

Novel Electromechanical Phenomena at the Nanoscale: Phenomenological Theory and Atomistic Modeling

Alexander K. Tagantsev, Vincent Meunier,
and Pradeep Sharma

Abstract

In the past two decades, the fact that "small is different" has been established for a wide variety of phenomena, including electrical, optical, magnetic, and mechanical behavior of materials. However, one largely untapped but potentially very important area of nanoscience involves the interplay of electricity and mechanics at the nanoscale. In this article, predicated on both phenomenological approaches and atomistic calculations, we summarize the state-of-the-art in understanding electromechanical coupling at the nanoscale. First, we address flexoelectricity—the coupling of strain gradient to polarization. Flexoelectricity exists in both piezoelectric and nonpiezoelectric dielectrics. As a high-order spatial-dispersion effect, the flexoelectricity becomes more and more important with the reduction of the spatial scale of the problem. Exploitation of this phenomenon and the associated nanoscale size effects can lead to tantalizing applications, such as "piezoelectric nanocomposites without using piezoelectric materials." The second issue concerns electromechanical effects at the dielectric/metal interface. An interface in solids typically exhibits a lower symmetry compared to that of the associated adhering materials. This symmetry reduction can drastically affect the electromechanical and dielectric behavior of the material at the nanoscale.

Introduction

The emergence of unusual size-dependent phenomena at submicron scales has given rise to intensely researched areas in the physical and biological sciences as well as several novel materials and device applications. This includes nanomechanics, plasmonics, nano-optics, and molecular electronics. However, one largely untapped but potentially important area of

nanoscience involves the relationship between electricity and mechanics at small length scales. Electromechanical interactions at the nanoscale are directly related to functionality found in single molecules and more generally in molecular systems. Key to the fundamental understanding of these electromechanical couplings is the interplay between intrinsic structural and

electronic properties, originating from quantum mechanical manifestations at the atomic level.

From a theoretical standpoint, an atomistic-level treatment of the coupling is very important and must be performed using accurate quantum mechanical techniques, also known as "first-principles" or *ab initio* methods. These methods have been successfully applied to ferroelectricity at the nanoscale—a phenomenon tightly related to electromechanics. As representative examples, one can mention the evaluation of the minimum thickness for films carrying ferroelectricity,¹ the description of ferroelectric superlattices² and closure domain patterns in ultrathin films,³ and the analysis of the domain wall structures.⁴ The reader is referred to a recent review article by Junquera and Ghosez⁵ and references therein for a comprehensive account.

In parallel to the purely *ab initio* approach, modifications of existing phenomenological theories to interpret the numerical results of atomistic calculations are desirable as well. A complete interpretation of the experimental data is not possible without a true multiscale approach involving the linkage of quantum level phenomena to continuum level interpretations.

In this review, predicated on both phenomenological approaches and atomistic calculations, we summarize the state-of-the-art of our understanding of electromechanical coupling at the nanoscale.

Customarily, when speaking about electromechanical coupling, one means the piezoelectric effect. Indeed, often piezoelectric coupling provides a good overall description of the electromechanical effects in materials. However, at smaller length scales, various electromechanical couplings—which are not piezoelectric in nature—become significant. This review is focused on such aspects of electromechanical coupling. Specifically, we will address the so-called flexoelectric phenomena and the surface-stimulated electromechanical effects.

Flexoelectricity and Electromechanical Coupling at the Nanoscale

In a piezoelectric material, an applied uniform strain can induce electric polarization (or vice versa). Crystallographic considerations indicate that this technologically important property is restricted to noncentrosymmetric crystal systems.⁶ Formally, the polarization vector P_i is related to the second-order strain tensor ϵ_{jk} through a third-order piezoelectric tensor d_{ijk} : $P_i = d_{ijk} \epsilon_{jk}$. Tensor transformation pro-

perties require that, under inversion-center symmetry, all odd-order tensors vanish. Thus, many common dielectrics (e.g., silicon) and NaCl are not piezoelectric, whereas ZnO and GaAs are. This is tantamount to extending the conventional piezoelectric constitutive law to include strain gradients (since it breaks the inversion-center symmetry):

$$P_i = \underbrace{d_{ijk} \varepsilon_{jk}}_{=0, \text{ for nonpiezo materials}} + f_{ijk} \frac{\partial \varepsilon_{jk}}{\partial x_l} \quad (1)$$

Here f_{ijk} are the so-called flexoelectric coefficients, which determine the strength of the flexoelectric response, and x_l represents the differentiation with respect to the coordinate axes, thus signifying the gradient of strain. While the piezoelectric property is nonzero only for selected materials, the strain gradient-polarization coupling (i.e., flexoelectric coefficients) is in principle nonzero for all dielectric materials, including those that are centrosymmetric. This implies that under a nonuniform strain, all dielectric materials are capable of producing a polarization. Here, one should stress that the new, second "flexoelectric term" in Equation 1 does not provide a complete description of the effect, in contrast to the first "piezoelectric term." The piezoelectric contribution, as controlled by and calculated from the lattice mechanics of an infinite crystal, provides a correct description for the piezoelectric effect measured in the case of both homogeneous strain and the polarization wave, which follows the acoustic wave in the piezoelectric. (The latter takes place because of mechanical strain in such a wave.) Also of importance is that the piezoelectric effect is not sensitive to the sample termination (i.e., to the composition of the last atomic layer at the surface of the sample.). In contrast, the flexoelectric contribution calculated from the lattice mechanics for an infinite crystal under a constant strain gradient (which can be described by the second term, f_{ijk} , in Equation 1) gives only a part of the total response of a finite sample to a constant strain gradient. The additional contributions, comparable to the first flexoelectric contribution, are controlled by the sample termination and properties of the surface. These are the surface flexoelectricity and surface piezoelectricity, in contrast to the static bulk flexoelectricity described by f_{ijk} . Another, remarkable feature of the flexoelectric response is that the term f_{ijk} for Equation 1 provides only a contribution to the amplitude of the polarization wave that follows the acoustic wave in a centrosymmetric material. The other contribu-

tion is controlled by the dynamic bulk flexoelectricity. The reader is referred to the following works for conceptual and theoretical foundations of this concept in crystalline materials.^{7,8}

The flexoelectric effect is appreciable only at "small" length scales. While the mechanical strain itself can be considered to be roughly size-independent, if the system under study is shrunk self-similarly from millimeters to nanometers, strain gradients will increase by six orders of magnitude. Through this size effect, it is possible to exploit flexoelectricity for new types of applications. Cross and co-workers suggested the possibility of creating piezoelectric "materials" without using piezoelectric materials.⁹ Recently, Sharma et al. have theoretically analyzed such novel classes of multifunctional materials.¹⁰ Cross et al.^{9,11} have fabricated nonpiezoelectric tapered pyramidal structures on a substrate that effectively act as piezoelectric metamaterials, as explained in the figure caption of Figure 1.

Cross and co-workers¹² have published studies on composites made of nonpiezoelectric materials reporting that a (Ba,Sr)TiO₃ (BST)-based structure has an effective piezoelectric modulus of 40 pC/N (cf. piezoelectric modulus 2.3 pC/N for quartz). One of the structures they have employed is shown in Figure 1.¹²

The central concept behind this idea is as follows: Imagine a composite consisting of a nonpiezoelectric matrix with embedded nonpiezoelectric inclusions, which in a limiting case could simply be holes. Upon application of a uniform strain, strain gradients will be created in the vicinity of the inclusions. Due to the flexoelectric effect, local polarization will ensue. If the size of the inclusions is "small" (thus leading to large strain gradients), an appreciable net average nonzero polarization across the entire composite may emerge. Thus the composite material will behave like a piezoelectric one even though its constituents are nonpiezoelectric. The shape of the inclusion and the topological arrangement are important for this application. For example, in the case of a circular inclusion, while local polarization will indeed be produced, the net average will be rendered zero. The shape of the inclusions must be noncentrosymmetric (e.g., triangular). In a recent theoretical work,¹⁰ this application and the necessary attendant conditions have been examined in detail.

Interestingly, the flexoelectric effect (as revealed by recent atomistic and calculations on prototype nanostructures)¹³ under certain circumstances can compete

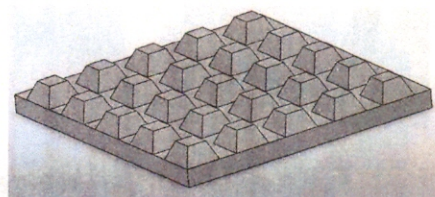


Figure 1. Diagrammatic sketch of a flexoelectric composite consisting of nonpiezoelectric (Ba,Sr)TiO₃ and air. The (Ba,Sr)TiO₃ component (pyramids mounted on a substrate) is shown. When set between two planar electrodes, this material imitates the direct piezoelectric effect under mechanical loading normal to the plane of the substrate. Adapted from Fu et al.¹²

with the piezoelectric response. This, for example, happens when the polarization response of a bent piezoelectric beam is examined. Since upon bending the tension and compression at the two sides of the bar are close in value, in the first approximation, the piezoelectric responses of these sides cancel each other. As a result, in a high-order approximation, only a small polarization response controlled by the piezoelectric effect appears. Taking into account flexoelectricity, an additional polarization response comes into play. This response increases with decreasing bar thickness, becoming appreciable at small thicknesses. It is equivalent to the emergence of size-dependent enhanced piezoelectricity in materials that are already piezoelectric (e.g., an enhancement in the effective piezoelectric constant of nearly 210% was found for a tetragonal BaTiO₃ cantilever beam 2 nm thick) (see Figure 2).

The evaluation of flexoelectric properties is a challenging task (both experimentally and theoretically). In the context of crystalline materials, a crude analysis to measure the magnitude of the static bulk flexoelectric coefficients, f_{ijk} , was first provided by Kogan,¹⁴ who estimated the coefficients to be on the order of e/a , where e is the electronic charge and a is the lattice parameter. This estimate was derived for "normal" dielectrics not exhibiting an additional lattice softness, which can result in an elevated value of the dielectric constant (such as in ferroelectrics). For "normal" dielectrics, this estimate applies to the rest of the aforementioned contributions to the effect. Taking into account such softness modifies this estimate for the bulk contributions to the form $(e\kappa)/(4\pi a)$, where κ is the dielectric constant. This softness does not affect or has much less effect on surface contributions.⁸

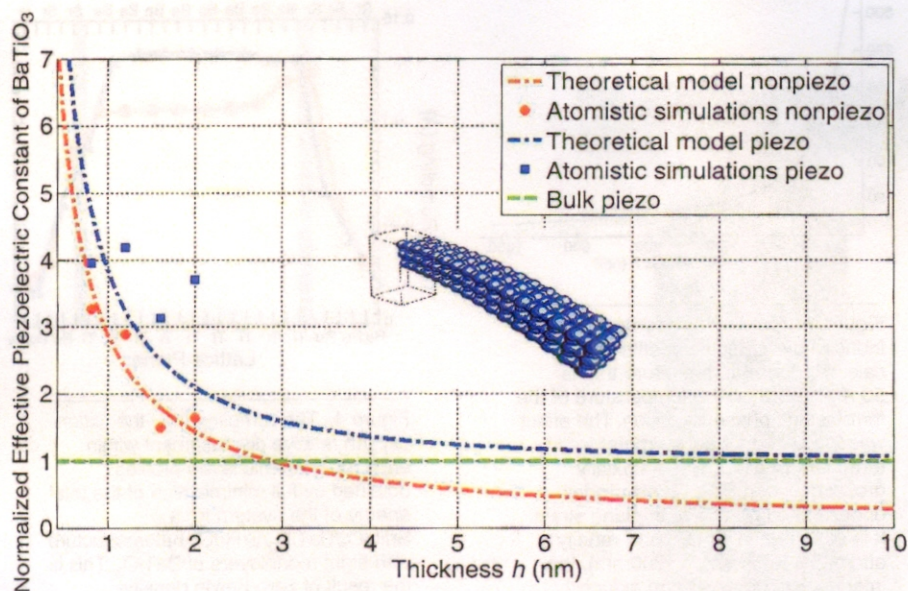


Figure 2. Normalized "effective" piezoelectric constant of a bent BaTiO_3 beam is plotted as a function of its thickness. The atomistic calculations for the case of cubic (nonpiezoelectric) BaTiO_3 are in good agreement with the theoretical model (red dotted line). In the case of tetragonal (piezoelectric) BaTiO_3 , the atomistic simulations are also able to capture the same order of magnitude as the theoretical model (blue dotted line). The green dashed line is for the piezoelectric bulk piezoelectric constant of BaTiO_3 . The theoretical model incorporates both flexoelectricity and piezoelectricity. The flexoelectric coefficients are obtained from *ab initio* calculations. The figure in the middle is an atomistic representation of a cantilever beam under bending. The beam is solidly mounted in the square dotted block. Adapted from Majdoub et al.¹²

Thus in materials with a high dielectric constant, one expects bulk contributions to control the flexoelectricity. Experimental measurements of the flexoelectric effect of high dielectric constant ceramics, such as lead magnesium niobate, barium strontium titanate, and lead zirconate titanate, by Cross and co-workers^{9,11,12} show that the magnitude of their flexoelectric coefficients are of the order of 10^{-6} C/m, which is two orders of magnitude larger than $(\epsilon\kappa)/(4\pi a)$. At the same time, Zubko et al.¹⁵ estimated the values of the components of the complete flexoelectric tensor for SrTiO_3 to be on the order of 10^{-8} C/m, which reasonably agrees with the estimate mentioned previously. Kholkin et al.¹⁶ also have addressed the flexoelectric effect in SrTiO_3 by using piezoelectric force microscopy. In this article, the authors demonstrated a manifestation of flexoelectric response in SrTiO_3 ceramic samples due to surface relaxation. The estimate of the flexoelectric constant obtained, however, was an order of magnitude smaller than that obtained by Zubko et al.¹⁵

On the theoretical side, *ab initio* and shell model results are available for nonferroelectric crystals (GaAs, GaP, ZnS, NaCl, and KCl) and ferroelectric crystals

(BaTiO_3 and SrTiO_3).¹⁷ For nonferroelectric crystals, the calculated values of the flexoelectric coefficients were found to be in the range of 10^{-12} – 10^{-11} C/m, which are smaller than those estimated for e/a . For ferroelectrics, the results of the calculations are in agreement within an order of magnitude of the rough theoretical estimates and experimental data obtained for SrTiO_3 crystals.

The concept of flexoelectricity is also used in the context of atomically thin membranes, where the polarization induced by the membrane bending is considered. The flexoelectric coefficient now is defined as the ratio of the dipole moment per unit area over the bending curvature (to avoid confusion, the term membrane flexoelectric coefficient will be used). Here atomistic calculations have been performed for carbon systems (Dumitrica et al.¹⁸ and Kalinin and Meunier¹⁹) and boron nitride sheets (Naumov et al.²⁰). Kalinin and Meunier used density functional theory (DFT) calculations for carbon systems, including polyacetylene and nanographitic ribbons. The membrane flexoelectric coefficients were estimated to be on the order of $0.1e$, compared to typical flexoelectric coefficients in biological membranes of

$(0.1\text{--}10)e$, depending on the mechanism.²¹ Note that this value, after appropriately translated to contrast with the bulk flexoelectric coefficients, is consistent with the aforementioned estimate, e/a .

Electromechanical Coupling at Interfaces

In the bulk of a dielectric, the electric polarization can be influenced by three types of macroscopic perturbations: the macroscopic electric field, the elastic deformation field, and a temperature variation. The responses to these perturbations correspond to the dielectric polarizability and piezoelectric, flexoelectric, pyroelectric, and thermopolarization effects.⁸ At the same time, close to the interface of the dielectric with a metal or another material, the electric polarization can be induced by a direct action of the interface (via the short-range interatomic coupling), which cannot be classified in terms of the polarization interacting with macroscopic perturbations. This effect can be termed as an interface poling effect. Levanyuk and Minyukov²² introduced a Landau theory description of this effect by adding a term linear in polarization (P) to the surface contribution to the free energy of the system ΔF

$$\Delta F = \int \eta P dS, \quad (2)$$

where η is a material parameter depending on the properties of the interface, and the integration is performed over the surface of the latter. Since, in general, any interface breaks the inversion symmetry, such a contribution to the free energy is readily allowed by the symmetry. This approach was recently employed for the description of the dielectric and ferroelectric properties of thin-film ferroelectric capacitors.^{23,24} In a thin-film ferroelectric capacitor, a remarkable manifestation of this effect is that when the two ferroelectric/metal interfaces are not identical, the poling action of the interfaces is equivalent to a dc electric field in the ferroelectric, which is proportional to $(\eta_1 - \eta_2)/h$. Here the subscripts correspond to the two interfaces, and h is the thickness of the ferroelectric film. In thin ferroelectric films, this poling effect, in principle, can affect their properties, leading, for example, to a smearing of the dielectric anomaly at the ferroelectric phase transition and the appearance of the piezoelectric effect in an originally centrosymmetric material. A more detailed analysis of the problem revealed that in a thin-film ferroelectric capacitor, the ferroelectric is poled not only by the interface poling effect but also by the true electric field that appears

due to the difference of the work functions of the two nonequivalent metallic interfaces.²⁵

Tagantsev's group recently offered a multiscale approach to the description of the impact of the interfaces on the properties of a metal-ferroelectric-metal heterostructure.²⁵ This approach combines the first-principles and phenomenological frameworks. The poling effect of nonequivalent metal-ferroelectric interfaces has been evaluated for a $\text{SrRuO}_3/\text{BaTiO}_3/\text{SrRuO}_3$ system with ideally flat (001) interfaces containing different B-site (a site in the perovskite unit cell) ions (Ti or Ru) in the border layer. Figure 3 presents a result of modeling for this system: the thickness dependence of the induced piezoelectric coefficient in the paraelectric state of the material. It is clear from this figure that, at least in the case of atomically flat interfaces, even in thin films of readily affordable thicknesses, the interface poling effect can be appreciable.

The interface poling effect can also essentially affect the switching phenomena in ferroelectrics²⁶ (i.e., polarization reversal driven by application of an electric field). Within a matrix of oppositely polarized material, the switching is made possible by the appearance and growth of domains with reverse polarization. As in other ordered systems, such as ferromagnets or superfluids and Type II superconductors, the nucleation of such domains in a homogeneous, defect-free material is associated with impracticably high energy barriers. Defects lower this barrier. In this context, the progress in understanding the ferroelectric switching is tightly related to that of the role of defects in the reverse domain nucleation. The poling effect of the interface that can be viewed as a planar defect makes one or a few of the polarization directions preferable and can substantially facilitate the polarization reversal. Estimates show that this effect may provide a reduction of the nucleation energy down to values corresponding to realistic switching rates, in the range from microseconds to minutes. Another interesting feature of the switching mechanism stimulated by the surface poling effect is that, in this case, the applied field can fully suppress the nucleation barrier so that reverse domain nucleation does not require thermal assistance.

Another issue associated with the behavior of the polarization at the interface is the screening ability of the ferroelectric/electrode interface. This issue is linked to the fact that the textbook wisdom, "Electric field in a short-circuited capacitor is zero," is not strictly speaking correct. When a short-circuited capacitor

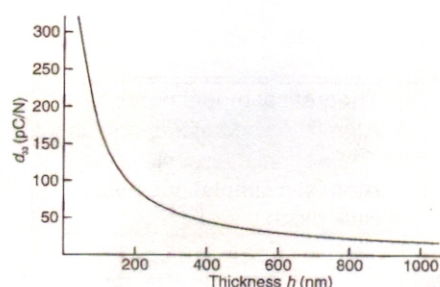


Figure 3. Termination asymmetry-induced piezoelectric coefficient d_{33} calculated for a temperature that is 50 K higher than the temperature of the ferroelectric phase transition. The effect was evaluated for an asymmetrically terminated BaTiO₃ film epitaxially grown between SrRuO₃ electrodes under 2% compressive in-plane strain. It is seen that in thin films of readily affordable thicknesses (200 nm), the interface poling effect can induce piezoelectric coefficients of practical interest (100 pC/N). Adapted from Gerra et al.²⁴

is charged, which is often the case for ferroelectric capacitors, the center of gravity of both the free charges at the electrode and the bound charges at the surface of the ferroelectric are displaced with respect to each other. First and foremost, this happens because of the thickness of the layer of the free chargers in the metal at the metal/ferroelectric interface, which is finite being about the so-called Thomas-Fermi screening length. As a result of this separation, two double electric layers form at the ferroelectric/electrode interfaces. When the capacitor is short-circuited, the voltage drop across these double electric layers is applied to the ferroelectric. This voltage drop characterizes the "screening quality" of the ferroelectric/electrode interface. Clearly, the parasitic field in the ferroelectric associated with this effect increases with decreasing film thickness. In view of the modern trend of miniaturization with the use of progressively thinner ferroelectric layers in applications, this voltage is undesirable. It was recently demonstrated using first principles calculations that the arrangement of the ionic polarization at the interface between a ferroelectric and conductive oxide can improve the screening ability of a ferroelectric/metal interface. Specifically, the ionic displacements, which control the polarization in the ferroelectric, can also occur inside the conductive oxide of the electrode. Results of modeling the $\text{SrRuO}_3/\text{BaTiO}_3/\text{SrRuO}_3$ system is presented in Figure 4.²⁴ At such an interface, the bound charge associated

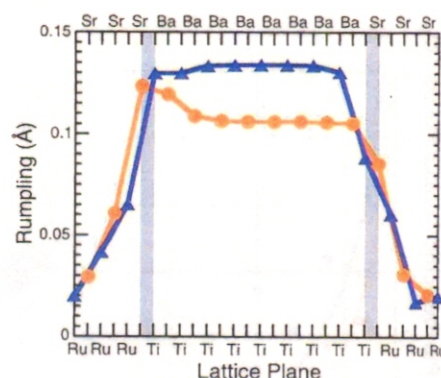


Figure 4. The rumpling (i.e., the cation-oxygen relative displacement within each (001) atomic layer) profiles obtained by full minimization of the total energy of the system for a $\text{SrRuO}_3/\text{BaTiO}_3/\text{SrRuO}_3$ heterostructure with eight monolayers of BaTiO_3 . This is the result of zero-Kelvin density-functional calculations for the stack, which is under a 2% compressive in-plane strain. It is seen that the ionic displacements, which control the polarization in the ferroelectric, can also occur inside the conductive oxide of the electrode. Thus, the bound charge associated with the variation of the ionic polarization at the interface is essentially shifted inside the electrode, where it can be screened *in situ* by its free carriers. This improves the screening ability of the electrode. Adapted from Gerra et al.²⁶

with the variation of the ionic polarization at the interface is essentially shifted inside the electrode, where it can be screened *in situ* by its free carriers. The result is an improvement (compared to the situation where the ionic displacements cannot go inside the electrode) of the "screening quality" of the ferroelectric/electrode interface, which manifests itself in improved ferroelectric and dielectric performance of the capacitor.^{27,28}

Conclusions and Open Issues

The discussion of flexoelectricity presented here clearly shows that further development in this area is likely to spur exploration into both the basic scientific underpinnings of these materials and development toward device applications. Indeed, various open issues remain: (1) relationship of flexoelectricity to polarization gradient theory;²⁹ (2) experimental demonstration of flexoelectricity-based devices; (3) interplay between flexoelectric and surface effects; and (4) the reconciliation of atomistically predicted flexoelectric properties and experimental results in ferroelectrics.