The origins of electromechanical indentation size effect in ferroelectrics
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**Working Definition of Piezoelectricity**

A *uniform* strain causes polarization and vice-versa

\[ P_i = d_{ijk} \varepsilon_{jk} \]

Odd order tensor cannot be sustained by centrosymmetric crystal—hence piezoelectricity is restricted to non-centrosymmetric crystals

**Beyond Uniform Strain and Polarization----Flexoelectricity**

\[ P_i = d_{ijk} \varepsilon_{jk} + \mu_{ijkl} \frac{\partial \varepsilon_{jk}}{\partial x_l} \]

In principle, flexoelectric coefficients are non-zero for all dielectrics (although may be negligibly small in some cases)—experimentally verified for many materials!

The curvature of CNT results in rehybridization of p-orbital. As a result, the center of electronic charge at each atomic site is displaced outwards from the nuclear charge.

**Theoretical Results: A regular piezoelectric material**

[Karapetian, Kachanov, Kalinin and co-workers]

Purely mechanical loading on an anisotropic piezoelectric material

\[ P = \frac{2aC_1}{\pi} w + \frac{2aC_2}{\pi} \psi_0 \]

For example, in the isotropic purely elastic half-space case (Oliver, Pharr)

\[ C_1 = \pi E_r \]

\[ s = \frac{\partial P}{\partial w} = \frac{2a}{\pi} C_1 \]

**Theoretical results: Effect of flexoelectricity on indentation**

We derived analytical solution of the indentation problem incorporating anisotropy, piezoelectricity and flexoelectricity----the solution fills 14 pages!

\[ s = \frac{\partial P}{\partial w} = \frac{2a}{\pi} C_1 - \frac{2C_3}{\pi a} \left( \delta e \frac{A}{A} - \delta + Aa \right) \]

**Indentation experiments**

In parallel, we conducted experiments with varying indentation size…..single crystal BaTiO₃

Berkovich indent on BTO surface: Load: 8mN; Depth into surface: 200nm

**Contact stiffness vs contact radius for BaTiO₃**

• Indentation experiments indicate a large size effect (see the star-data points). For example, compared to the size-independent behavior (red line), around 10 nm, there is a doubling of contact stiffness.

• Incorporation of flexoelectricity correctly captures the size-effect

• Another possible source of size-effect dislocation activity

**Contact stiffness vs contact radius for Quartz**

• No size-effect is observed for Quartz!

• This observation strengthens our argument that flexoelectricity is the cause of indentation size-effect since Quartz has very small flexoelectricity constants (in contrast to BaTiO₃) while the dislocation nucleation behavior between the two is not expected to be dramatically different.