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Electrets in soft materials: Nonlinearity, size effects, and giant electromechanical coupling

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Development of soft electromechanical materials is critical for several tantalizing applications such as soft robots and stretchable electronics, among others. Soft nonpiezoelectric materials can be coaxed to behave like piezoelectrics by merely embedding charges and dipoles in their interior and assuring some elastic heterogeneity. Such so-called electret materials have been experimentally shown to exhibit very large electromechanical coupling. In this work, we derive rigorous nonlinear expressions that relate effective electromechanical coupling to the creation of electret materials. In contrast to the existing models, we are able to both qualitatively and quantitatively capture the known experimental results on the nonlinear response of electret materials. Furthermore, we show that the presence of another form of electromechanical coupling, *flexoelectricity*, leads to size effects that dramatically alter the electromechanical response at submicron feature sizes. One of our key conclusions is that nonlinear deformation (prevalent in soft materials) significantly enhances the flexoelectric response and hence the aforementioned size effects.

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I. INTRODUCTION

Over the past several decades, electromechanical coupling has attracted intense attention due to its role in intriguing applications such as energy harvesting [1–4], micro- and nanoelectromechanical systems [5–8], and biology [9,10], among others. One of the most commonly observed electromechanical couplings is the piezoelectric effect, which is the basis for a large number of sensor and transducer applications. Piezoelectricity, as it is most commonly understood, involves the linear interconversion between electric fields and mechanical deformation. However, the atomistic mechanism of piezoelectricity constraints its existence only in certain crystal structures, such as barium titanate ($BaTiO_3$), zinc oxide (ZnO), and lead zirconate titanate (PZT). Such crystals are invariably hard, brittle, and poorly suited for the host of applications that require soft matter applications, e.g., soft robotics and stretchable and flexible electronics. As an example, polyvinylidene difluoride (PVDF) is among the few soft materials reported to show piezoelectricity [11]. Some biological materials with composite structure, such as bone and wood, exhibit piezoelectricity [12–14]. Recently, even ferroelectricity has been observed in some biological tissues [15,16].

Piezoelectricity is, however, not the only form of electromechanical coupling. For example, all insulating materials exhibit electrostriction and the so-called Maxwell stress effect whereby an application of electric field can deform the material. Although mathematically similar, electrostriction and Maxwell stress have different physical origins [17]. The notable aspect of these particular phenomena is that a converse effect does not exist; in other words, an electric field can deform the material, but deformation will not produce electricity. Furthermore, this particular coupling (in contrast to piezoelectricity) is nonlinear in nature [18,19]. One consequence of this is that reversal of the electric field will not reverse the direction of the mechanical deformation. These limitations of the Maxwell stress effect and/or electrostriction explain the usually larger emphasis on piezoelectric materials. A simple illustration of the Maxwell stress effect is schematically depicted in Fig. 1.

An interesting approach to creating piezoelectric materials, in particular, soft materials, is via the construction of electret materials. Although not widely noted, these materials use the basic notion of the Maxwell stress effect. The central idea involves embedding layers of charges or dipoles in a soft conventional (i.e., nonpiezoelectric) material. Such a charged state is unstable in principle; however, in practice, experiments have shown that for a class of polymer materials, such electret materials tend to be stable for appreciable durations. Such a material behaves *like* a piezoelectric material provided the elastic properties in the material are nonuniform, e.g., multilayers with charge layers at the interfaces or a foamy material containing charges on the void surfaces. Due to the nonlinear Maxwell stress effect, deformation of the sample induces a change in its preexisting macroscopic polarization, and similarly, a converse effect also exists. For all practical purposes, the "electret composite" behaves like a piezoelectric material. Experimentally, a two-way linear coupling between stress and the electric field can be detected even though microscopically the cause is the Maxwell stress effect. Via both the simple linear model that currently exists in the literature and our nonlinear derivations, it will become clear that a uniform

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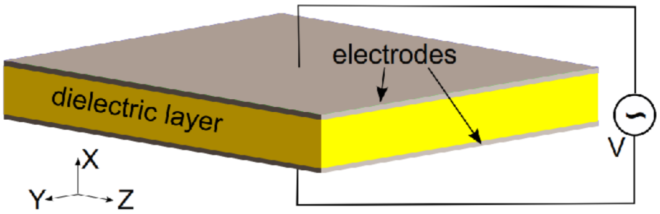

FIG. 1. (Color online) A dielectric film under external electric field undergoes a deformation proportional to the square of the applied voltage difference across its thickness direction. The deformation results from the Coulombic force between the bound charges and dipoles generated at the opposing surfaces in response to the electric field. The deformation changes in magnitude with the variation of the applied voltage difference but not the direction.

homogeneous material with electrets will not exhibit this effect: inhomogeneity in elastic material properties is a necessary condition for this apparent piezoelectric-like behavior. Usually, especially in cellular polymers like polypropylene, the air in the voids within the material is broken down through a corona charging process thus depositing charge. Experimental work has shown that electret-polypropylene foams can produce apparent piezoelectric coefficients up to 1200 pC/N, which is more than 6 times that of PZT [20].

The vast majority of the work on this topic is experimental in nature with only very simple linearized models that purport to interpret this patently nonlinear effect. In this work, we (i) provide mathematical derivations to transparently illustrate the mechanisms that lead to the "piezoelectric-like" behavior in electrets, (ii) predict the nonlinear electromechanical response of electret materials and compare it with known experiments and the existing linearized model, and (iii) illustrate the size effects due to the interplay between flexoelectricity and nonlinear deformation.

II. THEORETICAL FORMULATION AND THE MECHANISM OF ELECTRETS

Consider the electromechanical thermodynamic state of the film in Fig. 1 as described by two independent variables: deformation $\chi(\mathbf{X})$ and polarization $\mathbf{P}(\mathbf{X})$ (defined in the reference configuration), where $\mathbf{X} = (X,Y,Z)$ are the Lagrange coordinates of the material points [21–23]. Correspondingly, $\mathbf{x} = (x,y,z) = \chi(\mathbf{X})$ are the Euler coordinates. For this film, its thickness H is much smaller than its width and depth (both are equal to L). So it is assumed that the deformation χ and the polarization $\mathbf{P}$ only depend on the coordinate X and that the polarization $\mathbf{P}$ is along the X direction throughout the whole process of deformation or application of electric field. In other words, the following constraints are assumed:

$$\begin{aligned} x &= X + u(X), \quad y = Y\alpha(X), \\ z &= Z\beta(X), \quad \mathbf{P} = P_X(X)\mathbf{e}_X, \end{aligned} \tag{1}$$

where $\mathbf{e}_X$ is the unit vector in the X direction and P_X corresponds to the X component of the polarization $\mathbf{P}$.

Following the standard framework of continuum mechanics, we introduce the stretches in X (Y,Z) direction: $\lambda_1 = 1 + (\partial u/\partial X)$ $(\lambda_2 = \partial y/\partial Y = \alpha$, $\lambda_3 = \partial z/\partial Z)$, and the deformation gradient $\mathbf{F} = \mathrm{Grad}\chi$ with $J = \det \mathbf{F} = \lambda_1\lambda_2\lambda_3$ is the Jacobian, which represents the volume change due to the deformation. Note that, in this paper, $\mathrm{Grad}(\cdot) = \nabla_X(\cdot)$ and $\mathrm{grad}(\cdot) = \nabla_x(\cdot)$ are the gradient operators defined in the reference and current configurations, respectively. Similarly, $\mathrm{Div}(\cdot) = \nabla_X \cdot (\cdot)$ and $\mathrm{div}(\cdot) = \nabla_x \cdot (\cdot)$ are the divergence operators defined in these two different configurations. The electric field $\mathbf{e}$ is related to the potential ξ by $\mathbf{e} = -\mathrm{grad}\xi$. To account for energies associated with electric fields and loading devices, we shall first solve for the electric field via the Maxwell equations; that is, the electric field in the current configuration is determined by

$$\mathrm{div}[-\epsilon_0 \mathrm{grad}\xi + \mathbf{p}(x)] = \rho^e(x), \tag{2}$$

with the boundary conditions $\xi(x = 0) = 0$ and $\xi(x = h) = V$. Here h is the thickness of the deformed film, $\mathbf{p} = \mathbf{P}/J$ is the polarization defined in the current configuration, $\rho^e = \rho_0^e/J$ is the external charge density (per unit volume) in the current configuration, and ρ_0^e is the external charge density in the reference configuration.

Taking into account the elastic and electric field energies, we identify the total free energy of the system as

$$\begin{aligned} \frac{1}{L^2}F[\chi,\mathbf{P}] = &\int_0^H W(\lambda_1,\lambda_2,\lambda_3,\mathbf{P})dX \\ &+ \frac{\epsilon_0}{2}\int_0^h \lambda_2\lambda_3|\mathrm{grad}\xi|^2 dx \\ &+ [\lambda_2\lambda_3\xi(-\epsilon_0\mathrm{grad}\xi + \mathbf{p})]|_{x=0}^{x=h}, \end{aligned} \tag{3}$$

where $W(\lambda_1,\lambda_2,\lambda_3,P)$ is the stored or internal energy density of the material, the second term corresponds to the electric field energy, and the third term is the potential energy of the boundary electric device. Note that the parameter L in Eq. (3) is the sample size in the Y and Z directions. Thus L^2 represents the undeformed surface area, and the deformed surface area is simply $\lambda_2\lambda_3 L^2$. In this work, we employ the neo-Hookean hyperelastic model for the material with the elastic stored energy given by

$$\begin{aligned} &W_{\mathrm{elast}}(\lambda_1,\lambda_2,\lambda_3) \\ &\quad = \frac{\mu}{2}\left[J^{-2/3}\left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2\right) - 3\right] + \frac{\kappa}{2}(J-1)^2, \end{aligned}$$

where μ and κ are the shear modulus and the bulk modulus of the neo-Hookean material, respectively. This choice is not central to our main physical conclusions. Alternative constitutive laws may be considered easily. Given this, the internal energy is given by [23]

$$W = W_{\mathrm{elast}}(\lambda_1,\lambda_2,\lambda_3) + \frac{|\mathbf{P}|^2}{2(\epsilon - \epsilon_0)J}, \tag{4}$$

where ϵ and ϵ_0 are the absolute permittivities of dielectric material and vacuum, respectively. Note that the second term guarantees the usual linear dielectric behavior in the current configuration.

Based on symmetry, we observe that the stretches in the Y and Z directions are the same. So we have

$$\lambda_2 = \alpha = \lambda_3 = \beta = (J/\lambda_1)^{1/2}.$$

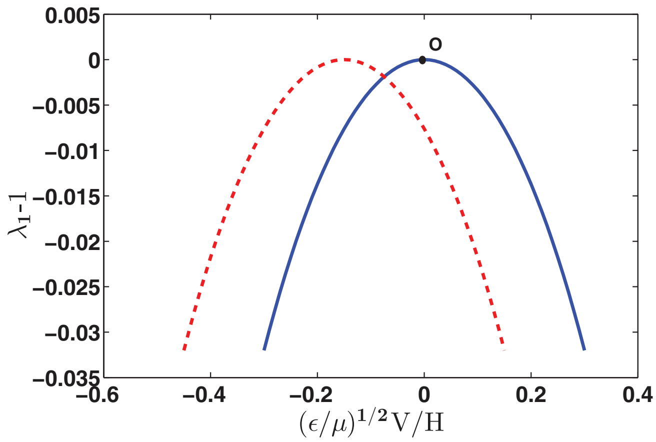

FIG. 2. (Color online) Strain-voltage curves of the dielectric film: solid line shows conventional dielectrics; dashed line shows electrets.

By the principle of minimum free energy

$$\min_{(\chi,\mathbf{P})} F[\chi,\mathbf{P}] \tag{5}$$

and using the standard variational calculus, we obtain the following two Euler-Lagrange equations that determine the equilibrium state of the incompressible ($J=1$) film:

$$\frac{P_X}{\epsilon-\epsilon_0}+\lambda_1^{-1}\frac{d\xi}{dX}=0, \tag{6a}$$

$$\frac{d}{dX}\left[\mu\left(\lambda_1-\lambda_1^{-2}\right)+\tilde{\Sigma}_1-\lambda_1^{-3/2}\tilde{\Sigma}_2\right]=0, \tag{6b}$$

where

$$\begin{aligned}\tilde{\Sigma}_1&=-\frac{1}{\lambda_1^2}\frac{d\xi}{dX}P_X+\frac{\epsilon_0}{2\lambda_1^3}\left|\frac{d\xi}{dX}\right|^2,\\ \tilde{\Sigma}_2&=-\frac{\epsilon_0}{2\lambda_1^2\lambda_2}\left|\frac{d\xi}{dX}\right|^2\end{aligned} \tag{7}$$

are the normal components of the Maxwell stress in the X, Y, and Z directions, respectively.

In the absence of external charges, i.e., $\rho^e=0$ in Eq. (2), using (6a) and (2) we find that the electric field $\mathbf{e}=-\text{grad}\xi$ is constant across the film. Accordingly, the stretch λ_1 is also independent of the coordinates. This implies that for the homogeneous dielectric film in Fig. 1, $\text{grad}\xi=V/h$ and $\lambda_1=h/H$. Using (6a) along with the free traction boundary condition, the mechanical equilibrium equation (6b) implies that

$$\mu\left(\lambda_1-\lambda_1^{-2}\right)+\frac{\epsilon}{\lambda_1^3}(V/H)^2=0, \tag{8}$$

where the terms $\mu(\lambda_1-\lambda_1^{-2})$ and $\frac{\epsilon}{\lambda_1^3}(V/H)^2$ correspond to the normal Piola-Kirchhoff stress and (modified) Maxwell stress, respectively. The latter is non-negative so that the mechanical stress is negative. Equation (8) determines the relation between strain and applied voltage, which is shown by the solid curve $\lambda_1=\lambda_1[(\epsilon/\mu)^{1/2}V/H]$ in Fig. 2. As we can see from Fig. 2, the solid curve has a saddle point at zero voltage, meaning $\lambda_1-1\propto(V/H)^2$, the characteristics of electrostriction.

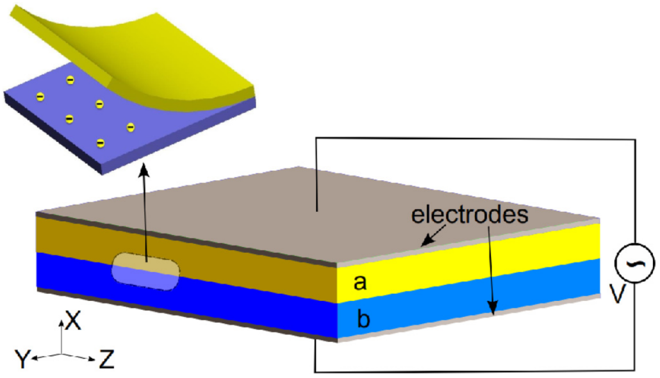

FIG. 3. (Color online) The constituent of an electret: a layer of net charge is deposited between two different dielectric films.

Is it possible to shift the solid line in Fig. 2 to the dashed line so that the strain varies almost linearly around zero voltage? This would be the telltale signature of a piezoelectric material. By inserting a layer of charge into the interface between two layers of different dielectric materials, the electromechanical behavior of the whole structure can be significantly changed so that the saddle point does not have to stay at the origin (Fig. 3). Properly choosing the material properties, the interface charge, and the thickness of the two layers enables us to tune the electromechanical properties of the artificially designed piezoelectric material.

Due to the presence of the charge density q_0, the right hand side of (2) can be written as $\rho^e=q_0\delta(x-h_b)$. Here $\delta(\cdot)$ is the Dirac delta function. This interface condition leads to the following relationship between the voltage on the top surface V_a and the voltage on the bottom surface $-V_b$:

$$-\epsilon_a\frac{V_a}{h_a}+\epsilon_b\frac{V_b}{h_b}=q_0, \tag{9}$$

where the subscript a (b) represents the corresponding variables in film a (b). Because

$$V_a+V_b=V, \tag{10}$$

we can express V_a and V_b as follows:

$$\frac{V_a}{h_a}=\frac{\epsilon_bV-q_0h_b}{\epsilon_ah_b+\epsilon_bh_a},\quad \frac{V_b}{h_b}=\frac{\epsilon_aV+q_0h_a}{\epsilon_ah_b\epsilon_bh_a}.$$

Then the equilibrium equation (8) becomes

$$\begin{aligned}&\mu_a\left(\lambda_a-\lambda_a^{-2}\right)+\frac{\epsilon_a}{\lambda_a}\left(\frac{\epsilon_bV-q_0h_b}{\epsilon_ah_b+\epsilon_bh_a}\right)^2=0,\\ &\mu_b\left(\lambda_b-\lambda_b^{-2}\right)+\frac{\epsilon_b}{\lambda_b}\left(\frac{\epsilon_aV-q_0h_a}{\epsilon_ah_b+\epsilon_bh_a}\right)^2=0,\end{aligned} \tag{11}$$

where $\lambda_a=h_a/H_a$ and $\lambda_b=h_b/H_b$ are the stretch λ_1 in layers a and b, respectively.

For small strain ($h-H\ll H$), we immediately have

$$3\mu_i(\lambda_i-1)\approx-\epsilon_i(V_i/H_i)^2\quad(i=a\text{ or }b).$$

Therefore, the total change of the thickness $\triangle u$ is given by

$$\begin{aligned}\triangle u &= h_a + h_b - H_a - H_b\\ &= -\frac{1}{3(\epsilon_a H_b + \epsilon_b H_a)^2}\left[q_0^2 H_a H_b\left(\frac{H_b\epsilon_a}{\mu_a} + \frac{H_a\epsilon_b}{\mu_b}\right)\right.\\ &\quad + 2q_0 H_a H_b \epsilon_a\epsilon_b V\left(\frac{1}{\mu_a} - \frac{1}{\mu_b}\right)\\ &\quad \left. + \epsilon_a\epsilon_b V^2\left(\frac{\epsilon_b H_a}{\mu_a} + \frac{\epsilon_a H_b}{\mu_b}\right)\right].\end{aligned}$$

We note that the above expression for $\triangle u$ contains three contributions. The first term is proportional to q_0^2 but independent of V. Once the electret is fabricated, this term does not change. The second term is linear with respect to both q_0 and V. The last term, which is proportional to V^2 and independent off q_0, is related to the Maxwell stress caused by the applied voltage V. For the nonelectret case, $q_0 = 0$, we only have this term. For this reason, the first two terms represent the electret effect, and the last term is simply the Maxwell stress effect term. We then define the change of the thickness with respect to the applied voltage as the effective piezoelectric coefficient:

$$\begin{aligned}d^{\text{eff}} &= \frac{du}{dV}\\ &= -\frac{2}{3(\epsilon_a H_b + \epsilon_b H_a)^2}\left[q_0 H_a H_b \epsilon_a\epsilon_b\left(\frac{1}{\mu_a} - \frac{1}{\mu_b}\right)\right.\\ &\quad \left. + \epsilon_a\epsilon_b V\left(\frac{\epsilon_b H_a}{\mu_a} + \frac{\epsilon_a H_b}{\mu_b}\right)\right], \qquad (12)\end{aligned}$$

where the first term, which corresponds to the electret effect mentioned above, is similar to the form reported in the literature [24] and the second term, the Maxwell stress effect, is linear with respect to V. It is also found from (12) that high d^{eff} is always obtained by using two soft materials with different shear moduli. However, for soft materials, the small-deformation assumption is certainly contraindicated. To properly account for nonlinear deformation, we must solve (11) numerically.

III. NONLINEAR ANALYSIS AND COMPARISON WITH EXPERIMENTAL RESULTS

We now proceed to analyze some key experimental results in the literature that have estimated the nonlinear response of porous cellular polymer film with charges deposited on the upper and lower internal surfaces of the void [20,25–28]. The voids, which are much softer than the bulk polymer, can be viewed as the second phase of the composite mentioned in the previous section. When this cellular polymer is deformed, the deformation exists mostly in the voids. The (experimentally) measured effective piezoelectric coefficient is reported to be fairly high (up to 1200 pC/N) for this material. For such high porosity, foam-like structures, the volume fraction of voids is often more than 50%, so that its Young's modulus in the thickness direction is on the order of 1 MPa. Similar to the double layered model (previously shown), a proposed triple layered model (as shown in Fig. 4) is used to predict the experimental results. We assume that the voltage difference across the top and bottom polymer layers is V_p, and V_a is the voltage difference across the air layer. We have

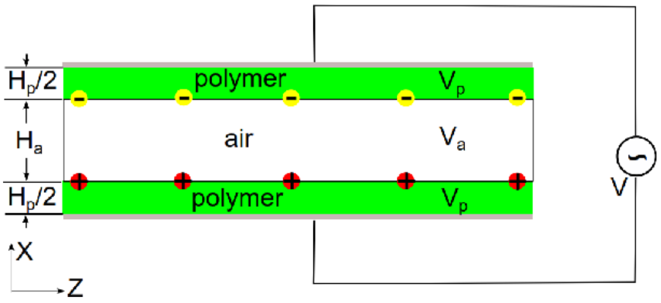

FIG. 4. (Color online) A simplified model for the ferroelectret in which opposite charges are deposited on the surfaces of voids.

$$-\epsilon_0\frac{V_a}{h_a} + \epsilon_p\frac{2V_p}{h_p} = -q_0. \qquad (13)$$

Using (13) and the equation $2V_p + V_a = V$, we can express V_a as

$$\frac{V_a}{h_a} = \frac{q_0 h_p + \epsilon_p V}{\epsilon_0 h_p + \epsilon_p h_a}. \qquad (14)$$

According to the experiments we seek to explain [20], the electret material studied here is composed of cellulose polypropylene (PP). Since the average Young's modulus of the whole structure is three orders lower than that of PP, it is reasonable to assume that the deformation in the PP layers is small in comparison to the pores ($\lambda_p = 1$). We adopt constitutive linearity (Hooke's law), although geometrical (deformation) nonlinearity is fully accounted for. The equilibrium equation is then given by

$$\frac{H_a}{H_p + H_a}Y(\lambda_a - 1) + \frac{\epsilon_0}{2}\left(\frac{V_a}{h_a}\right)^2 = 0, \qquad (15)$$

where Y is the average Young's modulus of the ferroelectret. Based on the data reported in the experiment, we set $Y = 0.8$ MPa, $H_a = 38\ \mu$m, $H_p = 32\ \mu$m, $q_0 = 10^{-3}$ C/m^2, and $\epsilon_p = 2.35\epsilon_0$. We substitute (14) into (15) to solve for λ_a. We obtain the effective piezoelectric coefficient by $d^{\text{eff}} = \frac{du}{dV}$.

In Fig. 5, the d^{eff} of the ferroelectret is calculated using the aforementioned nonlinear model and compared with the experimental results [20]. Evidently, our model captures the experimental results quite well. As already indicated earlier, the d^{eff} calculated here contains two parts which emerge from the electret effect and a third contribution due to the Maxwell stress effect. Since the Maxwell stress effect is one way coupling, here we propose that it is better to define a piezoelectric coefficient $\bar{d}^{\text{eff}}$ without the contribution of the Maxwell stress effect. In practice, this $\bar{d}^{\text{eff}}$ is calculated as the difference between the d^{eff} of the two cases with $q_0 \neq 0$ and $q_0 = 0$.

Using this new definition of the effective piezoelectric coefficient, $\bar{d}^{\text{eff}}$ is plotted in Fig. 6 as a function of applied voltage V. Due to the nonlinear dependency of the displacement on the applied voltage V, the effective piezoelectric coefficient $\bar{d}^{\text{eff}}$ is no longer a *constant* but varies with the magnitude of the applied potential difference. As already indicated, we expect

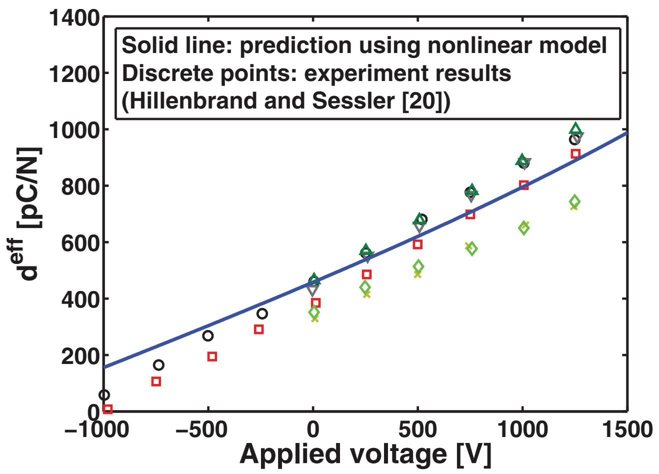

FIG. 5. (Color online) The variation of d^{eff} with respect to the applied voltage across the films.

such nonlinear behavior to be significant for soft materials. In contrast, the linear model proposed by Kacprzyk [24] corresponds to the minimum of the $\bar{d}^{\mathrm{eff}}$ where the whole structure does not deform much. Clearly, as evident from both our numerical results and the experiments, the studied soft materials exhibit strong nonlinearities, and the linear model simply cannot be used.

IV. FLEXOELECTRICITY

At submicron or nanometer length scales, additional electromechanical coupling effects can become important. We consider here the phenomenon of flexoelectricity. As a form of electromechanical coupling, flexoelectricity links strain gradients to polarization [29–34]. Different from piezoelectricity, which is restricted to only certain crystal structures, flexoelectricity (like the Maxwell stress effect), in principle, exists in all dielectrics. Since strain gradients scale with sample size (as opposed to strain, which is roughly scale invariant), we can expect size effects as feature sizes shrink towards the nanoscale. Numerous experimental [35–40] and theoretical [32,41–47] studies (primarily on hard materials with two notable exceptions) have addressed the importance of flexoelectricity on electromechanical coupling at small scales. Several works have also recently appeared that develop a first principles approach to flexoelectricity [48–53]. In this work, we elucidate the interaction of flexoelectricity with nonlinear deformation and electrets. The central formulation remains the same as in Sec. II except for the addition of two additional terms to the energy:

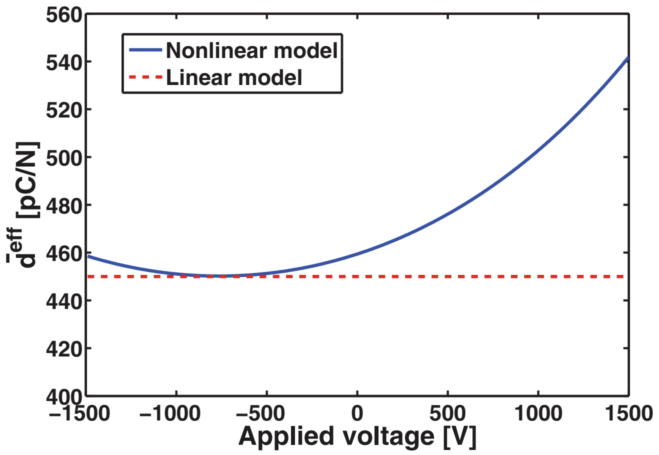

FIG. 6. (Color online) The piezoelectric effect of the ferroelectret.

$$W(\boldsymbol{\lambda},\boldsymbol{\Lambda},\mathbf{P}) = W_{\mathrm{elast}}(\boldsymbol{\lambda}) + \frac{g}{2}(\Lambda_1)^2 + f\Lambda_1 P_X + \frac{|\mathbf{P}|^2}{2(\epsilon-\epsilon_0)J}, \tag{16}$$

where $\boldsymbol{\lambda} = (\lambda_1,\lambda_2,\lambda_3)$ and $\boldsymbol{\Lambda} = (\Lambda_1,\Lambda_2,\Lambda_3) = (\frac{d\lambda_1}{dX},\frac{d\lambda_2}{dX},\frac{d\lambda_3}{dX})$ are the stretches and the strain gradients in vectorial form and g and f are material properties associated with the flexoelectricity. Note that, due to the introduction of the strain gradient, the stretches or strains may not be uniform throughout the film as in the previous nonflexoelectric case.

The one-dimensional (1D) governing equations are then derived to be

$$\begin{gathered} \frac{P_X}{\epsilon-\epsilon_0} + f\Lambda_1 + \lambda_1^{-1}\frac{d\xi}{dX} = 0, \\ \frac{d}{dX}\left[\mu\left(\lambda_1 - \lambda_1^{-2}\right) + \left(\tilde{\Sigma}_1 - \lambda_1^{-3/2}\tilde{\Sigma}_2\right) - \frac{d}{dX}(g\Lambda_1 + fP_X)\right] = 0. \end{gathered} \tag{17}$$

V. NONLINEARITY AND SIZE EFFECT

We reanalyze the equilibrium electromechanical state of the electret shown in Fig. 3. It is worthwhile to mention that, at the interface between the two layers, not only the potential and the displacement fields but also the stretches should be continuous in order to avoid the strain gradient singularity. We solve the problem numerically using the finite-element based partial differential equation solver [54]. Due to the highly nonlinear nature of the problem, the quartic (fourth-order) 1D finite element is used to carry out the computation.

For illustration, we use polypropylene cellular film and PVDF for layers a and b, respectively. The material properties are from the literature [55,56]: for layer a, $\mu_a = 0.95$ MPa, $f_a = 46.79$ Nm/C, $g_a = 1.28 \times 10^{-8}$ N, $\epsilon_a = 2.35\epsilon_0$; for layer b, $\mu_b = 2.0$ GPa, $f_b = 179.0$ Nm/C, $g_b = 5.42 \times 10^{-7}$ N, $\epsilon_b = 9.5\epsilon_0$. The flexoelectric coefficient of PVDF has been experimentally measured [56]. However, there is no report on the flexoelectric coefficient of polypropylene cellular film; in this work, we have assumed a reasonable value which is within the range of known values for common polymer materials. Also, the value of g is estimated for the present problem. As motivated by Maranganti and Sharma [57], the characteristic nonlocal elastic length scale can be approximated by the radius of gyration. Accordingly, we set $\sqrt{g/3\mu} = R_g$, where R_g is the radius of gyration of the polymers studied.

Piezoelectricity is a linearized material property and should exist without the application of the external electric field (but under the action of applied traction). Thus, for this case, we set the voltage difference between the top and the bottom surfaces to be zero. The effective piezoelectric coefficient is then calculated by $d^{\mathrm{eff}} = d\tilde{D}_X/dt_0^e$, where

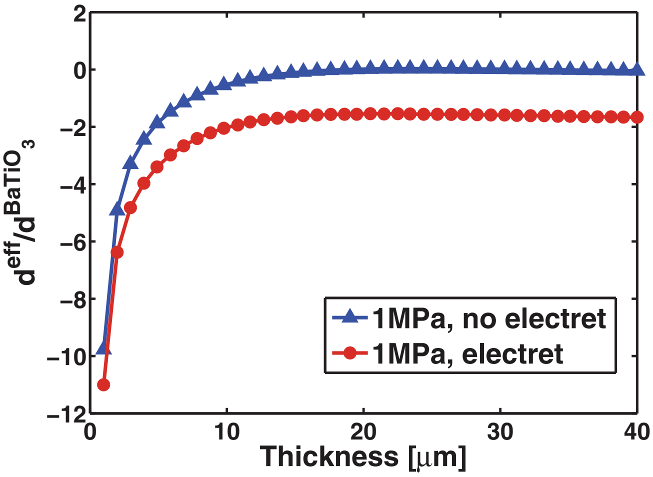

FIG. 7. (Color online) Size effect in electrets due to the flexoelectricity.

$\tilde{D}_X = -\epsilon_0\lambda_1^{-2}\xi_{,X} + \lambda_1^{-1}P_X$ is the correspondence of the electric displacement in the reference configuration and t_0^e is the applied surface traction.

To elucidate the interaction of the Maxwell stress effect and flexoelectricity, we compute the effective piezoelectric coefficient as a function of both thickness and applied mechanical stress (Fig. 7). Note that the two cases marked by "electret" and "no electret" correspond to the interface charge densities $q_0 = 10^{-3}$ C/m^2 and $q_0 = 0$, respectively. The piezoelectric coefficient d^{eff} is normalized by the d_{33} of barium titanate, which is around 78 pC/N. It is found that, above 20 μm, the size effect is minor, so that d^{eff} is practically size independent beyond this size scale. However, when the thickness decreases below this value, d^{eff} increases rapidly with the reduction of thickness. Eventually, below a certain size, the gradient strain energy grows very rapidly, and the system minimizes its energy by forcing the reduction in both the strain and the strain gradients: this feature is certainly nonclassical. More significantly, the "no electret" also exhibits a nonzero d^{eff} as the thickness becomes smaller, which is remarkable since we are dealing with inherently nonpiezoelectric materials.

VI. SUMMARY

With layers of charges or dipoles inserted inside, heterogeneous electret materials provide a simple yet effective way of coaxing nonpiezoelectric materials to exhibit an unusually large apparent piezoelectric response. Experimental studies indicate that the electromechanical coupling in the electret material is highly nonlinear. In this paper, we provide a simple treatment of this nonlinearity, taking into account large deformations expected from soft materials. The effective piezoelectric coefficients predicted by our theoretical model show excellent agreement with the experimental results, both qualitatively and quantitatively, in sharp contrast to the linear model that is often used in the literature. Accounting for the phenomenon of flexoelectricity, we also explore the interaction of size effects with electret materials. In particular, we find that "giant" electromechanical coupling can be achieved by judiciously exploiting the nonlinearity in electret soft materials and size effects due to flexoelectricity.

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