

Surface Electric Gibbs Free Energy and Its Effect on the Electromechanical Behavior of Nano-Dielectrics

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Abstract: This paper considers the surface effect through the surface and bulk electric Gibbs free energy. The analytical expressions are derived for the effective elastic, dielectric and piezoelectric modulus for nano-structural elements in electromechanical coupling problems. Numerical examples for PZT are given to illustrate the size effects on the electromechanical properties of nano-particles, nano-wires and nano-films quantitatively. The solution shows that the electromechanical properties of piezoelectric nano-material are size-dependent but the size effects on the elastic property and dielectric property are different.

Keywords: Electric Gibbs free energy; Surface effect; Surface stress; Surface polarization

1 Introduction

When the size of the structure element reduces, even to nanometer scale, the properties of the material will be different from the ones in macroscopic scale, which is called size effect. For the elastic material, the size effect on the elastic properties of nano-sized structure element has been studied by many researchers. Zhou and Huang (2004) employed molecular dynamic simulations to demonstrate that the effective elastic modulus of a thin free-standing film can either increase or decrease as the film thickness decreases depending upon the crystallographic orientations. Sharma et al. (2003) investigated the deformation around a spherical nanoinhomogeneity. Yang (2004) derived the effective modulus of elastic materials with nano-voids. Dingreville et al. (2005) developed a framework to incorporate the surface free energy into the continuum theory of mechanics, and then they demonstrated that the overall elastic behavior of structural elements (such as particles, wires, films) is size-dependent.

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For dielectrics, the surface effect includes both surface stress and surface polarization which is induced due to the dangling bonds on the surface. The rearrangement of the bonding at surfaces causes a charge displacement that may greatly affect the polarization properties of the surface with respect to the bulk (Brandino and Cicero, 2007). In Slavchov *et al.* (2006), the effect of the surface polarization was studied with the help of a definition of surface dielectric constants for surface. The effect of the surface polarization in polar perovskites was investigated by means of the first principles in Fechner *et al.* (2008). Camacho and Nossa (2009) showed that the influences of surface polarization on the dielectric properties of quantum dots arrays are significant. The electric Gibbs free energy variational principle has been established with the strain/electric field gradient effects, as well as the effects of surface and electrostatic force (Hu and Shen, 2009). The flexoelectric effect has also been investigated with the surface effects and the electrostatic force (Shen and Hu, 2010; Hu and Shen, 2010). The electromechanical behavior of dielectrics is characterized by its elastic, dielectric and piezoelectric modulus. For nano-sized dielectrics, the ratio of surface area to volume becomes high, so the surface polarization and stress turn out to be significant when considering the overall electromechanical behavior of nano-sized structural elements. Consequently, the effective elastic, dielectric and piezoelectric modulus of nano-sized structural elements should be considered, and become size-dependent. It is necessary to develop a theoretical framework to investigate the effects of surface electric Gibbs free energy on the effective electromechanical modulus of nano-sized dielectrics, which can be considered as the extension of the elastic framework in Dingreville *et al.* (2005) to piezoelectric materials .

In this paper, the surface effect is taken into account, through the surface and bulk electric Gibbs free energy. The analytical expressions are derived for the effective elastic, dielectric and piezoelectric modulus for nano-structural elements in electromechanical coupling problems such as nano-particles, nano-wires and nano-films. The size dependency of the overall elastic, dielectric and piezoelectric modulus of such nano-sized structural elements is investigated.

2 Electric Gibbs free energy

The local environment of the atoms on the free surface is different from that of the ones in the bulk, so does the energy of them. The excess energy of the surface atoms is called the surface free energy (Dingreville *et al.*, 2005). In this paper, we consider the electric Gibbs free energy by choosing the strain and the electric field as the independent variables. The surface electric Gibbs free energy density can be defined as the reversible work involved in creating a unit area of new surface obtained from an isothermal, isobaric thermodynamic system. Consider a repre-

sentative volume near the free surface of a bulk dielectric crystal, and assume the surface is flat and homogeneous. Similar to Dingreville et al. (2005), in an area A_0 in the undeformed configuration, the Lagrange description of the surface electric Gibbs free energy density can be defined as

$$\Gamma = \frac{1}{A_0} \sum_{n=1}^N w_n, \quad (1)$$

where N is the amount of atoms underneath the area A_0 . w_n is the surface electric Gibbs free (excess) energy of near-surface atom n defined by the difference between its total electric Gibbs free energy and that of an atom deep in the interior of a large bulk crystal, which depends on the location of the atom.

Assuming the surface electric Gibbs free energy density Γ is a smooth function of the surface strain and the surface electric-field, then it can be expanded as follow,

$$\begin{aligned} \Gamma(\boldsymbol{\varepsilon}_{\alpha\beta}^S, E_\xi^S) &= \Gamma_0 + \frac{\partial\Gamma}{\partial\boldsymbol{\varepsilon}_{\alpha\beta}^S} \boldsymbol{\varepsilon}_{\alpha\beta}^S + \frac{\partial\Gamma}{\partial E_\xi^S} E_\xi^S + \\ &\quad \frac{1}{2} \frac{\partial^2\Gamma}{\partial\boldsymbol{\varepsilon}_{\alpha\beta}^S \partial\boldsymbol{\varepsilon}_{\kappa\lambda}^S} \boldsymbol{\varepsilon}_{\alpha\beta}^S \boldsymbol{\varepsilon}_{\kappa\lambda}^S + \frac{\partial^2\Gamma}{\partial\boldsymbol{\varepsilon}_{\alpha\beta}^S \partial E_\xi^S} \boldsymbol{\varepsilon}_{\alpha\beta}^S E_\xi^S + \frac{1}{2} \frac{\partial^2\Gamma}{\partial E_\xi^S \partial E_\psi^S} E_\xi^S E_\psi^S + \\ &\quad \frac{1}{6} \frac{\partial^3\Gamma}{\partial\boldsymbol{\varepsilon}_{\alpha\beta}^S \partial\boldsymbol{\varepsilon}_{\kappa\lambda}^S \partial\boldsymbol{\varepsilon}_{\gamma\eta}^S} \boldsymbol{\varepsilon}_{\alpha\beta}^S \boldsymbol{\varepsilon}_{\kappa\lambda}^S \boldsymbol{\varepsilon}_{\gamma\eta}^S + \frac{1}{2} \frac{\partial^3\Gamma}{\partial\boldsymbol{\varepsilon}_{\alpha\beta}^S \partial\boldsymbol{\varepsilon}_{\kappa\lambda}^S \partial E_\xi^S} \boldsymbol{\varepsilon}_{\alpha\beta}^S \boldsymbol{\varepsilon}_{\kappa\lambda}^S E_\xi^S + \\ &\quad \frac{1}{2} \frac{\partial^3\Gamma}{\partial\boldsymbol{\varepsilon}_{\alpha\beta}^S \partial E_\xi^S \partial E_\psi^S} \boldsymbol{\varepsilon}_{\alpha\beta}^S E_\xi^S E_\psi^S + \frac{1}{6} \frac{\partial^3\Gamma}{\partial E_\xi^S \partial E_\psi^S \partial E_\delta^S} E_\xi^S E_\psi^S E_\delta^S \quad (2) \\ &= \Gamma_0 + \Gamma_{\alpha\beta}^{(1)} \boldsymbol{\varepsilon}_{\alpha\beta}^S + \Lambda_\xi^{(1)} E_\xi^S + \frac{1}{2} \Gamma_{\alpha\beta\kappa\lambda}^{(2)} \boldsymbol{\varepsilon}_{\alpha\beta}^S \boldsymbol{\varepsilon}_{\kappa\lambda}^S + \Pi_{\alpha\beta\xi}^{(2)} \boldsymbol{\varepsilon}_{\alpha\beta}^S E_\xi^S + \\ &\quad \frac{1}{2} \Lambda_{\xi\psi}^{(2)} E_\xi^S E_\psi^S + \frac{1}{6} \Gamma_{\alpha\beta\kappa\lambda\gamma\eta}^{(3)} \boldsymbol{\varepsilon}_{\alpha\beta}^S \boldsymbol{\varepsilon}_{\kappa\lambda}^S \boldsymbol{\varepsilon}_{\gamma\eta}^S + \frac{1}{2} \Pi_{\alpha\beta\kappa\lambda\xi}^{(3)} \boldsymbol{\varepsilon}_{\alpha\beta}^S \boldsymbol{\varepsilon}_{\kappa\lambda}^S E_\xi^S + \\ &\quad \frac{1}{2} \Xi_{\alpha\beta\xi\psi}^{(3)} \boldsymbol{\varepsilon}_{\alpha\beta}^S E_\xi^S E_\psi^S + \frac{1}{6} \Lambda_{\xi\psi\delta}^{(3)} E_\xi^S E_\psi^S E_\delta^S \end{aligned}$$

where $\boldsymbol{\varepsilon}_{\alpha\beta}^S$ is the Lagrange surface strain relative to the undeformed crystal lattice, and E_α^S is the Lagrange surface electric field. In the later, we will denote the bulk Lagrange strain and electric field as $\boldsymbol{\varepsilon}_i$ and E_i respectively. In this paper, Roman indices range from 1 to 3 and Greek indices range from 1 to 2, unless otherwise indicated. Γ_0 , $\Gamma_{\alpha\beta}^{(1)}$, $\Lambda_\xi^{(1)}$, $\Gamma_{\alpha\beta\kappa\lambda}^{(2)}$, \dots are material and surface dependent, which can be either measured experimentally or computed using atomistic simulations for a given material surface. Higher order items are neglected here.

By using differential relation between surface stress, surface electric displacement and surface electric Gibbs free energy density, the expressions of surface stress and

surface electric displacement can also be obtained,

$$\begin{aligned}\sigma_{\alpha\beta}^S &= \frac{\partial\Gamma}{\partial\varepsilon_{\alpha\beta}^S} = \Gamma_{\alpha\beta}^{(1)} + \Gamma_{\alpha\beta\kappa\lambda}^{(2)}\varepsilon_{\kappa\lambda}^S + \Pi_{\alpha\beta\xi}^{(2)}E_{\xi}^S + \frac{1}{2}\Gamma_{\alpha\beta\kappa\lambda\gamma\eta}^{(3)}\varepsilon_{\kappa\lambda}^S\varepsilon_{\gamma\eta}^S \\ &\quad + \Pi_{\alpha\beta\kappa\lambda\xi}^{(3)}\varepsilon_{\kappa\lambda}^SE_{\xi}^S + \frac{1}{2}\Xi_{\alpha\beta\xi\psi}^{(3)}E_{\xi}^SE_{\psi}^S \\ D_{\xi}^S &= -\frac{\partial\Gamma}{\partial E_{\xi}^S} = -\Lambda_{\xi}^{(1)} - \Pi_{\alpha\beta\xi}^{(2)}\varepsilon_{\alpha\beta}^S - \Lambda_{\xi\psi}^{(2)}E_{\psi}^S - \frac{1}{2}\Pi_{\alpha\beta\kappa\lambda\xi}^{(3)}\varepsilon_{\alpha\beta}^S\varepsilon_{\kappa\lambda}^S \\ &\quad - \Xi_{\alpha\beta\xi\psi}^{(3)}\varepsilon_{\alpha\beta}^SE_{\psi}^S - \frac{1}{2}\Lambda_{\xi\psi\delta}^{(3)}E_{\psi}^SE_{\delta}^S\end{aligned}\quad (3)$$

In these expressions, $\Gamma_{\alpha\beta}^{(1)}$ and $\Lambda_{\xi}^{(1)}$ give, respectively, the residual stress and the residual electric displacement on the free surface respectively, and they present the surface stress and the surface electric displacement when the surface strain and the surface electric-field do not exist. The two-dimensional fourth-order tensor $\Gamma_{\alpha\beta\kappa\lambda}^{(2)}$ presents the surface elasticity tensor, $\Lambda_{\xi\psi}^{(2)}$ presents the surface dielectric tensor, and $\Pi_{\alpha\beta\xi}^{(2)}$ presents the surface piezoelectric tensor. The two-dimensional sixth-order tensor $\Gamma_{\alpha\beta\kappa\lambda\gamma\eta}^{(3)}$ can be viewed as the tensor of the third-order elastic constants of the surface, $\Lambda_{\xi\psi\delta}^{(3)}$ can be viewed as the tensor of the third-order dielectric constants of the surface, $\Pi_{\alpha\beta\kappa\lambda\xi}^{(3)}$ and $\Xi_{\alpha\beta\xi\psi}^{(3)}$ can be viewed as the tensor of the third-order piezoelectric constants of the surface.

Since the surface stress and surface electric displacement are obtained, the surface electric Gibbs free energy can be derived by

$$U_{surface} = \int_{S_0} \left[\int_0^{\varepsilon_{\alpha\beta}^S} \sigma_{\alpha\beta}^S d\varepsilon_{\alpha\beta} \right] dS_0 + \int_{S_0} \left[\int_0^{E_{\xi}^S} D_{\xi}^S dE_{\xi} \right] dS_0. \quad (4)$$

Substituting Eq. (3) into Eq. (4), we have

$$\begin{aligned}U_{surface} &= \int_{S_0} \left[\Gamma_{\alpha\beta}^{(1)}\varepsilon_{\alpha\beta}^S + \Lambda_{\xi}^{(1)}E_{\xi}^S + \frac{1}{2}\Gamma_{\alpha\beta\kappa\lambda}^{(2)}\varepsilon_{\alpha\beta}^S\varepsilon_{\kappa\lambda}^S + 2\Pi_{\alpha\beta\xi}^{(2)}\varepsilon_{\alpha\beta}^SE_{\xi}^S \right. \\ &\quad \left. + \frac{1}{2}\Lambda_{\xi\psi}^{(2)}E_{\xi}^SE_{\psi}^S + \frac{1}{6}\Gamma_{\alpha\beta\phi\lambda\gamma\eta}^{(3)}\varepsilon_{\alpha\beta}^S\varepsilon_{\kappa\lambda}^S\varepsilon_{\gamma\eta}^S + \Pi_{\alpha\beta\kappa\lambda\xi}^{(3)}\varepsilon_{\alpha\beta}^S\varepsilon_{\kappa\lambda}^SE_{\xi}^S \right. \\ &\quad \left. + \Xi_{\alpha\beta\xi\psi}^{(3)}\varepsilon_{\alpha\beta}^SE_{\xi}^SE_{\psi}^S + \frac{1}{6}\Lambda_{\xi\psi\delta}^{(3)}E_{\xi}^SE_{\psi}^SE_{\delta}^S \right] dS_0\end{aligned}\quad (5)$$

Consider a particle in a spherical coordinate, by using the coordinate transformation the relationship between the surface tensors and the bulk tensors can be written as

(Dingreville et al., 2005)

$$\varepsilon_{\alpha\beta}^S = t_{\alpha i} t_{\beta j} \varepsilon_{ij} |_S, \quad (6)$$

$$E_{\xi}^S = t_{\xi n} E_n |_S, \quad (7)$$

where the t_{ij} is the transformation matrix which is given by

$$[t_{ij}] = \begin{bmatrix} \frac{a}{cd_1 d_2} \cos \theta \cos \phi & \frac{a^2}{bcd_1 d_2} \sin \theta \cos \phi & -\frac{d_2}{d_1} \sin \phi \\ -\frac{a}{bd_2} \sin \theta & \frac{1}{d_2} \cos \theta & 0 \\ \frac{1}{d_2} \sin \phi \cos \theta & \frac{a}{bd_1} \sin \phi \sin \theta & \frac{a}{cd_1} \cos \phi \end{bmatrix}$$

where a , b and c are the semi-axes of the ellipsoid while $a \leq b \leq c$, and

$$d_1 = \sqrt{\cos^2 \theta \sin^2 \phi + \frac{a^2}{b^2} \sin^2 \theta \sin^2 \phi + \frac{a^2}{c^2} \cos^2 \phi},$$

$$d_2 = \sqrt{\frac{a^2}{b^2} \sin^2 \theta + \cos^2 \theta}.$$

Then the surface electric Gibbs free energy stored on the whole surface of the particle is

$$\begin{aligned} U_{surface} = & \frac{V_0}{a} \tau_{ij} \varepsilon_{ij} + \frac{V_0}{2a} Q_{ijkl} \varepsilon_{ij} \varepsilon_{kl} + \frac{V_0}{6a} P_{ijklpq} \varepsilon_{ij} \varepsilon_{kl} \varepsilon_{pq} + \frac{V_0}{a} e_n E_n + \frac{V_0}{2a} W_{nm} E_n E_m + \\ & \frac{V_0}{6a} V_{nmr} E_n E_m E_r + \frac{2V_0}{a} X_{ijn} \varepsilon_{ij} E_n + \frac{V_0}{a} Y_{ijnm} \varepsilon_{ij} E_n E_m + \frac{V_0}{a} Z_{ijkln} \varepsilon_{ij} \varepsilon_{kl} E_n \end{aligned} \quad (8)$$

where the tensors in Eq.(8) are defined as

$$\tau_{ij} = \frac{a}{V_0} \int_{S_0} \Gamma_{\alpha\beta}^{(1)} t_{\alpha i} t_{\beta j} dS_0,$$

$$Q_{ijkl} = \frac{a}{V_0} \int_{S_0} \Gamma_{\alpha\beta\kappa\lambda}^{(2)} t_{\alpha i} t_{\beta j} t_{\kappa k} t_{\lambda l} dS_0,$$

$$e_n = \frac{a}{V_0} \int_{S_0} \Lambda_{\xi}^{(1)} t_{\xi n} dS_0,$$

$$W_{nm} = \frac{a}{V_0} \int_{S_0} \Lambda_{\xi\psi}^{(2)} t_{\xi n} t_{\psi m} dS_0,$$

$$V_{nmr} = \frac{a}{V_0} \int_{S_0} \Lambda_{\xi\psi\delta}^{(3)} t_{\xi n} t_{\psi m} t_{\delta r} dS_0,$$

$$X_{ijn} = \frac{a}{V_0} \int_{S_0} \Pi_{\alpha\beta\xi}^{(2)} t_{\alpha i} t_{\beta j} t_{\xi n} dS_0,$$

$$P_{ijklpq} = \frac{a}{V_0} \int_{S_0} \Gamma_{\alpha\beta\phi\lambda\gamma\eta}^{(3)} t_{\alpha i} t_{\beta j} t_{\kappa k} t_{\lambda l} t_{\gamma p} t_{\eta q} dS_0,$$

$$Y_{ijnm} = \frac{a}{V_0} \int_{S_0} \Xi_{\alpha\beta\zeta\psi}^{(3)} t_{\alpha i} t_{\beta j} t_{\zeta n} t_{\psi m} dS_0,$$

$$Z_{ijkln} = \frac{a}{V_0} \int_{S_0} \Pi_{\alpha\beta\kappa\lambda\xi}^{(3)} t_{\alpha i} t_{\beta j} t_{\kappa k} t_{\lambda l} t_{\xi n} dS_0.$$

The total electric Gibbs free energy is made up by the surface electric Gibbs free energy and the electric Gibbs free energy in the bulk of the material as

$$U = U_{surface} + U_{bulk}, \quad (9)$$

where the U_{bulk} can be obtained by

$$U_{bulk} = \int_{V_0} \int_0^{\epsilon_{ij}} \frac{\partial \Phi}{\partial e_{ij}} de_{ij} dV_0 + \int_{V_0} \int_0^{E_n} \frac{\partial \Phi}{\partial e_n} de_n dV_0, \quad (10)$$

where Φ is the electric Gibbs potential in the bulk. After expanding it into a series of bulk strain and bulk electric field, we got

$$\begin{aligned} \Phi = & \frac{1}{2} c_{ijkl} \epsilon_{ij} \epsilon_{kl} - \frac{1}{2} a_{nm} E_n E_m - d_{ijn} \epsilon_{ij} E_n + \frac{1}{6} c_{ijklpq}^{(3)} \epsilon_{ij} \epsilon_{kl} \epsilon_{pq} - \\ & \frac{1}{6} a_{nmr}^{(3)} E_n E_m E_r - \frac{1}{2} s_{ijnm}^{(3)} \epsilon_{ij} E_n E_m - \frac{1}{2} d_{ijkln}^{(3)} \epsilon_{ij} \epsilon_{kl} E_n + \dots \end{aligned} \quad (11)$$

where c_{ijkl} and $c_{ijklpq}^{(3)}$ are, respectively, the second- and third-order elastic constants of the material, and a_{nm} and $a_{nmr}^{(3)}$ are, respectively, the second- and third-order dielectric constants, d_{ijn} is the second-order piezoelectric coefficient, $s_{ijnm}^{(3)}$ and $d_{ijkln}^{(3)}$ are third-order piezoelectric coefficients.

Substituting Eq. (11) into Eq. (10) with neglecting the higher order terms, one has

$$U_{bulk} = \int_{V_0} \left[\frac{1}{2} c_{ijkl} \varepsilon_{ij} \varepsilon_{kl} - \frac{1}{2} a_{nm} E_n E_m - 2d_{ijn} \varepsilon_{ij} E_n + \frac{1}{6} c_{ijklpq}^{(3)} \varepsilon_{ij} \varepsilon_{kl} \varepsilon_{pq} - \frac{1}{6} a_{nmr}^{(3)} E_n E_m E_r - s_{ijnm}^{(3)} \varepsilon_{ij} E_n E_m - d_{ijkln}^{(3)} \varepsilon_{ij} \varepsilon_{kl} E_n \right] dV_0 \quad (12)$$

Then the total electric Gibbs free energy of the particle is derived as

$$U = V_0 \cdot \tau_{ij} \cdot \varepsilon_{ij} + V_0 \cdot e_n \cdot E_n + \frac{1}{2} V_0 \left[\frac{1}{a} Q_{ijkl} + c_{ijkl} \right] \varepsilon_{ij} \varepsilon_{kl} + \frac{1}{2} V_0 \left[\frac{1}{a} W_{nm} - a_{nm} \right] E_n E_m + \frac{1}{6} V_0 \left[\frac{1}{a} P_{ijklpq} + c_{ijklpq}^{(3)} \right] \varepsilon_{ij} \varepsilon_{kl} \varepsilon_{pq} + \frac{1}{6} V_0 \left[\frac{1}{a} V_{nmr} - a_{nmr}^{(3)} \right] E_n E_m E_r + 2V_0 \left[\frac{1}{a} X_{ijn} - d_{ijn} \right] \varepsilon_{ij} E_n + V_0 \left[\frac{1}{a} Z_{ijkln} - d_{ijkln}^{(3)} \right] \varepsilon_{ij} \varepsilon_{kl} E_n + V_0 \left[\frac{1}{a} Y_{ijnm} - s_{ijnm}^{(3)} \right] \varepsilon_{ij} E_n E_m \quad (13)$$

3 Size effect on effective modulus

Because of the existence of the surface, strictly speaking, the total energy can be no longer obtained only through content in the bulk. When the size of the structure unit is in macroscopic level or even in microscopic level, the effect brought by the surface free energy on the performance of the material is so small that it can be neglected. But when the characteristic dimension of the structure decreases to the nano-size, the size effect exists.

For the composite material, the effective modulus is often used to characterize its properties due to its inhomogeneity. Analogously, when the characteristic dimension of the particle is in nano scale, since the ratio of the surface to volume is large enough, the particle can be treated as heterogeneous body, and the effective modulus should be introduced to characterize the properties of the particle.

Due to surface stresses and surface electric field, the self-equilibrium state of the particle is different from the perfect bulk crystal lattice. The strain $\hat{\varepsilon}_{ij}$ and electric field \hat{E}_i that describe the electromechanical deformation from the perfect crystal lattice to the self-equilibrium state of the particle can be found by minimizing the

total electric Gibbs free energy. Thus, one has

$$\begin{aligned} & \frac{\partial U}{V_0 \partial \varepsilon_{ij}} \Big|_{\varepsilon_{ij}=\hat{\varepsilon}_{ij}, E_n=\hat{E}_n} \\ &= \tau_{ij} + \left[\frac{1}{a} Q_{ijkl} + c_{ijkl} \right] \hat{\varepsilon}_{kl} + \frac{1}{2} \left[\frac{1}{a} P_{ijklpq} + c_{ijklpq}^{(3)} \right] \hat{\varepsilon}_{kl} \hat{\varepsilon}_{pq} + 2 \left[\frac{1}{a} X_{ijn} - d_{ijn} \right] \hat{E}_n + \\ & 2 \left[\frac{1}{a} Z_{ijkln} - d_{ijkln}^{(3)} \right] \hat{\varepsilon}_{kl} \hat{E}_n + \left[\frac{1}{a} Y_{ijnm} - s_{ijnm}^{(3)} \right] \hat{E}_n \hat{E}_m = 0 \end{aligned} \quad (14)$$

and

$$\begin{aligned} & \frac{\partial U}{V_0 \partial E_n} \Big|_{\varepsilon_{ij}=\hat{\varepsilon}_{ij}, E_n=\hat{E}_n} \\ &= e_n + \left[\frac{1}{a} W_{nm} - a_{nm} \right] \hat{E}_m + \frac{1}{2} \left[\frac{1}{a} V_{nmr} - a_{nmr}^{(3)} \right] \hat{E}_m \hat{E}_r + 2 \left[\frac{1}{a} X_{ijn} - d_{ijn} \right] \hat{\varepsilon}_{ij} + \\ & \left[\frac{1}{a} Z_{ijkln} - d_{ijkln}^{(3)} \right] \hat{\varepsilon}_{ij} \hat{\varepsilon}_{kl} + 2 \left[\frac{1}{a} Y_{ijnm} - s_{ijnm}^{(3)} \right] \hat{\varepsilon}_{ij} \hat{E}_m = 0 \end{aligned} \quad (15)$$

This constitutes a set of nine quadratic equations which needs to be solved numerically for the six components of self-equilibrium strain tensor and three components of self-equilibrium electric field vector.

When the self-equilibrium strain and self-equilibrium electric-field are small, the quadratic terms in Eqs. (14) and (15) can be neglected. Thus, the self-equilibrium strain and self-equilibrium electric-field can be obtained as

$$\begin{aligned} \hat{\varepsilon}_{ij} = & \left[\left(\frac{1}{a} Q_{klij} + c_{klij} \right) - 4 \left(\frac{1}{a} X_{ijn} - d_{ijn} \right) \left(\frac{1}{a} W_{mn} - a_{mn} \right)^{-1} \left(\frac{1}{a} X_{klm} - d_{klm} \right) \right]^{-1} \\ & \cdot \left[2 \left(\frac{1}{a} X_{klt} - d_{klt} \right) \left(\frac{1}{a} W_{rt} - a_{rt} \right)^{-1} e_r - \tau_{kl} \right] \end{aligned} \quad (16)$$

$$\begin{aligned} \hat{E}_n = & \left[\left(\frac{1}{a} W_{mn} - a_{mn} \right) - 4 \left(\frac{1}{a} X_{ijn} - d_{ijn} \right) \left(\frac{1}{a} Q_{klij} + c_{klij} \right)^{-1} \left(\frac{1}{a} X_{kln} - d_{kln} \right) \right]^{-1} \\ & \cdot \left[2 \left(\frac{1}{a} X_{rtm} - d_{rtm} \right) \left(\frac{1}{a} Q_{pqrt} + c_{pqrt} \right)^{-1} \tau_{pq} - e_m \right] \end{aligned} \quad (17)$$

Then, the effective elastic, dielectric and piezoelectric modulus tensors of the particle can be obtained as

$$\bar{c}_{ijkl} = \frac{\partial^2}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} \left(\frac{U}{V_0} \right) \Big|_{\varepsilon_{ij}=\hat{\varepsilon}_{ij}, E_n=\hat{E}_n} = c_{ijkl} + \frac{1}{a} Q_{ijkl} + \left[\frac{1}{a} P_{ijklpq} + c_{ijklpq}^{(3)} \right] \hat{\varepsilon}_{pq} + 2 \left[\frac{1}{a} Z_{ijkln} - d_{ijkln}^{(3)} \right] \hat{E}_n \quad (18)$$

$$\bar{a}_{nm} = -\frac{\partial^2}{\partial E_n \partial E_m} \left(\frac{U}{V_0} \right) \Big|_{\varepsilon_{ij}=\hat{\varepsilon}_{ij}, E_n=\hat{E}_n} = a_{nm} - \frac{1}{a} W_{nm} - \left[\frac{1}{a} V_{nmr} - a_{nmr}^{(3)} \right] \hat{E}_r - 2 \left[\frac{1}{a} Y_{ijnm} - s_{ijnm}^{(3)} \right] \hat{\varepsilon}_{ij} \quad (19)$$

$$\bar{d}_{ijn} = -\frac{1}{2} \frac{\partial^2}{\partial \varepsilon_{ij} \partial E_n} \left(\frac{U}{V_0} \right) \Big|_{\varepsilon_{ij}=\hat{\varepsilon}_{ij}, E_n=\hat{E}_n} = d_{ijn} - \frac{1}{a} X_{ijn} - \left[\frac{1}{a} Z_{ijkln} - d_{ijkln}^{(3)} \right] \hat{\varepsilon}_{kl} - \left[\frac{1}{a} Y_{ijnm} - s_{ijnm}^{(3)} \right] \hat{E}_m \quad (20)$$

It can be found that the contribution of the surface electric Gibbs free energy to the effective elastic, dielectric and piezoelectric modulus tensors of the dielectric particle is inversely proportional to the particle size. It will be shown numerically in the next section that the surface electric Gibbs free energy contribution is negligible unless the particle size reaches the nanoscale.

4 Numerical examples and discussions

To illustrate size effect on the piezoelectric material when the electromechanical coupling is taken into consideration, three typical structure elements, nano-sized particles, wires and films are discussed in this section.

All the structure units are made by the same transversely isotropic piezoelectric material, and the bulk constants of the material are given in the appendix, which are taken from Dunn and Taya (1993). The surface material properties can be calculated via molecular dynamics. However, for piezoelectric materials, such work is still needed. Here, we choose approximations for the surface constants according to Huang and Yu (2006), and the surface property tensor $\Gamma_{\alpha\beta\kappa\lambda}^{(2)}$, $\Lambda_{\xi\psi}^{(2)}$ and $\Pi_{\alpha\beta\xi}^{(2)}$ for PZT are assumed that $\Gamma_{1111}^{(2)} = \Gamma_{2222}^{(2)} = 7.56J/m^2$, $\Gamma_{1122}^{(2)} = \Gamma_{2211}^{(2)} = 3.72J/m^2$, $\Gamma_{1212}^{(2)} = 1.92J/m^2$, $\Lambda_{11}^{(2)} = \Lambda_{22}^{(2)} = 1.2 \times 10^{-17}C^2/Nm$ and $\Pi_{111}^{(2)} = 3 \times 10^{-8}C/m$. The residual stresses and electric displacements on the free surface are assumed that $\Gamma_{11}^{(1)} = \Gamma_{22}^{(1)} = 1N/m$ and $\Lambda_1^{(1)} = \Lambda_2^{(1)} = 1 \times 10^{-8}C/m$. The characteristic dimension is the radius for the spherical particles, the side length of the square section for the wires, and the half thickness for the films.

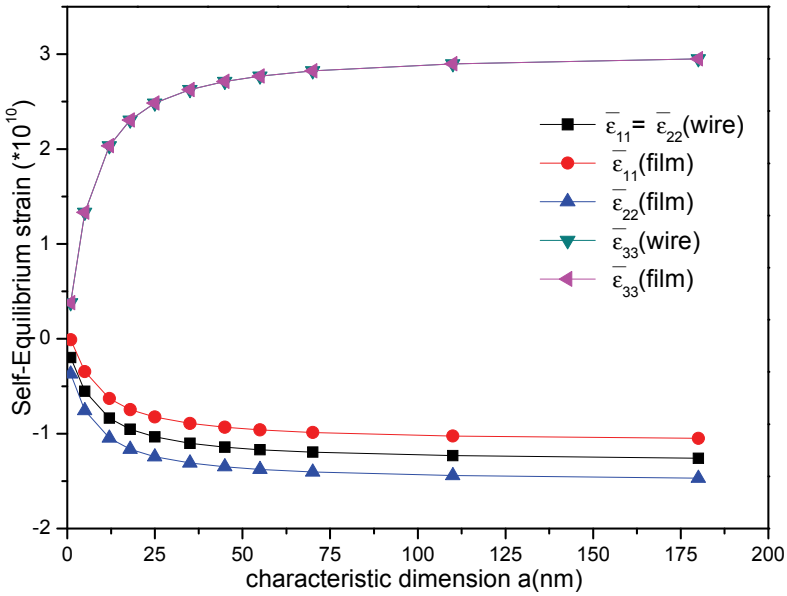


Figure 1: Variation of self-equilibrium strain for wires and films

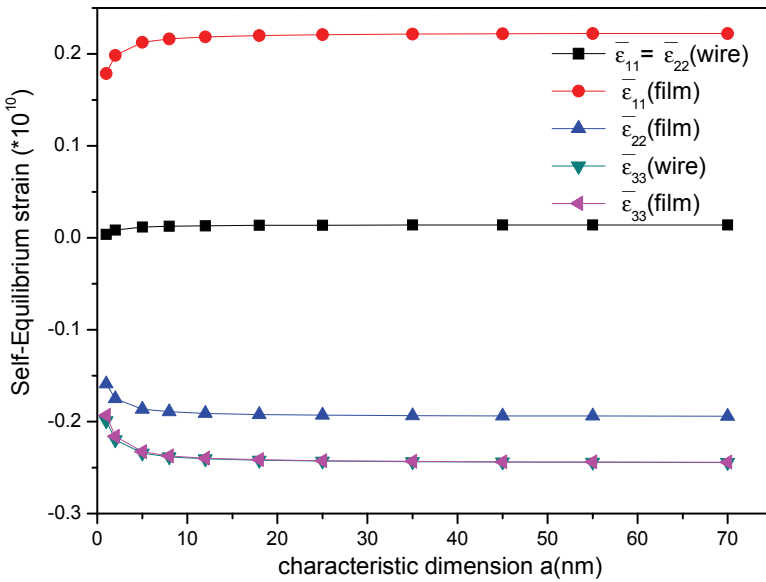


Figure 2: Self-equilibrium strain for wires and films in purely elastic state

The self-equilibrium strain for nano-wires and nano-films are plotted in Fig.1. From this figure, one can found that, when the size is less than 50 nm, all the components of the self-equilibrium strain change significantly, and they all approach to the corresponding value of the bulk with the increase of the characteristic dimension. Size effect becomes very week and even can be neglected when it is larger than 100nm. As a comparison, the corresponding results for purely elastic state are plotted in Fig. 2. Fig. 2 shows that, when the size approaches to 10 nm, the self-equilibrium strains already fairly approach to the bulk value. It can be concluded that the electromechanical coupling makes the size effect more obvious.

The self-equilibrium electric field is plotted in Fig. 3, the size effects on the self-equilibrium electric field in x_3 direction are almost the same for the wire and film and are significant in the region from 2 nm to 80 nm. However, for the film the size effect on the self-equilibrium electric field in x_2 direction occurs only when the size is less than 5 nm.

All the effective elastic, dielectric and piezoelectric modulus for the particle, wires and films are calculated. Because of the similarity among the variation behavior of particle, wires and film, only the effective modulus of the particle are taken as an example to elucidate the regularity of the size effect, as shown in Fig. 4 to Fig. 6 which are, respectively, the effective elastic, dielectric, and piezoelectric modulus. The effective elastic modulus increases with decreasing the radius, while the effective dielectric modulus and effective piezoelectric modulus decrease with decreasing the radius. The effective elastic modulus increases significantly when the size is under 2 nm, while the effective dielectric modulus decreases significantly when the size is less than 5 nm.

Regarding to the effective piezoelectric modulus, it is obvious that the size effects on different components of the piezoelectric modulus tensors are different. When the radius is 1 nm, \bar{d}_{333} is ten times larger than the bulk value of d_{333} , but \bar{d}_{232} and \bar{d}_{131} is, respectively, only twice of bulk values of d_{232} and d_{131} .

5 Summary

In this study, the surface effect is taken into account, through the surface and bulk electric Gibbs free energy. The analytical expressions are derived for the effective elastic, dielectric and piezoelectric modulus for nano-structural elements in electromechanical coupling problems. Furthermore, the solution shows that the electromechanical properties of piezoelectric nano-material are size-dependent but the size effects on the elastic property and dielectric property are different. Finally, numerical examples for PZT are given to illustrate the size effects on the electromechanical properties of nano-particle, nano-wires and nano-films quantitatively.

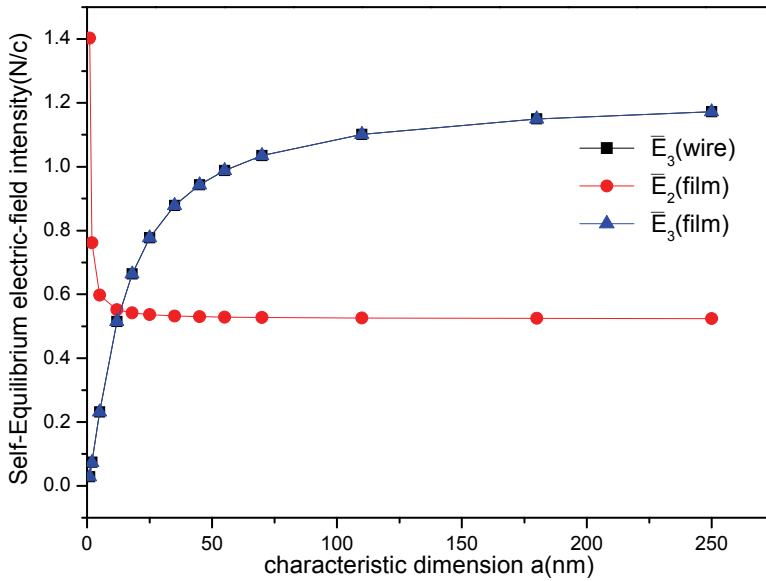


Figure 3: Variation of self-equilibrium electric-field for wires and films

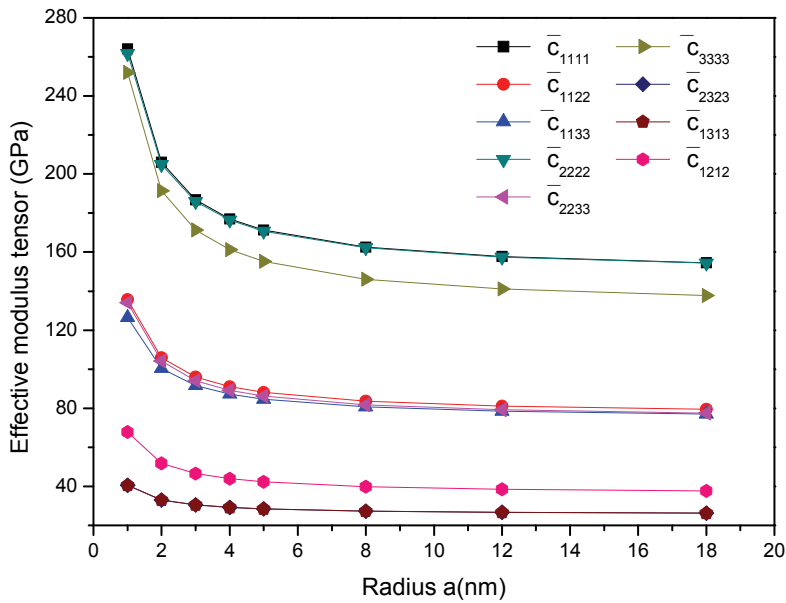


Figure 4: Variation of effective elastic modulus for spherical particle

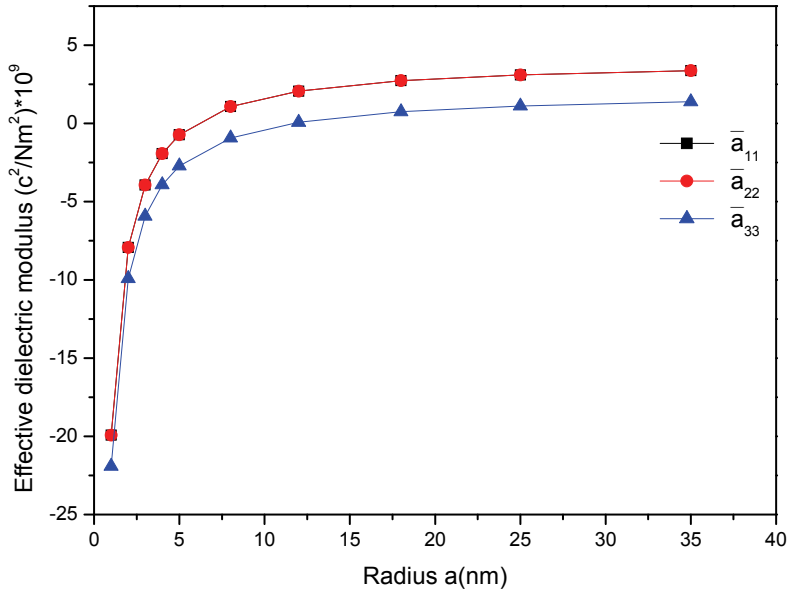


Figure 5: Variation of effective dielectric modulus for spherical particle

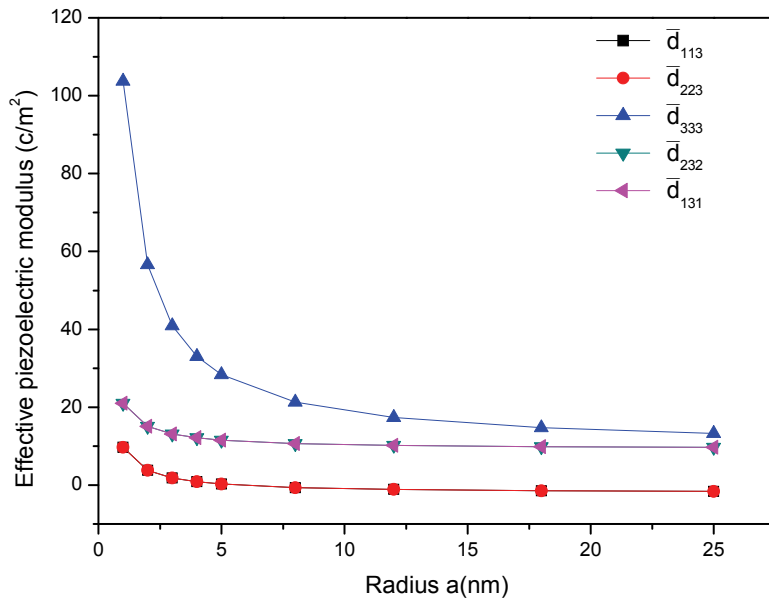


Figure 6: Variation of effective piezoelectric modulus for spherical particle

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Appendix

PZT (Dunn and Taya, 1993)

$$c^E = \begin{bmatrix} 148 & 76.2 & 74.2 & 0 & 0 & 0 \\ & 148 & 74.2 & 0 & 0 & 0 \\ & & 131 & 0 & 0 & 0 \\ & & & 25.4 & 0 & 0 \\ & & & & 25.4 & 0 \\ & & & & & 36.9 \end{bmatrix} \text{ GPa},$$

$$a = \begin{bmatrix} 4.071 & 0 & 0 \\ & 4.071 & 0 \\ & & 2.08 \end{bmatrix} \times 10^{-9} \text{ C}^2/\text{Nm}^2,$$

$$d = \begin{bmatrix} 0 & 0 & -2.1 \\ 0 & 0 & -2.1 \\ 0 & 0 & 9.5 \\ 0 & 9.2 & 0 \\ 9.2 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \text{ C/m}^2.$$

References

- Brandino, G.P., Cicero, G.** (2007): Polarization properties of (1100) and (1120) SiC surfaces from first principles. *Phys. Rev. B.* 76, 085322.
- Camacho, A.S., Nossa, J.F.** (2009): Geometric dependence of the dielectric properties of quantum dots arrays. *Microelectronics Journal* 40, 835-837.
- Dingreville, R., Qu, J.M., Cherkaoui, M.** (2005): Surface free energy and its effect on the elastic behavior of nano-sized particles, wires and films. *Phys. Solids.* 53, 1827-1854.
- Dunn, M.L., Taya, M.** (1993): Micromechanic predictions of the effective electroelastic moduli of piezoelectric composites. *Int. J. Solids Struct.* 30, 161-175.
- Fechner, M., Ostanin, S., Mertig, I.** (2008): Effect of the surface polarization in polar perovskites studied from first principles. *Phys. Rev. B* 77, 094112.

- Hu, S. L., Shen, S.** (2009): Electric field gradient theory with surface effect for nano-Dielectrics. *CMC: Computers, Material & Continua* 13: 63-87.
- Hu, S. L., Shen, S.** (2010): Variational principles and governing equations in nano-dielectrics with flexoelectric effect. *Sci China Phys Mech Astron* 53: 1497-1504.
- Huang G.Y., Yu S.W.** (2006): Effect of surface piezoelectricity on the electromechanical behaviour of a piezoelectric ring. *Phys. Stat. Sol. (b)* 243: R22-R24.
- Sharma P., Ganti S., Bhate N.** (2003): Effect of surfaces on the size-dependent elastic state of nano-inhomogeneities. *Applied Physics Letters* 82: 535-537.
- Shen, S., Hu, S. L.** (2010): A theory of flexoelectricity with surface effect for elastic dielectrics. *J. Mech. Phys. Solids* 58: 665-677.
- Slavchov, R., Ivanov, T., Radoev, B.** (2006): Effect of the surface polarizability on electrostatic screening in semiconductors. *J. Phys.: Condens. Matter* 18: 5873-5879.
- Varadan, V.V., Roh, Y.R., Varadan, V.K., Tancrell, R.H.** (1989): Measurement of all the elastic and dielectric constants of poled PVDF films. In 1989 Ultrasonics Symposium. IEEE, Montreal, Quebec, Canada, pp. 727-730.
- Yang F.** (2004): Size dependent effective modulus of elastic composite materials: spherical nanocavities at dilute concentrations. *Journal of Applied Physics* 95: 3516-3520.
- Zhou L.G., Huang H.** (2004): Are surfaces elastically softer or stiffer? *Applied Physics Letters* 84: 1940-1942.

