Reciprocity failure in piezoelectric polymer composite

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Abstract

Reciprocity principles, which entail equivalent outcome on exchange of cause and effect, are widely used and accepted. We present a piezoelectric composite system designed so that reciprocity does not hold; sensitivity is substantially enhanced. Reciprocity failure is observed in which the piezoelectric direct effect (stress causes polarization) sensitivity d^d_{kij} is unequal to the converse effect (electric field causes deformation) sensitivity d^c_{kij}. The piezoelectric polymer PVDF under isothermal conditions on a polymer substrate obeys reciprocity. Reciprocity failure occurs when a bumpy contact condition causes stress gradients. Reciprocity failure with strong frequency dependence occurs in the presence of thermal flux that is modulated by force: a non-equilibrium condition. Non-reciprocal effects give rise to a maximum enhancement of a factor of five in sensitivity.

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1 Introduction

Reciprocity entails interchange of cause and effect, with equivalent outcome. Reciprocity principles are particularly useful in many fields of study. The concept is distinct from that of time reversibility. Reciprocity may apply even in the presence of energy dissipation, in which time reversibility no longer holds. Reciprocity concepts are known in many settings, including elasticity [1] [2] [3], optics [4], electrical network theory, dielectric materials [5] and piezoelectric materials [6]. In elasticity, the Maxwell-Betti [1] [2] reciprocity theorem may be stated as the displacement due to elastic deformation at location 2 caused by a force applied at location 1 is equal to the displacement at location 1 caused by an equal force at location 2. Work is independent of the order of application of forces and the matrix of influence coefficients is symmetric. In elastic reciprocity it is necessary that a stored energy function exist [7]. General reviews are provided, with emphasis on waves and optics, in Ref. [4] and on acoustic waves in Ref. [8]. Piezoelectric materials, by virtue of their chiral asymmetry, couple electric and mechanical variables. Reciprocity in piezoelectric materials [6] states that the electrical effect of a mechanical cause is equivalent to the mechanical effect of a corresponding electrical cause. As in elasticity, piezoelectric reciprocity makes use of assumptions of equilibrium and of the existence of an energy function. Reciprocity with equilibrium assumptions is in contrast to the Onsager [9] [10] reciprocal relations that relate currents of heat and electricity and thermodynamic driving forces. The Onsager relations were derived using statistical mechanics as a consequence of the time reversibility of microscopic dynamics. Non-reciprocal effects are of interest in that they are linked to internal freedom in materials. For example non-reciprocal effects can arise from an asymmetric dielectric tensor in magneto-optical materials [11] and are useful in optical and other wave isolators.

Piezoelectric materials provide coupling between electrical and mechanical field variables by virtue of their chiral asymmetry. These materials are widely used in transducers, sensors, actuators, and in emitters and detectors of sound and ultrasound. Specifically, piezoelectric materials produce an electric displacement vector $\mathcal{D}_i$ when mechanically stressed via the direct effect sensitivity d^d_{kij} (in pC/N), Eq. 1, and they deform in response to an electric field via the converse effect sensitivity d^c_{kij} (in pm/volt), Eq. 2. Moreover the electric displacement depends on electric field via K_{ij} which is the dielectric tensor at constant stress and temperature. Too, $\mathcal{D}_i$ can depend on temperature change ΔT via the pyroelectric effect; p_i is the pyroelectric coefficient at constant stress. The strain ϵ_{ij}, depends upon stress σ_{kl} via the elastic compliance J_{ijkl}, upon electric field $\mathcal{E}_k$ in piezoelectric materials with modulus tensor d^c_{kij} the converse effect at constant temperature, and on temperature change ΔT via the thermal expansion α_{ij} [6].

$$\mathcal{D}_i = d^d_{ijk}\sigma_{jk} + K_{ij}\mathcal{E}_j + p_i\Delta T \tag{1}$$

$$\epsilon_{ij} = J_{ijkl}\sigma_{kl} + d^c_{kij}\mathcal{E}_k + \alpha_{ij}\Delta T \tag{2}$$

In the context of piezoelectricity, reciprocity entails equality between the coefficients for the converse effect and for the direct effect: $d^c_{kij} = d^d_{kij}$. Reciprocity arises from the assumption of equilibrium and the existence of an energy function [6]; reciprocity is so universally accepted in this setting that the same symbol d is used for both sensitivity tensors. We remark that there is a similar correspondence between the thermal expansion α and the piezocaloric sensitivity in which mechanical stress causes a change in entropy.

In this article, reciprocity failure is demonstrated experimentally in a piezoelectric composite layer with a bumpy contact condition; a frequency dependent reciprocity failure occurs in the presence of thermal flux. Sensitivity is enhanced by up to a factor of five. The concepts may be generalized to other coupled field phenomena.

2 Experimental Method

Experiments were designed to relax several assumptions underlying reciprocity and to obtain enhanced sensitivity.

In the experiments, polyvinylidene fluoride PVDF polymer was used because it is piezoelectric, pyroelectric and flexoelectric. These characteristics allow experimental conditions that probe the limits of reciprocity.

The PVDF films, type DT 1-028K/L, manufactured by Measurement Specialties, Inc., were 28 μm thick and 12.5 mm wide; they were provided with thin metal coating for electrical contact and with electrodes; the total thickness was 40 μm. The magnitude of the d_{33} piezoelectric coefficient was reported as 33 pC/N [12]. Charges for the direct effect were measured using a charge amplifier Kistler 5010 and a digital oscilloscope Tektronix TDS 3014B. A preamplifier SRS SR560 with high and low pass filter capability was used to minimize noise in the experiments. For the converse effect (deformation from electric field), a function generator SRS DS345, a lock-in amplifier SR850 DSP and a fiber optic displacement sensor MTI 2000 were used. The temperature of the PVDF film was controlled using a Cambion Cambridge, MA thermoelectric module and measured using a digital thermometer Omega 871A with Type K thermocouples. The PVDF film was secured in place on a substrate using a UHU acid free glue-stick. For initial studies a Nylon 6-6 substrate was used. The piezoelectric sensitivity was then measured using both the direct and converse effect at ambient temperature $\sim 22\,^\circ$C. For the direct effect (electric polarization from mechanical stress), a speaker of resistance 4 Ω was mounted above the PVDF film with a 12.7 mm diameter polycarbonate rod transmitting force from the speaker to the piezoelectric element [13]. The speaker was calibrated by applying a known current and measuring the force via an analytical balance. A nominal input voltage of 20 V p-p from a 50 Ω source impedance was used. The resulting charge developed by the PVDF was measured with the charge amplifier. The lower limit on frequency was due to drift; the upper limit was due to the tendency of the unconstrained rod to vibrate off the specimen. To eliminate pyroelectric noise effects due to air currents, the specimen was placed in a polymer enclosure insulated with mineral wool.

For the converse effect, the function generator was used to supply a 20 V p-p sine wave directly to the PVDF film. A small mirror was cemented to the surface with cyanoacrylate adhesive, allowing a fiber optic displacement sensor to be used to measure the displacement of the piezoelectric in response to the input voltage. The fiber optic sensor emits light from one set of fibers and detects reflected light from another set of fibers to determine displacement. Its end is not in contact with the mirror or any part of the specimen. Again, a polymer enclosure filled with insulation was used to shield the specimen and maintain uniform temperature. Axial displacement on the order 1 nm (50 pm/V × 20V = 1 nm) entailed a signal-to-noise ratio of about 5×10^{-3}. Therefore a lock-in amplifier with a long time constant of 100 seconds was used to measure the amplitude of the displacement. The lower limit on frequency was due to drift and the requisite long time constants. The instrument configuration is shown in Figure 1.

To relax the assumptions underlying reciprocity, a bumpy surface was provided to allow advancing contact in a two layer composite; also to allow the possibility of heat flux modulated by force. To that end, a layer of tin granules was placed on the top surface of the PVDF. Granules of two sizes, 1 mm and 150 μm were used in separate experiments. A copper foam block 8.3 mm thick resting on top of the tin granules served as a heat sink. A small preload of 0.5 N was applied to the polycarbonate rod to keep it in place over the specimen. The piezoelectric specimen was securely fastened to a Newport 270 vertical stage to allow for fine adjustments underneath the speaker. The additional layers on top of the PVDF increased the noise superposed on the direct effect signal by a factor of ten so the signal-to-noise ratio decreased to about 5. As above, a lock in amplifier was used to extract the signal. To determine the effect of surface bumps in the boundary conditions, the d_{33} piezoelectric coefficient was first measured at ambient temperature with both direct and converse methods.

Effects of thermal flux were determined using a thermoelectric module to heat or cool the two layer composite. A thin aluminum plate was coupled to the module with thermally conductive grease and the piezoelectric sheet was cemented to that plate. Thermocouples were placed on the top and bottom surfaces of the PVDF film to determine temperature and infer gradients. To determine the effect of heat flux, 1 amp was supplied to the thermoelectric module creating a 1°C temperature difference across the PVDF. The average temperature of the PVDF film was 35.5 ± 0.5°C. The sensitivity was then measured with the PVDF at a uniform temperature of 35.5 ± 0.5°C. To maintain a uniform temperature, warm air was flowed into the insulated chamber. In combination with the thermoelectric module, the warm air was used to control the temperature gradient in the PVDF film.

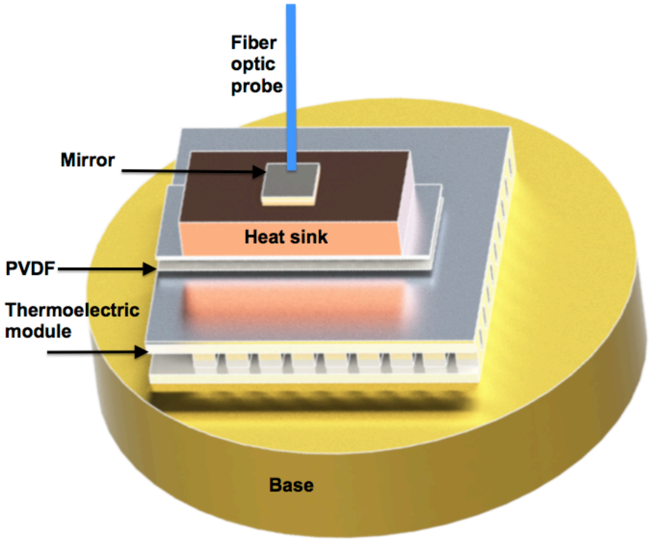

Figure 1: Diagram of experimental apparatus: configuration for measuring deformation produced by electric field. Electrodes and environment chamber are not shown.

3 Results

The observed direct and converse piezoelectric sensitivity for PVDF at ambient temperature on a polymer Nylon substrate is displayed in Figure 2. The direct effect and converse sensitivities were the same, indicating reciprocity is obeyed. Moreover the sensitivity agrees with reported values. The units pC/N and pm/V are equivalent.

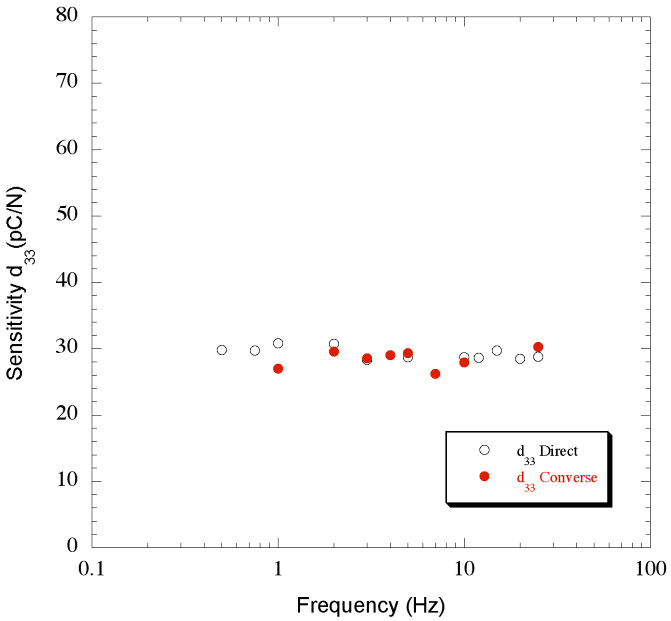

Figure 2: Direct ○ and converse ● piezoelectric sensitivities of PVDF are equal at ambient temperature on a polymer Nylon substrate; reciprocity is obeyed.

Figure 3 shows the effect of a bumpy surface which alters stress transfer, on the effective d_{33} piezoelectric coefficient of the PVDF composite using the direct and converse effects. Direct effect sensitivity at ambient temperature was about 55-60 pC/N, and varied little over several decades (factors of ten) of frequency. The measured d_{33} coefficient using the converse effect at ambient temperature matched closely with reported values; the average sensitivity was approximately 30 pC/N. The difference reveals reciprocity failure.

Figures 4 and 5 show the effects of a thermal gradient, about 1°C, and of uniform elevated temperature on the piezoelectric response. The average temperature with and without the gradient was about 35.5 ± 0.5°C. The measured sensitivity using the converse effect increased from 30 to 40 pC/N independent of frequency, for both the uniform elevated temperature and for elevated temperature plus a gradient. The sensitivity measured with the direct effect, however, shows a marked frequency dependence for 150 μm granules; frequency dependence was much less for the 1 mm granules. As the frequency decreased, the measured sensitivity increased. This frequency dependence occurred only in the presence of heat flux and was not observed when the specimen was heated to a uniform temperature.

4 Assumptions and causes

Reciprocity failure from contact with a bumpy surface at constant temperature arises as follows. Local indentation of the piezoelectric film by a bumpy surface gives rise to an additional polarization due to gradient piezoelectricity [14], also called the flexoelectric effect [15]. PVDF is known to exhibit such gradient effects. Flexoelectric gradient effect sensitivity is intrinsic to the material. Although it can be evoked by local bending or indentation of the PVDF, it is distinct from mechanical effects seen in sandwich structures [16]. In the present experiments, flexoelectric effects contribute to the overall direct effect sensitivity, so the measured d_{33} is an effective sensitivity. By contrast, converse effect measurements entail observing deformation due to an electric field; the deformation is free to occur and the bumps have no influence. Flexoelectric effects are expected to be reciprocal provided an energy function exists and that the same kind of gradient prevails in both direct and converse effects. That would entail a gradient in field to correspond to the gradient in stress imposed by contact of bumps. Such a gradient does not occur in the converse effect experiments because the surface in contact is free to expand and contract. Also, uniform electrodes provide

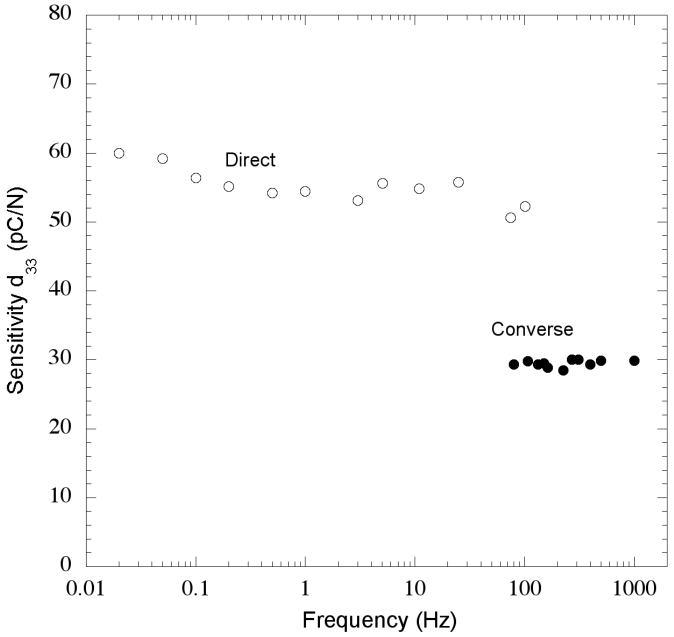

Figure 3: Reciprocity failure, $d^c_{kij} \neq d^d_{kij}$, for PVDF composite with a bumpy contact condition at ambient temperature, 150 μm tin powder.

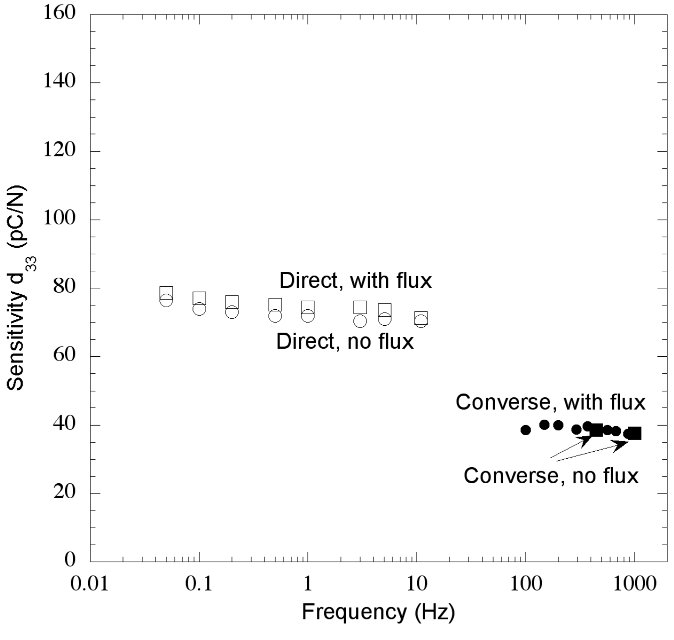

Figure 4: Reciprocity failure, $d^c_{kij} \neq d^d_{kij}$, for PVDF composite with a bumpy contact condition, 1 mm tin beads, no heat flux, direct effect ○, converse effect ■, and effect of heat flux, direct effect □, converse effect ●, uniform temperature 35.5°C.

the electrical boundary conditions so that the imposed electric field is uniform with no gradient. Specifically, following the transparent derivation of Nye [6], reciprocity arises from differentiation of an energy function

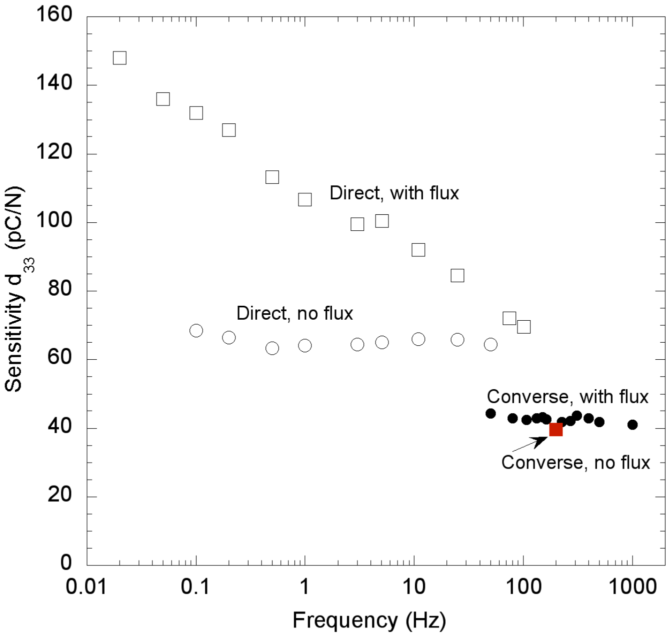

Figure 5: Reciprocity failure, $d^c_{kij} \neq d^d_{kij}$, for PVDF composite with a bumpy contact condition, 150 μm tin powder, no heat flux, direct effect ○ , converse effect ■, and effect of heat flux, direct effect □, converse effect ●, uniform temperature 35.5°C.

U with respect to electric field and mechanical stress,

$$-\frac{\partial^2 U}{\partial \mathcal{E}_k \partial \sigma_{ij}}_T = \frac{\partial \epsilon_{ij}}{\partial \mathcal{E}_k}_{\sigma,T} = \frac{\partial \mathcal{D}_k}{\partial \sigma_{ij}}_{\mathcal{E},T} \tag{3}$$

The condition of constant stress σ is satisfied when one applies an electric field, because there is no constraint on the resulting strain. However when force, hence stress, is applied, the condition of constant field $\mathcal{E}$ is satisfied only in the mean by use of the charge amplifier which holds the voltage across the piezoelectric element to zero. Locally the field varies due to the heterogeneous stress distribution imposed by the bumpy surface contact as force is applied. The effect of locally heterogeneous field does not average to zero because the material has a flexo-electric sensitivity.

Reciprocity failure from energy flux arises as follows. The contact area changes with applied force, modulating the heat flux. This gives rise to an additional electric polarization via the pyroelectric effect. Coupled field reciprocity considered here assumes equilibrium and the existence of a conserved energy density, hence also assumes zero flux. Energy flux combined with a contact condition can give rise to singular or negative stiffness [17] that is stable, or to large enhancements of effective piezoelectric sensitivity [18] of a ceramic disc. The frequency dependence favoring low frequency in such effects is a consequence of thermal time constants associated with thermal conductivity [17]. Smaller granules in contact give rise to a stronger modulation hence a more pronounced non-reciprocal effect.

Non-equilibrium conditions alone are not sufficient to generate deviations from reciprocity. For example, in viscoelastic materials that dissipate mechanical energy, the elastic - viscoelastic correspondence principle is used to obtain analytical solutions to viscoelastic problems if a solution for the same geometry is known in elasticity. For physical properties that are probed by sinusoidal excitation, one replaces each variable that represents a physical property by a complex quantity [19] in which the imaginary part represents the dissipative aspect and the real part represents the effect of stored energy.

The observed effects cannot be due to difference between adiabatic and isothermal properties because that effect is too small. Similarly the lateral constraint imposed by the substrate in 3-D elasticity has too small an effect to contribute appreciably.

The system studied here is a composite of two layers, the piezoelectric polymer and the granules. Multilayer composites can be made but require designed electrical connectivity to obtain the effects observed in the two layer composite.

5 Conclusion

To conclude, reciprocity is obeyed if the piezoelectric polymer is subjected to globally and locally uniform stress or field under isothermal conditions. Reciprocity failure is observed when a bumpy contact condition causes stress gradients. Reciprocity failure with strong frequency dependence is observed in the presence of thermal flux that is modulated by force. Enhancement of sensitivity occurs in both cases. There is potential for large enhancement of effective piezoelectric sensitivity in composites of this type. Moreover, the concepts illustrated here for piezoelectric materials may be generalized to other coupled field phenomena such as thermoelastic and magnetoelastic.

Acknowledgment

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