Piezoelectric Solids and Transducers

Macroscopic View of Piezoelectricity: The Constitutive Relations

Arguably the most important sub-class of ferroelectric solids is the piezoelectrics (origin: piezo Greek for pressure). These are materials in which an applied pressure or stress produces a large surface charge Q and associated displacement vector $\vec{D}$ in the solid. For reasons that will be come clear in a moment, this is called the "direct" piezoelectric effect. Historically the "direct" piezoelectric effect was observed in Rochelle salt, quartz, topaz, and some other materials by Curie brothers (Pierre and Jacques) in 1880. They applied various mechanical forces to these materials and measured charge on their surfaces. From a practical standpoint, the direct piezoelectric effect is responsible for a large number of useful devices, such as strain gauges, spark igniters ("Bic flick"), etc. Because all such devices are converting mechanical energy into electrical energy, they are called "transducers" (more on these shortly.

In 1881 a scientist named Lippman predicted that piezoelectric effects should be reciprocal. That is, an applied charge (or electric) field should produce a pressure (or stress). This is called the converse (or inverse) piezoelectric effect. Later around 1910, P. Langevin in France utilized this effect to build a sonar generator from quartz capacitors. But, quartz is not a very good piezoelectric material, so the sonar was not very useful in World War I. But it became a critical factor in World War II and a very useful technology for maritime technology as well with the advent of stronger piezoelectric materials, such as lead zirconate titanate (PZT).

General observation about piezoelectrics:

- All ferroelectric materials are piezoelectric, and these tend to be the best for transducer application. Useful classes are: (1) Perovskites e.g., $BaTiO_3$ (barium titanate), (2) PZT (lead zirconate, lead titanate), (3) PVF_2 (polyvinylidenflouride), the first useful piezoelectric polymer (i.e., plastic).

- But many non-ferroelectric crystals display significant piezoelectricity, e.g., SiO_2 (quartz), AlN (aluminum nitride), ZnO (zinc oxide).

- And even the III-V compound semiconductors, GaAs, InSb, etc, exhibit piezoelectricity, but it tends to be weak. Nevertheless, the piezoelectric effect at the microscopic level can have profound impact on free-carrier-phonon scattering, as we will see later in transport theory.

Independent of the type of piezoelectric material, there are general expressions called the constitutive relations that couple the macroscopic thermodynamic variables, electric field, displacement vector, stress, and strain. These relations come in pairs, one defining a mechanical variable, and the other an electrical variable. For example, one can write.

$$P_m = C_{mn} \cdot \eta_n - e_{mp} E_p \qquad \text{(inverse piezoelectric effect)} \qquad (1)$$

and

$$D_m = \varepsilon_{mp} E_p + e_{mn} \cdot \eta_n \qquad \text{(direct piezoelectric effect)} \qquad (2)$$

where P_m is the stress, η_n is the strain component (relabeled from e_n in the chapter on elasticity to avoid confusing with the electric charge e), E_p is the applied electric field, C_{mn} are the stiffness coefficients, ε_{mp} is the dielectric constant (possibly tensorial), and e_{mn} are the piezoelectric stress coefficients, named after their connection between stress and field in (1). Note the adoption here of the repeated-index convention; i.e., any subscript that occurs twice is implicitly summed over. That is, (1) really means

$$C_{mn} \cdot \eta_n - e_{mp} E_p \equiv \sum_{n=1}^{6} C_{mn} \cdot \eta_n - \sum_{p=1}^{3} e_{mp} E_p$$

Also, since the stress and strain have six components (reduced notation) and the electric field and displacement have three, the piezoelectric stress matrix is necessarily *non-square*. It is a 6x3 matrix when relating P to E, and it is a 3x6 matrix when relating D to P. As expected, the 3x6 form is just the 6x3 form *transposed*. And as with the stiffness matrix, more and more of its elements become zero as the symmetry of the piezoelectric crystal heightens. Note that non-square matrices are very common in "mixed-force" phenomena; i.e., those that connect physical variables belonging to different canonical pairs in the 1st law of thermodynamics. Another example is electro-optic effect.

An alternative constitutive formulation is

$$\eta_m = S_{mn} \cdot P_n + d_{mp} E_p \qquad (3)$$

and

$$D_m = d_{mn} \cdot P_n + \varepsilon_{mp} E_p \tag{4}$$

where S_{mn} are the compliance coefficients, and the d_{mn} are elements of the piezoelectric strain coefficient.   Whether the pair (1) and (2), or the pair (3) and (4) are used usually depends on practical issues, such as boundary conditions on the sample (e.g., when the boundary is mechanically "free", i.e., "unclamped", then (3) and (4) are convenient because the left side of (3) can be set to zero. This is often done in the analysis of MEMS devices such as membranes and cantilevers).

Independent of the formulation, the piezoelectric stress and strain coefficients are defined so that "bigger is better." And often there is a particular axes in the solid for which the stress or strain coefficients describing the response is a maximum. In the case of the stress coefficient, it is usually called e_{xx} (or e_{11}), and the size of this particular coefficient is often used to qualify piezoelectrics. For example, in crystalline quartz, $e_{11} = 0.17$ Cb/m^2. And in ceramic PZT, $e_{11} = 30.0$ Cb/m^2. Roughly speaking, these define the useful range of piezoelectric materials. And in spite of quartz being so inferior to PZT, it still gets used because of its low cost and low acoustic attenuation at high frequencies.

Non-Centrosymmetry: A Litmus Test for Piezoelectricity

A sufficient condition for piezoelectricity in a solid is that it *not be* centrosymmetric.

Fig. 1
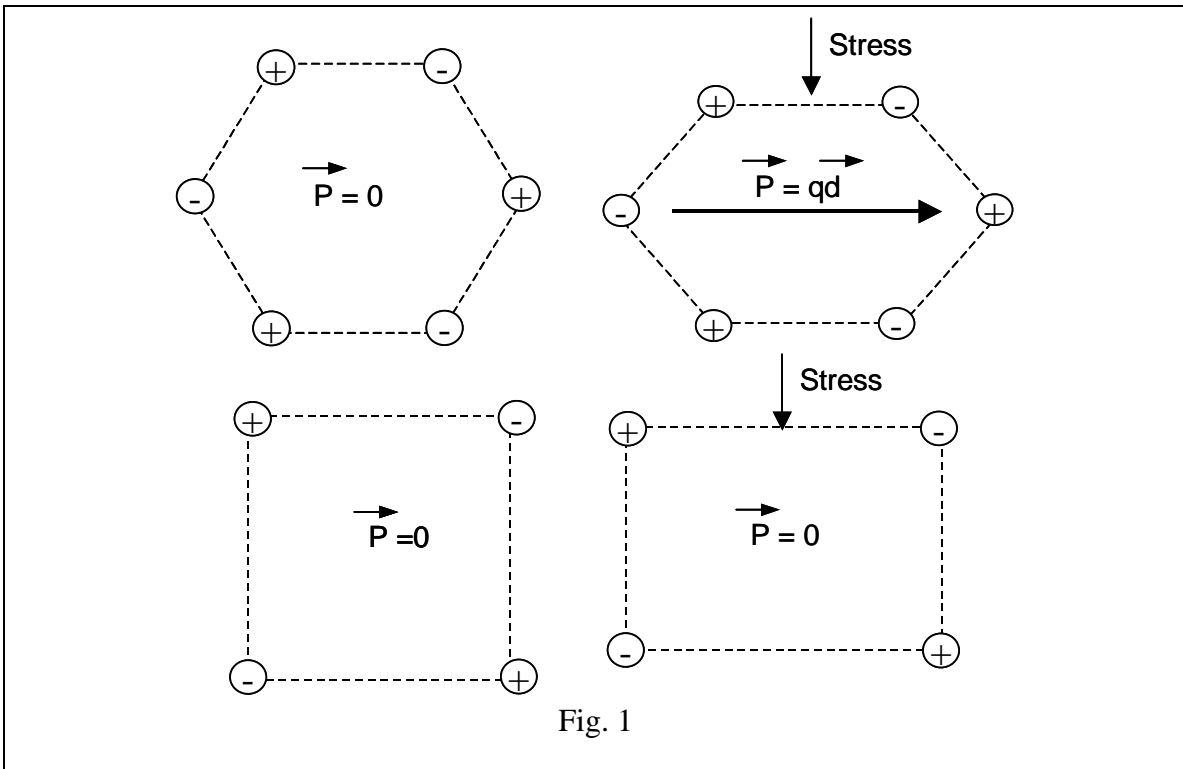
For crystalline solids, symmetry conditions generally involve a virtual geometric operation on the solid with respect to a *specific point*. For the centrosymmetry condition, one seeks a center point and an axis through that point for which inversion (i.e., moving the observation point from $\vec{r}$ to $-\vec{r}$, or equivalently, keeping the observation point fixed and moving the crystal from $\vec{r}$ to $-\vec{r}$) yields the same *atomic form* no matter what the angular orientation of the axis. A good example is shown in the Fig. 1 below where a unit cell is shown for a two-dim honeycomb and square lattice. Both are ionic materials with two oppositely-charge atoms. In the absence of external forces, both are electrical neutral and have no built-in dipole moment because of cancellation. Clearly, if we choose the reference point at the geometric center of each unit cell, we get two different answers for the inversion operation. For the square lattice, inversion leads to the same atomic form, so this lattice is centrosymmetric. But for the honeycomb, it leads to an atomic change, so the ionic honeycomb is non-centrosymmetric. Logically, the act of testing for centrosymmetry, or any symmetry condition for that matter, always proceeds by seeking affirmation, and then deducing the opposite if affirmation is not found.

To verify the correlation between centrosymmetry and piezoelectric behavior, Fig. 1 also shows (right side) the qualitative result of applying a uniaxial stress and assuming an elastic (i.e., Hooke's law) response. The strained square lattice continues to have no polarization since $\vec{P}$ is still the sum of atomic dipoles that cancel in pairs. But the strained honeycomb develops a non-zero $\vec{P}$ due to non-cancellation of the atomic dipoles, and thus should exhibit a piezoelectric effect (Homework problem). If a macroscopic crystal is created from a lattice of such honeycombs, there would be a net balanced positive charge on the right side of the crystal (perpendicular to the applied stress) and a net negative charge on the left side. This would create a net *surface* charge on both sides - the telltale sign of piezoelectricity.

The above definition is rather clear-cut and elegant, but only applicable in crystals. In noncrystalline materials, a centrosymmetry condition can still be tested, provided the material is homogeneous. But they are not tested not against the microscopic atomic form. Instead, it gets applied to macroscopic physical measurements. We start by choosing a specific *axis* and *direction* and a macroscopic physical quantity, usually a vector quantity such as the electric field, a stress, etc. We then measure a second physical quantity, usually

a tensorial quantity, such as the electric susceptibility, the stiffness, etc. If an inversion of the field quantities along *the chosen axis* leaves the tensorial quantities unchanged, then the crystal is said to be centrosymmetric with respect to that tensor quantity. The description of this procedure is rather vague in many books because they will often drop off the "with respect to" clause and just label crystals as centrosymmetric and noncentrosymmetric. This is because all physical quantities within a given tensorial rank have the same behavior. For example, all physical quantities described by 2nd, 4th, or other *even* rank tensors are always centrosymmetric in homogeneous material. This is obvious for quantities of 2nd rank, which can always be written as $X_i = Y_{ij} Z_j$ where Yij is the (matrix) quantity of interest. The test for centrosymmetry involves sign reversal of X_i and Z_j, which trivially leaves Y_{ij} unchanged. Therefore, the crystal is centrosymmetric *with respect to Y_{ij}.*

A good example of a quantity having centrosymmetry is the dielectric constant (or electric susceptibility) through $D_i = \varepsilon_{ij} E_j$. A second and less obvious example is the elastic stiffness. At its most basic level, the stiffness is a 4th rank tensor having $3^{\wedge 4}$ or 81 components. In our earlier discussion of elasticity theory, this was reduced to 36 components by treating the solid as motion-free. Note that the centrosymmetry with respect to *these definitions* of dielectric constant and stiffness does not necessarily mean that the *overall* dielectric constant or stiffness is centrosymmetric. Other effects can break the symmetry by virtue of their odd-order (usually 3rd) tensorial behavior. For example, the dielectric constant can be disturbed by a strong strain (piezo-optic, or acousto-optic effect), or the stiffness can be changed by a strong electric field (piezoelectric "stiffening"). As we will see shortly, the fundamental physical quantity and the change induced can (and usually do) have different tensorial behavior.   This is one of the more confusing points in the theory of "mixed-force" phenomena in solids, for which piezoelectricity is a paradigm.

Symmetry Operations with Respect to a Point: A Quick Return to Ferroelectricity (to be covered later)

The centrosymmetry condition for crystals pertains to inversion with respect to a fixed point in space, any point. Not surprisingly, there are other operations besides inversion that can be defined with respect to the fixed point, and that together classify all crystals into distinct *groups*. They are: (1) mirror-plane imaging, (2) $2\pi/n$ rotation about a

fixed axis through the point, where n = 1, 2, 3, 4, or 6, and (3) 2π/n rotation (where n = 1, 2, 3, 4, or 6) about a fixed axis plus inversion through the point.[1] As stated earlier, the logical goal in these symmetry operations is to seek a point (plus any associated plane, axis, etc.) that yield affirmation, and then deduce non-affirmation if no such point can be found. Note that these point symmetry operations are unrelated to the spatial-symmetry (e.g., translational symmetry) operations that we applied to test for the condition of a Bravais lattice and that ultimately determine the number of possible unique Bravais lattices to be 14. So the point-symmetry operations and the subsequent crystal classification are a great example of an elegant mathematical field called Group Theory.

It turns out that the point-symmetry operations result in 32 different *groups* of crystals, each group satisfying a unique combination of point-symmetry conditions. Of these, 20 are non-centrosymmetric.   Of these 20, ten also possess a *unique* polar axis. By definition, along such an axis the atomic form (or at least one physical property) is dissimilar and not related by any point-symmetry operation associated with the crystal *group*. These remaining ten groups are the ones that can display pyroelectricity.

Quick Return to Ferroelectricty: Yet another Necessary Condition (to be covered later)

The conditions of non-centrosymmetry and a unique polar axis apply as well to ferroelectricty as to piezoelectricity and pyroelectricty. But they are not the only *necessary* conditions. Another condition is that the crystal also possess a unit cell with a non-centered total charge. By this we mean that the center-of-charge does not coincide with the center-of-mass. Mathematically the center of mass is given by

$$\vec{R}_C = \frac{1}{M}\sum_{i=1}^{N} m_i \cdot \vec{r}_i \qquad \text{where} \qquad M = \sum_{i=1}^{N} m_i$$

where N is the number of atoms in the cell and $\vec{r}_i$ are the vectors to each atom from a chosen coordinate system. The charge center is given by

$$\vec{R}_Q = \frac{1}{Q}\sum_{i=1}^{N} |q_i| \cdot \vec{r}_i \qquad \text{where} \qquad Q = \sum_{i=1}^{N} |q_i|.$$

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[1] A great reference on these operations and their mathematical description is found in "Physical Properties of Crystals: Their Representation by Tensors and Matrices," J.F. Nye (Oxford, London, 1976).

When $\vec{R}_C$ and $\vec{R}_Q$ coincide, one does *not get* ferroelectricty.   In BaTiO$_3$, for example, the necessary non-coincidence results from the quasi-mobile Ti atom that can move relative to its nominal position at the center of the cubic unit cell, and get "locked-in" to a non-centered location at T < T$_C$. Similar atomic mobility occurs in PZT and other ferroelectrics. Now we see why historically the phenomena of piezoelectricity and pyroelectricity were discovered decades before the explanation and confirmation of ferroelectricity. Ferroelectricity is much more complicated and rare because it entails chemical as well as symmetrical conditions.

Electric-to-Acoustic Transducers

By definition, transducers are devices that convert energy (or power) from one physical domain into another. Electric motors are a good but rather complicated example. A better example from an electronics viewpoint has been the piezoelectric transducer. Arguably the most useful piezoelectric transducer structure has been the simple parallel-plate capacitor. It is the basis for ultrasonic ("thickness-mode") transducers and RF thin-film bulk acoustic resonator (FBARs), for example.

Before getting into the details it is good to state two assumptions implied by the constitutive relations:

(1) Electric-to-acoustic transducers are almost always reciprocal in the sense that if a given stress yields a certain voltage (or current), then that given voltage (or current) will produce the same stress in reverse.

(2) Electro-acoustic transducers are usually linear in the sense that $V_{out} = AP_{in}$ or, reciprocally, $P_{out} = BV_{in}$, where P$_{in}$ and P$_{out}$ are the input and output stresses, respectively.
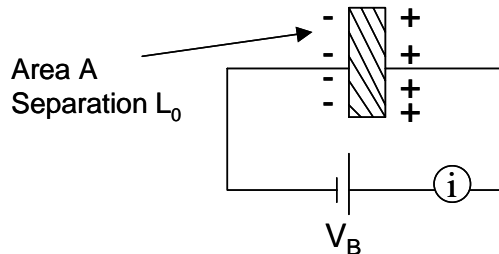

Fig. 2

<u>Parallel-Plate Capacitor with Normal Dielectric (receive mode)</u>

If a homogeneous solid is placed between the plates of a parallel-plate capacitor, the electric field and stress inside the solid will both be uniform if the thickness of the capacitor L_0 is much less than the width, and much less than the acoustic-wavelength λ.   In this case we can write (from electrostatics) $C = \varepsilon_0 \varepsilon r A/L_0$ and $Q = CV$. Hence, at a constant voltage $\delta Q = \delta C \cdot V$. Suppose this change of capacitance is caused by a change in thickness through a perpendicular component of stress. This perpendicular force will change the plate separation and, hence, change the charge on the plates as

$$\delta Q \simeq \frac{dC}{dL} \cdot \delta L = \frac{-\varepsilon AV}{L_0^2} \cdot \delta L = \frac{-\varepsilon AV}{L_0} \cdot \delta[(L - L_0)/L_0] \equiv \frac{-\varepsilon AV}{L_0} \cdot \delta \eta$$

where $\varepsilon \equiv \varepsilon_r \varepsilon_0$, and the last step is aimed at introducing a familiar elastic quantity, the strain $\eta \equiv (L-L_0)/L_0$. This looks very similar to a piezoelectric effect, but is not. The clue is the linear proportionality to the bias voltage, V. In essence, the bias is disrupting the *centrosymmetry* inside the capacitor at the macroscopic scale, thereby allowing a coupling of strain to charge. But as we shall see shortly, this "electrostrictive"-type effect is much weaker than high-quality piezoelectricity.

If we assume the stress is sinusoidal in time, then $\delta \eta$ will also be sinusoidal in time and so will δQ. Hence,

$$i = \frac{-\varepsilon AV}{L_0} \frac{\delta \eta}{\delta t} \rightarrow \frac{-\varepsilon AV}{L_0} \frac{d\eta}{dt}$$

where i is the current through the external circuit. If the stress is uniaxial and the response of the solid is elastic, $P = Y \eta$ where Y is the Young's modulus. Hence,

$$\frac{d\eta}{dt} \simeq \frac{1}{Y} \frac{dP}{dt}$$

A useful figure-of-merit for this or any other transducer is the coupling parameter between the physical domains, in this case between the elastic and electrical. We assume one plate of the capacitor is coupled to a separate material in which there is a unidirectional acoustic plane wave of amplitude P_0. Defining a transmission coefficient τ for propagation

of stress across the interface, we can write $P \approx \tau \cdot P_{inc} \approx \tau \cdot P_0 \sin(\omega t)$, where P_{inc} is the incident stress. So,

$$\frac{d\eta}{dt} \approx \frac{1}{Y}\frac{dP}{dt} \approx \frac{\tau}{Y}\omega P_0 cos(\omega t)$$

and

$$i(t) \approx \frac{-\varepsilon AV}{L_0}\frac{\tau}{Y}\omega P_0 cos(\omega t) = \frac{-\omega CV\tau}{Y}P_0 cos(\omega t)$$

A useful coupling parameter is the responsivity $\mathfrak{R}_I \equiv \dfrac{i_{rms}}{P_{inc,rms}} = \dfrac{\varepsilon AV}{L_0}\dfrac{\tau}{Y}\omega = \omega CV\tau/Y$ [A/W]

Example: Glass capacitor @ 10 MHz coupled to water. $A = 1$ mm^2, $L_0 = 0.1$ mm. Solving we get $C_0 = 3.5$ pF, and because $Y = 73$ GPa for glass, $\varepsilon_r = 4.0$, and $\tau \sim 0.1$, we get $\mathfrak{R}_I \sim 3 \times 10^{-16} \cdot V$ [A/Pa]. So for a typical voltage of 100 V, $\mathfrak{R}_I \sim 3 \times 10^{-14}$ [A/Pa]. This is a very low responsivity, too low to be useful in electronics. To get more responsivity we could increase A, but this starts to make the transducer cumbersome. We could also increase V/L_0, but this is limited by dielectric breakdown effects to $\sim 10^5$ V/cm. A better solution is to fill the capacitor with a good piezoelectric material.

<u>Parallel-Plate Capacitor filled with Piezoelectric (receive mode)</u>

As with a normal dielectric capacitor, we assume the bias voltage is fixed and apply a pressure, i.e., stress, perpendicular to the plates. With a piezoelectric, two things will happen: (1) a change of charge on plates from electrostatics and (2) a change of charge on the plates from the direct piezoelectric effect. To calculate the net effect, we use a modified version of the constitutive Eqn (2) that concentrates just on the plates of the capacitor, guided by the analysis given above. We will assume that there is one predominant piezoelectric stress coefficient e_{xx} along the direction of the E field inside the capacitor (this is not too restrictive… if the piezoelectric material in the capacitor has a different predominant stress coefficient, say e_{yy} or e_{zz}, we could just re-orient the appropriate axes to make it align with the E field). We know on the plates that there will be a surface free-charge density σ, and an electric field perpendicular to the plates $E = \sigma/\varepsilon$. Therefore, $D \equiv eE = \sigma$, also perpendicular to the plates. And since E is uniform between the plates, so

should be D, so we can multiply the left side of Eqn (2) by the area of the plates A to get

$D \cdot A = \sigma \cdot A = Q$.   Similarly, since $E = V/L_0$ and $C = \varepsilon A/L_0$, we can write $\varepsilon E =$

$(C \cdot L_0/A)(V/L_0) = C \cdot V/A$. So multiplying the last term in Eqn (2) by A yields the "capacitor-model" version of the direct piezoelectric relation:

$$Q = CV + e_{xx}\eta_1 A$$

piezoelectric stress coefficient   strain along x axis

(this also shows clearly that since the strain is unitless, e_{xx} must have units Cb/m^2). And

the current in the external circuit becomes:

$$i(t) = \frac{dQ}{dt} = \left(\frac{dC}{dL}\right)V\frac{dL}{dt} + e_{xx}A\left(\frac{d\eta_1}{dt}\right)$$

All piezoelectrics are still elastic and sides of the capacitor are usually "unclamped", so that

$P_1 = Y\eta_1$. Hence, if a sinusoidal stress wave impinges on the capacitor, we have

$$P_1 \simeq \tau P_{inc} \approx \tau P_0 sin(\omega t)$$

and

$$i(t) \simeq \frac{-C \cdot V\tau}{Y}\omega P_0 cos(\omega t) + \frac{e_{xx}A}{Y}\tau \cdot \omega P_0 cos(\omega t).$$

So the responsivity is

$$\Re_I \approx \frac{\tau}{Y}\omega\left(e_{xx}A - C \cdot V\right)$$

Example: PZT capacitor @ 10 MHz (a common frequency for medical ultrasound): $e_{11} \approx 25$

Cb/m^2, $\varepsilon_r \sim 1700$, $A = 1$ mm^2, $L_0 = 0.1$ mm, $Y \approx 4.8 \times 10^{10}$ N/m^2, $\tau \approx 0.1$ (usually the transducers are coupled to "soft" tissue, which is close in acoustic impedance to water, creating a low transmission of stress from the capacitor to the outside medium)

$$\Re_I = 1.3 \times 10^{-10} + 2.0 \times 10^{-11} \text{ [A/Pa]}$$

The direct piezoelectric effect dominates.

And we get $\Re_I \approx 1.5 \times 10^{-10}$ [Amp/Pa] – 430 times more responsive than the glass capacitor !

PZT Capacitors as Ultrasonic Generators

One of the most useful aspects of piezoelectric capacitors is that they can be used both as linear transmitters and receivers. This makes them analogous to electronic transistors in many ways. But unfortunately, the transducers can not provide power gain. To predict the performance of piezoelectrics as transmitters, we drive the capacitor with a sinusoidal voltage source and "radiate" acoustic stress according to the same formalism we just followed. The appropriate piezoelectric constitutive relation is the inverse expression Eqn (1)

$$P_1 = C_{11}\eta_1 - e_{11}\ E_1$$

As in the case of a receiving capacitor, we expect the piezoelectric term to dominate so that

$$P_1 \approx -e_{11}\ E_1 = -e_{11}\ (V_0/L_0)$$

and the transmitted stress under sinusoidal drive is

$$P(t)\ \approx \tau e_{xx}\left(\frac{V_0 \cos(\omega t)}{L_0}\right)$$

For systems applications, a more useful parameter is absolute radiated power.

$$P_{rms} = I \cdot A = \frac{|P|^2}{2Z_0} \cdot A = \left(\frac{\tau e_{11}V_0}{L_0}\right)^2 \frac{A}{2Z_0}$$

where I is the acoustic intensity and Z_0 is the acoustic impedance of the transmitting medium.[2] (note here that P_{rms} is a power and P is a stress)
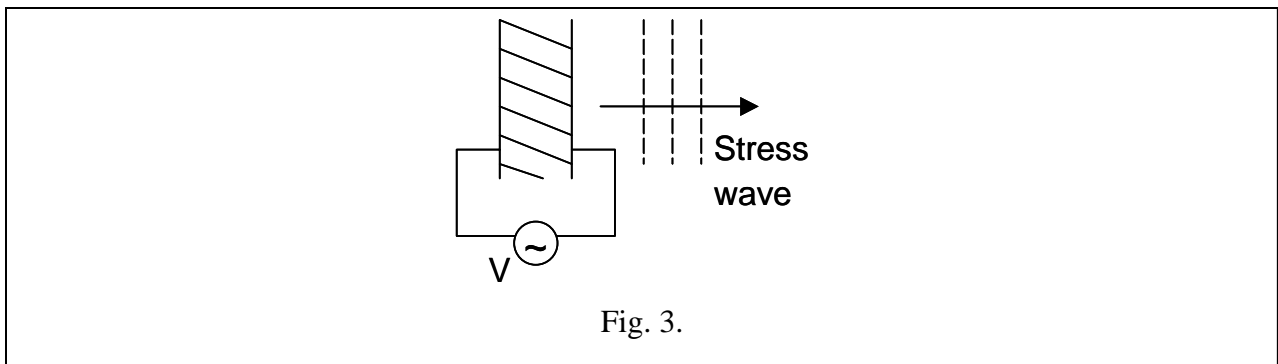

Fig. 3.

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[2] See any good book on acoustics, such as "Fundamentals of Acoustics," L. E. Kinsler, A. R. Frye, A. B. Coppens, and J. V. Sanders 4th Ed (John Wiley, New York, 2000)

Example: PZT generator into water: $A = 1$ mm^2, $L_0 = 0.1$ mm, $e_{xx} = 25$ Cb/m^2, $Z_0 \equiv \rho \cdot c =$ (1000 KG/m^3)·(1400 m/s) ≈ 1.4 MRayl (water), and $\tau \sim 0.1$ (owing to the acoustic impedance mismatch between PZT and water). So, $P_{rms} \approx 2.2 \times 10^{-4} (V_0)^2$ [W], and at a typical drive voltage of $V_0 = 10$ V, $P_{rms} = 22.0$ mW. This is a clear statement of why PZT piezoelectric generators are so important - they can produce useful levels of power with modest drive voltages !

A Summary of Important Piezoelectric Materials for Electronics

We have seen by example how handy the piezoelectric stress coefficients are, at least in capacitor calculations. As stated earlier the piezoelectric stress reduces to a 3x6 (or 6x3) matrix representation of the 3rd rank tensor $\overline{\overline{e}}$. And like the stiffness and compliance matrices, the number of vanishing components goes up with heightened symmetry of the crystal. Because most of the useful piezoelectric materials for electronics have rather high symmetry, it is useful to classify the materials by the number of unique non-zero elements. (1) One unique nonzero element. The popular non-centrosymmetric cubic Zincblende crystals (group "43m") have only one unique element but appearing three times:

$$\begin{pmatrix} 0 & 0 & 0 & e_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & e_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & e_{14} \end{pmatrix}$$

GaAs, InP, InSb, and other important non-centrosymmetric III-V semiconductors fall into this class, as do several II-VI compound semiconductors (e.g., CdTe and ZnSe). The e_{12} and stiffness coefficients for GaAs are listed in Table I.

(2) Two unique nonzero elements. By reducing the symmetry to trigonal (32),[3] we get the piezoelectric stress matrix shown below with two independent coefficients.   The classic example here is crystalline quartz, having the numerical values listed in Table I. Note that e_{11} for quartz is only marginally larger than e_{14} for GaAs.

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[3] the interested student should look back to 215A notes #5, Table I where the 14 Bravais lattices were classified by decreasing degrees of symmetry.

$$\begin{pmatrix} e_{11} & -e_{11} & 0 & e_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -e_{14} & 2e_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

(3) Three unique nonzero elements. By going down to hexagonal (group 6mm) crystals, we get the form below. Two important examples here are AlN and ZnO, which have the same Wurtzite crystal structure and very nearly the same piezoelectric stress coefficients.

$$\begin{pmatrix} 0 & 0 & 0 & 0 & e15 & 0 \\ 0 & 0 & 0 & e15 & 0 & 0 \\ e31 & e31 & e33 & 0 & 0 & 0 \end{pmatrix}$$

(4) Four unique nonzero elements. By reducing the symmetry further to trigonal, we get one more important class of piezoelectric materials with 4 unique elements. The prime examples here are $LiNbO_3$, $BaTiO_3$, and its derivatives, such as $BaSrTio_3$.

$$\begin{pmatrix} 0 & 0 & 0 & 0 & e15 & -e22 \\ -e22 & e22 & 0 & e15 & 0 & 0 \\ e31 & e31 & e33 & 0 & 0 & 0 \end{pmatrix}$$

	Symmetry	Stiffness Coefficients ($\times 10^{10}$ Newton/m^2)						
Material	**Group**	**C11**	**C12**	**C13**	**C14**	**C33**	**C44**	**C66**
GaAs	Cubic 43m	11.9	5.3				6.0	
Quartz	Trig 32	8.7	0.7	1.3	-1.8	10.7	5.8	
AlN	Hexagonal 6mm	41	14	10		39	12	13.5
LiNbO$_3$	Trigonal 3m	20.3	5.3	7.5	0.9	24.5	6.0	7.5
	Piezoelectric Constants (Coulomb/m^2)						**ε_r**	**Density (Kg/m^3)**
Material	**e11**	**e14**	**e15**	**e22**	**e31**	**e33**	**ε_r**	**ρ**
GaAs		0.154					12.8	5317
Quartz	0.171	-0.044					4.27-4.34 depending on direction	2650
AlN			-0.48		-0.58	1.55	8.5	3230
LiNbO$_3$			3.7	2.5	0.2	1.3	85 (in "a" plane) 29 in "c" plane	4644

Non-Crystalline Materials.

By now it should be clear that these forms of the piezoelectric stiffness matrix can apply even to noncrystalline materials. After all, the quantities it relates - the stress to the electric field, or the displacement to the strain - are all macroscopic thermodynamic quantities. So it should not be surprising that the strongest piezoelectric materials, which still tend to be the "exotic" ceramics, can still be ascribed a specific form of piezoelectric stiffness matrix. Perhaps the best-known example is PZT-5H, which fits in to the hexagonal 6mm point group, the same as AlN and ZnO. But its three non-zero stress coefficient e_{33}, has a value typically between 25 and 30 Cb/m^2 !   So there is research aimed at developing single-crystal films of PZT in the hopes of getting an even bigger e_{33} than this.

Dr. Culjat will be providing more material on polymeric piezoelectrics (e.g., PVDF) during his guest lecture.