experimentally confirmed (Baskaran et al., 2011, 2012; Chu and Salem, 2012) and further elucidation is a subject of future research. It is worthwhile to note that the term "flexoelectricity" was first coined in the context of liquid crystals (Meyer, 1969; deGennes, 1974). A substantial literature on flexoelectricity in thermotropic liquid crystals does exist—a detailed discussion of which is beyond the scope of the current paper. The reader is simply referred to a recent text that summarizes much of the literature on that topic (Eber and Buka, 2012).

Flexoelectricity results in the size-dependency of electromechanical coupling and researchers (including us) have advocated several tantalizing applications that can result through its exploitation. For example, the notion of creating piezoelectric materials without using piezoelectric materials (Sharma et al., 2007, 2010; Chandratre and Sharma, 2012; Fu et al., 2007), giant piezoelectricity in inhomogeneously deformed nanostructures (Majdoub et al., 2008a, 2009a), enhanced energy harvesting (Majdoub et al., 2008b, 2009b), the origins of nanoindentation size effects (Gharbi et al., 2011), renormalized ferroelectric properties (Catalan et al., 2004; Eliseev et al., 2009, 2011), the origins of the dead-layer effect in nanocapacitors (Majdoub et al., 2009) among others. In fact, Chandratre and Sharma (2012) have recently shown that graphene can be coaxed to behave like a piezoelectric material merely by creating holes of certain symmetry. The artificial piezoelectricity thus produced was found to be almost as strong as that of well-known piezoelectric substances such as quartz. Such a constructed graphene nanoribbon may be considered to be the thinnest known piezoelectric material. We briefly elaborate on this notion (Fig. 2). Consider a material consisting of two or more different non-piezoelectric dielectrics —as a concrete example that has been studied in the past we may think of a (dielectric) graphene nanoribbon impregnated

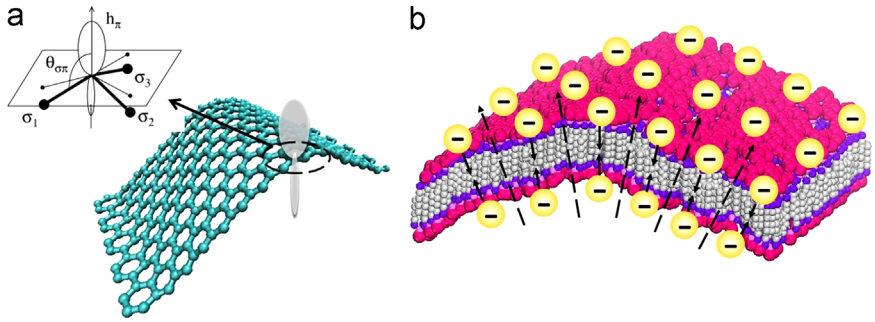

Fig. 1. Flexoelectricity in membranes. (a) Bending of graphene: upon bending, the symmetry of the electron distribution at each atomic site is broken, which leads to the polarization normal to the graphene ribbon; an infinite graphene sheet is semi-metallic; however, finite graphene nanoribbons can be dielectric depending upon surface termination. (b) Bending of a lipid bilayer membrane: due to bending, both the charge and dipole densities in the upper and lower layers become asymmetric. This asymmetry causes the normal polarization in the bilayer membrane.