a material. Requires a polarization that remains within a material in the absence of the application of an external field, in turn requiring a non-enantiomorphic polar symmetry in the composition of the material.

Cross References

- ► Non-Centrosymmetric
- ► Ferroelectric
- ► Acoustics Based Biosensors

Piezoelectric Drop-on-Demand

► Piezoelectric Microdispenser

Piezoelectric Ink Jet

► Piezoelectric Microdispenser

Piezoelectric Materials for Microfluidics

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Synonyms

Lead zirconate titanate; PZT; Zinc oxide; Quartz; AlN; Electroactive materials; Electromechanically coupled materials; Artificial muscle materials; Electrets

Definition

Piezoelectricity means *squeeze* or *pressure* electricity, from the Greek *pieze* which means to press or squeeze. The casual definition of piezoelectric materials is that they develop an electric charge differential along an axis of ► piezoelectric polarization if placed under appropriate mechanical strain, called the ► direct piezoelectric effect, and deform if an electric field is applied along the same axis of polarization, the converse piezoelectric effect. The electric field to mechanical strain coupling occurs when the positive and negative charge of the individual ions within the material do not displace symmetrically upon the application of an external strain. Strictly speaking, piezoelectric materials exhibit electric polarization upon the application of a stress and vice versa. Often the casual and strict definitions are the same, though confusion may arise with the casual definition. All piezoelectric materials are ► anisotropic, and there are useful examples of piezoelectric materials that are single crystals, polycrystalline ceramics, and polymers. Many of the known piezoelectric materials have at one time or another been used as sensors or actuators in microfluidics, for which their rapid response and large force transmission have been beneficial, though researchers have had to learn to overcome small strains, thermal losses, aging, and difficulties in fabrication, especially in process compatibility.

Overview

Piezoelectric materials offer the ability to directly transform (transduct) from electrical to mechanical energy and vice versa, convenient for microtechnology in sensing and actuation; a material is said to be piezoelectric if an applied stress generates an electric field within, and vice versa. They may be used to provide static and dynamic deformation at frequencies up to several gigahertz, depending on the motion to be induced, the scale of the device, and the material used. Compared to other methods of power transduction, including electrostatic, electrostrictive, magnetostrictive, and electromagnetic means, piezoelectric transduction typically provides large forces at small strain rates ($< 1\%$ strain typically) for actuation, and relatively large voltages and small currents for sensing. Piezoelectricity is usually treated as a linear interaction between mechanical and electrical phenomena, though this assumption is generally invalid for high-power applications or in materials with either large losses or large deformations (polymers). The ► hysteresis in such conditions is the deviation from linear transduction. This is different than the typically weak ► electrostrictive [2] behaviour of many insulating materials which exhibit a strain proportional to the square of the applied field, though some materials, like ► relaxor ferroelectrics are exceptions. Single crystal materials are usually naturally polarized, implying they may be used without additional treatment, while polycrystalline and polymeric materials must be polarized with either an applied electric field or an applied strain prior to use.

Recognition of the piezoelectric effect has been known since ancient times [6]. Theophrastus noted in 314 BC the attraction of small pieces of straw and wood to tourmaline after heating, but recognition of the presence of an electrostatic field causing the attraction had to wait for the nineteenth century, along with a name provided by Brewster in 1824: ► pyroelectricity. All pyroelectric materials are piezoelectric; Jacques and Pierre Curie studied piezoelectric materials in the 1880's and were able to describe many of the characteristics of the phenomena used in applications today. Once synthetic quartz and high-performance materials like barium titanate, lead zirconate titanate and subsequent variations became available in the 1950's and 60's, a wide variety of applications beyond sonar became feasible.

Many of the piezoelectric materials used for applications are single crystals or polycrystalline matrices of single-crystal grains. Overall, crystalline media may be organized into thirty-two crystal classes or point groups based on their symmetry; the names of some of these groups are commonly known; triclinic, orthorhombic, cubic, and isotropic are especially well-known. ► Hermann–Mauguin notation [1] is often used to precisely describe the properties of these materials. For example, triclinic materials are represented with either a 1 or –1, depending on whether or not the material has ► inversion symmetry, respectively. Of these thirty-two crystal classes, twenty-one possess no centre of symmetry; they are said to be ► non-centrosymmetric or to lack inversion symmetry, and all but one of these classes are piezoelectric. The exception is class 432, which has other symmetries which negate the non-centrosymmetric nature of the crystal structure. The remaining crystal classes which are piezoelectric are 1, 2, m, 222, mm2, 23, 3, 3m, 32, 4, –4, 422, 4mm, –42m, –43m, 6, –6, 622, 6mm, and –62m.

Out of these twenty piezoelectric classes, ten also lack symmetric characteristics along a particular axis, and are therefore able to retain a natural ionic charge separation in the crystalline structure along that axis—a ► spontaneous polarization—that forms an electric dipole which remains even without an externally applied electric field. This is in contrast to all insulating or dielectric materials which polarize to form such dipoles only with an externally applied field. These crystal groups are *pyroelectric*, including 1, 2, m, mm2, 3, 3m, 4, 4mm, 6, and 6mm. A crystal belonging to one of these crystal groups that has a polarization that may be reversed through the application of an external electric field is said to be ► ferroelectric. A distinct characteristic of ferroelectric materials, in the strictest definition, is the presence of hysteresis. All ferroelectric materials are both piezoelectric and pyroelectric. Lead zirconium titanate (PZT or $Pb_xZr_{(1-x)}O_3$) is one of the most important ferroelectric materials, class 6mm, though PZT is only found in polycrystalline form as a ► perovskite ABO_3.

Most piezoelectric materials tend to be quite capacitive. The pyroelectric nature of all polarized piezoelectric materials can cause the development of significant charging across the material due to thermal expansion coupled to the direct piezoelectric effect causing a charge displacement from the thermal strain; voltages of 1 kV are not unheard of in PZT after a temperature change of 50 °C, and caution is warranted in any application. However, a piezoelectric material will lose its spontaneous polarization if its temperature is raised above the ► Curie temperature, near the temperature of maximum dielectric constant, the ► Curie–Weiss temperature. Since the mechanical and electrical behavior are coupled, a change in boundary conditions in one domain will change the behavior of the material in the other domain. By leaving a polarized piezoelectric element open-circuited, the mechanical stiffness of the material will be higher, called stress stiffening. Similarly, mechanically clamping a piezoelectric element will tend to increase the impedance.

With polycrystalline and amorphous *piezoelectric* materials, a spontaneous polarization can rarely be obtained as a consequence of the natural ordering within the material during fabrication. Some form of applied strain or electric field is necessary to polarize the material before use. A common sensor material, polydivinylfluoride (PVDF), is stretched to polarize it, while standard PZT must have a large ($> 10\,\mathrm{kV/cm}$) electric field applied to it to order the electric Weiss domains, or groups of dipoles, in the general direction of the applied field. It is a common misconception that polarization of these materials implies the dipole polarization is rotated to be aligned with the electric field or that the atomic structure itself is realigned within the material. In reality, the atomic structure is essentially fixed, preventing such rotation or realignment. Once polarized, the material can be said to be a member of the pseudocrystal group ∞ mm, and is often represented as a 6 mm material. Generally, the domains are randomly oriented beforehand.

At times, particularly with amorphous materials, the term *electret* is used instead of *piezoelectric* to describe a material; the term was introduced as an electric counterpart to the magnet, defined as all materials that are able to retain at least a quasi-permanent electric polarization within, and perhaps trap charge on the surface (or within in a porous material). Polytetrafluorethylene (PTFE) is a powerful electret material. The critical difference among the terms is that electrets retain polarization in thermodynamic *non*equilibrium, pyroelectric materials retain polarization in equilibrium, ferroelectrics permit the equilibrium polarization to be reversed along the polarization axis, and piezoelectric materials may or may not have any polarization at all.

Basic Methodology

Modeling Linear Piezoelectricity

Equations for structural dynamics within the solid material, along with the standard equations for electrostatics, are sufficient to model most piezoelectric materials and their applications. The full electromagnetic equations are

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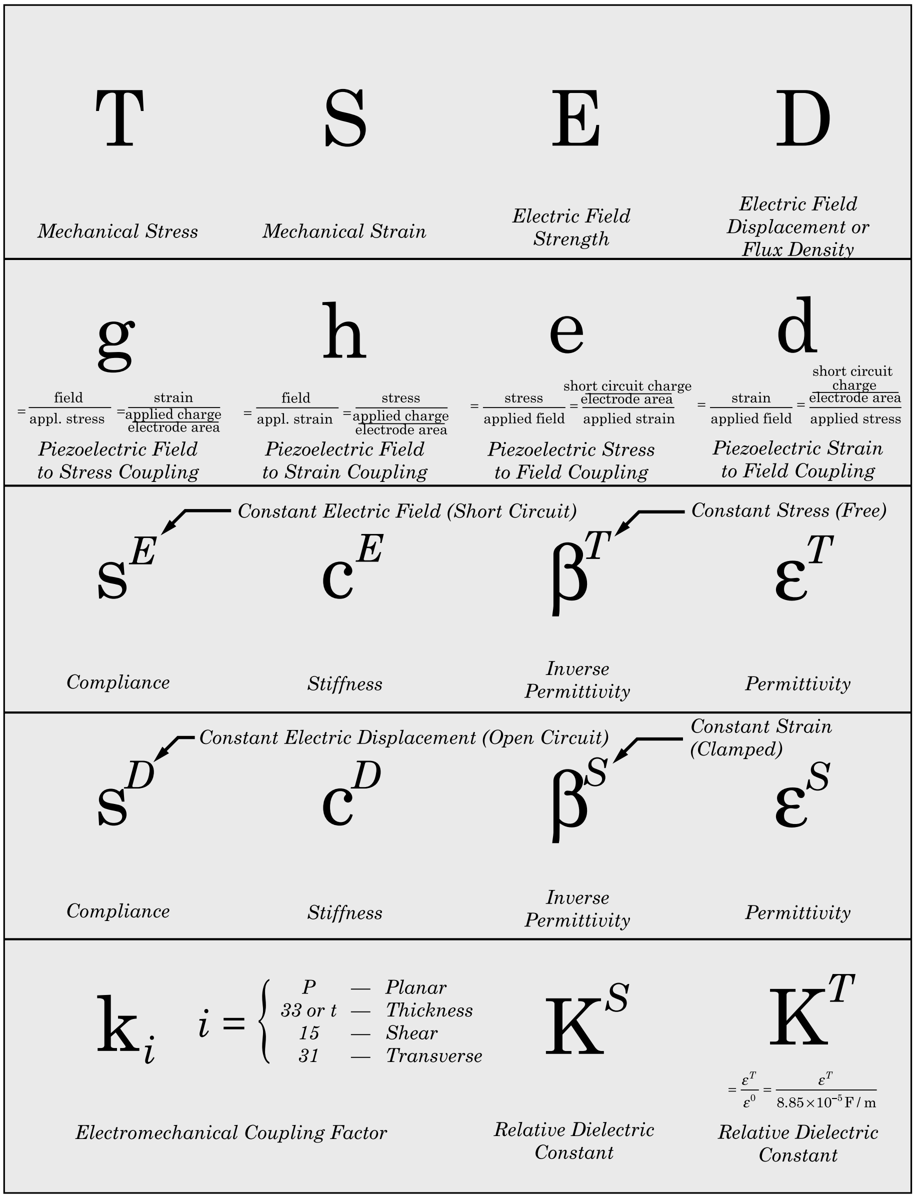


Piezoelectric Materials for Microfluidics, Figure 1 Variables used in linear piezoelectric material analysis

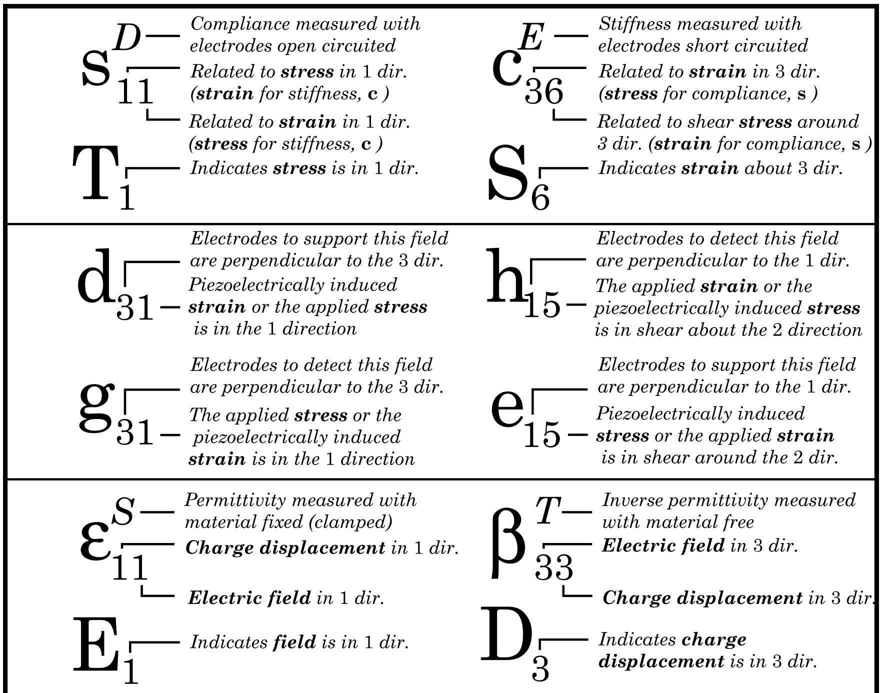
unnecessary since the mechanical motion propagates at $\sim 10^3$ m/s, several orders of magnitude less than the electric field, permitting the so-called *quasistatic* assumption. For the same reason, magnetic fields are typically weak and may be safely ignored. Still, equations to describe the electrical and mechanical behaviour are needed in addition to the constitutive equations for the material.

Using Auld's notation [1], the full tensor form of the linear constitutive equations with the strain and charge displacement as dependent on the stress and applied field may be written as

$$\mathbf{T} = \mathbf{c}^E : \mathbf{S} - \tilde{\mathbf{e}} \cdot \mathbf{E}$$

$$\mathbf{D} = \mathbf{e} : \mathbf{S} + \tilde{\boldsymbol{\varepsilon}}^S \cdot \mathbf{E} \tag{1}$$

where the terms are defined with units in Figs. 1 and 2 (using contracted notation to be described later). The tilde ($\sim$) is a transpose while the single and double dots represent an inner product across one and two dimensions



Units

Variable	Name	Derived Units (MKS)	Fundamental Units
c	*Stiffness*	Pa	$kg / m \cdot s^2$
s	*Compliance*	1 / Pa	$m \cdot s^2 / kg$
T	*Stress*	Pa	$kg / m \cdot s^2$
S	*Strain*	—	—
d	*Piezo. Strain Coefficient*	m / V *or* C / N	$C \cdot s^2 / kg \cdot m$
g	*Piezo. Voltage Coefficient*	m•V / N *or* N•m / C	m^2 / C
e	*Piezo. Stress Coefficient*	C / m^2	C / m^2
h	*Piezo. Stiffness Coefficient*	V / m	$kg \cdot m / C \cdot s^2$
ε	*Permittivity*	F / m	$C^2 \cdot s^2 / kg \cdot m^3$
β	*Inverse Permittivity*	m / F	$kg \cdot m^3 / C^2 \cdot s^2$
D	*Electric Charge Displacement*	F•V / m	C / m^2
E	*Electric Field Strength*	V / m	$kg \cdot m / C \cdot s^2$
K	*Relative Dielectric Constant* ($\varepsilon/\varepsilon_0$)	—	($\varepsilon_0 = 8.85 \times 10^{-5}$ F / m)
k	*Electromechanical Coupling Factor*	—	—

Piezoelectric Materials for Microfluidics, Figure 2 Description of subscripts used in piezoelectric analysis

of the adjacent tensors, respectively. In piezoelectric materials analysis, the contravariant basis vectors are typically Cartesian, therefore orthonormal and so the covariant basis is not needed. Upon choosing a coordinate system, an indicial notation may be adopted [14],

$$T_{ij} = c^{E}_{ijkl} S_{kl} + e_{mij} E_m$$

$$D_i = e_{ijk} S_{jk} + \varepsilon^{S}_{ik} E_k \,, \tag{2}$$

where summation is assumed across repeated subscripts in products of terms, i. e., k and l in $c^{E}_{ijkl} S_{kl}$; all of the subscripts range from 1 to 3. The strain S_{ij} is given by astrain-displacement relationship $S_{ij} = \frac{1}{2}\left(u_{i,j} + u_{j,i}\right)$ where the comma in the subscript represents a spatial derivative ($u_{i,j} = \partial u_i / \partial x_j$). The momentum equation is $T_{ij,i} + f_i = \rho \ddot{u}_j$ where $\ddot{u} = \partial^2 u_j / \partial t^2$ and f_i represents a body force. The time-dependent electric field, E_i, and charge displacement, D_i, may be related through the polarization and permeability equation $D_i = \varepsilon_0 E_i + P_i$ where P_i is the polarization. A scalar potential φ may be defined to represent the electric field, $E_i = \varphi_{,i}$, while the charge displacement is *spatially* constant along a particular direction, $D_{i,i} = 0$.

A piezoelectric Poynting energy flux akin to those defined for nonpiezoelectric acoustic waves and electromagnetic waves is given by $-\left(T_{ij}\dot{u}_j - \varphi\dot{D}_j\right)$.

In attempting to use these equations to solve problems, a complete and consistent set of electromechanical boundary conditions are needed. Tiersten [13] provides such a derivation, though solution of anything beyond simple problems requires computation. Fortunately, the mechanical and electrical boundary conditions are usually separable; $u_i = u_i^*$ or $n_i T_{ij} = n_i T_{ij}^*$, and $n_i D_i = n_i D_i^*$ or $\varphi = \varphi^*$. The starred terms represent constants, time-varying values, or values defined within another media adjacent to the piezoelectric material. The outward vector normal to the boundary surface is given by n_i.

Even in the most anisotropic of materials substantial symmetry exists in Eq. (2), permitting contraction of the subscripts [4] and giving a simpler form for the constitutive equation;

$$\begin{aligned} T_p &= c_{pq}^E S_q + e_{mp} E_m \\ D_n &= e_{nr} S_r + \varepsilon_{nm}^S E_m , \end{aligned} \tag{3}$$

where p, q, and r range from 1 to 6, while m and n range from 1 to 3. There is *not* a one-to-one correspondence between the two representations in Eqs. (2) and (3). For example, the strain S_{ij} is $S_p = 2^{|\mathrm{sgn}(i-j)|}$. For this reason and the confusion that can arise in defining the momentum and strain-displacement equations, one must use care in solving problems with the contracted notation. The value of p in terms of i,j varies notoriously between authors, but the IEEE standard [4] is the most commonly accepted version; here $p = \frac{1}{2}(i+j)(1-|\mathrm{sgn}(i-j)|) + |\mathrm{sgn}(i-j)|(9-i-j)$ for i,j = 1,2,3; here the vertical bars $|\cdot|$ represent an absolute value while $\mathrm{sgn}(\cdot)$ is the *signum*, zero when x is zero and the sign of x otherwise.

Most solutions found by solving the complete set of piezoelectric material equations are very simple approximations. Computation, typically using finite element analysis software, is often necessary for practical cases. The ability to handle piezoelectric materials in commercially available finite element analysis software varies, though ANSYS (ANSYS Inc., Canonsburg, PA, USA) and COMSOL (COMSOL Inc., Burlington, MA, USA) are two well-known packages with decent implementations. However, a one-dimensional model of the piezoelectric material behavior offers many of the salient features without the complexity.

Piezoelectricity in One Dimension: Transducer Equations

If we assume a longitudinal plane wave propagates along the z-axis—assumed to be a principal axis of the material—the only non-zero displacement will also be along the z- or 3-axis, $u = u(z,t)$ and the strain will be $S_{33} = \partial u/\partial z$. Further, assuming the applied electric field is only along the 3-axis, $E_3 = E$ while $E_1 = E_2 = 0$, we may find the resulting constitutive equations from substitution into Eq. (2), closely following the approach used by Dieulesaint and Royer [3]:

$$\begin{aligned} T_{ij} &= c_{ij33}^E S_{33} + e_{3ij} E_3 \\ D_i &= e_{i33} S_{33} + \varepsilon_{i3}^S E_3 \end{aligned} , \tag{4}$$

where i must be equal to j. If we set $i = j = 1$, the motion would be transverse to the applied field (setting i and j to 2 would give the same result), while if $i = j = 3$, the motion is parallel. Taking the latter option with Eq. (4),

$$\begin{aligned} T_{33} &= c_{3333}^E S_{33} + e_{333} E_3 \\ D_3 &= e_{i33} S_{33} + \varepsilon_{33}^S E_3 \end{aligned} \rightarrow \begin{aligned} T &= c^E S + eE \\ D &= eS + \varepsilon^S E \end{aligned} , \tag{5}$$

where we discard the subscripts here and subsequently. The electric field, E, may be eliminated from Eq. (5):

$$T = \left(c^E + \frac{e^2}{\varepsilon^S}\right)\frac{\partial u}{\partial z} - \frac{e}{\varepsilon^S} D, \tag{6}$$

giving

$$\frac{\partial T}{\partial t} = \left(c^E + \frac{e^2}{\varepsilon^S}\right)\frac{\partial^2 u}{\partial z \partial t} - \frac{e}{\varepsilon^S}\frac{\partial D}{\partial t} \tag{7}$$

if we take a time derivative. The quantity $\left(c^E + \frac{e^2}{\varepsilon^S}\right) \equiv c^D$; this relation is also true for the tensor form, and indicates the relationship between the constant-field stiffness c^E and the constant field displacment c^D. There are relations between all of the coefficients as described later. The current passing through the piezoelectric element is given by $I = \int \frac{\partial D}{\partial t} dA$ where A is the cross-sectional area perpendicular to the z-axis. Since the wave is planar, $\frac{\partial D}{\partial t}$ is a constant across the cross-sectional area A, so $\frac{\partial D}{\partial t} = I/A$, and Eq. (7) simplifies to

$$\frac{\partial T}{\partial t} = c^D \frac{\partial^2 u}{\partial z \partial t} - \frac{eI}{\varepsilon^S A}. \tag{8}$$

Differentiating Eq. (8) with respect to z,

$$\frac{\partial^2 T}{\partial t \partial z} = c^D \frac{\partial^3 u}{\partial z^2 \partial t} = c^D \frac{\partial^2 v}{\partial z^2}, \tag{9}$$

noting $I = I(t)$ alone, and $v = \partial u/\partial t$. From the momentum equation, if the body force $f = 0$,

$$\frac{\partial T}{\partial z} = \rho \frac{\partial^2 u}{\partial t^2} \implies \frac{\partial^2 T}{\partial z \partial t} = c^D \frac{\partial^2 v}{\partial z^2} = \rho \frac{\partial^2 v}{\partial t^2}, \quad (10)$$

The latter part of Eq. (10), $c^D \partial^2 v/\partial z^2 = \rho\, \partial^2 v/\partial t^2$, may be solved as a wave equation:

$$v(x, t) = \mathrm{e}^{\jmath \omega t} \left(V_1 \mathrm{e}^{-\jmath kz} + V_2 \mathrm{e}^{\jmath kz} \right). \quad (11)$$

where the circular frequency-wavenumber ratio is related to the material properties by $\omega/k = \sqrt{c^D/\rho}$ and $\jmath = \sqrt{-1}$; the first and second parts of the solution in Eq. (11) are waves traveling in the positive and negative z-directions, respectively.

An acoustic impedance may be defined as $Z = T/v = \sqrt{c^D \rho}$ —the latter term found by substituting Eq. (11) into Eq. (10)—and used to describe the stress wave propagation by substitution of Eq. (11) into Eq. (8) and integrating,

$$T = \mathrm{e}^{\jmath \omega t} \left[\frac{kc^D}{\omega} \left(-V_1 \mathrm{e}^{-\jmath kz} + V_2 \mathrm{e}^{\jmath kz} \right) + \jmath \frac{eI_0}{\omega \varepsilon^S A} \right]. \quad (12)$$

Notice that the wave is *electroelastic*, with a propagating electric field wave in addition to the elastic behavior, and that $I = I_0 \mathrm{e}^{\jmath \omega t}$.

The relationship between the mechanical and electrical behavior may now be determined using the stress and particle velocity fields for a piezoelectric element of homogeneous composition, finite thickness t, and constant cross-sectional area A as shown in Fig. 3. Note the polarization of the material indicated by the arrow adjacent to P. The stress T, when expressed on the faces of the piezoelectric element normal to the z-axis, becomes the force delivered by the element:

$$\begin{aligned} F_1 = AT|_{z=z_1} &= \mathrm{e}^{\jmath \omega t} \cdot \left[\frac{Akc^D}{\omega} \left(-V_1 \mathrm{e}^{-\jmath kz_1} + V_2 \mathrm{e}^{\jmath kz_1} \right) + \jmath \frac{eI_0}{\omega \varepsilon^S A} \right], \\ F_2 = AT|_{z=z_2} &= \mathrm{e}^{\jmath \omega t} \cdot \left[\frac{Akc^D}{\omega} \left(-V_1 \mathrm{e}^{-\jmath kz_2} + V_2 \mathrm{e}^{\jmath kz_2} \right) + \jmath \frac{eI_0}{\omega \varepsilon^S A} \right]. \end{aligned} \quad (13)$$

The velocities on the faces $z = z_1$ and $z = z_2$ are given by

$$\begin{aligned} v_1 &= -v|_{z=z_1} \\ &= -\mathrm{e}^{\jmath \omega t} \left(V_1 \mathrm{e}^{-\jmath kz_1} + V_2 \mathrm{e}^{\jmath kz_1} \right), \\ v_2 &= v|_{z=z_2} \\ &= \mathrm{e}^{\jmath \omega t} \left(V_1 \mathrm{e}^{-\jmath kz_2} + V_2 \mathrm{e}^{\jmath kz_2} \right) \end{aligned} . \quad (14)$$

Using Eq. (14), it is possible to eliminate V_1 and V_2 from the force Eq. (13);

$$\begin{aligned} V_1 \mathrm{e}^{\jmath \omega t} &= -\frac{v_1 \mathrm{e}^{\jmath kz_2} + v_2 \mathrm{e}^{\jmath kz_1}}{2\jmath \sin kd}, \\ V_2 \mathrm{e}^{\jmath \omega t} &= \frac{v_1 \mathrm{e}^{-\jmath kz_2} + v_2 \mathrm{e}^{-\jmath kz_1}}{2\jmath \sin kd} \end{aligned} \quad (15)$$

where $d = z_2 - z_1$, giving

$$\begin{aligned} F_1 &= \frac{kc^D A}{\jmath \omega} \left[\frac{v_1}{\tan kd} + \frac{v_2}{\sin kd} \right] + \jmath \frac{eI_0}{\omega \varepsilon^S} \\ F_2 &= \frac{kc^D A}{\jmath \omega} \left[\frac{v_1}{\sin kd} + \frac{v_2}{\tan kd} \right] + \jmath \frac{eI_0}{\omega \varepsilon^S} \end{aligned} \quad (16)$$

making use of several trignometric identities.

From the field displacement equation in Eq. (5), the applied voltage V is given by

$$\begin{aligned} V &= \int_{z_1}^{z_2} E\, dz \\ &= \int_{z_1}^{z_2} \left(-\frac{e}{\varepsilon^S} S + \frac{D}{\varepsilon^S} \right) dz \\ &= -\frac{e}{\varepsilon^S} u|_{z=z_1}^{z_2} + \frac{1}{\varepsilon^S} \int_{z_1}^{z_2} D\, dz \\ &= \frac{e}{\varepsilon^S} \left(u|_{z=z_1} - u|_{z=z_2} \right) + \frac{I_0 d}{\jmath A \omega \varepsilon^S} \end{aligned} \quad (17)$$

since $D = (1/A) \int I_0\, \mathrm{d}A = I_0/(\jmath \omega A)$, implying $\int_{z_1}^{z_2} D\, \mathrm{d}z = I_0 d/(\jmath \omega A)$. Since $u = -\jmath \omega v$ and the *static* or *shunt capacitance* is $C_0 = \frac{\varepsilon^S A}{d}$,

$$V = -\jmath \left[\frac{\omega e}{\varepsilon^S} (v_1 - v_2) + \frac{I_0}{\omega C_0} \right], \quad (18)$$

forming the third of three equations which may be combined to give a matrix relationship between the input voltage and current and the output forces and velocities on the

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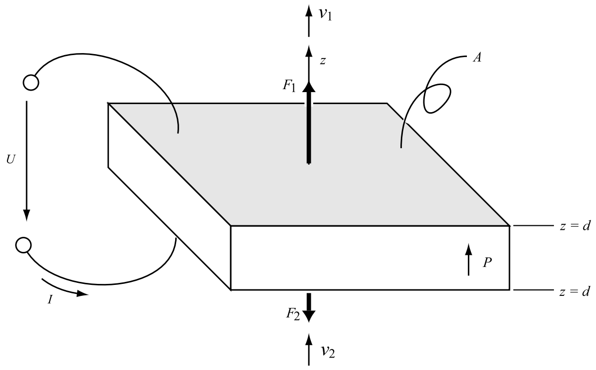

Piezoelectric Materials for Microfluidics, Figure 3 Schematic of a piezoelectric element to illustrate the process of analysis

faces of the piezoelectric element:

$$\begin{bmatrix} F_1 \\ F_2 \\ V \end{bmatrix} = -\jmath \begin{bmatrix} \frac{\zeta}{\tan kd} & \frac{\zeta}{\sin kd} & -\frac{e}{\omega\varepsilon^S} \\ \frac{\zeta}{\sin kd} & \frac{\zeta}{\tan kd} & -\frac{e}{\omega\varepsilon^S} \\ \frac{\omega e}{\varepsilon^S} & -\frac{\omega e}{\varepsilon^S} & \frac{1}{\omega C_0} \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \\ I \end{bmatrix} \tag{19}$$

if $\zeta \equiv \frac{kc^D A}{\omega}$ as the mechanical impedance, with units of mass/time. Notice that

- The output forces F_1 and F_2 are linearly proportional to the input current I and piezoelectric stress coefficient e, and inversely proportional to the permittivity ε^S and circular frequency ω.
- The change in velocity across the element $v_1 - v_2$ is linearly proportional to the input voltage V and permittivity ε^S, and inversely proportional to the circular frequency ω and piezoelectric stress coefficient e.

Approximating Transducer Behavior with Equivalent Circuit Equations

From the expression in Eq. (19) most forms of equivalent circuit models of piezoelectric elements may be found. The Van Dyke circuit [14] is the simplest, using discrete electrical components combined to approximate the piezoelectric element's behavior. I tis used to represent the electrical impedance about one resonance of a freely suspended piezoelectric element, using a shunt capacitor in parallel with an inductor, resistor, and capacitor placed in series to represent the *motional* or resonance behavior of the element. A multivibrator Van Dyke model may be formed by adding additional motional legs, each representing another resonance. Since it lacks any explicit treatment of the output force and velocity, it is not especially useful beyond electrical characterization (see Smits' method below). Other circuit models incorporate the mechanical behavior, and the most prevalent of these are the *Mason* [14] and Krimholtz–Leedom–Matthaei [7] (KLM) circuits.

The Mason equivalent circuit may be derived directly from Eq. (19). It is sometimes called a *transmission-line* circuit model since the transcendental terms in the matrix appear in the same way when modeling power transmission lines. Most importantly, the circuit represents more than one resonance with these transcendental terms. Consider first an element that does not have piezoelectricity, implying the piezoelectric stress coefficient $e = 0$. The force-velocity relationships in the nonpiezoelectric element would then be

$$F_i = \frac{v_1 + v_2}{\jmath \sin kd}\zeta + (\jmath\zeta \tan kd/2)\, v_i \tag{20}$$

for $i = 1, 2$. This relates the force and velocity on one face of the nonpiezoelectric element to the other face. For an element that is piezoelectric, $e \neq 0$, and we can use the third equation in Eq. (19) to determine the actual force due to the applied voltage by substitution in the top two equations.

Piezoelectric Coefficient Relations

Typically, a piezoelectric material's properties are measured through a series of experiments on a set of samples, and these measurements give results easily substituted into the matrix representations of the material. Unfortunately, very few of the components within each of the matrices are defined with the measured data, but the remaining data may be calculated using relations between the coefficients. At times, not enough data are provided to do this; for whatever reason, the data set is incomplete. This problem is especially common with piezoelectric material manufacturers. Further complicating the problem, companies sometimes provide redundant data that are inconsistent—calculated results from some of the provided data does not match the rest of the data that are provided.

The simplest relationship between the electrical property tensors is the inverse relationship between the permittivity, $\boldsymbol{\varepsilon}$, and the inverse permittivity, $\boldsymbol{\beta}$. The equations are

$$\boldsymbol{\beta}^S = \boldsymbol{\varepsilon}^{S^{-1}} \qquad \text{and} \qquad \boldsymbol{\beta}^T = \boldsymbol{\varepsilon}^{T^{-1}}. \tag{21}$$

Other relations transform the matrix representation of the permittivity or inverse permittivity from one set of boundary conditions (either fixed stress or fixed strain) to the other; for the permittivity,

$$\boldsymbol{\varepsilon}^S = \boldsymbol{\varepsilon}^T - \mathbf{d}\,\mathbf{c}^E\tilde{\mathbf{d}} = \boldsymbol{\varepsilon}^T - \mathbf{e}\,\mathbf{s}^E\,\tilde{\mathbf{e}}, \tag{22}$$

and for the inverse permittivity,

$$\boldsymbol{\beta}^S = \boldsymbol{\beta}^T + \mathbf{h}\,\mathbf{s}^D\,\tilde{\mathbf{h}} \;=\; \boldsymbol{\beta}^T + \mathbf{g}\,\mathbf{c}^D\,\tilde{\mathbf{g}} \tag{23}$$

Again, there is a simple inverse relationship between the mechanical coefficient matrices, namely, the stiffness, **c** and the compliance, **s**;

$$\mathbf{c}^E = \mathbf{s}^{E^{-1}} \quad \text{and} \quad \mathbf{c}^D = \mathbf{s}^{D^{-1}}. \tag{24}$$

The boundary conditions on the mechanical property matrices may be changed with the following transformations:

$$\mathbf{c}^D = \mathbf{c}^E + \tilde{\mathbf{e}}\,\boldsymbol{\beta}^S\,\mathbf{e} \;=\; \mathbf{c}^E + \tilde{\mathbf{h}}\,\boldsymbol{\varepsilon}^S\,\mathbf{h}, \tag{25}$$

for the stiffness, and

$$\mathbf{s}^D = \mathbf{s}^E + \tilde{\mathbf{g}}\,\boldsymbol{\varepsilon}^T\,\mathbf{g} \;=\; \mathbf{s}^E + \tilde{\mathbf{d}}\,\boldsymbol{\beta}^T\,\mathbf{d}, \tag{26}$$

for the compliance.

Unfortunately, there are no inverse relations between the piezoelectric coefficients. But, there are a wide collection of equations that describe one piezoelectric quantity in terms of the others. The following is a complete list of these equations:

$$\mathbf{d} = \boldsymbol{\varepsilon}^T\mathbf{g} = \mathbf{e}\mathbf{s}^E, \tag{27}$$

$$\mathbf{g} = \boldsymbol{\beta}^T\mathbf{d} = \mathbf{h}\mathbf{s}^D, \tag{28}$$

$$\mathbf{h} = \boldsymbol{\beta}^S\mathbf{e} = \mathbf{g}\mathbf{c}^D, \tag{29}$$

and

$$\mathbf{e} = \boldsymbol{\varepsilon}^S\,\mathbf{h} \;=\; \mathbf{d}\,\mathbf{c}^E. \tag{30}$$

Through substitution between these equations, many more relations between the variables can be expressed. Written differently, the relations are clearer. In the following equation, the dots within the parentheses represent where the variable at the top of each column would be placed to form the equation for the variable on the left side of each row:

$$\begin{array}{ccccc} & \mathbf{d} & \mathbf{g} & \mathbf{h} & \mathbf{e} \\ \mathbf{d} = & (\cdot) & \boldsymbol{\varepsilon}^T(\cdot) & \boldsymbol{\varepsilon}^T\,(\cdot)\,\mathbf{s}^E & (\cdot)\,\mathbf{s}^E \\ \mathbf{g} = & \boldsymbol{\beta}^T\,(\cdot) & (\cdot) & (\cdot)\mathbf{s}^D & \boldsymbol{\beta}^S\,(\cdot)\,\mathbf{s}^D. \\ \mathbf{h} = & \boldsymbol{\beta}^S\,(\cdot)\,\mathbf{c}^E & (\cdot)\,\mathbf{c}^D & (\cdot) & \boldsymbol{\beta}^S\,(\cdot) \\ \mathbf{e} = & (\cdot)\,\mathbf{c}^E & \boldsymbol{\varepsilon}^S\,(\cdot)\,\mathbf{c}^D & \boldsymbol{\varepsilon}^S\,(\cdot) & (\cdot) \end{array} \tag{31}$$

Experiment and Use

Physically measuring the coefficients of a piezoelectric material can be pursued in several different ways. Two of the most popular are the IEEE method [14] and Smits' technique [11]. Smits' technique has the advantage in that it requires fewer samples to be made by eliminating the radial resonator shape, especially important when considering the time necessary to make, machine, electrode, pole, and test piezoelectric material. Further, Smits' method uses exact equations in the calculation of the material constants, makes possible the calculation of loss data at the same time, and the electric and mechanical constants are measured at the same frequency unlike the IEEE method.

The technique is iterative, but the iteration process is strongly convergent. To determine all of the coefficients of a given piezoelectric material, four different geometries must be used. Each of these geometries encourage a particular vibration mode shape which reduce the number of material coefficients that are participating in the motion to a reasonable number. Named after the desired mode shape, the *thickness/shear* resonator, the *length expansion* resonator with perpendicular field, the *thickness expansion* plate resonator, and the *length expansion* resonator with parallel field provide different material constants when using Smits' technique on each of them. Convergence criteria and proof are provided in Smits' paper [11], but he claims that convergence to the correct values is usually achieved in eight iterations.

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Manufacturing Methods

There are numerous ways to manufacture piezoelectric materials, roughly divided into crystal-growth methods for the single crystal media and a collection of techniques for polycrystalline piezoelectric media. The most obvious and troublesome difference in fabricating piezoelectric materials is the presence of lead in lead-based polycrystalline piezoelectrics like PZT; the lead is present in solid solution and tends to leach from the ceramic during sintering unless a source of lead is provided to maintain equilibrium. For all piezoelectric materials that exhibit remnant polarization, charging effects can be a problem during processing, enough to cause arcing and device failure or substrate cracking.

Among the crystal-growth techniques, the Czochralski (CZ) crystal growth technique is most common, particularly for lithium niobate, lithium tantalate, barium gallium orthophosphate (BGO), langasite, There are other techniques, and this is an active area of research. The development of single-crystal high-strain relaxor ferroelectrics like lead manganese niobate-lead titanate (PMN-PT) [8] using the high-temperature flux technique is a notable example of another approach.

For ceramic materials, there are many approaches available to a researcher for fabrication, including the simple pellet press, tape casting, screen printing, sputter deposition (especially PZT and ZnO), sol-gel techniques for thin films, pulsed-laser deposition, and the hygrothermal technique [10] for deposition of quality PZT onto titanium.

Key Research Findings

During World War II, the discovery of PZT was a fortuitous and remarkable improvement on the state of the art in piezoelectric materials engineering. Since then, modest improvements in performance of piezoelectric materials have been made, with the discovery of single-crystal high-strain PMN-PT materials [8] an important milestone. In the past few years, however, methods for studying and manipulating the structure of ceramics on the scale of the unit cell and lower—the grain structure, the ferroelectric domains, and the structure of the unit cells themselves—have appeared [5]. These techniques are especially well-suited for improving the quality of piezoelectric materials; a recent potassium-sodium niobate/lithium tantalate/lithium antimonate ceramic has a piezoelectric performance equivalent to PZT while eliminating toxic lead [12]. Further, given the need to fabricate ►thin-film devices with features measured in nanometers in conjunction with micro- and nanofluidics, an understanding of the nature of polarization and ferroelectric domain growth in materials compatible with fabrication at these scales is vital. The applications for this technology span many disciplines: nonvolatile memory for computer technology, sensors and sensors for medical and biological diagnostics and actuators and microwave devices for consumer applications [9].

Future Directions for Research

The development of characterization and fabrication methods approaching the unit-cell size of known piezoelectric materials has reenergized the area of piezoelectric materials research in the past few years. By tailoring the structure of piezoelectric materials to maximize the polarizability, strength, and maximum strain, major advances are just beginning to appear. Work on applying the replete knowledge of bulk piezoelectric materials to thin-film materials research remains incomplete, from fabrication of PMN-PT to lead-free ceramics at small scales.

Looking beyond ceramic materials to electrets, polymer and elastomeric piezoelectric materials, and so-called electroactive materials, a wide-open field of research in high-strain piezoelectric materials is appearing. Using the same technology to manipulate the chemical and physical structures of complex ionic or nanotube-imbibed polymers, strains of well over 50 % have been obtained in this new class of material, many examples of which are biocompatible. Improvements in reliability, tolerance of extreme ambient conditions, and modeling are important areas that remain to be considered.

Cross References

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