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# Thermodynamic modeling of pyroelectric and piezoelectric properties of cellular polymers

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A thermodynamic approach is presented to model devices manufactured with cellular polymers. They are heterogeneous nonpolar space-charge electrets that exhibit much higher piezoelectricity than the well-known ferroelectric polymers. Their pyroelectric and piezoelectric properties are characterized by adequate coefficients which quantify the performance of devices manufactured with those materials. The method presented in this contribution to calculate those coefficients is exact and consistent avoiding *ad hoc* simplifications introduced in other approaches. The results obtained by this method allow drawing conclusions regarding device optimization.

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## I. INTRODUCTION

Electrets have been widely used in electromechanical and pyroelectric devices taking advantage of the voltage induced in a load by the motion of the electret relative at least to one electrode.[1–4] Until recently, the best space-charge polymer electrets were highly insulating nonpolar polymers and the best piezoelectric polymer electrets were semicrystalline polar polymers with ferroelectric properties. Recently it has been shown that heterogeneous nonpolar space-charge electrets can exhibit much higher piezoelectricity than the well-known ferroelectric polymers.[1,5–7]

In the cellular or porous polymer electret materials the voids serve not only to reduce the polymer mass and hardness but also to form giant dipoles when charged to opposite polarities on their upper and lower internal surfaces. These dipoles are easily deformed, and large changes in their dipole moments may therefore be expected upon application of mechanical, electrical, or even thermal stress. The resulting macroscopic behavior is very similar to those of ferroelectric and piezoelectric polymers, even though the microscopic origins of the observed phenomena are very different and many fundamental and applied aspects of the physics of heterogeneous space-charge electrets have not been explored so far.

This contribution is concerned with the elaboration of a model that allows the deduction of the coefficients that characterize the pyroelectric and electromechanical properties of devices manufactured with such materials. It is a thermodynamic approach which, in addition to the thermal and mechanical energies, includes the electric energy. With this generalized thermodynamic model it is possible to analyze the conversion among thermal, mechanical, and electrical energies and not only between thermal and mechanical energies, which is the traditional scope of thermodynamics.

After an overview of the electrostatics of such devices, a thermodynamic system is defined. It is in contact with three reservoirs; besides the two traditional ones, i.e., one at constant pressure and the other one at constant temperature, it is also in contact with a battery that plays the role of a reservoir at constant electrical voltage. It will be shown that the calculation of all physical quantities of interest in such systems becomes straightforward by applying the first law of thermodynamics. It is more general than the model introduced by Dreyfus and Lewiner[8] which is restricted to electromechanical properties.

## II. DEFINITIONS AND PHYSICAL CONCEPTS

Charged polymer foams are unusual materials since piezoelectricity and pyroelectricity are not caused by symmetry breaking on a microscopic level but arise from the material heterogeneity coupled with a nonsymmetric charge distribution. For a description of their pyroelectric and piezoelectric (actuator and sensor modes) properties, the measurable quantities are the charge on the electrodes, $q$, the temperature, $T$, the thickness of the sample, $x$, the external applied force, $\Delta F$, and the voltage across the electrodes, $V$. In terms of those quantities the pyroelectric, $k_{(\mathrm{py})}$, actuator, $k_{(a)}$, and sensor, $k_{(s)}$, coefficients are defined as[7]

$$k_{(\mathrm{py})} = \left.\frac{\Delta q}{\Delta T}\right|_{p}, \tag{1a}$$

$$k_{(s)} = \left.\frac{\Delta q}{\Delta F}\right|_{V}, \tag{1b}$$

$$k_{(a)} = \left.\frac{\Delta x}{\Delta V}\right|_{p}. \tag{1c}$$

The polymer foil employed (usually of polypropylene) in the construction of such devices usually consists of three layers:[1,6,7,9,10] two continuous layers with a thickness of a few microns without any voids sandwiching a dominant mid-section layer with a large number of flat voids. The lateral dimensions of these voids are about 100 $\mu$m and the vertical dimensions are up to about 10 $\mu$m as shown in Fig. 1.

During corona charging of these films large electric fields cause Paschen breakdown of the gas inside the voids[11–13] of the polymer. The charges generated during the plasma discharge are trapped on the surface of the voids and form oriented macroscopic dipoles that are nearly aligned with the axis along the thickness of the foam. The existence of these aligned dipoles combined with a highly compliant foam is

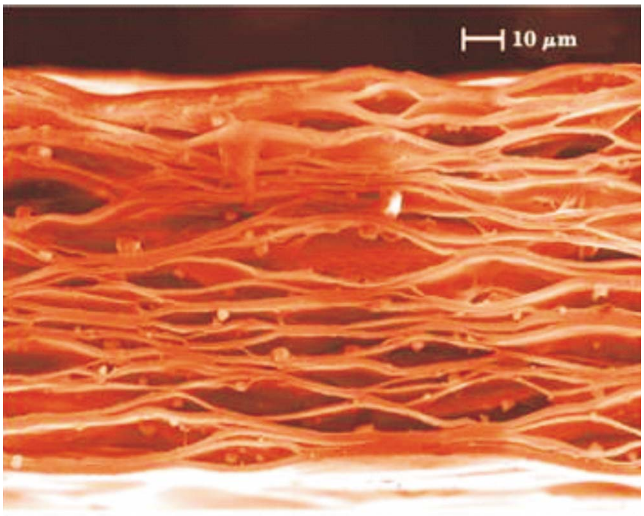

FIG. 1. (Color online) Electron scanning microscopy (SEM) images of a cross section of a cellular polypropylene film.

the factor that leads to significant macroscopically observable piezoelectric and pyroelectric couplings in the thickness direction. Specifically the piezoelectric coupling coefficient in this direction is quite high; experimentally measured values range up to 200 pC/N in cellular polypropylene.[1,5] To improve the performance of those materials it is of essence to retrieve further information about the constitution of such dipoles.

### A. Electrostatics

In Fig. 2 the model of a charged cellular polymer is schematized. The devices under consideration have a thickness which is much smaller than the other dimensions, allowing a one-dimensional approximation. In this figure three layers are shown but it can be easily generalized to a $N$-layer model which is more appropriate to a material whose image is shown in Fig. 1.

The gas voids have relative permittivity, $\varepsilon_g$, and are represented by $N$ layers with thicknesses given by $x_{gi}$, where $i=1,\ldots,N$. The polymer matrix is represented by the layers with thicknesses given by $x_{pi}$, where $i=1,\ldots,N+1$. The charge densities on the electrodes are $\sigma_a$ and $\sigma_b$. The charge densities on the surfaces of the gas layers, which model the voids inside the polymer, are $\sigma_{gi}$, where $i=1,\ldots,N$. The external surfaces of the polymer (in Fig. 2 represented by the thicknesses $x_{pa}$ and $x_{pb}$) usually are compact, and spatial charges on these layers may be generated while poling. It is important to take those charges into consideration since they contribute to the electrical field inside the device but specifics of their distribution are irrelevant to our treatment, wherefrom they may be represented by charge layers $\sigma_{pa}$ and $\sigma_{pb}$, which are located at mean distances $x_{pa}$ and $x_{pb}$ from the electrodes $a$ and $b$, respectively.[9,10,13] $V$ is the electric tension between the electrodes $a$ and $b$. The space charges and the charges on the surfaces of the voids (or gas layers) are trapped and do not change when low voltages are applied between the electrodes of the device.

The one-dimensional assumption simplifies considerably the electrostatic description since the electric fields inside the sample depend only on the charges that generate them and not on their distance to these charges. We avoid the use of the electric displacement vector in order to simplify notation since a charged porous polymer presents microscopic (due to the electric permittivity of the polymer $\varepsilon_p$) and macroscopic polarizations due to the charges on the internal surfaces of the voids.

In Fig. 2 a rectangular Gaussian surface is drawn which contains the electrode $a$ and is extended up to gas layer $i=3$. Applying Gauss' law (the field inside the electrode $a$ is zero since it is metallized) one concludes that the electric field $E_{g3}$ is given by

$$E_{gi} = \frac{\sigma_a - \sigma_{pa} + \sigma_{gi}}{\varepsilon_0 \varepsilon_g} \qquad i = 1,2,\ldots,N, \tag{2}$$

where the International System of units (SI) has been used. The absolute electric permittivity of the gas is given by $\varepsilon_0\varepsilon_g$ where $\varepsilon_0$ is the electric permittivity of the vacuum and $\varepsilon_g$ is the relative permittivity of the gas. The electric fields inside the outermost layers (capping layers) with thicknesses $x_{pa}$ and $x_{pb}$ are obtained in a similar way and yield

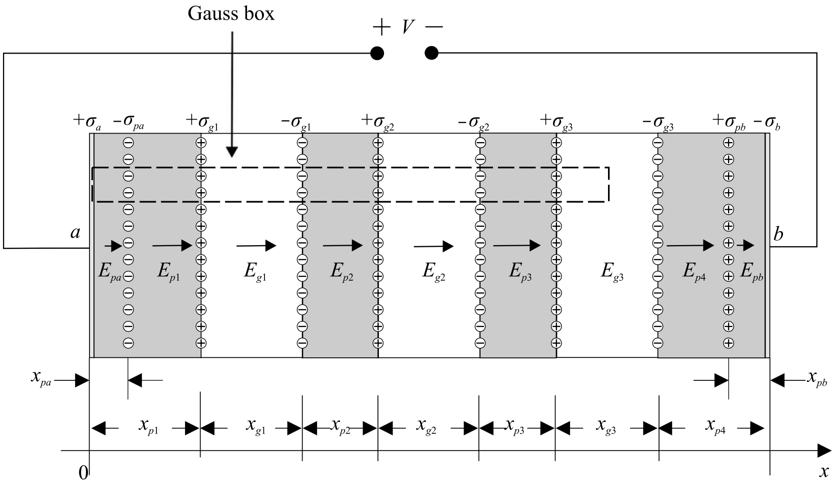

FIG. 2. Simplified model of a cellular film with $N=3$.

$$E_{pa} = \frac{\sigma_a}{\varepsilon_0 \varepsilon_p} \quad \text{and} \quad E_{pb} = \frac{\sigma_a - \sigma_{pa} + \sigma_{pb}}{\varepsilon_0 \varepsilon_p}, \tag{3}$$

respectively. $\varepsilon_p$ is the relative permittivity of the polymer. Inside the polymer layers all fields have the same value, i.e.,

$$E_{p1} = E_{p2} = \cdots = E_{pN} = E_{p(N+1)} = E_p, \tag{4}$$

where

$$E_p = \frac{\sigma_a - \sigma_{pa}}{\varepsilon_0 \varepsilon_p}. \tag{5}$$

Employing Kirchhoff's second law to the system, one obtains

$$\begin{aligned} V + E_{pa}x_{pa} + E_{p1}(x_{p1} - x_{pa}) + E_{g1}x_{g1} + \cdots + E_{pN}x_{pN} + E_{gN}x_{gN} \\ + E_{p(N-1)}(x_{p(N-1)} - x_{pb}) + E_{pb}x_{pb} = 0, \end{aligned} \tag{6}$$

and with the insertion of Eqs. (2)–(5) into Eq. (6) an expression for the charges on electrodes *a* and *b* is obtained,

$$\sigma_{a,b} = \frac{(\varepsilon_g x_p + \varepsilon_p x_g)\sigma_{pa,pb} - \varepsilon_g(\sigma_{pa}x_{pa} + \sigma_{pb}x_{pb}) - \varepsilon_p x_g \sigma_{\text{eff}} - \varepsilon_0 \varepsilon_g \varepsilon_p V}{(\varepsilon_g x_p + \varepsilon_p x_g)}. \tag{7}$$

The term $\sigma_{a,b}$ refers to electrode *a* or *b* and the proper index has to be chosen: $\sigma_a$ for electrode *a* or $\sigma_b$ for electrode *b* with the corresponding index *pa* or *pb* in the term $\sigma_{pa,pb}$. The thicknesses $x_g$ and $x_p$ are the respective sums of the thickness of the individual gas and polymer layers and can be determined experimentally,

$$x_g = \sum_i x_{gi}, \quad i = 1, \ldots, N \quad \text{and} \quad x_p = \sum_i x_{pi}, \quad i = 1, \ldots, N + 1. \tag{8}$$

The effective charge density $\sigma_{\text{eff}}$ is defined by

$$\sigma_{\text{eff}} = \frac{\sum_i \sigma_{gi} x_{gi}}{x_g}. \tag{9}$$

Equation (7), in terms of the effective charge $\sigma_{\text{eff}}$, reduces the electrostatic *N*-layer model into a one-layer model as schematized in Fig. 3. This simplification has experimental support since while charging the sample the electric breakdown only starts when the electric-field strength in the pores is inconformity with Paschen's law when applied to gaps having a width equal to $x_g$.[12,14]

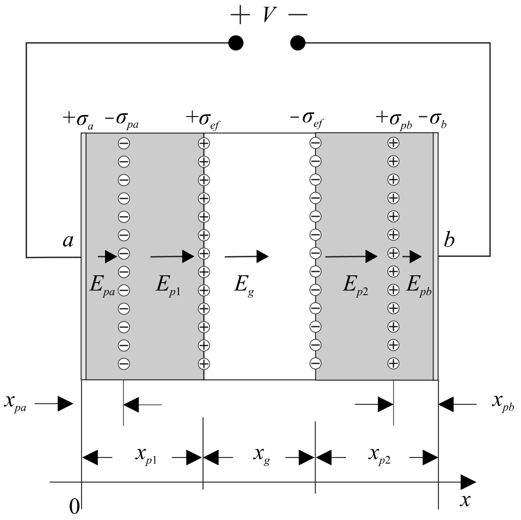

FIG. 3. Equivalent one-layer model.

From Fig. 3 and Eqs. (7)–(9) it becomes evident that the variables of the charged electret are the charge density $\sigma_a$ on electrode *a*, the thickness of the gas layer $x_g$, and the tension *V* that keeps the system in electrostatic equilibrium (the spatial charges, $\sigma_{pa}$ and $\sigma_{pb}$, and the charges on the surfaces of the voids, $\sigma_{gi}$ with $i=1,\ldots,N$, are trapped and have definitive values).

The thermodynamic analysis requires the knowledge of the electric energy of the cellular polymer, $U_{\text{el}}$. It can be calculated by[15]

$$U_{\text{el}} = \frac{1}{2}\int \vec{E} \cdot \vec{D} dv, \tag{10}$$

where *dv* is a volume element of the whole sample and $D=\varepsilon_0 \varepsilon E$ is the electric displacement in a dielectric with permittivity $\varepsilon$. Applying this expression to the model schematized in Fig. 3 we obtain

$$\begin{aligned} U_{\text{el}} = \frac{A}{2}\{\varepsilon_0 \varepsilon_p[E_{pa}^2 x_{pa} - E_p^2(x_p - x_{pa} - x_{pb})] \\ + \varepsilon_0 \varepsilon_g[E_g^2 x_g + E_{pb}^2 x_{pb}]\}, \end{aligned} \tag{11}$$

where *A* is the area of the electrodes. With Eqs. (2)–(5), this expression can be written in terms of charge densities as

$$\begin{aligned} U_{\text{el}} = \frac{A}{2}\Bigg\{ \frac{1}{\varepsilon_0 \varepsilon_p}[\sigma_a^2 x_{pa} + (\sigma_a - \sigma_{pa})^2(x_p - x_{pa} - x_{pb}) \\ + (\sigma_a - \sigma_{pa} - \sigma_{pb})^2 x_{pb}] + \frac{1}{\varepsilon_o \varepsilon_g}(\sigma_a - \sigma_{pa} + \sigma_{\text{eff}})^2 x_g \Bigg\}. \end{aligned} \tag{12}$$

The space charges, $+\sigma_{pa}$ and $-\sigma_{pb}$, are fixed and their role in the performance of the device is passive. Therefore, without loss of generality, we may consider the space charges as located immediately below the surface of the polymer and we may set the distances to the surfaces as negligible, i.e.,

$$x_{pa} \cong x_{pb} \cong 0. \tag{13}$$

This assumption simplifies Eq. (7) to

$$\sigma_a = \sigma_{pa} - \frac{\varepsilon_p x_g \sigma_{\text{eff}} + \varepsilon_0 \varepsilon_g \varepsilon_p V}{(\varepsilon_g x_p + \varepsilon_p x_g)}, \tag{14}$$

which is a relation among the charge density $\sigma_a$ on electrode $a$, the internal effective charges $\sigma_{\text{eff}}$, the thickness of the layer of gas $x_g$, and the tension $V$ between electrodes $a$ and $b$, establishing a constraint among these variables. This equation constitutes a sort of "electrical" equation of state, a consideration that is shown to be important when applying the first law of thermodynamics to this system.

Equation (11) simplifies to

$$U_{\text{el}} = \frac{A}{2\varepsilon_0 \varepsilon_p \varepsilon_g}[(\sigma_a - \sigma_{pa})^2 \varepsilon_g x_p + (\sigma_a - \sigma_{pa} + \sigma_{\text{eff}})^2 \varepsilon_p x_g], \tag{15}$$

showing that the electric energy is a function of $\sigma_a$ and $x_g$,

$$U_{\text{el}} = U_{\text{el}}(\sigma_a, x_g), \tag{16}$$

wherefrom

$$dU_{\text{el}} = \left(\frac{\partial U_{\text{el}}}{\partial \sigma_a}\right)_{x_g} d\sigma_a + \left(\frac{\partial U_{\text{el}}}{\partial x_g}\right)_{\sigma_a} dx_g \tag{17}$$

or

$$dU_{\text{el}} = \frac{A}{\varepsilon_0 \varepsilon_p \varepsilon_g}\Bigg\{[(\sigma_a - \sigma_{pa} + \sigma_{\text{eff}})(\varepsilon_g x_p + \varepsilon_p x_g) + \varepsilon_p x_g \sigma_{\text{eff}}]d\sigma_a + \left[\frac{1}{2}(\sigma_a - \sigma_{pa} + \sigma_{\text{eff}})^2 \varepsilon_p\right]dx_g\Bigg\}, \tag{18}$$

which, with the aid of Eq. (14), can be written as

$$dU_{\text{el}} = -AVd\sigma_a + \frac{1}{2\varepsilon_0 \varepsilon_g}(\sigma_a - \sigma_{pa} + \sigma_{\text{eff}})^2 \varepsilon_p dx_g. \tag{19}$$

The first term in this expression is the energy spent to add or to remove a charge $Ad\sigma_a$ to the electrode $a$. This observation has consequences in the thermodynamic analysis that follows.

### B. Thermodynamics

The electrostatic analysis showed that the model with $N$ layers of gas (that simulate the voids of the cellular polymer) in electrostatic terms is equivalent to a model with only one layer of gas, simplifying the analysis that follows. In this approach the system can be represented by the scheme in Fig. 4. It consists of two layers of compact polymer with thicknesses $x_{p1}$ and $x_{p2}$ (total polymer thickness of $x_p = x_{p1} + x_{p2}$) with electrodes $a$ and $b$ metallized on its surfaces and a layer of gas with thickness $x_g$ representing the voids of the polymer. The charges $\sigma_a$ and $-\sigma_b$ are the charge densities on the electrodes $a$ and $b$, each one with area $A$. With switch $S_w$ at position 3 the device operates in short circuit and the voltmeter represented by the encircled $V$ indicates that $V = V_{\text{int}}$, i.e., the tension between the electrodes induced by the charged electret. This tension has been overlooked by some authors.[9] When the switch $S_w$ is in position 2 an electromotive force, represented by the battery, is connected to the electrodes and the voltmeter indicates that $V = V_b$. The spring constant $k_{st}$ represents the "Blätterteig" morphology of the voided structure. In this morphology the voids are interconnected up to some degree, and under quasistatic compression some of the gas may leave the device. The degree of interconnection relates to the softness of the material, and it is an important factor in applications that exploit the electromechanical properties of the material. In the case of pyroelectric applications little interconnection is desirable in order to have a large gas expansion. In whichever application a large quantity of voids inside the device is desirable since a change in its thickness induces large changes in the dipole moments formed by the trapped charges on the surfaces of the voids.

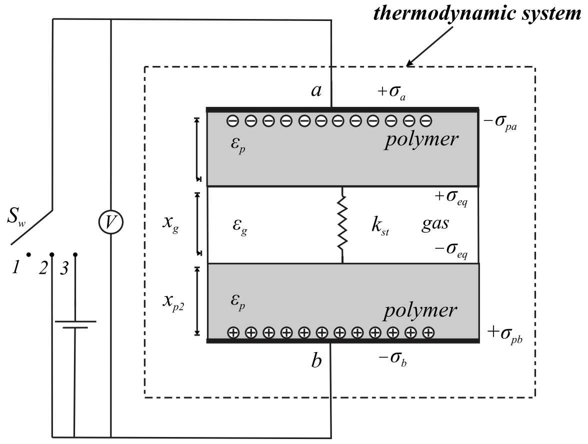

FIG. 4. The dash-dotted line represents the thermodynamic system in contact with bath at constant temperature and pressure, $T$ and $p$, respectively. The battery represents an electromotive force and the encircled $V$ represents a voltmeter.

The dashed line in Fig. 4 indicates the thermodynamic system to be analyzed. It is in contact with a constant pressure, $p$, and constant temperature, $T$, reservoir. The battery outside the system, switch $S_w$ in position 2, plays the role of a "voltage bath" that keeps the system at constant voltage, $V_b$.

Depending on the kind of application the device schematized in Fig. 4 operates in different operation modes: *open circuit*, switch $S_w$ in position 1, which is inconvenient in technological applications; *constant voltage*, in this mode of operation, switch $S_w$ in position 2, a voltage equal to that of the battery $V = V_b$ is applied to the system as shown in Fig. 4; and *short circuit*, in this case, switch $S_w$ in position 3, the battery is shut out of the circuit and the voltmeter measures a voltage $V = V_{\text{int}}$, i.e., the voltage induced between the electrodes by the charged electret.

### C. Pyroelectric coefficient

The pyroelectric coefficient, $k_{(\mathrm{py})}$, given by Eq. (1a) will be calculated with the device in short-circuit operation mode (switch $S_w$ in position 3). When heat $\Delta Q$ is supplied to the system its temperature raises from $T$ to $T+\Delta T$, expanding the device causing a rearrangement in the charge distribution of the device.

To achieve significant thermal expansion a large amount of gas inside the device is desirable; this may be realized either by sealing the device, and therefore locking the gas inside, or by utilizing a material with high degree of disconnection between the voids. The large coefficient of thermal expansion of the gas is what provides the change in polarization inside the ferroelectret and consequently determines the amount of displaced charge $\Delta(A\sigma_a)$ on the electrode $a$.

To calculate the pyroelectric coefficient, Eq. (1a), we apply the first law of thermodynamics to the system which, for short-circuit operation mode, reads

$$dU_{\mathrm{tot}} = dQ + dW. \tag{20}$$

$dQ$ is the heat supplied to the system and corresponds to the heat absorbed by the polymer, $dQ_p$, and by the gas, $dQ_g$, or

$$dQ = dQ_p + dQ_g. \tag{21}$$

The effect of heat on the elastic structure is to soften the polymer, which yields the expansion of the gas, changing therefore the elastic energy of the device. On the charge distribution its effect can be neglected for low temperatures; the stability of the material does not go beyond 200 °C.

The change in total energy, $dU_{\mathrm{tot}}$, can be dismembered into the change in internal energy of the polymer $dU_p$, in the gas inside the voids $dU_g$, in the electric energy $dU_{\mathrm{el}}$, and in the elastic energy $dU_{st}$,

$$dU_{\mathrm{tot}} = dU_p + dU_g + dU_{\mathrm{el}} + dU_{st}. \tag{22}$$

The conformal or elastic energy of the voided structure of the device is

$$U_{st} = \frac{1}{2}k_{st}x_g^2, \tag{23}$$

where $x_g$ is the thickness of the gas layer (or the "total" size of the voids). The equilibrium position of the equivalent spring $k_{st}$ is taken as $x_g=0$. This is a reasonable assumption since the thickness of the gas layer $x_g$ is formed by many disconnected (small) voids[16] and the width $x_g$ is the addition of the thicknesses of these voids. For a change in temperature from $T$ to $T+dT$ the gas layer increases its thickness from $x_g$ to $x_g+dx_g$ and the elastic energy of the sample is dependent on the temperature, i.e.,

$$U_{st} = U_{st}(x_g, T) \tag{24}$$

and

$$dU_{st} = k_{st}x_g dx_g + \frac{1}{2}x_g^2 \kappa dT, \tag{25}$$

where $\kappa$ is the rate of change of the string constant $k_{st}$ with the temperature $T$,

$$\kappa = \frac{dk_{st}}{dT}, \tag{26}$$

characterizing the softening of the spring constant.

The work of expansion performed by the system, $dW$, is the sum of the expansion work performed by the polymer, $dW_p$, and by the gas inside the voids, $dW_g$,

$$dW = dW_p + dW_g. \tag{27}$$

The gas expands against the pressure of the reservoir, $p$, and realizes the work $dW_{st}=-pAdx_g$. The resistance to expansion offered by the spring, $k_{st}$, is taken into account by the first term on the right-hand side of Eq. (25). If the spring were considered to be outside the thermodynamic system, the concept would be different; the gas would expand against the pressure of the reservoir and against the pressure exerted by the spring, $p_{st}=k_{st}x_g/A$, and $dW_{st}=-(p+p_{st})Adx_g$ while in this case $dU_{st}=0$. Therefore if $dx_p$ is the change in polymer thickness, the work of expansion of the gas and of the polymer is given by

$$dW_g = -pAdx_g \quad \text{and} \quad dW_p = -pAdx_p, \tag{28}$$

respectively. With those considerations the first law of thermodynamics, Eq. (20), becomes

$$\begin{aligned} dU_p + dU_g + dU_{\mathrm{el}} + k_{st}x_gAdx_g + \frac{1}{2}x_g^2\kappa dT \\ = dQ_p + dQ_g - pAdx_p - pAdx_g. \end{aligned} \tag{29}$$

The polymer and the gas constitute subsystems where the first law of thermodynamics holds, i.e.,

$$dU_p = dQ_p - pdv_p \quad \text{and} \quad dU_g = dQ_g - pdv_g, \tag{30}$$

yielding further simplification in Eq. (29). With the result given for $dU_{\mathrm{el}}$ by Eq. (18) the first law of thermodynamics expressed by Eq. (29) becomes

$$\frac{A}{\varepsilon_0\varepsilon_p\varepsilon_g}\{[K1]d\sigma_a - A[K2]dx_g\} = -k_{st}x_g\Delta x_g - \frac{x_g^2}{2}\kappa\Delta T, \tag{31a}$$

where the terms $[K1]$ and $[K2]$ are given by

$$\begin{aligned} [K1] &= (\sigma_a - \sigma_{pa} + \sigma_{\mathrm{eff}})(\varepsilon_g x_p + \varepsilon_p x_g) + \varepsilon_p x_g \sigma_{\mathrm{eff}} \quad \text{and} \\ [K2] &= \frac{(\sigma_a - \sigma_{pa} + \sigma_{\mathrm{eff}})^2 \varepsilon_p}{2}. \end{aligned} \tag{31b}$$

Integrating Eq. (31a) to the first order in $\Delta\sigma_a$ and considering the elastic force $-k_{st}x_g$ to be constant for small displacements $\Delta x_g$, the pyroelectric coefficient $k_{\mathrm{py}}$, after some algebraic manipulation, becomes

$$k_{\mathrm{py}} = \left.\frac{A\Delta\sigma_a}{\Delta T}\right|_p = - \frac{A(\sigma_a - \sigma_{pa} + \sigma_{\mathrm{eff}})^2 \varepsilon_p x_g + \varepsilon_0 \varepsilon_p \varepsilon_g (2k_{st} + AT\kappa) x_g^2}{2T[(\sigma_a - \sigma_{pa} + \sigma_{\mathrm{eff}})(\varepsilon_g x_p + \varepsilon_p x_g) + \varepsilon_p x_g \sigma_{\mathrm{eff}}]}, \tag{32}$$

where we used the volume expansion coefficient, $\alpha$, of ideal gases,

$$\alpha = \frac{\Delta x_g}{x_g \Delta T} = \frac{1}{T}. \tag{33}$$

In the case of high mechanical stiffness the pyroelectric coefficient is significant and Eq. (32) simplifies to

$$k_{\mathrm{py}} = \left.\frac{A\Delta\sigma_a}{\Delta T}\right|_p = - \frac{\varepsilon_0 \varepsilon_p \varepsilon_g (2k_{st} + AT\kappa) x_g^2}{2T[(\sigma_a - \sigma_{pa} + \sigma_{\mathrm{eff}})(\varepsilon_g x_p + \varepsilon_p x_g) + \varepsilon_p x_g \sigma_{\mathrm{eff}}]}. \tag{34}$$

All quantities in Eqs. (32) and (34) are known or can be obtained experimentally (inclusive $k_{(\mathrm{py})}$) yielding the effective charge $\sigma_{\mathrm{eff}}$ defined by Eq. (9). This allows one to draw conclusions about the charges on the surfaces of the voids, i.e., $\sigma_{gi}$ where $i=1,\ldots,N$, which so far have been elusive to direct measurement.

### D. Sensor coefficient

The sensor coefficient is given by Eq. (1b), where an applied external force $\Delta F$ generates a change in charge $\Delta q = A\Delta\sigma_a$ on electrode $a$. This coefficient is calculated in constant voltage operation mode (switch $S_w$ in position 2), and a voltage $V=V_b$ is applied to the system as shown in Fig. 4. No heat is supplied to the system and

$$dQ = 0. \tag{35}$$

In Fig. 4 the battery, representing the electromotive force, is located outside the thermodynamic system and plays the role of a voltage reservoir. Therefore in the thermodynamic approach the change in electric energy $dU_{\mathrm{el}}$ is split into an external part given by the work performed by the battery on the system,

$$dW_{\mathrm{el}} = AV_b d\sigma_a, \tag{36}$$

and an internal one due to the change in thickness of the sample,

$$dU_{\mathrm{el}} = \frac{A}{2\varepsilon_0 \varepsilon_p \varepsilon_g}(\sigma_a - \sigma_{pa} + \sigma_{\mathrm{eff}})^2 \varepsilon_p dx. \tag{37}$$

There has been no agreement among some authors regarding the electric energy in these systems; some considered only the electromagnetic energy stored inside the gas layer[9,10] while others considered the energy of charges in vacuum.[8] For an ideal gas and incompressible polymer, when no heat is delivered to the system, the corresponding changes in internal energy are zero. Therefore,

$$dU_p = 0 \quad \text{and} \quad dU_g = 0. \tag{38}$$

The change in elastic internal energy is obtained from Eq. (25) with $\Delta T=0$,

$$dU_{st} = k_{st} x_g dx_g. \tag{39}$$

The expansion work of the gas against the pressure of the reservoir, $p$, is $dW = -pAdx_g$, and the first law of thermodynamics can be written as

$$\frac{A}{2\varepsilon_0 \varepsilon_g}(\sigma_a - \sigma_{pa} + \sigma_{\mathrm{eff}})^2 dx_g + k_{st} x_g dx_g = -pAdx_g + AV_b d\sigma_a, \tag{40}$$

where we used the results given by Eqs. (36)–(39). The external pressure which maintains the device in equilibrium conditions is given by

$$p = -\frac{(\sigma_a - \sigma_{pa} + \sigma_{\mathrm{eff}})^2}{2\varepsilon_0 \varepsilon_g} - \frac{k_{st}}{A} x_g + V_b \frac{d\sigma_a}{dx_g}. \tag{41}$$

The variables $x_g$, $V$, and $\sigma_a$ are constrained by Eq. (14). For constant voltage operation mode, $V=V_b$, the constraint between the displaced charge $d\sigma_a$ and the change in width $dx_g$ is

$$d\sigma_a = -\frac{\varepsilon_p(\sigma_a - \sigma_{pa} + \sigma_{\mathrm{eff}})}{(\varepsilon_g x_p + \varepsilon_p x_g)} dx_g. \tag{42}$$

Using this expression in Eq. (41) and performing the derivative of $p$ relative to $\sigma_a$, the following expression, linear in $\Delta\sigma_a$, is obtained for the sensor coefficient $k_{(s)}$:

$$k_{(s)} = \left.\frac{\Delta\sigma_a}{\Delta p}\right|_V = -\frac{\varepsilon_0 \varepsilon_p \varepsilon_g (\sigma_a - \sigma_{pa} + \sigma_{\mathrm{eff}})}{\varepsilon_p(\sigma_a - \sigma_{pa} + \sigma_{\mathrm{eff}})^2 - \frac{k_{st}}{A} L_{\mathrm{el}} \varepsilon_0 \varepsilon_g}, \tag{43a}$$

where the electric thickness, $L_{\mathrm{el}}$, is defined by

$$L_{\mathrm{el}} = \varepsilon_g x_p + \varepsilon_p x_g. \tag{43b}$$

For a material with large amount of gas we may presume that

$$\frac{x_p}{x_g} \to 0 \quad \text{and} \quad L_{\mathrm{el}} \to \varepsilon_p x_g, \tag{44}$$

and Eq. (43a) can be simplified to

$$k_{(s)} = \left.\frac{d\sigma_a}{dp}\right|_V = -\frac{x_g}{V_b}\left(1 - \frac{p_{st} x_g}{V_b}\right), \tag{45a}$$

where the voltage $V_b$ is given by Eq. (14) and the elastic pressure of the device $p_{st}$ is defined by

$$p_{st} = \frac{k_{st} x_g}{A}. \tag{45b}$$

The first term of Eq. (45a) shows, as expected, that the sensor sensitivity is proportional to the amount of gas in the device and inversely proportional to the voltage of the battery; high voltages of the battery turn the device less sensitive or "electrically" more rigid. The second term inside the parenthesis of the right side of Eq. (45a) shows how the elasticity of the material influences the sensitivity of the sensor.

### E. Actuator coefficient

The actuator coefficient, $k_{(a)}$, is calculated in short-circuit operation mode with switch $S_w$ in position 3 and with voltage between the electrodes $V_{\text{int}}$. The applied voltage to the system, say $\Delta V = \Delta V_{\text{int}}$, induces a variation in the thickness of the device, $\Delta x_g$, while the external stress, $p$, is kept constant. The first law of thermodynamics is identical to Eq. (40) with $V_{\text{int}}$ in place of $V_b$, i.e.,

$$\frac{A}{2\varepsilon_0\varepsilon_g}(\sigma_a - \sigma_{pa} + \sigma_{\text{eff}})^2 dx_g + k_{st} x_g dx_g = -pA dx_g + A V_{\text{int}} d\sigma_a. \tag{46}$$

After performing the derivative $dV_{\text{int}}/dx_g$ and keeping only the terms in the first order of $\Delta V_{\text{int}}$, the following result for the actuator coefficient is obtained after some algebraic manipulation:

$$k_{(a)} = \left.\frac{\Delta x}{\Delta V}\right|_p = \left.\frac{\Delta x_g}{\Delta V_{\text{int}}}\right|_p = -\frac{\sigma_a + \sigma_{pa} + \sigma_{\text{eff}}}{2(p + p_{st})}. \tag{47}$$

This result shows as expected that the sensitivity is proportional to the charge of the device and inversely proportional to the elastic stress of the polymeric structure. The softer the polymer the higher the actuator sensitivity.

## III. CONCLUSIONS

A method to analyze electromechanical and pyroelectric devices based on the first law of thermodynamics and elementary electrostatics is presented. It provides a consistent approach to calculate pyroelectric, sensor, and actuator, and the accuracy of the results depends on the fidelity with which the model describes the device. It shows that it is important to consider the restraints under which the coefficients given by Eqs. (1a)–(1c) are defined. This has not been taken into consideration by some authors[6,9,10] leading to equalities such as $k_{(a)}|_p = k_{(s)}|_V$ which is not correct in the exact treatment. The thermodynamic treatment, besides showing how to deal properly with the electric energy (some authors considered it to be only due to the electric field in the gas[9,10] while others[8] considered it to be just the energy of electric charges in the vacuum), also shows how to consider the elastic properties of the device matrix. Last but not least, this method facilitates the task of setting up the problem in which all physical quantities of interest are properly taken in account: heat, electric charges, electromotive forces, mechanical stresses, changes in volume, elasticity, etc., elucidating the interconnection among all those factors avoiding misconceptions or ill-conceived approximations.

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