Int. J. Solids Structures, 1968, Vol. 4, pp. 637 to 642. Pergamon Press. Printed in Great Britain

POLARIZATION GRADIENT IN ELASTIC DIELECTRICS

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Abstract—By inclusion of the polarization gradient in the stored energy function of elastic dielectrics, the classical theory of piezoelectricity is extended to accommodate an electro-mechanical interaction in centro-symmetric (including isotropic) materials and a surface energy of deformation and polarization.

1. TOUPIN'S VARIATIONAL PRINCIPLE

As a preliminary to an extension of the classical theory of electro-mechanical interaction in elastic, dielectric continua, a review is given, in this section, of a linear version of Toupin's [1] variational principle for the equilibrium equations of classical piezoelectricity.

In a body occupying a volume V bounded by a surface S, separating V from an outer vacuum V', it is assumed that

$$-\delta\int_{V^*} H\,\mathrm{d}V+\int_V (f_i\delta u_i+E_i^0\delta P_i)\,\mathrm{d}V+\int_S t_i\delta u_i\,\mathrm{d}S = 0, \tag{1.1}$$

where H is the electric enthalpy density, $V^* = V+V'$, u_i is the displacement, P_i is the polarization and f_i, E_i^0 and t_i are the external body force, electric field and surface traction, respectively. Toupin separates the electric enthalpy density into an energy density of deformation and polarization, say W^{L}, and a remainder:

$$H = W^{\mathrm{L}}(S_{ij}, P_i)-\tfrac{1}{2}\varepsilon_0\varphi_{,i}\varphi_{,i}+\varphi_{,i}P_i, \tag{1.2}$$

where S_{ij} is the strain,

$$S_{ij} = \tfrac{1}{2}(u_{j,i}+u_{i,j}), \tag{1.3}$$

φ is the potential of the Maxwell self-field,

$$E_i^{\mathrm{MS}} = -\varphi_{,i}, \tag{1.4}$$

and ε_0 is the permittivity of a vacuum.

For independent variations of u_i, P_i and φ,

$$\delta H = T_{ij}\delta S_{ij}-\bar{E}_i\delta P_i-\varepsilon_0\varphi_{,i}\delta\varphi_{,i}+\varphi_{,i}\delta P_i+P_i\delta\varphi_{,i}, \tag{1.5}$$

where T_{ij} is the stress and $\bar{E}_i$ is the effective local electric force:

$$T_{ij} \equiv \frac{\partial W^{\mathrm{L}}}{\partial S_{ij}} = T_{ji}, \qquad \bar{E}_i \equiv -\frac{\partial W^{\mathrm{L}}}{\partial P_i}. \tag{1.6}$$

By the chain rule of differentiation,

$$\delta H = -T_{ij,i}\delta u_i-(\bar{E}_i-\varphi_{,i})\delta P_i-(-\varepsilon_0\varphi_{,ii}+P_{i,i})\delta\varphi+(T_{ij}\delta u_j)_{,i}+[(-\varepsilon_0\varphi_{,i}+P_i)\delta\varphi]_{,i}. \tag{1.7}$$

Inserting (1.7) in (1.1) and applying the divergence theorem, we have

$$\int_{V^*} [(T_{ij,i}+f_j)\delta u_j+(\bar{E}_i-\varphi_{,i}+E_i^0)\delta P_i+(-\varepsilon_0\varphi_{,ii}+P_{i,i})\delta\varphi]\,\mathrm{d}V$$
$$+\int_S [(t_j-n_iT_{ij})\delta u_j+n_i(\varepsilon_0[\![\varphi_{,i}]\!]-P_i)\delta\varphi]\,\mathrm{d}S = 0; \tag{1.8}$$

whence follow the Euler equations

$$\begin{aligned} T_{ij,i}+f_j &= 0, \\ \bar{E}_i-\varphi_{,i}+E_i^0 &= 0, \\ -\varepsilon_0\varphi_{,ii}+P_{i,i} &= 0, \text{ in } V; \\ \varphi_{,ii} &= 0, \text{ in } V'; \end{aligned} \tag{1.9}$$

and the boundary conditions

$$\begin{aligned} n_iT_{ij} &= t_j, \\ n_i(-\varepsilon_0[\![\varphi_{,i}]\!]+P_i) &= 0. \end{aligned} \tag{1.10}$$

where $[\![\varphi_{,i}]\!]$ is the jump in $\varphi_{,i}$ across S.

The energy density of deformation and polarization is taken to be

$$W^{\mathrm{L}} = \tfrac{1}{2}a_{ij}P_iP_j+\tfrac{1}{2}c_{ijkl}S_{ij}S_{kl}+f_{ijk}S_{ij}P_k \tag{1.11}$$

so that, from (1.6),

$$\begin{aligned} -\bar{E}_j &= a_{jk}P_k+f_{klj}S_{kl}, \\ T_{ij} &= f_{ijk}P_k+c_{ijkl}S_{kl}. \end{aligned} \tag{1.12}$$

Equations (1.3), (1.9) and (1.12), with boundary conditions (1.10), constitute the classical theory of piezoelectricity in the form given by Toupin.

2. POLARIZATION GRADIENT

The extension of the classical theory, to be considered, is obtained simply by adding a functional dependence of W^{L} on the polarization gradient. This addition may be justified on several grounds. First of all, the order of the differential equations is thereby not raised, so that we are not adding effects of higher order than those already included. Alternatively, suppose we were to start by assuming dependence of W^{L} on the displacement and polarization and their gradients and truncate after the first gradients. The requirement of invariance of W^{L}, in a rigid translation and rotation of the deformed and polarized body, eliminates dependence on the displacement and rotation only; leaving the strain, polarization and polarization gradient. Finally, from the point of view of lattice theories of crystals [2, 3], based on the "shell model" [4] of the atom, the polarization gradient represents the long wave approximation to the shell–shell and core–shell interactions between atoms which logically should accompany the core–core interaction between atoms, despite their possibly small magnitude.

In addition to taking the polarization gradient into account, we shall also include the kinetic energy and employ Hamilton's principle, so that (1.1) is replaced by

$$\delta\int_{t_0}^{t_1}\mathrm{d}t\int_{V^*}(\tfrac{1}{2}\rho\dot{u}_i\dot{u}_i-H)\,\mathrm{d}V+\int_{t_0}^{t_1}\mathrm{d}t\left[\int_V(f_i\delta u_i+E_i^0\delta P_i)\delta V+\int_S t_i\delta u_i\,\mathrm{d}S\right]=0, \tag{2.1}$$

where

$$H = W^{\mathrm{L}}(S_{ij}, P_i, P_{j,i}) - \tfrac{1}{2}\varepsilon_0 \varphi_{,i}\varphi_{,i} + \varphi_{,i}P_i. \tag{2.2}$$

As usual [5],

$$\delta \int_{t_0}^{t_1} \mathrm{d}t \int_V \tfrac{1}{2}\rho \dot{u}_i \dot{u}_i \,\mathrm{d}V = -\int_{t_0}^{t_1} \mathrm{d}t \int_V \rho \ddot{u}_j \delta u_j \,\mathrm{d}V.$$

Then, by the same procedure as that employed in the preceding section,

$$\begin{aligned} T_{ij,i} + f_j &= \rho \ddot{u}_j, \\ \bar{E}_j + E_{ij,i} - \varphi_{,j} + E_j^0 &= 0, \\ -\varepsilon_0 \varphi_{,ii} + P_{i,i} &= 0, \text{ in } V, \\ \varphi_{,ii} &= 0, \text{ in } V'; \end{aligned} \tag{2.3}$$

and, on S,

$$\begin{aligned} n_i T_{ij} &= t_j, \\ n_i(-\varepsilon_0[\varphi_{,i}] + P_i) &= 0, \\ n_i E_{ij} &= 0, \end{aligned} \tag{2.4}$$

where

$$\bar{E}_i \equiv -\frac{\partial W^{\mathrm{L}}}{\partial P_i}, \qquad E_{ij} \equiv \frac{\partial W^{\mathrm{L}}}{\partial P_{j,i}}, \qquad T_{ij} \equiv \frac{\partial W^{\mathrm{L}}}{\partial S_{ij}} = T_{ji}. \tag{2.5}$$

For W^{L}, we take

$$W^{\mathrm{L}} = b_{ij}^0 P_{j,i} + \tfrac{1}{2}a_{ij}P_iP_j + \tfrac{1}{2}b_{ijkl}P_{j,i}P_{l,k} + \tfrac{1}{2}c_{ijkl}S_{ij}S_{kl} + d_{ijkl}P_{j,i}S_{kl} + f_{ijk}S_{ij}P_k + g_{ijk}P_iP_{k,j}. \tag{2.6}$$

Then, from (2.5),

$$\begin{aligned} -\bar{E}_j &= a_{jk}P_k + g_{jkl}P_{l,k} + f_{klj}S_{kl}, \\ E_{ij} &= g_{kij}P_k + b_{ijkl}P_{l,k} + d_{ijkl}S_{kl} + b_{ij}^0, \\ T_{ij} &= f_{ijk}P_k + d_{klij}P_{l,k} + c_{ijkl}S_{kl}. \end{aligned} \tag{2.7}$$

Equations (1.3), (2.3) and (2.7), with boundary conditions (2.4), form the equations of the extended theory. The significance of the linear term $b_{ij}^0 P_{j,i}$, in W^{L}, is considered in Section 4.

3. CENTROSYMMETRIC MATERIALS

One of the properties of the extended theory is its accommodation of an electromechanical interaction, through the coefficient d_{ijkl}, even for materials with centrosymmetry. For example, for centrosymmetric cubic symmetry [6],

$$\begin{aligned} f_{ijk} &= 0, \qquad g_{ijk} = 0, \qquad b_{ij}^0 = b_0\delta_{ij}, \qquad a_{ij} = a\delta_{ij}, \\ b_{ijkl} &= b\delta_{ijkl} + b_{12}\delta_{ij}\delta_{kl} + b_{44}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) + b_{77}(\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}), \\ c_{ijkl} &= c\delta_{ijkl} + c_{12}\delta_{ij}\delta_{kl} + c_{44}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}), \\ d_{ijkl} &= d\delta_{ijkl} + d_{12}\delta_{ij}\delta_{kl} + d_{44}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}), \end{aligned} \tag{3.1}$$

where

$$b = b_{11} - b_{12} - 2b_{44}, \qquad c = c_{11} - c_{12} - 2c_{44}, \qquad d = d_{11} - d_{12} - 2d_{44}, \tag{3.2}$$

δ_{ij} is the Kronecker delta and δ_{ijkl} is unity if all indices are alike and zero otherwise. Then, from (2.5), (2.6) and (3.1),

$$\begin{aligned} -\bar{E}_i &= aP_i, \\ E_{ij} &= b\delta_{ijkl}P_{l,k} + b_{12}\delta_{ij}P_{k,k} + b_{44}(P_{j,i} + P_{i,j}) + b_{77}(P_{j,i} - P_{i,j}) \\ &\quad + d\delta_{ijkl}S_{kl} + d_{12}\delta_{ij}S_{kk} + 2d_{44}S_{ij} + b_0\delta_{ij}, \\ T_{ij} &= d\delta_{ijkl}P_{l,k} + d_{12}\delta_{ij}P_{k,k} + d_{44}(P_{j,i} + P_{i,j}) \\ &\quad + c\delta_{ijkl}S_{kl} + c_{12}\delta_{ij}S_{kk} + 2c_{44}S_{ij}. \end{aligned} \tag{3.3}$$

Upon substituting (3.3) in (2.3) and employing (1.3), we find the "displacement" equations of motion:

$$\begin{aligned} &\tfrac{1}{2}c\delta_{ijkl}(u_{l,ki} + u_{k,li}) + c_{12}\delta_{ij}u_{k,ki} \\ &\quad + c_{44}(u_{j,ii} + u_{i,ji}) + d\delta_{ijkl}P_{l,ki} + d_{12}\delta_{ij}P_{k,ki} + d_{44}(P_{j,ii} + P_{i,ji}) + f_j = \rho\ddot{u}_j \\ &\tfrac{1}{2}d\delta_{ijkl}(u_{l,ki} + u_{k,li}) + d_{12}\delta_{ij}u_{k,ki} + d_{44}(u_{j,ii} + u_{i,ji}) - aP_j - \varphi_{,j} \\ &\quad + b\delta_{ijkl}P_{l,ki} + b_{12}\delta_{ij}P_{k,ki} + b_{44}(P_{j,ii} + P_{i,ji}) + b_{77}(P_{j,ii} - P_{i,ji}) + E_j^0 = 0, \\ &\qquad -\varepsilon_0\varphi_{,ii} + P_{i,i} = 0. \end{aligned} \tag{3.4}$$

For isotropic materials, it is only necessary to set

$$b = c = d = 0.$$

Then (3.4) become, in vector notation,

$$\begin{aligned} c_{44}\nabla^2\mathbf{u} + (c_{12} + c_{44})\nabla\nabla\cdot\mathbf{u} + d_{44}\nabla^2\mathbf{P} + (d_{12} + d_{44})\nabla\nabla\cdot\mathbf{P} + \mathbf{f} &= \rho\ddot{\mathbf{u}}, \\ d_{44}\nabla^2\mathbf{u} + (d_{12} + d_{44})\nabla\nabla\cdot\mathbf{u} + (b_{44} + b_{77})\nabla^2\mathbf{P} + (b_{12} + b_{44} - b_{77})\nabla\nabla\cdot\mathbf{P} - a\mathbf{P} - \nabla\varphi + \mathbf{E}^0 &= 0, \\ -\varepsilon_0\nabla^2\varphi + \nabla\cdot\mathbf{P} &= 0. \end{aligned} \tag{3.5}$$

It is apparent that, in both cases, the displacement and polarization fields are coupled through the constants d_{ijkl}.

4. SURFACE ENERGY OF DEFORMATION AND POLARIZATION

It will be observed that the energy density W^{L}, in (2.6), contains a linear term, $b_{ij}^0P_{j,i}$, in the polarization gradient. The removal of the resulting n_iE_{ij} from a boundary results in a polarization and strain localized at the surface. The accompanying surface energy can be found as follows.

The energy density W^{L}, given by (2.6), can be written in the alternative form

$$W^{\mathrm{L}} = \tfrac{1}{2}b_{ij}^0P_{j,i} + \tfrac{1}{2}T_{ij}S_{ij} - \tfrac{1}{2}\bar{E}_iP_i + \tfrac{1}{2}E_{ij}P_{j,i} \tag{4.1}$$

through the use of (2.7). Then, in the case of equilibrium, application of the chain rule, the divergence theorem, the boundary conditions and the equations of equilibrium results in the following expression for the *total* energy:

$$\int_{V^*} W\,\mathrm{d}V = \frac{1}{2}\int_S n_i b_{ij}^0 P_j\,\mathrm{d}S + \frac{1}{2}\int_V (f_i u_i + E_i^0 P_i)\,\mathrm{d}V + \frac{1}{2}\int_S t_i u_i\,\mathrm{d}S. \tag{4.2}$$

Hence, in the absence of external forces, we have

$$\int_{V^*} W\,\mathrm{d}V = \frac{1}{2}\int_S n_i b_{ij}^0 P_j\,\mathrm{d}S. \tag{4.3}$$

Accordingly, the surface energy of deformation and polarization per unit area (the surface tension) is

$$T = \tfrac{1}{2}[n_i b_{ij}^0 P_j]_S. \tag{4.4}$$

This energy is to be added to the bond energy, per unit area, to obtain the total energy per unit area required to separate the material into two parts along a surface S [7].

As an example, consider the case of a free (100) surface of a semi-infinite, centrosymmetric, cubic crystal. In this case, the resulting fields are one-dimensional and the equations of equilibrium, (3.4), for the half space $x_1 \geqslant 0$, reduce to

$$\begin{aligned} c_{11}u_{1,11} + d_{11}P_{1,11} &= 0, \\ d_{11}u_{1,11} + b_{11}P_{1,11} - aP_1 - \varphi_{,1} &= 0, \\ -\varepsilon_0\varphi_{,11} + P_{1,1} &= 0, \end{aligned} \tag{4.5}$$

while the boundary conditions, on $x_1 = 0$, become

$$\begin{aligned} c_{11}u_{1,1} + d_{11}P_{1,1} &= 0, \\ d_{11}u_{1,1} + b_{11}P_{1,1} &= -b_0, \\ -\varepsilon_0\varphi_{,1} + P_1 &= 0. \end{aligned} \tag{4.6}$$

Consider the functions

$$u_1 = A_1\,\mathrm{e}^{-x_1/l}, \qquad P_1 = A_2\,\mathrm{e}^{-x_1/l}, \qquad \varphi = A_3\,\mathrm{e}^{-x_1/l}. \tag{4.7}$$

Upon substituting (4.7) into the equilibrium equations (4.5), we find

$$A_3 = -lA_2/\varepsilon_0 = lc_{11}A_1/\varepsilon_0 d_{11} \tag{4.8}$$

$$l = \left(\frac{c_{11}b_{11} - d_{11}^2}{c_{11}(a + \varepsilon_0^{-1})}\right)^{\frac{1}{2}}. \tag{4.9}$$

Positive definiteness of W^{L} requires the radicand in (4.9) to be positive.

With (4.8), the first and third of the boundary conditions (4.6) are satisfied identically and the second yields

$$A_1 = -\frac{b_0 d_{11}}{c_{11} l(a + \varepsilon_0^{-1})}. \tag{4.10}$$

Whence, from (4.8),

$$A_2 = \frac{b_0}{l(a + \varepsilon_0^{-1})}, \qquad A_3 = -\frac{b_0}{a\varepsilon_0 + 1}. \tag{4.11}$$

Thus, there are a strain and a polarization, at the surface, which decay exponentially into the interior with decay constant l. The surface energy of deformation and polarization per unit area (the surface tension) is, from (4.4) and (4.11),

$$T = -\frac{b_0^2}{2l(a+\varepsilon_0^{-1})}. \tag{4.12}$$

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(*Received* 17 *October* 1967)

Абстракт—Учитывая включение градиента поляризаций в функцию сохранения энергии упругих диэлектриков расширается классическая теория пьезоэлектричества путем учета электро-механической реакции в осесимметрических /включая изотропные/ материалах и поверхностной энергии деформации и поляризации.