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Impact of the flexocaloric effect on polarization in the flexoelectric layer

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ABSTRACT

The paper presents a theoretical study on the distribution of polarization and mechanical stresses in the flexoelectric layer accounting for the flexocaloric effect. It is assumed that the flexoelectric material has neither piezoelectric nor electrostrictive properties. Particular attention is given to the boundary conditions at the media interface. The analysis is carried out in the framework of a one-dimensional model. It is demonstrated that the correct formulation of the boundary conditions requires to consider the square of the deformation gradient. The presence of this term results in the existence of the boundary layer at the flexoelectric interface, in which, according to our estimates, the deformation gradient can reach 10^6–$10^7\,\mathrm{m}^{-1}$.

1. Introduction

Virtually all dielectrics can be polarized while being subjected to an inhomogeneous deformation. This phenomenon, i.e. the relation between the polarization and the deformation gradient, is called flexoelectric effect (FEE) (Tagantsev, 1986). The effect is versatile and, unlike to the piezoelectric effect, exists for crystals of arbitrary symmetry. Despite the fact that FEE is known for a very long time, see e.g., Tagantsev (1986), Gharbi et al. (2011), Majdoub et al. (2008), Yudin and Tagantsev (2013), and has been revealed not only in crystals but also in biological materials (Deng et al., 2014b; Petrov, 2002), considerable interest in flexoelectrics appeared mainly in the last decade. Such a tendency can be explained by the advent of nanostructured metamaterials (Ma et al., 2011; Ma and Eric Cross, 2002; Sharma et al., 2010) with piezoelectric properties due to FEE. In addition, the evaluation of the flexoelectric coefficients derived by Kogan (1964) from theoretical considerations was underestimated. Since the flexoelectric effect is proportional to the dielectric constant (Kogan, 1964; Tagantsev, 1986), its highest values to be achieved for ferroelectrics. Experiments conducted on ferroelectrics with perovskite structure have shown that the measured value of FEE is three orders higher than the theoretical estimate (Ma and Eric Cross, 2002; Zubko et al., 2007). Moreover, the FEE should increase by reducing the size of the sample and can be very significant on the nanoscale. The enormous impact of the flexoelectricity on the electric properties of flexoelectric thin films was demonstrated by Catalan et al. (2004). Consequently, flexoelectricity must be considered for the energy harvesting applications (Deng et al., 2014a) and when calculating the ferroelectric memory elements such as thin films, nanowires, and nanodots (Eliseev et al., 2009). Finally, the temperature dependence of the flexoelectric coefficients leads to the flexocaloric effect, that is a temperature or entropy change of an inhomogeneously deformed sample under an electric field (Starkov and Starkov, 2014). This effect is especially attractive for the creation of the efficient solid-state cooling systems (Starkov et al., 2012).

The correct description of the finite size flexoelectric requires a proper formulation of the boundary conditions on the surface of the body. These conditions for the polarization were established a long time ago (Eliseev et al., 2009; Indenbom et al., 1981). However, the modification of the usual elasticity boundary conditions for the flexoelectric material was obtained only in 2011 (Yurkov, 2011). The paper of Liu (2014) helped to formulate the boundary conditions for a variety of problems. The equations describing the state of the flexoelectric are derived, as a rule, from variational principles based on the condition of minimum of the thermodynamic potential W (Eliseev et al., 2009; Sharma et al., 2010; Yudin and Tagantsev, 2013; Yurkov, 2011). The boundary conditions, according to the calculus of variations, shall be determined by the same potential W (Gelfand and Fomin, 2000). Unfortunately, most of the works dedicated to this problem use ordinary boundary conditions of the theory of elasticity (Nye, 1985). Note also that

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the flexoelectric terms in the thermodynamic potential increase the order of the differential equations describing the behavior of flexoelectric. Therefore, along with the modification of conventional electrical and elastic boundary conditions, it is necessary to take into account the emergence of additional boundary conditions (Yurkov, 2011). In the vast majority of papers devoted to the theory of flexoelectricity these conditions are not even mentioned. The purpose of this paper is to investigate, with a focus on the correct description of the boundary conditions, the impact of FEE on the distribution of polarization and deformation in a thin flexoelectric layer. For simplicity, it is assumed that the flexoelectric has neither piezoelectric or electrostrictive properties.

2. Variational principles for flexoelectricity

For the description of a flexoelectric occupying a volume V and bounded by the surface S, we will use the energy density w. We introduce also the displacement vector $\mathbf{u}$ with the components u_i, $(i = 1, 2, 3)$, and the potential φ. In the usual way, using the above notations, we define the electric field $E = -\varphi_{,i}$, the deformation tensor $u_{ij} = (u_{i,j} + u_{j,i})/2$, and the deformation gradient $v_{ijk} = u_{k,ij}$. Hereafter, the subscript after the comma denotes partial differentiation with respect to Cartesian coordinates x_1, x_2, x_3. It is assumed that the energy density w as well as the electric field E_i depends on the deformation tensor u_{ij} and its gradient v_{ijk}. Then the total internal energy of the material body W (excluding the potential energy of, e.g., a mechanical loading device or energy of electrodes) stored in the volume V has the form

$$W \equiv \int_V w(u_{ij}, v_{ijk}, E_i)\mathrm{d}V. \tag{1}$$

The variation of (1) with respect to u_{ij}, v_{ijk}, E_i gives

$$\delta W = \int_V (\sigma_{ij}\delta u_{ij} + \tau_{ijk}\delta v_{ijk} + D_i\delta E_i)\mathrm{d}V, \tag{2}$$

where $\{\sigma_{ij}, \tau_{ijk}, D_i\}$ are, respectively, the stress tensor, the higher-order stress tensor (Mindlin, 1965), and the electric displacement

$$\sigma_{ij} = \frac{\partial w}{\partial u_{ij}}, \quad \tau_{ijk} = \frac{\partial w}{\partial v_{ijk}}, \quad D_i = \frac{\partial w}{\partial E_i}. \tag{3}$$

In the above equations, Eqs. (2) and (3), we have used the Einstein summation convention in which repeated indices are summed over. Note that the variables σ_{ij}, τ_{ijk}, D_i and u_{ij}, v_{ijk}, E_i are the generalized forces and coordinates which are conjugate to each other. Return to the original independent variables u_i, φ. Using the Gauss theorem, the volume integrals in (2) can be converted to the surface integrals over S

$$\delta W = \int_V \left[(\sigma_{jk,j} - \tau_{ijk,ij})\delta u_k + D_{i,i}\delta\varphi\right]\mathrm{d}V + \int_S [(\sigma_{jk} - \tau_{ijk,i})n_j\delta u_k + \tau_{ijk}n_i\delta u_{k,j} + D_j n_j\delta\varphi]\mathrm{d}S, \tag{4}$$

where n_j are components of the vector normal to the surface S. According to (4), the extremal condition (1) leads to equations

$$\varsigma_{jk,j} = 0, \qquad D_{i,i} = 0, \tag{5}$$

in which the generalized stress ς_{jk} is given by $\varsigma_{jk} = \sigma_{jk} - \tau_{ijk,i}$. It is necessary to mention that the values of $\delta u_{k,j}$ cannot be considered as independent because they are determined by the values of δu_k on the surface S. In view of this, we represent $\delta u_{k,j}$ in the form of

$$\delta u_{k,j} = \mathrm{d}_j^{\parallel}\delta u_k + n_j\mathrm{d}^{\perp}\delta u_k, \tag{6}$$

i.e. the derivative can be decomposed into normal and tangential components (Mindlin, 1965)

$$\mathrm{d}^{\perp} \equiv n_k\frac{\partial}{\partial x_k}, \quad \mathrm{d}_j^{\parallel} \equiv (\delta_{jk} - n_j n_k)\frac{\partial}{\partial x_k}, \tag{7}$$

with δ_{jk} as the Kronecker symbol. After substituting (6) into (4) and accounting for (5), we obtain

$$\delta W = \int_S (T_k\delta u_k + R_k\mathrm{d}^{\perp}\delta u_k + n_k D_k\delta\varphi)\mathrm{d}S. \tag{8}$$

Here we have introduced the notations

$$T_k \equiv n_i\varsigma_{ik} + n_i n_j\tau_{ijk}(\mathrm{d}_l^{\parallel} n_l) - \mathrm{d}_j^{\parallel}(n_i\tau_{ijk}), \tag{9}$$

$$R_k \equiv n_i n_j\tau_{ijk}. \tag{9}$$

From (8), it is evident that the following 14 boundary conditions must be satisfied at the surface of flexoelectric:

$$\begin{aligned} &[\varphi] = 0, \quad [u_k] = 0, \quad [\mathrm{d}^{\perp}u_k] = 0, \\ &[R_k] = 0, \quad [T_k] = 0, \quad [n_k D_k] = 0. \end{aligned} \tag{10}$$

The symbol $[X]$ denotes the jump of a function X when passing through the interface. The first 4 conditions are standard and correspond to the continuity of the displacement and potential. The continuity of the normal component of the electric displacement $n_k D_k$ is also included in the standard electrostatic boundary conditions (Nye, 1985). At the same time, the condition of continuity of T_k is a generalization of the continuity condition for $n_i\sigma_{ij}$ in the usual theory of elasticity. Only the conditions of continuity of $\mathrm{d}^{\perp}u_k$ and R_k are introduced here for the first time. Thus, the electroelastic field in the flexoelectric must satisfy 4 equations (5), 14 conditions at the interfaces between the media (10), and 7 conditions at the external boundaries. The latter ones may be in the specification of u_k, $\mathrm{d}^{\perp}u_k$, φ or T_k, R_k, $D_k n_k$, or a combination of these conditions. In particular, according to (9), the next relations must be satisfied for the case of free external boundaries

$$n_k D_k = 0, \quad T_k = 0, \quad R_k = 0. \tag{11}$$

It worth to emphasize that the above derivation of the equations and boundary conditions for the flexoelectric does not depend on the form of w. It can be easily generalized to the case of w depending on the polarization P and its derivatives. The derivation of the elastic boundary conditions for the specific case of the quadratic dependence of w on the generalized forces is available in Yurkov (2011). For the general case, the boundary conditions can be found in Liu (2014).

3. Linearized theory for the flexoelectric layer

As an example of the model application, we discuss the problem of the flexoelectric layer. The thickness of the flexoelectric is denoted by l and the applicate axis is directed perpendicular to the layer. We consider the scalar case, i.e. assume the existence of a single component of the displacement vector depending only on $z = x_3$. A prime denotes the derivative with respect to z. The potential difference across the layer boundaries is denoted by U. It is believed that these boundaries are free from stress. This means, that the natural boundary conditions of the form (10) (Gelfand and Fomin, 2000) are fulfilled for the displacement and polarization. The energy density in a one-dimensional model for the specified layer is written in the form (Catalan et al., 2004; Zubko et al., 2013)

$$w = \frac{a}{2}P^2 + \frac{b}{4}P^4 + \frac{c}{2}(u')^2 - f^{(1)}Pu'' - f^{(2)}P'u' + \frac{g}{2}(P')^2 + \frac{h}{2}(u'')^2 + P\varphi' + \frac{\varepsilon_0}{2}(\varphi')^2. \tag{12}$$

Here $\{a, b\}$ are the Ginzburg–Landau coefficients, c elasticity modulus, $f^{(1),(2)}$ flexoelectric coefficients, $\{g, h\}$ gradient coefficients, ε_0 dielectric constant. For the case of interest, Eq. (5) takes the form of $D' = 0$, $\varsigma' = 0$, where

$$D = \varepsilon_0 E + P, \quad \varsigma = cu' + fP' - hu''', \tag{13}$$