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Flexoelectric properties of ferroelectrics and the nanoindentation size-effect

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ABSTRACT

Recent works have established the critical role of flexoelectricity in a variety of size-dependent physical phenomena related to ferroelectrics including giant piezoelectricity at the nanoscale, dead-layer effect in nanocapacitors, dielectric properties of nanostructures among others. Flexoelectricity couples strain gradients to polarization in both ordinary and piezoelectric dielectrics. Relatively few experimental works exist that have determined flexoelectric properties and they all generally involve some sort of bending tests on micro-specimens. In this work, we present a straightforward method based on nanoindentation that allows the evaluation of flexoelectric properties in a facile manner. The key contribution is the development of an analytical model that, in conjunction with indentation load–displacement data, allows an estimate of the flexoelectric constants. In particular, we confirm the experimental results of other groups on $BaTiO_3$ which differ by three orders of magnitude from atomistic predictions. Our analytical model predicts (duly confirmed by our experiments) a strong indentation size-effect due to flexoelectricity.

1. Introduction

Piezoelectricity exists only in non-centrosymmetric crystals. However, a somewhat under-appreciated fact is that all dielectrics polarize when subjected to inhomogeneous strain. This phenomenon, the coupling of strain gradients to polarization, is known as flexoelectricity. Phenomenologically, the total polarization can be expressed as:

$$P_i = \underbrace{d_{ijk}\varepsilon_{jk}}_{=0,\ for\ centrosymmetric\ materials} + \mu_{ijkl}\frac{\partial \varepsilon_{jk}}{\partial x_l}. \quad (1)$$

Recently, flexoelectricity has generated much excitement due to the elucidation of several insights relevant at the nanoscale. For example, Catalan et al. (2004) have studied the impact of flexoelectricity on the dielectric properties and Curie temperature of ferroelectric materials while Cross and coworkers (1999, 2006) have proposed tantalizing notions such as "piezoelectric composites without using piezoelectric materials". Eliseev et al. (2009) have investigated the renormalization of properties of ferroelectric nanostructures due to the spontaneous flexoelectric effect as well as developed analytical approaches to derive size-effects in such nanostructures (Eliseev and Morozovska, 2009). One of us has demonstrated strong size-dependent enhancement of the apparent piezoelectric coefficient in materials that are intrinsically piezoelectric (Majdoub et al., 2008a, 2009b) as well as explored ramifications for energy harvesting (Majdoub et al., 2008b, 2009c). More recently Majdoub et al. (2009a) have also demonstrated, through first principles and theoretical calculations, that the so-called dead-layer effect in nanocapacitors may be strongly influenced by flexoelectricity. The reader is referred to reviews by Tagantsev (1986, 1991), Tagantsev et al. (2009) for further details.

Relatively few experimental works exists on the determination of flexoelectric properties of crystals. Cross and co-worker's pioneering work provided some of the first data on various perovskites like PMN, PZT, BST, and $BaTO_3$ (Ma and Cross, 2001, 2002, 2003, 2006; Fu et al., 2006, 2007). More, recently Zubko et al. (2007) have published the experimental characterization of the complete flexoelectric tensor for $SrTiO_3$. The afore-mentioned experimental approaches are predicated on bending experiments and are decidedly non-trivial. In parallel, various groups have also made atomistic predictions of flexoelectric properties. For example, one of us (Maranganti and Sharma, 2009) presented results for a number of dielectrics of technological and scientific interest. Dumitrica et al. (2002), Kalinin and Meunier (2008) discuss graphene and very recently, Hong et al. (2010) presented a first principles approach and consequent data for both $SrTiO_3$ and $BaTO_3$. While the theoretical works of various groups are all in agreement, the experimentally estimated flexoelectric constant of $BaTO_3$ is 3 orders of magnitude higher compared to the atomistically predicted value. The reasons for this discrepancy are still an open research issue (and beyond the scope of the present paper).

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In this paper, we present a nano-indentation based methodology to extract flexoelectricity properties of dielectrics. The key contribution is the development of an analytical model of indentation of a ferroelectric surface duly incorporating both piezoelectricity and flexoelectricity. This analytical model can then be used with rather easily generated load–displacement data to extract the desired properties. The outline of the paper is as follows: in Section 2, we present the mathematical problem followed by an approximate analytical solution. Experimental work is described in Section 3 and our major results are presented in Section 4. Implications of the present work, including the identification of the indentation size-effect due to flexoelectricity are discussed in Section 5 where we also summarize our conclusions. Some initial results on the indentation size-effects were communicated earlier by us in a rapid communication (Gharbi et al., 2009).

2. Indentation problem for piezoelectric-flexoelectric half-space

We consider the indentation of a transversely isotropic material by a circular flat indenter of radius a as shown in Fig. 1. Recently, Kalinin et al. (2004), Karapetian et al. (2005), have developed closed form solutions for piezoelectric half-space indentation problem for the cases of flat, spherical and conical indenters using the correspondence principle (Karapetian et al., 2002). The objective of this section is to present the mathematical development leading to expressions that inter-relate applied concentrated force P, concentrated charge Q, indentation depth w and tip potential ψ_0.

According to Majdoub et al. (2008a), the governing equations of a continuum with simultaneous presence of piezoelectricity and flexoelectricity valid for a dielectric occupying a volume V bounded by a surface S in a vacuum V' are:

$$\begin{aligned} &\nabla\cdot\sigma + f = \rho\ddot{u} \text{ where } \sigma = c:S + d\cdot P + (e-f):\nabla P \text{ in } V,\\ &\overline{E} + \nabla\cdot\widetilde{E} - \nabla\varphi + E^0 = 0 \text{ in } V,\\ &-\varepsilon_0\Delta\varphi + \nabla\cdot P = 0 \text{ in } V\\ &\Delta\varphi = 0 \text{ in } V', \end{aligned} \quad (2)$$

where

$$\begin{aligned} &-\overline{E} = a\cdot P + g:\nabla P + f:\nabla\nabla u + d:S,\\ &\widetilde{E} = b:\nabla P + e:S + g\cdot P. \end{aligned}$$

The second order tensor a is the reciprocal dielectric susceptibility and the fourth order tensor c is the elastic tensor. d and f are the third order piezoelectric tensor and the fourth order flexoelectric tensor respectively. The fourth order tensor b is the polarization gradient–polarization gradient coupling tensor. The fourth order tensor e corresponds to polarization gradient and strain coupling and g is the polarization-polarization gradient coupling tensor. For sake of simplicity, we note the term $(f-e)$ by f in the rest of our theoretical development.

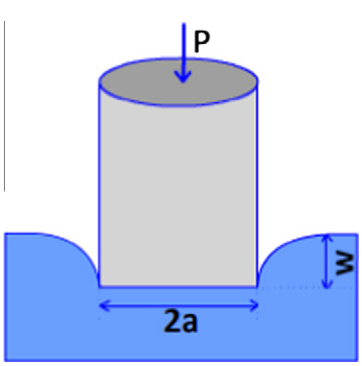

Fig. 1. Schematic of a transversely isotropic medium indented by circular flat indenter.

The corresponding boundary conditions are:

$$\begin{aligned} &\sigma.n = t,\\ &\widetilde{E}.n = 0,\\ &(-\varepsilon_0\|\varphi\| + P)\cdot n = 0. \end{aligned} \quad (3)$$

In anticipation of eventually applying perturbation theory to solve the rather complicated boundary value problem stated above, we define that for any $i,j = 1,2,3,\ q = \frac{q_1}{a} = \frac{f_{ij}}{ad^*}$, where $\left(d^* = \frac{|d_{15}|+|d_{31}|+|d_{33}|}{3}\right)$. Then, constitutive equations for the case of transversely isotropic material may be explicitly written as follows:

$$\frac{\sigma_{ij}}{ad^*} = \frac{C_{ijkl}}{ad^*}S_{kl} + \varepsilon_0^{-1}\frac{d_{kij}}{ad^*}P_k - q\varepsilon_0^{-1}P_{l,k}, \quad (4)$$

$$\frac{D_i}{ad^*} = \frac{d_{ikl}}{ad^*}S_{kl} - \varepsilon_0^{-1}\frac{a_{ik}}{ad^*}P_k + qS_{kl,j}.$$

We re-write equilibrium equations $\partial\sigma_{ij}/\partial x_i = 0$ and equation of electrostatics $\partial D_i/\partial x_i = 0$ to obtain a system of four equations for displacements u_x, u_y, u_z and polarizations P_x, P_y and P_z.

$$\frac{C_{ijkl}}{ad^*}S_{kl,i} + \varepsilon_0^{-1}\frac{d_{kij}}{ad^*}P_{k,i} - q\varepsilon_0^{-1}P_{l,ki} = 0, \quad (5)$$

$$\frac{d_{ikl}}{ad^*}S_{kl,i} - \varepsilon_0^{-1}\frac{a_{ik}}{ad^*}P_{k,i} + qS_{kl,ji} = 0.$$

The remaining equation is:

$$P_{i,i} - \varepsilon_0\psi_{,ii} = 0. \quad (6)$$

2.1. Solution of the problem for the case of circular flat indenter

The complexity of the above equations precludes an exact solution. We employ the perturbation approach, as (for example) used quite successfully by Holmes in a different context Holmes (1995).The present boundary value problem is a singular perturbation problem and accordingly, we separately present both "inner" and "outer" solutions.

2.1.1. Outer solution

The perturbation expansion is carried out in terms of the small parameter q.:

$$\begin{aligned} &u_x^{outer} = u_x^0 + o(q), \quad u_y^{outer} = u_y^0 + o(q),\\ &u_z^{outer} = u_z^0 + o(q), \quad P_x^{outer} = P_x^0 + o(q),\\ &P_y^{outer} = P_y^0 + o(q), \quad P_z^{outer} = P_z^0 + o(q). \end{aligned} \quad (7)$$

For purely mechanical problem (zero electrical conditions, $\psi = 0$ for $(0 \leqslant \rho \prec \infty)$ the boundary conditions are:

$$\begin{aligned} &u_z^{outer} = w \text{ for } 0 \leqslant \rho < a,\\ &\sigma_{zz}^{outer} = 0 \text{ for } \rho > a,\\ &\tau_z^{outer} = 0 \text{ for } 0 \leqslant \rho < \infty. \end{aligned} \quad (8)$$

For purely electrical problem (zero mechanical conditions, $u_z = 0$ for $(0 \leqslant \rho \prec \infty)$:

$$\begin{aligned} &\psi^{outer} = \psi_0 \text{ for } 0 \leqslant \rho < a,\\ &D_z^{outer} = 0 \text{ for } \rho \succ a. \end{aligned} \quad (9)$$

Inserting (7) into (5) and considering the leading order terms only, we obtain the outer system of equations. This corresponds to $q = 0$ (absence of flexoelectricity)—i.e., the case of a purely piezoelectric material solved exactly by Karapetian et al. (2005). For the sake of completeness, Karapetian et. al.'s solution is summarized in