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Phenomenological piezoelectricity of polymer insulators

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We present expressions for the tensile and bending piezoelectric response as a function of the free charge density and initial polarization present in a dielectric. We pay attention to giving a clear definition of the piezoelectric coefficients. We use our results to analyze some literature data, interpreting the decay in poly(vinyl fluoride) during annealing as being wholly dipolar, but in poly(vinylidene fluoride) there is a mixed space charge and dipolar regime with some results remaining unexplained.

I. INTRODUCTION

Plastic insulating materials can exhibit strong piezoelectric properties. The theory of piezoelectricity is well established for inorganic crystalline substances,[1,2] but the organic polymers differ from the traditional materials in several respects. While the standard theory undoubtedly applies to individual polymer crystallites, the materials themselves have widely different morphologies, varying from wholly amorphous, through the partially crystalline to the almost wholly crystalline, though single crystals are not normally obtained and the crystallites may, in addition, show a domain structure. A second point of difference is that the polymers are frequently dipolar. Again, there is a wide gradation from nonpolar (polytetrafluoroethylene, PTFE), through adventitious dipoles (low-density polyethylene, LDPE) and dipolar main chains [poly(ethylene terephthalate), PETP] to wholly oriented crystal phases [β-phase poly(vinylidene fluoride), PVDF]. Lastly, the piezoelectric activity is frequently associated with space charge within the material, or surface charges. On inspecting the review literature, it has become clear that the basic theory of piezoelectricity in these materials is in some disarray,[3–5] while the extension to the composite morphologies found in practice is in a much weaker state.[6]

We are interested in using gross piezoelectric measurements as an adjunct to the detailed spatial information provided by pressure-pulse techniques.[7,8] In this case, we need to be able to interpret the piezoelectric signals induced across the thickness of a planar sample in terms of the distribution of polarization, charge, and intrinsic piezoelectricity as a function of depth within the sample. For this purpose, the details of the behavior at the crystallite level are not apposite, and some form of mean-field averaging on this scale is called for. While there are some approaches to evaluating the response in this form,[6,7,9,10] we have found them to be somewhat incomplete and in places rather confusing. In the present paper, we give a consolidated account of the various effects, first taken one at a time and then all together, and we take care to distinguish the local (but mean-field-averaged) piezoelectric coefficients from the observed effects at the electrodes. This separation has not been too clear in the past. While some effects can be evaluated directly, others depend upon knowing the corresponding microscopic response functions, and we make no attempt to obtain numerical values for the latter quantities in the present work.

II. CALCULATION OF THE TENSILE PIEZOELECTRIC EFFECTS

We begin by calculating the measured response in the thickness direction to a simple stretching of a film. The distortion is illustrated on a much exaggerated scale in Fig. 1. We assume for the sake of simplicity that the material is homogeneous, at least for length scales compara-

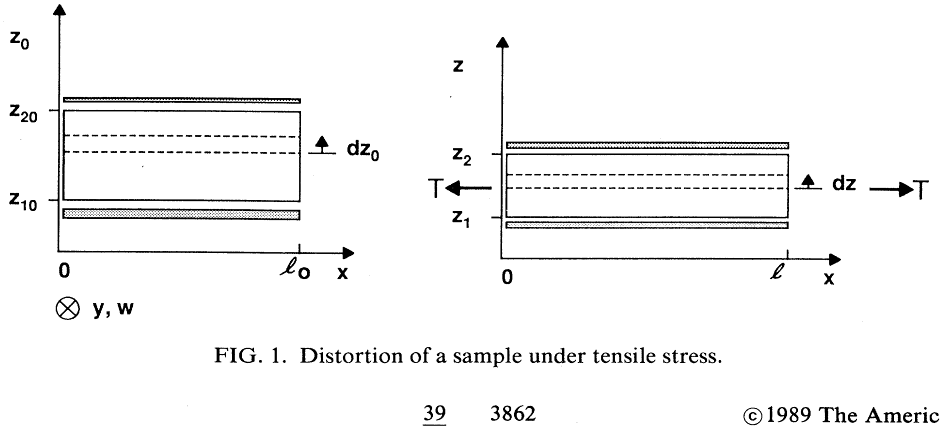

FIG. 1. Distortion of a sample under tensile stress.

ble to the thickness, and isotropic. If this were not the case, then the full apparatus of tensor notation would be required. This is straightforward though cumbersome,[11] and the complication is unnecessary in the present context. Also for the sake of simplicity, we assume that the material is clamped in the third orthogonal or y direction, so that the width w remains fixed. We adopt this restriction in order to make the calculation simple and lift it further on in the paper. In this geometry we are dealing with what is usually labeled as the d_{31} piezoelectric strain coefficient, and its close allies. We start by computing the observed effects due to the geometrical distortion of the charge density and the polarization, then we deal with the strain dependence of the dielectric constant and the polarization, and finally we handle cases in which the dielectric constant is coupled to the other source of piezoelectricity. We restrict ourselves to the case of a short-circuited sample, which is the normal experimental situation for highly resistive materials.

A. Space charge

A slice of the material, originally of thickness dz_0 and length l_0, is extended by the tensile force to a length $l_0+\Delta l$. The strain S is given by the Young modulus Y and the tensile stress X:

$$S=\Delta l/l_0 \ , \tag{1}$$

$$S=X/Y \ . \tag{2}$$

At the same time, there is a contraction in the thickness direction:

$$dz=dz_0(1-\sigma S) \ , \tag{3}$$

where σ is the Poisson ratio. Both Y and σ are the values appropriate to clamping in the y direction, so we expect that $\sigma \leq 1$, where the equality applies if the volume of the material stays constant. Since the space charge is conserved, so its density changes

$$\rho=\rho_0/[(1-\sigma S)(1+S)] \ , \tag{4}$$

where ρ_0 is the initial density. The electrode area increases by the factor $(1+S)$. It is evident that since the distortion in the thickness direction is uniform, then the space charge induces charges on the upper and lower electrodes in precisely the same ratios as before. There is consequently no piezoelectric effect and we can write

$$\Delta Q=0 \quad \text{(space charge)} \ , \tag{5}$$

where ΔQ is the change in induced charge on the lower electrode. This result holds whatever voltage may be applied to the electrodes, so long as it remains fixed, and it is valid for any spatial dependence $\rho_0(z_0)$ of the charge density.

B. Polarization

In assessing the effects of polarization, one must be quite careful about defining what is being taken into consideration. Here, we make the assumption that under distortion, the number of dipoles is preserved, their individual dipole moments stay the same, and their directions remain unaltered. While the first two assumptions are quite sensible, it will be clear that the last one is merely an approximation, because the shearing of the sample implies a local rotation of the material for all but the principal axis directions. In the interest of clarity, we choose to throw the consequences of this rotation into the extrinsic e_e coefficient discussed later. This usage has been adopted previously.[12] Alternative assumptions can be made, such as the conservation of the quantity $(-\partial P/\partial z)$.[6]

We now have the equations

$$D=\epsilon_0\epsilon_\infty E+P \ , \tag{6}$$

$$P=n\langle p\rangle \ , \tag{7}$$

$$\partial D/\partial z=0 \ , \tag{8}$$

$$\int E\,dz=0 \ , \tag{9}$$

where ϵ_∞ is the high-frequency dielectric constant, E is the electric field, P the polarization due to the dipoles, n the dipole concentration, $\langle p\rangle$ the local mean dipole moment in the z direction, and the sample contains no charge and is short circuited. Our third assumption is equivalent to holding $\langle p\rangle$ fixed at its undisturbed value $\langle p_0\rangle$ during the distortion. The number density obeys a relation identical to (4):

$$n=n_0/[(1-\sigma S)(1+S)] \ . \tag{10}$$

Now if we integrate across the sample thickness, we obtain

$$Dt=\int P\,dz \ , \tag{11}$$

where

$$t=z_2-z_1 \ . \tag{12}$$

The charge Q on the lower plate is given by

$$\begin{aligned} Q&=Dlw \\ &=\frac{lw}{t}\int P\,dz \\ &=\frac{l_0(1+S)w}{t_0(1-\sigma S)}\int dz_0\frac{n_0\langle p_0\rangle}{(1-\sigma S)(1+S)}(1-\sigma S) \\ &=\frac{l_0w}{t_0}\frac{1}{(1-\sigma S)}\int n_0\langle p_0\rangle dz_0 \ . \end{aligned} \tag{13}$$

Expanding this to first order, and recalling that we measure only the change ΔQ of the induced charge, we obtain

$$\begin{aligned} \Delta Q&=\frac{l_0w}{t_0}\sigma S\int n_0\langle p_0\rangle dz_0 \\ &=l_0w\sigma S\int dz_0\,P_0/t_0 \ . \end{aligned} \tag{14}$$

Here, P_0 is the polarization in the undistorted sample. This particular contribution to the piezoelectric response is thus proportional to the average initial polarization.

C. Intrinsic and extrinsic strain coefficients

If the material has an appropriate crystal structure, then it will automatically show a piezoelectric effect under strain, given by[1,2]

$$D=\epsilon_0\epsilon_\infty E+e_i S \;, \tag{15}$$

where e_i is the intrinsic piezoelectric strain coefficient. In the stretching mode, S is constant over the volume of the sample. Under short-circuit, space-charge-free conditions, this equation integrates to give

$$\Delta Q=Dlw=lwe_i S\approx l_0 we_i S \;. \tag{16}$$

This contribution will arise only in anisotropic materials, and even then will vanish if the material is composed of randomly oriented crystallites.

We now reach the awkward question of extrinsic piezoelectricity. Under tensile stress, any direction fixed in the material will tend to rotate away from the z axis. This mechanical distortion would cause a corresponding rotation of any dipoles within the sample. Evidently, when the dipoles are initially randomly distributed then $\langle p_0\rangle=0$. Under strain, dipoles partially aligned in the $+z$ direction and dipoles partially aligned in the $-z$ direction will produce offsetting changes so the mean moment remains unchanged, $\langle p\rangle=0$. In the general case, neither of these quantities need be zero. While it might be possible to construct pathological cases where $\langle p_0\rangle=0$ but $\langle p\rangle\neq0$, it seems more likely that a high local moment $\langle p_0\rangle$ in the relaxed state would lead to a high moment $\langle p\rangle$ in the strained state, and conversely. Since the free volume may change under strain, other microscopic effects are possible.[13] To a first approximation, one would expect these to also give sample contributions that go up as the local polarization goes up. Hence, we are led to the *definition* of an extrinsic piezoelectric coefficient e_e

$$D=\epsilon_0\epsilon_\infty E+e_e S \;, \tag{17}$$

and to a *working hypothesis*

$$e_e=cP_0 \;, \tag{18}$$

where c is a dimensionless constant that can be found only by detailed microscopic modeling. Given these two equations, one can essentially repeat the calculations of the previous section, obtaining the result (correct to first order)

$$\begin{aligned}\Delta Q&=\frac{l_0 w}{t_0}cS\int n_0\langle p_0\rangle dz_0\\&=l_0 wcS\int dz_0\, P_0/t_0 \;.\end{aligned} \tag{19}$$

This signal simply enhances the polarization signal given by Eq. (14).

D. Strain gradient coefficients and dielectric-constant changes

In principle, there can be further contributions to the piezoelectric response arising from the gradient of the strain, leading to an equation of the form.[14]

$$D=\epsilon_0\epsilon_\infty+g\, dS/dz \;, \tag{20}$$

where g is the piezoelectric strain gradient coefficient. This, in turn, might have both intrinsic and extrinsic parts g_i and g_e, respectively. Again, we anticipate that the extrinsic coefficient will be linear in the polarization, and write

$$g_e=c^*P_0 \;. \tag{21}$$

In the case of purely tensile strain, the strain gradient is zero and so there are no contributions to the induced charge from these terms.

The dielectric constant is also a function of density and hence of strain, and we write it in the form

$$\epsilon_\infty=\epsilon_{\infty 0}(1+\alpha_\epsilon S) \;, \tag{22}$$

where $\epsilon_{\infty 0}$ is the unstrained value and α_ϵ is the strain coefficient. Microscopic models for this coefficient have been conveniently summarized elsewhere.[9] While imposing uniform strain could give rise to an anisotropic dielectric constant, there is no confusion in the present case because only the z-directed response comes into play. In the absence of space charge and polarization we have merely that

$$D=\epsilon_0\epsilon_\infty E \;, \tag{23}$$

while Eq. (8) remains valid. Using the short-circuit condition, Eq. (9), we see directly that $D=0$ irrespective of the strain, so $\Delta Q=0$ for tensile strain. We note that this is not true if a voltage is applied to the sample.

E. Interaction with the dielectric constant

So far, the possible effects have been considered singly. However, there is an important interaction between changes of the dielectric constant and any space charge or polarization present. This arises because $(D-P)/\epsilon_0\epsilon_\infty$ gives the electric field E, but it is E that is subject to the boundary condition imposed by the applied voltage. Thus the combinations (D/ϵ_∞) and (P/ϵ_∞) are the quantities of physical importance. Indeed, in the case of nonpolar dielectrics, the only contribution to pressure pulse signals comes from the (ρ,ϵ_∞) interaction.[9]

Under static tension several of the combined terms are inactive. The strain is uniform so the dielectric constant is also uniform. In this case, the space charge behaves exactly as in Sec. II A above, and there is no change in the induced charge on either electrode. The strain gradient terms are self-evidently zero.

In the absence of space charge, and with a uniform dielectric constant, the calculations of Secs. II B and II C can be repeated, giving the same results as before. Even with space charge present, it is easy to see that by integrating the expression

$$D=\epsilon_0\epsilon_\infty E+P+(e_i+e_e)S \tag{24}$$

over the thickness of the sample, the electric field term vanishes and we obtain for the flux density D_1 at $z=z_1$ a linear sum of the contributions evaluated earlier. Hence we get from Eqs. (5), (14), (16), and (19) that

$$\Delta Q=\frac{l_0 w}{t_0} S \left[e_i t_0+(\sigma+c)\int P_0\, dz_0\right] . \tag{25}$$

We recall that the parameters e_i and c have to be estimated from microscopic models, while σ can be obtained from the mechanical deformation. The most notable feature of this result is that the charge density does not appear at all.

III. CALCULATION OF THE BENDING PIEZOELECTRIC EFFECTS

When a sample is slightly bent under end loading, it deforms into a circular arc of radius of curvature R, measured to the neutral plane, as shown in Fig. 2. The tensile strain in a layer located at radius r is

$$S=(r-R)/R\ , \tag{26}$$

and there is a corresponding radial compression (for $r>R$) or radial expansion (for $r<R$) which varies with position. The calculation of the change in the induced charge on the lower electrode is straightforward and follows the same lines as before. However, it is algebraically tedious, so the details are given in the Appendix. If we ignore the strain dependence of the dielectric constant, we obtain

$$\begin{aligned}\Delta Q=&\frac{l_0 w}{2Rt_0}\left[-(1+\sigma)\int \rho_0(z_2-z_0)(z_1-z_0)dz_0\right]\\&+\frac{l_0 w}{Rt_0}\int P_0(z_m-z_0)dz_0\\&+\frac{l_0 w}{Rt_0}\left[\int e_e(z_0-z_m)dz_0+g_i t_0+\int g_e\, dz_0\right] ,\end{aligned} \tag{27}$$

where

$$z_m=(z_1+z_2)/2\ .$$

There are three features of note in this result. The induced charge varies as $(1/R)$ as expected,[15] while the intrinsic piezoelectric term vanishes because one half of the sample is in compression and the other half in extension. The weight in factors in the integrals for ρ_0 and P_0 are symmetric with respect to inversion of the z axis, so the signal amplitude does not depend on the sign of R (this symmetry is implicit in the strain gradient term[14]).

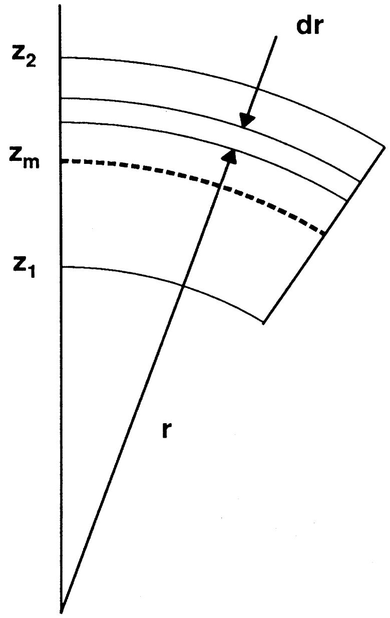

FIG. 2. Distortion of a sample under bending.

The strain dependence of the dielectric constant gives rise to two additional terms

$$\begin{aligned}\Delta Q^{*}=\frac{l_0 w}{Rt_0}\alpha_\epsilon&\left[-\int \rho_0(z_1-z_0)(z_2-z_0)dz_0/2\right.\\&\left.-\int P_0(z_0-z_m)dz_0\right] .\end{aligned} \tag{28}$$

This induced charge depends upon the first moment of the polarization but in a more complicated way on the charge distribution.

IV. THE UNCLAMPED CASE

Real experimental data is usually obtained by using an unconstrained sample, in which case the width w also changes during the stressing of the sample. The calculations given above can be readily modified to take this geometry into account. Under tension, it is simple to show that Eq. (25) still holds, though now σ refers to the familiar unclamped Poisson ratio. The bending case is somewhat more awkward because two curvatures are involved. The details are given in the Appendix, and the result is

$$\begin{aligned}\Delta Q=&\frac{l_0 w_0}{Rt_0}(\sigma-1)\int P_0(z_0-z_m)dz_0-\frac{l_0 w_0}{2Rt_0}(1-\sigma)\int \rho_0(z_2-z_0)(z_1-z_0)dz_0\\&+\frac{l_0 w_0}{Rt_0}\left[g_i t_0+\int g_e\, dz_0+\int e_e(z_0-z_m)dz_0\right]+\frac{l_0 w_0}{Rt_0}\alpha_\epsilon\left[-\int P_0(z_0-z_m)dz_0-\int \rho_0(z_1-z_0)(z_2-z_0)dz_0/2\right] .\end{aligned} \tag{29}$$

While there are now different coefficients for the polarization and space-charge terms, and a different weighting factor for the polarization, the same general pattern holds: a first moment of the polarization and a second moment of the charge density are the leading quantities. All other terms remain unchanged.

V. DISCUSSION AND APPLICATION

The chief results of this work are given in Eqs. (25) and (27)–(29). While the derivation of Eq. (25) is straightforward, the equations for the bending case require some care because of the coordinate distortion which takes place. It is clear that the chief contribution in the tensile case comes from the polarization, whereas in the bending case both the polarization and the charge density are involved. In carrying out the calculation, one must take care to include the change of electrode area as well as the variation of the terms in the line integral.

One possible effect that we have not taken into account is that the charge density might give rise to an extrinsic piezoelectric coefficient, due to the replacement of the initially isotropic surroundings by anisotropic surroundings under shear. In a nonpolar material, this could be taken care of by an adjustment in the value of α_e, though this would not be appropriate in a case where dipolar and charge effects were of comparable size. The other feature that we have not specifically included is any detailed effect of the composite structure of many plastic materials. Other workers have addressed this probem[13,16,17] but have been forced to introduce simple mixing relations, with or without an arbitrary parameter describing a compensation charge. We feel that the assessment of local fields (on the scale of crystallite dimensions) is important for establishing the strength of the polarization in the material, but that these details are not appropriate for evaluating the observed signals. Our procedure amounts to taking the actual charge and polarization for a given z coordinate, and averaging over the area of the sample. Since the charge induced on each electrode depends on these average values, properly weighted with respect to the z coordinate, it seems to us that our results are suitable for interpreting the experimental data.

We wish to draw attention to the question of the extrinsic piezoelectric coefficient. We have chosen to define the change of polarization under strain in a very specific way that seems to us to make good physical sense: the number of dipoles is conserved, the molecular dipole moments are unperturbed in both magnitude and direction, and the polarization P varies proportional to the density of the material. All additional effects such as rotation of the dipoles under strain, alteration of the libration amplitude,[12] or other secondary effects are taken into the coefficient e_e. Other choices are possible, such as[6] conservation of $\partial P/\partial z$ or conservation of P, and the definition of e_e has to be adjusted accordingly.

The experimental results are often expressed in terms of an apparent tensile coefficient $\langle d_{31} \rangle$ and an apparent bending coefficient $\langle \beta_{31} \rangle$, which in the present notation are

$$\langle d_{31} \rangle = \frac{\Delta Q}{w l_0} \frac{1}{YS} \quad \text{(tensile)} , \tag{30a}$$

$$\langle \beta_{31} \rangle = \frac{\Delta Q}{w_0 l_0} R \quad \text{(bending)} . \tag{30b}$$

We have used the notation $\langle \ \rangle$ to emphasize the fact that the observed quantities are weighted averages of the internal distributions. The precise form of the averaging was not clear in earlier work,[6,7] but it is now explicitly given in the equations derived in this paper.

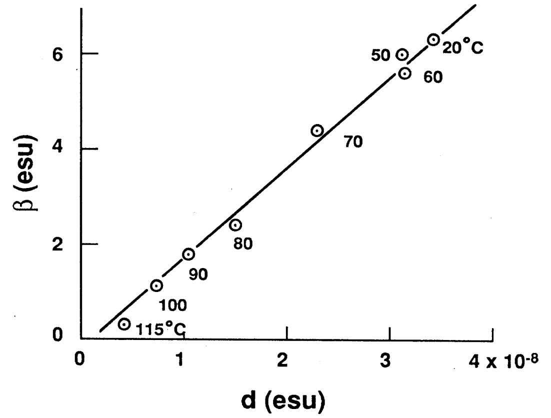

FIG. 3. Data of Kawai (Ref. 15) for poly(vinyl fluoride). The annealing temperature (Celsius) is indicated against the experimental points.

We are now able to offer an interpretation of some of the earlier experimental work. We first consider the data for PVF [poly(vinyl fluoride)] obtained by Kawai.[15] We replot his results in Fig. 3, and we see that the $\langle \beta_{31} \rangle$ and $\langle d_{31} \rangle$ coefficients fall together as the sample is annealed. It is unlikely that space charge and polarization anneal out at the same rate,[18] so we infer that there was never any space charge in the sample. The same argument applies to the e_i and g_i terms in Eqs. (25) and (29), respectively, and the almost negligible intercept supports this. If the polarization were uniform, then the only term left in Eq. (29) would be the term in g_e. However, since the quantity $\langle \beta_{31} \rangle \sim 200$ nC/m is quite comparable to values found for PVDF,[7,15] it seems more realistic to suppose that the sample was nonuniformly polarized. The value of $\langle d_{31} \rangle \sim 0.1$ pC/N is low, and this may merely reflect an accidental near-cancellation of σ and c. Thus, while we are unable to determine the details of the behavior, we are able to deduce that the response is entirely due to dipoles in this material.

The annealing of PVDF reported by Kawai[15] presents interesting features. Again, the tensile coefficient is low compared with later work,[7] although the bending coefficient is comparable. While the original plots of $\langle \beta_{31} \rangle$ and $\langle d_{31} \rangle$ against temperature suggest that $\langle d_{31} \rangle$ begins to anneal at 50 °C while the reduction in $\langle \beta_{31} \rangle$ is delayed until about 75 °C, the plot of one against the other shown in Fig. 4 is more informative. At the lower temperatures, $\langle d_{31} \rangle$ anneals steadily while $\langle \beta_{31} \rangle$ stays nearly fixed, suggesting that polarization is beginning to collapse but that the space charge which exists as a countercharge in this material[13] stays trapped and accounts for the intercept on the $\langle \beta_{31} \rangle$ axis. At approximately 90 °C, this charge detraps and discharges more rapidly than the polarization, so there is a break in the plot and the $\langle \beta_{31} \rangle$ coefficient now drops more rapidly than the $\langle d_{31} \rangle$ coefficient. The intercept which now appears on

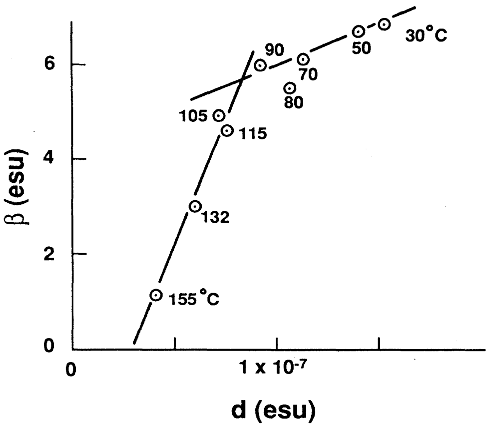

FIG. 4. Data of Kawai (Ref. 15) for poly(vinylidene fluoride). Annealing temperatures are given in degrees Celsius.

the $\langle d_{31}\rangle$ axis suggests that the polarization is nearly uniform, leading to finite contributions to the tensile response but only small contributions to the bending response. Clearly, these arguments need to be supported by comparison with results obtained by other experimental techniques.

Finally, we consider the work of Fukada *et al.*[7] Their PVDF samples were irradiated by an electron beam which had a stopping distance of 13 μm in samples of thickness 25 μm. Consequently, they expected to have a thin charge layer in the middle of the sample and one half of the sample polarized. As they point out, conduction should force the residual charge density to conform to the residual polarization. To a good approximation, we can represent the sample as shown in Fig. 5, and we have a charge per unit area $\sigma_d = P_0$. With some experimental scatter, these authors obtained a proportionality between the bending and tensile piezoelectric responses:

$$\langle \beta_{31}\rangle / \langle d_{31}\rangle = 2.7\times 10^4 \text{ N/m (experimental)} . \qquad (31)$$

They postulated a uniform stress coefficient d_{31} and a uniform stress gradient coefficient f_{31} (analogous to the strain gradient coefficient) over the piezoelectrically active half of the sample in order to account for their result, without relating these quantities directly to the polarization and the charge density. By referring to Eqs. (25), (29), and (30), we see that the observed proportionality will now occur if the intrinsic terms in g_i and e_i are unimportant. The material is known to have an extrinsic strain term in e_e, because this is what gives rise to their laser-induced pressure pulse (LIPP) signals.[19] We expect the dielectric constant term to be unimportant. With these simplifications we obtain

$$\begin{aligned}\langle \beta_{31}\rangle &\simeq \frac{1}{t_0}(\sigma-1)\int P_0(z_0-z_m)dz_0 \\ &\quad -\frac{(1-\sigma)}{2t_0}P_0(z_2-z_m)(z_1-z_m) \\ &\quad +\int cP_0(z_0-z_m)dz_0/t_0 \ , \\ \langle d_{31}\rangle &= \frac{1}{Yt_0}(\sigma+c)\int P_0 dz_0 \ ,\end{aligned} \qquad (32)$$

and carrying out the integrations using the geometry of Fig. 5 yields the ratio

$$\langle \beta_{31}\rangle / \langle d_{31}\rangle = \frac{Yt_0}{4} \ . \qquad (33)$$

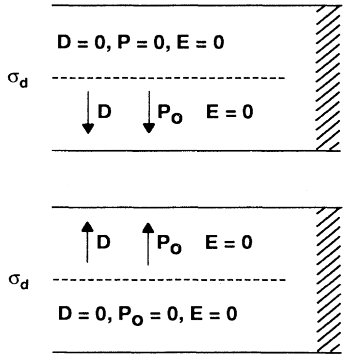

FIG. 5. Electrical state of the samples used by Fukada *et al.* (Ref. 7). The remaining charge is located approximately at the middle of the sample.

Substituting the values $Y = 1.6\times 10^9$ N/m^2 and $t_0 = 25$ μm, the right-hand side of Eq. (33) comes to 1×10^4 N/m, and so is a factor of 2.7 too low. The original authors reached the same result, though they used only a very general description of the piezoelectric response. We agree with them that it seems necessary to invoke other terms to account for the discrepancy. Fukada *et al.* suggested that the strain gradient terms in g_i and g_e were involved.[7] While it seems surprising that these terms should account for the major part of the response, one theoretical attack[16] gives a similar result, though all such calculations must be treated with caution.[5] The ratio would be increased if there were a negative e_i term, but the original data (Fig. 6 of Ref. 7) show that there is no constant offset in the $\langle d_{31}\rangle$ measurements. It follows that the experimental data remains unexplained.

In conclusion, we have shown that while the theory of the tensile piezoelectric coefficient due to permanent dipoles and to space charge is straightforward, the theory of the bending coefficient contains some subtleties, and the mechanical constraints on the sample must be accounted for in some detail. We have stressed that the definition of the extrinsic coefficient e_e depends on what basic assumption has been made with regard to the behavior of the polarization during distortion of the material. By analyzing examples drawn from the experimental literature, we have shown that qualitative and sometimes quantitative deductions can be made about the relaxation processes taking place in poled polymer dielectrics. Finally, we caution that the strong correlations noted between the piezoelectric response and dielectric constant[20] are invalid when space charge is involved, while spatially inhomogeneous dielectrics can exhibit additional effects.[21]

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APPENDIX: BENDING PEIZOELECTRIC RESPONSE.

1. Constrained sample

We first consider the clamped case, so that the width w is held fixed. The sample is bent as shown in Fig. 2. The Poisson equation for this geometry is

$$\frac{1}{r}\frac{\partial}{\partial r}(rD)=\rho \ , \tag{A1}$$

which integrates to give

$$rD=r_1D_1+\int_{r_1}^{r}\rho(r')r'\,dr' \ . \tag{A2}$$

The equation for the displacement is

$$D=\epsilon_0\epsilon_\infty E+P+eS+g(dS/dr) \ , \tag{A3}$$

where

$$e=e_i+e_e \ ,$$

$$g=g_i+g_e \ ,$$

$$S=(r-R)/R \ .$$

We impose the short-circuit condition

$$\int_{r_1}^{r_2}E\,dr=0 \ , \tag{A4}$$

and this yields

$$\int_{r_1}^{r_2}\frac{D}{\epsilon_\infty}dr=\int_{r_1}^{r_2}(P+eS+g/R)\frac{dr}{\epsilon_\infty} \ . \tag{A5}$$

Now we substitute for D from the Poisson equation, and introduce the strain dependence of ϵ_∞,

$$\epsilon_\infty=\epsilon_{\infty 0}(1+\alpha_\epsilon S) \ . \tag{A6}$$

On expanding to first order in the strain, i.e., in $(1/R)$, and using the binomial theorem where appropriate, we get

$$\begin{aligned}r_1D_1\int_{r_1}^{r_2}\left[\frac{1}{r}-\frac{1}{r}\frac{\alpha_\epsilon S}{\epsilon_{\infty 0}}\right]dr &=-\int_{r_1}^{r_2}\frac{dr}{r}(1-\alpha_\epsilon S)\int_{r_1}^{r}\rho(r')r'dr' \\ &\quad+\int_{r_1}^{r_2}dr[P(1-\alpha_\epsilon S)+eS+g/R] \ .\end{aligned} \tag{A7}$$

We now need to refer the integrals to the undistorted coordinate z_0. We have

$$dr=dz_0(1-\sigma S) \ . \tag{A8}$$

This can be integrated exactly, and the result involves logarithmic functions of r which eventually must be expanded. We have verified that the same final results are obtained, to first order in $(1/R)$, by using the approximate form

$$dr\simeq dz_0[1-\sigma(z_0-z_m)/R] \ .$$

In particular, this yields

$$r_2-r_1=t_0+\text{second-order terms} \ .$$

The term in α_ϵ on the left-hand side of Eq. (A7) vanishes to first order, leaving

$$D_1t_0(1-\tfrac{1}{2}t_0/R)+\text{second-order terms} \ . \tag{A9}$$

The quantity of interest is the charge Q_1, given by

$$\begin{aligned}Q_1&=D_1l_1w\\ &=D_1l_0w(1+S_1)\\ &=\frac{l_0w(1+S_1)}{t_0(1-\frac{1}{2}t_0/R)}\left[r_1D_1\int_{r_1}^{r_2}\left[\frac{1}{r}-\frac{1}{r}\frac{\alpha_\epsilon S}{\epsilon_{\infty 0}}\right]dr\right] \ ,\end{aligned} \tag{A10}$$

where l_1 and S_1 are, respectively, the length and the strain at the bottom electrode. The quantity Q_1 is found by substituting the right-hand side (rhs) of Eq. (A7). The terms in the rhs which involve S and $(1/R)$ are already $O(1/R)$ and can be replaced by the corresponding integrals over the undeformed z_0 variable, giving

$$Q_1=Q_{1S}+Q_{1P}+Q_{1\rho} \ ,$$

where

$$\begin{aligned}Q_{1S}&=\frac{l_0w}{Rt_0}\int_{z_1}^{z_2}(e_i+e_e)(z_0-z_m)dz_0+\frac{l_0w}{Rt_0}\int_{z_1}^{z_2}(g_i+g_e)dz_0-\frac{l_0w}{Rt_0}\alpha_\epsilon\int_{z_1}^{z_2}P_0(z_0-z_m)dz_0\\ &\quad+\frac{l_0w}{Rt_0}\alpha_\epsilon\int_{r_1}^{r_2}\frac{(r-R)}{r}dr\int_{r_1}^{r}\rho(r')r'\,dr' \ ,\\ Q_{1\rho}&=-\frac{l_0w(1+S_1)}{t_0(1-\frac{1}{2}t_0/R)}\int_{r_1}^{r_2}\frac{dr}{r}\int_{r_1}^{r}\rho(r')r'\,dr' \ ,\\ Q_{1P}&=\frac{l_0w(1+S_1)}{t_0(1-\frac{1}{2}t_0/R)}\int_{r_1}^{r_2}P_0\,dr \ .\end{aligned} \tag{A11}$$

The fourth term in Q_{1S} is handled by integrating by parts, then doing a series expansion of the logarithmic term so obtained. The result is

$$\frac{l_0 w}{Rt_0}\alpha_\epsilon \int_{r_1}^{r} \rho(r)(r_2-r)[\tfrac{1}{2}r-\tfrac{1}{2}r_1+O(1/R)]dr \simeq \frac{l_0 w}{Rt_0}\alpha_\epsilon \int_{z_1}^{z_2} \rho_0(z_2-z_0)(z_0-z_1)dz_0/2 \ .$$

The term in the polarization becomes

$$\begin{aligned} Q_{1P} &= \frac{l_0 w(1+S_1)}{t_0(1-\frac{1}{2}t_0/R)}\int_{z_1}^{z_2} \frac{P_0}{(1+S)}dz_0 \\ &\simeq \frac{l_0 w(1+S_1)}{t_0(1-\frac{1}{2}t_0/R)}\int (P_0-P_0 S)dz_0 + \text{second-order terms} \\ &= \frac{l_0 w}{t_0}\int P_0\, dz_0 + \frac{l_0 w}{t_0}\int P_0(S_1-S+\tfrac{1}{2}t_0/R)dz_0 \\ &= \frac{l_0 w}{t_0}\int P_0\, dz_0 + \frac{l_0 w}{Rt_0}\int P_0[z_1-z_m-z_0+z_m+\tfrac{1}{2}(z_2-z_1)]dz_0 \\ &= \frac{l_0 w}{t_0}\int P_0\, dz_0 - \frac{l_0 w}{Rt_0}\int P_0(z_0-z_m)dz_0 \ . \end{aligned} \tag{A12}$$

The term in the charge density is first integrated by parts, giving

$$\begin{aligned} Q_{1\rho} &= +\frac{l_0 w(1+S_1)}{t_0(1-\frac{1}{2}t_0/R)}\int_{r_1}^{r_2} \ln(r/r_2)\rho(r)r\, dr \\ &= -\frac{l_0 w}{t_0}\frac{(1+S_1)}{1-\frac{1}{2}t_0/R}\int_{z_1}^{z_2} dz_0 \frac{\rho_0(z_0)}{(1+S)}\ln(r_2/r) \ . \end{aligned} \tag{A13}$$

We expand the logarithm as a power series in the small quantity $(r_2-r)/r$, which leads to

$$\begin{aligned} Q_{1\rho} = -\frac{l_0 w}{t_0}&\frac{1+S_1}{1-\frac{1}{2}t_0/R} \\ &\times \int_{z_1}^{z_2} \rho_0(z_0)(1+S)^{-1}r \\ &\times \left[\frac{r_2-r}{r}-\frac{1}{2}\frac{(r_2-r)^2}{r^2}+\cdots\right]dz_0 \ . \end{aligned} \tag{A14}$$

In order to obtain the result correct to first order in $(1/R)$, the leading term in the square brackets must be replaced using the equivalent of Eq. (3) in bending geometry:

$$\begin{aligned} dr &= dz_0(1-\sigma S) \\ &\simeq dz_0[1-\sigma(z-z_m)/R] \ , \end{aligned} \tag{A15}$$

whence

$$\begin{aligned} r-R &= (z-z_m)-\sigma(z-z_m)^2/2R \\ &\quad + \text{second-order terms} \ . \end{aligned} \tag{A16}$$

Substituting in, we find

$$\begin{aligned} Q_{1\rho} &= -\frac{l_0 w}{t_0}\int \rho_0(z_0)(z_2-z_0)dz_0 - \frac{l_0 w}{t_0}\int \rho_0(z_0)(z_2-z_0)[S_1+\tfrac{1}{2}t_0/R-S-\tfrac{1}{2}(z_2-z_0)/R-\sigma(z_0-z_1)/2R]dz_0 \\ &= -\frac{l_0 w}{t_0}\int \rho_0(z_0)(z_2-z_0)dz_0 - \frac{l_0 w}{2Rt_0}\int \rho_0(z_0)(z_2-z_0)(z_1-z_0)(1+\sigma)dz_0 \ . \end{aligned} \tag{A17}$$

The signal obtained upon bending, ΔQ_1, is due to the change in induced charge, and it amounts to

$$\begin{aligned} \Delta Q_1 = \frac{l_0 w}{Rt_0}\Big[&-\int P_0(z_0-z_m)dz_0 - \tfrac{1}{2}\int \rho_0(z_0)(z_2-z_0)(z_1-z_0)(1+\sigma)dz_0 + \int e_e(z_0-z_m)dz_0 \\ &+ \int (g_i+g_e)dz_0 - \tfrac{1}{2}\alpha_\epsilon \int \rho_0(z_2-z_0)(z_1-z_0)dz_0 - \alpha_\epsilon \int P_0(z_0-z_m)dz_0 \Big] \ . \end{aligned} \tag{A18}$$

We note that the integral involving e_i vanishes. This is the final result for the constrained case.

2. Unconstrained sample

When there are no sideways constraints, we have to be more careful because of the double curvature that occurs. Fortunately, we can choose a *local* set of coordinates as illustrated in Fig. 6. The (r,θ,ϕ) set is orthogonal, and a small shift in position from any given point is associated with a distance ds, where

$$ds^2 = dr^2 + (r\, d\theta)^2 + (r^*\, d\phi)^2 \ . \tag{A19}$$

Here, R^* is the radius of curvature of the neutral plane measured in the transverse or w direction, and r^* is the radial position of a general point measured from the same axial position.

We will not repeat the calculation in detail for this case, but simply indicate the changes that have to be made. From expression (A19) we can find the metric coefficients for this set of coordinates, and hence write down the proper form for the Poisson equation:

$$\frac{1}{rr^*}\frac{\partial}{\partial r}(rr^*D)=\rho\ . \tag{A20}$$

The equation corresponding to Eq. (4) is

$$\rho=\rho_0/[(1-\sigma S)^2(1+S)]\ , \tag{A21}$$

and Eq. (10) has to be similarly modified. In computing the induced charge, we note that the width w_1 of the lower electrode is now different from the undistorted width:

$$w_1=w_0(1-\sigma S_1)\ . \tag{A22}$$

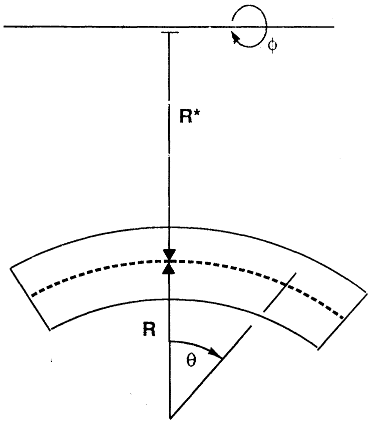

FIG. 6. The local coordinates in the unconstrained case are radius R measured from the center of longitudinal curvature, angle θ measured about an axis through this center, and angle ϕ measured about an axis parallel to the beam and passing through the center of transverse curvature.

With these modifications incorporated, the final result in the unconstrained case turns out to be Eq. (29) to first order in the curvature.

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